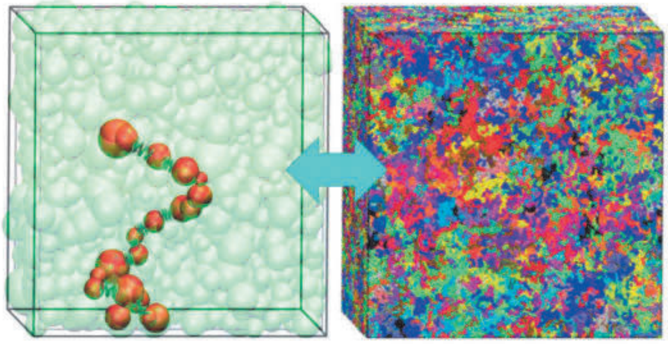
Deutsche Bunsen-Gesellschaft
für physikalische Chemie

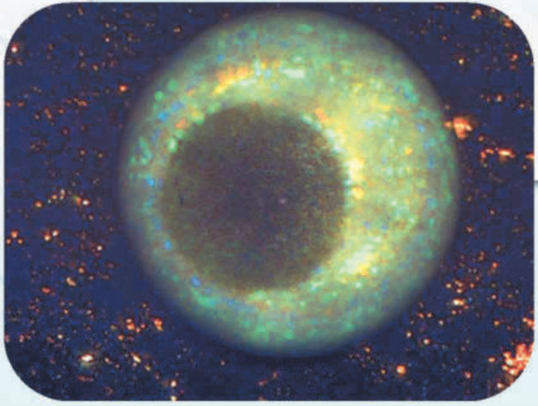
120th BUNSEN – TAGUNG

10 – 12 May 2021
virtual event

BOOK OF ABSTRACTS



Multi-Scale Modelling Physical Chemistry of Colloids



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Deutsche Bunsen-Gesellschaft
für physikalische Chemie

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HOST

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Deutsche Bunsen-Gesellschaft
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ADVERTISEMENTS

MONDAY, 10 May 2021

16:00	**OPENING & AWARD CEREMONY**	*Chair: P. Nuernberger*
17:15	**OPENING LECTURE: Daan Frenkel**, University of Cambridge **IL1**	*Chair: B. Dick*

TUESDAY, 11 May 2021

08:30	**PLENARY LECTURE: Colin D. Bain**, University of Durham **IL2**					*Chair: W. Kunz*	
	S01	**S02**	**S03**	**S04**	**S05**	**S06**	
	Key Topic: Colloids	**Key Topic: Multi-Scale Modelling**	**Reaction Kinetics & Dynamics**	**Catalysis**	**Transport & Storage**	**Thermo-dynamics**	
Chair	*A. Wittemann*	*P. Virnau*	*K. Boldt*	*M. Wächtler*	*K. Exner*	*H. Motschmann*	
09:20	Disch L02.01	**KEYNOTE** Diezemann L01.01	Grandjean L06.01	Noei L04.01	Dalpke L10.01	Mewes L09.01	
09:40	Rehbock L02.02		Wortmann L06.02	Diwald L04.02	Görtz L10.02	Aicher L09.02	
10:00	**Zsigmondy** König L02.03	Sebastiani L01.02	Holtmann L06.03	Mohrhusen L04.03	Genreith-Schriever L10.03	Lopez L09.03	
10:20		Piccini L01.03	Schmid L06.04	Bergwinkl L04.04	Xiao L10.04	Herrmann L09.04	
10:40	**COFFEE BREAK & EXHIBITION**						**EXHIBITION**
	S01	**S02**	**S03**	**S04**	**S05**	**S06**	
	Key Topic: Colloids	**Key Topic: Multi-Scale Modelling**	**Reaction Kinetics & Dynamics**	**Catalysis**	**Transport & Storage**	**Spectroscopy**	
Chair	*N. Vogel*	*K. Kremer*	*M. Schnell*	*J. Paier*	*A. Turchanin*	*A.-N. Unterreiner*	
11:25	**Steinkopff** Venzmer L02.04	Berger L01.04	Schlichting L06.05	Hess L04.05	**KEYNOTE** Maier L10.05	Strate L07.01	
11:45		Knippenberg L01.05	Krohn L06.06	Hohner L04.06		Dohmen L07.02	
12:05	Petry L02.05	**KEYNOTE** Smiatek L01.06	Zühlke L06.07	**KEYNOTE** Schröder L04.07	Schepp L10.06	Obenchain L07.03	
12:25	Kozlowska L02.06		Fischli L06.08		Getschmann L10.07	Fischer L07.04	
12:45	**LUNCH BREAK**						
13:30	**PLENARY LECTURE: Marjolein Dijkstra**, Utrecht University **IL3**					*Chair: R. Ludwig*	
	S01	**S02**	**S03**	**S04**	**S05**	**S06**	
	Key Topic: Colloids	**Key Topic: Multi-Scale Modelling**	**Reaction Kinetics & Dynamics**	**Industrial Topics**	**Award Winners & DFG**	**Spectroscopy**	
Chair	*S. Disch*	*M. Vogel*	*B. Rathke*	*P. Nuernberger*	*J. Janek*	*A. Slenczka*	
14:20	Förster L02.07	**KEYNOTE** van der Vegt L01.07	Fries L06.09	**Hamamatsu** Brandl	**Ewald-Wicke** Exner L11.01	van der Linde L07.05	
14:40	Zámbó L02.08		Kutta L06.10	**Carl Zeiss** Grimmelsmann	**Paul-Bunge 2020** Werrett	Crandall L07.06	
15:00	Rusch L02.09	Deußen L01.08	Winter L06.11	**McKinsey** Ketels	**Nernst-Haber-Bodenstein** Heinke L11.02	Mukhopadhyay L07.07	
15:20	**KEYNOTE** Wagner L02.10	Dünweg L01.09	Wille L06.12	**Roche** Steinbacher	**Paul-Bunge 2021** Taub	Peper L07.08	
15:40		Bernhardt L01.10	Kautek L06.13	**LIOP-TEC** Gutmann	DFG Wachter L11.03	Greis L07.09	
16:00 - 18:00	**POSTER SESSION**						

WEDNESDAY, 12 May 2021

08:30	**PLENARY LECTURE: Nadja C. Bigall,** Leibniz University Hannover **IL4** *Chair: S. Schauermann*					
	S01	**S02**	**S03**	**S04**	**S05**	**S06**
	Key Topic: Colloids	**Key Topic: Multi-Scale Modelling**	**Key Topic: Colloids**	**Key Topic: Multi-Scale Modelling**	**yPC-Forum**	**Spectroscopy**
Chair	*T. Hellweg*	*L. Stelzl*	*S. Förster*	*C. Allolio*	*yPC-Team*	*S. Tschierlei*
09:20	**KEYNOTE** Mulvaney L02.11	Schmid L01.11	Mees L02.26	Markthaler L01.26	**Chancengleichheit und Diversity in der Wissenschaft** Dehnen/Guggolz/Pecher L12	Küllmer L07.10
09:40		Presselt L01.12	Dehli L02.27	Hsu L01.27		Gerke L07.11
10:00	Vogel L02.12	**KEYNOTE** Rudzinski L01.13	Lübkemann L02.28	Yelash L01.28		Choi L07.12
10:20	Wang L02.13		Prasser L02.29	Daoulas L01.29		Czerwieniec L07.13
10:40	**COFFEE BREAK**					
	S01	**S02**	**S03**	**S04**	**S05**	**S06**
	Key Topic: Colloids	**Key Topic: Multi-Scale Modelling**	**Key Topic: Colloids**	**Theory & Data Science**	**Agnes Pockels-Session**	**Spectroscopy**
Chair	*T. König*	*R.Cortes-Huerto*	*J. Simmchen*	*M. Roemelt*	*K. Boldt / J. Lauth*	*R. Kutta*
11:05	Hellweg L02.14	**KEYNOTE** Peter L01.14	Dvoyashkin L02.30	Ko L08.01	Günther	Leier L07.14
11:25	Schad L02.15		Wittemann L02.31	Yachmenev L08.02	Lau	Gessner L07.15
11:45	Kühnhammer L02.16	Stelzl L01.15	Eslami L02.32	Zimmermann L08.03	Schubert	Brünker L07.16
12:05	**Liesegang** Dimova L02.17	Exner L01.16	Gutmann L02.33	Feldt L08.04	Tichter	**KEYNOTE** van Wilderen L07.17
12:25		Adams L01.17	Bettscheider L02.34	Frank L08.05	Westermayr	
12:45	**LUNCH BREAK**					
13:30	**PLENARY LECTURE: Tristan Bereau,** University of Amsterdam **IL5** *Chair: C. Peter*					
	S01	**S02**	**S03**	**S04**	**S05**	**S06**
	Key Topic: Colloids	**Key Topic: Multi-Scale Modelling**	**Biophysical Chemistry**	**Theory & Data Science**	**Electrochemistry**	**Spectroscopy**
Chair	*S.Roth*	*F. Schmid*	*S. Techert*	*M. Beyer*	*J. P. Hofmann*	*I. Fischer*
14:20	Huber L02.18	Valsson L01.18	**KEYNOTE** Müller-Werkmeister L03.01	**KEYNOTE** Roemelt L08.06	Weitzel L05.01	Unruh L07.18
14:40	Kuzminskaya L02.19	Paier L01.19			Eisele L05.02	Boden L07.19
15:00	Scotti L02.20	Martina L01.20	Kielb L03.02	Oncak L08.07	Grieshammer L05.03	Keppler L07.20
15:20	Aftenieva L02.21	**KEYNOTE** Behler L01.21	Metcalfe L03.03	Fritsch L08.08	Schlenkrich L05.04	Meyer L07.21
15:40	Lauth L02.22		Schwieger L03.04	Busch L08.09	Vargas-Barbosa L05.05	Gawrilow L07.22
16:00	**COFFEE BREAK**					
	S01	**S02**	**S03**	**S04**	**S05**	**S06**
	Key Topic: Colloids	**Key Topic: Multi-Scale Modelling**	**Biophysical Chemistry**	**Theory & Data Science**	**Electrochemistry**	**Spectroscopy**
Chair	*M. Gradzielski*	*D. Horinek*	*B. Herzog*	*J.-M. Mewes*	*N.Vargas-Barbarossa*	*K.-M. Weitzel*
16:15	Karg L02.23	Allolio L01.22	Wank L03.05	Peters L08.10	**KEYNOTE** Brummel L05.06	Ober L07.23
16:35	Simmchen L02.24	Stieffenhoffer L01.23	Selvaggio L03.06	Hertl L08.11		Moritz L07.24
16:55	**Ostwald** Butt L02.25	Ader L01.24	Kozuch L03.07	Roos L08.12	Mrkonjić Zajkoska L05.07	Wächtler L07.25
17:15		Dettmann L01.25	Hoernke L03.08	Henkel L08.13	Erbes L05.08	Mezger L07.26
17:40 - 18:00	**AWARD CEREMONY & CLOSING SESSION**					

EXHIBITION

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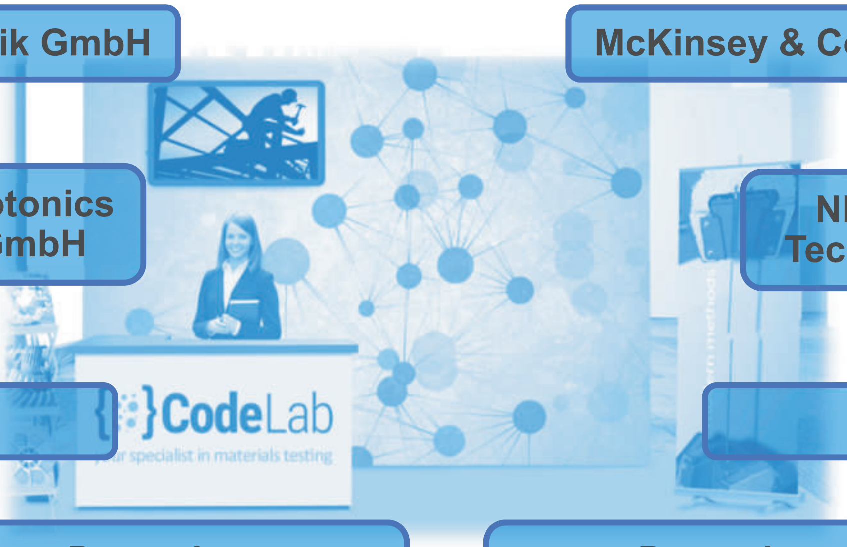
EXHIBITORS



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THE INDUSTRIAL TOPICS SESSION

Tuesday, May 11th, 2:20 – 4:00 pm

PRESENTERS

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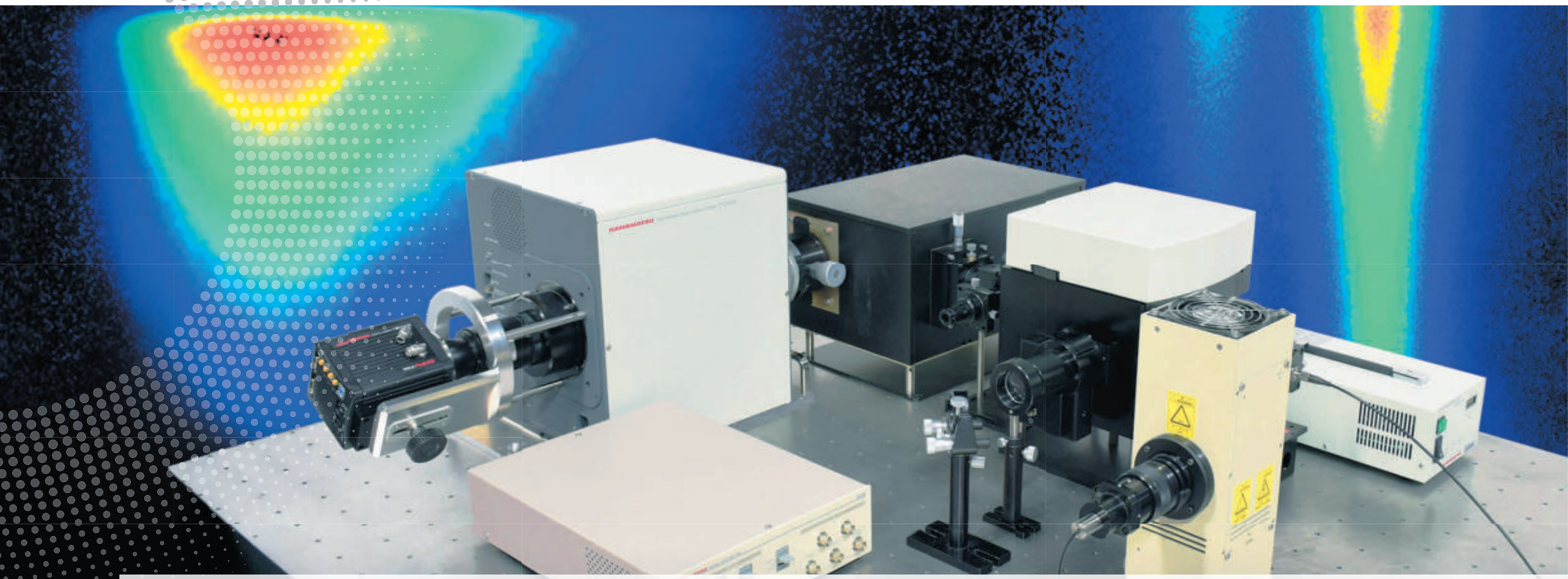

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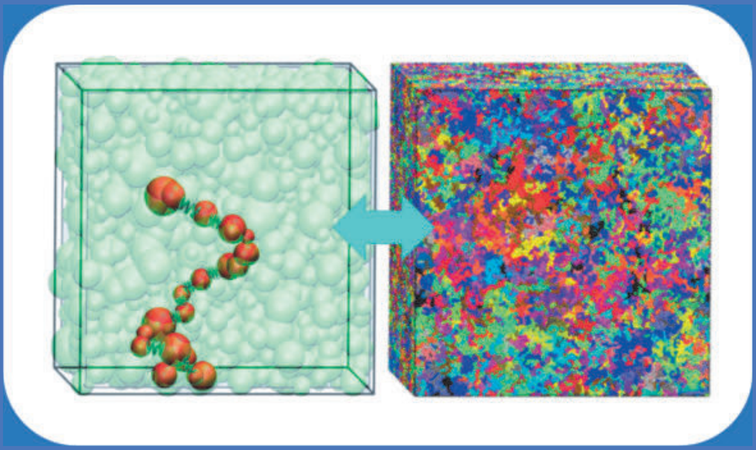
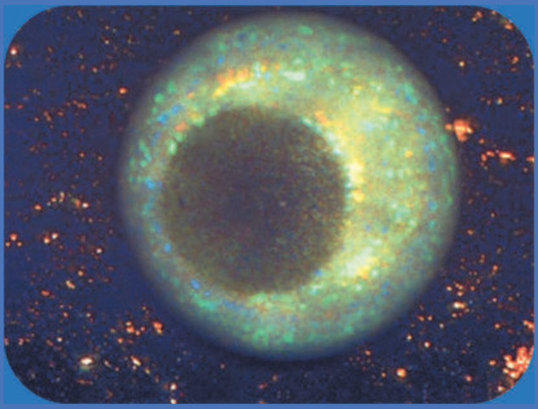


LECTURE SCHEDULE



Monday, 10 May 2021, 04:00 p.m.

04.00 p.m. **OPENING CEREMONY**

OPENING LECTURE

virtual Audimax

Chair: *Bernhard Dick, Regensburg*

05.15 p.m.
IL1
Entropy, Colloids and COVID19
D. Frenkel, Cambridge/GB

Tuesday, 11 May 2021, 08:30 a.m.

PLENARY LECTURE

virtual Audimax

Chair: *Werner Kunz, Regensburg*

08.30 a.m.
IL2
Physical Chemistry of Drying Droplets
C. D. Bain, Durham/GB

Tuesday, 11 May 2021, 09:20 – 10:40 a.m.

TUESDAY MORNING Parallel Sessions 1

KEY TOPIC: Physical Chemistry of Colloids

virtual room S01

Chair: *Alexander Wittemann, Konstanz*

09.20 a.m.
L02.01
Field Dependence of Magnetic Disorder in Nanoparticles
S. Disch, Köln/DE, D. Zákutná, Köln/DE, D. Honecker, Luxembourg/LU

09.40 a.m.
L02.02
Colloidal FeAu core-shell nanoparticles by laser ablation synthesis
C. Rehbock, Essen/DE, S. Barcikowski, Essen/DE

10.00 a.m.
L02.03
Keynote Lecture: Zsigmondy Scholarship
Functional optical surfaces by colloidal self-assembly
T. A. F. König, Dresden/DE

KEY TOPIC: Multi-Scale Modelling

virtual room S02

Chair: *Peter Virnau, Mainz*

09.20 a.m.
L01.01
Keynote Lecture
Force probe simulations using an adaptive resolution scheme
G. Diezemann, Mainz/DE, M. Oestereich, Mainz/DE, J. Gauss, Mainz/DE

10.00 a.m.
L01.02
Ion Conductivity Simulations in Nanostructured Materials with First Principles Resolution
D. Sebastiani, Halle/DE, C. Dressler, Halle/DE

10.20 a.m.
L01.03
Atomistic simulations of catalytic confined environments from supramolecular systems to biomass conversion
G. Piccini, Lugano/CH

Reaction Dynamics and Kinetics

virtual room S03

Chair: *Klaus Boldt, Konstanz*

09.20 a.m.
L06.01
Hydrogen-Bonded Ion Pair in Excited-State Proton Transfer
A. Grandjean, Saarbrücken/DE, J. L. Pérez Lustres, Berlin/DE, S. Muth, Regensburg/DE, D. Maus, Saarbrücken/DE, G. Jung, Saarbrücken/DE

09.40 a.m.
L06.02
Monitoring the photochemistry of a formazan over 12 orders of magnitude in time
S. Wortmann, Regensburg/DE, R. J. Kutta, Regensburg/DE, P. Nuernberger, Regensburg/DE

10.00 a.m.
L06.03
Unraveling the photo-induced dynamics of N^6,N^6-dimethyladenine by time-resolved spectroscopy and ab initio calculations
R. Holtmann, Kiel/DE, V. Lukaszczuk, Kiel/DE, F. Temps, Kiel/DE

10.20 a.m.
L06.04
Why substitution matters - temperature dependency of excited states of Ru(II) complexes
M.-A. Schmid, Braunschweig/DE, R. Nau, Ulm/DE, S. Amthor, Ulm/DE, S. Rau, Ulm/DE, S. Tschierlei, Braunschweig/DE

Catalysis

virtual room S04

Chair: *Maria Wächtler, Jena*

09.20 a.m.
L04.01
Operando ambient pressure HAXPES studies of Cu/ZnO(10-14) and Cu/ZnO(000-1) model catalysts for methanol synthesis
H. Noei, Hamburg/DE, R. Gleißner, Hamburg/DE, M. Wagtsaffe, Hamburg/DE, C. Goodwin, Stockholm/SE, M. Soldemo, Stockholm/SE, M. Shipilin, Stockholm/SE, P. Lömker, Hamburg/DE, C. Schlueter, Hamburg/DE, P. Amann, Stockholm/SE, A. Nilsson, Stockholm/SE, A. Stierle, Hamburg/DE

09.40 a.m.
L04.02
TiO_2 and $BaTiO_3$ nanoparticles: gas phase functionalization and separation of photogenerated charges
E. Neige, Salzburg/AT, T. Schwab, Salzburg/AT, G. Zickler, Salzburg/AT, O. Diwald, Salzburg/AT

10.00 a.m.
L04.03
Electron Transfer in mixed Oxide-Oxide Model Catalysis: Impact of Ti^{3+} on the (Photo)Chemistry of Methanol at Tungsten Oxide Clusters deposited on Rutile TiO_2
L. Mohrhusen, Oldenburg/DE, J. Kräuter, Oldenburg/DE, M. Grebien, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE

10.20 a.m.
L04.04
Consecutive photoinduced electron transfer (conPET): The mechanism of the photocatalyst rhodamine-6G.
S. Bergwinkl, Regensburg/DE, F. Brandl, Regensburg/DE, C. Allacher, Regensburg/DE, B. Dick, Regensburg/DE

Transport and Storage

virtual room S05

Chair: *Kai Exner, Essen*

09.20 a.m.
L10.01
Carbon Nanomembranes from Alkanethiol Monolayers
R. Dalpke, Bielefeld/DE, N. Biere, Bielefeld/DE, D. Emmrich, Bielefeld/DE, F. Paneff, Bielefeld/DE, D. Naberezhnyi, Bielefeld/DE, I. Ennen, Bielefeld/DE, M. Westphal, Bielefeld/DE, A. Beyer, Bielefeld/DE, P. Dementyev, Bielefeld/DE, A. Hütten, Bielefeld/DE, D. Anselmetti, Bielefeld/DE, A. Gölzhäuser, Bielefeld/DE

09.40 a.m.
L10.02
Investigation of a redox mass for rechargeable oxide batteries: $(Fe_{1-x}Mn_x)_yO_z$ with a $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ scaffold
D. Görtz, Aachen/DE, M. Schroeder, Aachen/DE

10.00 a.m.
L10.03
The Intrinsic Structural Resistance of a Grain Boundary to Transverse Ionic Conduction
A. R. Genreith-Schriever, Cambridge/GB

10.20 a.m.
L10.04
Discrete Modeling of Space Charge Zones in Solids
C. Xiao, Stuttgart/DE, C. C. Chen, Stuttgart/DE, R. Usiskin, Stuttgart/DE, J. Maier, Stuttgart/DE

Thermodynamics

virtual room S06

Chair: *Hubert Motschmann, Regensburg*

09.20 a.m.
L09.01
Liquid Thermodynamics from First Principles: Accurate Gibbs Energies Through Integration of Scaled DFT Forces
J. -M. Mewes, Bonn/DE

09.40 a.m.
L09.02
Role and activity of Fe^{3+} and In^{3+} impurities on coarsening and functional properties in MgO nanoparticle derived ceramics
K. Aicher, Salzburg/AT, T. Schwab, Salzburg/AT, M. Niedermaier, Salzburg/AT, G. Zickler, Salzburg/AT, M. Reissner, Wien/AT, O. Diwald, Salzburg/AT

10.00 a.m.
L09.03
Polyelectrolyte conformation and dynamics in solution measured by rheology and pulsed field gradient NMR
C. G. Lopez, Aachen/DE, W. Richtering, Aachen/DE, J. Linders, Essen/DE, C. Mayer, Essen/DE

10.20 a.m.
L09.04
Molecular self-assembly and boronate ester synthesis at the liquid-solid interface, a STM study
N. Herrmann, Leuven/BE, N. Bilbao, Leuven/BE, K. S. Mali, Leuven/BE, X. Feng, Dresden/DE, S. De Feyter, Leuven/BE

Tuesday, 11 May 2021, 10:40 – 11:25 a.m.

10.40 a.m. **COFFEE BREAK**

EXHIBITION OPENS

Tuesday, 11 May 2021, 11:25 – 12:45 p.m.

KEY TOPIC: Physical Chemistry of Colloids

virtual room S01

Chair: *Nicolas Vogel, Erlangen-Nürnberg*

11.25 a.m.
L02.04
Keynote Lecture: Steinkopff Prize
Surfactants and polymers active at interfaces: Examples of industrial Colloid and Interface Science
J. Venzmer, Essen/Deutschland

12.05 p.m.
L02.05
Luminescent Europium Doped Yttrium Oxide Nano Discs
J. Petry, Hamburg/DE, R. Komban, Hamburg/DE, C. Gimmler, Hamburg/DE, H. Weller, Hamburg/DE

12.25 p.m.
L02.06
Solubility of proteins from extended molecular DLVO theory
M. Kozlowska, Eggenstein-Leopoldshafen/DE, S. Pusara, Eggenstein-Leopoldshafen/DE, W. Wenzel, Eggenstein-Leopoldshafen/DE

KEY TOPIC: Multi-Scale Modelling

virtual room S02

Chair: *Kurt Kremer, Mainz*

11.25 a.m.
L01.04
MD Simulations with Near MP2 Accuracy - Adsorption in Zeolites
F. Berger, Berlin/DE, M. Rybicki, Berlin/DE, J. Sauer, Berlin/DE

11.45 a.m.
L01.05
Conformational changes as driving force for phase recognition
S. Knippenberg, Hasselt/BE, S. Osella, Warsaw/PL

12.05 p.m.
L01.06
Keynote Lecture
Challenges in Biopharmaceutical Development: Modelling at Different Length Scales
J. Smiatek, Stuttgart/Deutschland

Reaction Dynamics and Kinetics

virtual room S03

Chair: *Melanie Schnell, Hamburg*

11.25 a.m.
L06.05
Estimating the Octane Number via a 2-Zone-Cylinder-Model
Schlichting, Stuttgart/DE, T. Methling, Stuttgart/DE, C. Janzer, Stuttgart/DE, U. Riedel, Cottbus/DE, M. Köhler, Stuttgart/DE

11.45 a.m.
L06.06
Nucleation enhancement of weakly-bound species: A molecular love story of CO_2 and Toluene
J. Krohn, Zürich/CH, C. Li, Shanghai/CN, M. Lippe, Zürich/CH, R. Signorell, Zürich/CH

12.05 p.m.
L06.07
Acceleration of Mannich reaction in electrospray droplets
M. Zühlke, Potsdam/DE, J. A. Koenig, Potsdam/DE, C. Prüfert, Potsdam/DE, D. Riebe, Potsdam/DE, T. Beitz, Potsdam/DE, H.-G. Löhmannsröben, Potsdam/DE

12.25 p.m.
L06.08
Mechanisms for Regioselective Synthesis of Anisotropic Nano-Heterostructures
D. Fischli, Konstanz/DE, F. Enders, Konstanz/DE, S. Sutter, Konstanz/DE, R. Köser, Konstanz/DE, S. Monter, Konstanz/DE, K. Boldt, Konstanz/DE

Catalysis

virtual room S04

Chair: *Joachim Paier, Berlin*

11.25 a.m.
L04.05
New insight into the mechanism of CO oxidation and water-gas shift reaction over Au catalysts using operando spectroscopies
C. Hess, Darmstadt/DE, M. Ziemba, Darmstadt/DE, J. Weyel, Darmstadt/DE

11.45 a.m.
L04.06
How Does an Ionic Liquid Adsorb on a Pt(111) Surface? A Combined Study by Infrared Reflection Absorption Spectroscopy and Density Functional Theory Calculations
C. Hohner, Erlangen/DE, G. Fickenscher, Erlangen/DE, L. Fromm, Erlangen/DE, A. Görling, Erlangen/DE, J. Libuda, Erlangen/DE

12.05 p.m.
L04.07
Keynote Lecture
Ligand-Induced Heterogeneous Catalysis: Selective Hydrogenation of Acrolein on Ligand-Modified Pd(111)
C. Schröder, Kiel/DE, M. C. Schmidt, Kiel/DE, P. Haugg, Kiel/DE, A. - K. Baumann, Kiel/DE, S. Schauermann, Kiel/DE

Transport and Storage

virtual room S05

Chair: *Andrey Turchanin, Jena*

11.25 a.m.
L10.05
Keynote Lecture
The effect of long-range order on charge transport in self-assembled nanocrystal and nanocluster superlattices
A. Maier, Tübingen/DE, N. Mukharamova, Hamburg/DE, I. Vartanyants, Hamburg/DE, F. Fetzer, Tübingen/DE, M. Hodas, Tübingen/DE, O. Geladari, Tübingen/DE, P. Frech, Tübingen/DE, K. Braun, Tübingen/DE, M. Fleischer, Tübingen/DE, F. Schreiber, Tübingen/DE, A. Schnepf, Tübingen/DE, M. Scheele, Tübingen/DE, D. Lapkin, Hamburg/DE

12.05 p.m.
L10.06
Combined experimental and theoretical study of $Li_{(1-x)}FePO_4$ as a function of the state of lithiation
J. Schepp, Marburg/DE, L. Janin, Marburg/DE, S. Adams, Singapore/SG, K.-M. Weitzel, Marburg/DE

12.25 p.m.
L10.07
Cation Exchange Reactions on Semiconductor Nanoparticle Gel Networks
S. Getschmann, Hannover/DE, F. Lübkemann, Hannover/DE, P. Rusch, Hannover/DE, B. Schremmer, Hannover/DE, M. Rosebrock, Hannover/DE, D. Müller, Hannover/DE, N. C. Bigall, Hannover/DE

Spectroscopy

virtual room S06

Chair: *Andreas-Neil Unterreiner, Karlsruhe*

11.25 a.m.
L07.01
Rotational and translational motion in ionic liquids by means of high field and field cycling NMR relaxometry
A. Strate, Rostock/DE, N. Nübler, Rostock/DE, L. Kuban, Rostock/DE, T. van Alphen, Rostock/DE, R. Ludwig, Rostock/DE

11.45 a.m.
L07.02
Microwave Study of Mono-Cholorobenzaldehydes
M. M. Dohmen, Göttingen/DE, S. Arnold, Hartsville/US, J. Garrett, Hartsville/US, P. Pinacho, Hamburg/DE, M. Schnell, Hamburg/DE, G. Brown, Hartsville/US, D. A. Obenchain, Göttingen/DE

12.05 p.m.
L07.03
Docking preference and geometry of 1-naphthol complexes revealed by rotational spectroscopy
D. A. Obenchain, Göttingen/DE, M. M. Quesada-Moreno, Hamburg/DE, R. T. Saragi, Valladolid/ES, A. Lesarri, Valladolid/ES, M. Schnell, Hamburg/DE

12.25 p.m.
L07.04
Stark-spectroscopic investigations of large organic molecules and their clusters with water in superfluid helium nanodroplets
J. Fischer, Regensburg/DE, F. Schlaghaufer, Regensburg/DE, A. Slenczka, Regensburg/DE

Tuesday, 11 May 2021, 12:45 – 01:30 p.m.

12.45 p.m. **LUNCH BREAK**

Tuesday, 11 May 2021, 01:30 p.m.

PLENARY LECTURE

virtual Audimax

Chair: *Ralf Ludwig, Rostock*

01.30 p.m.
IL3
Towards Inverse Design of Soft Materials: Crystals, Quasi Crystals, Liquid Crystals
M. Dijkstra, Utrecht/NL

Tuesday, 11 May 2021, 02:20 – 04:00 p.m.

KEY TOPIC: Physical Chemistry of Colloids

virtual room S01

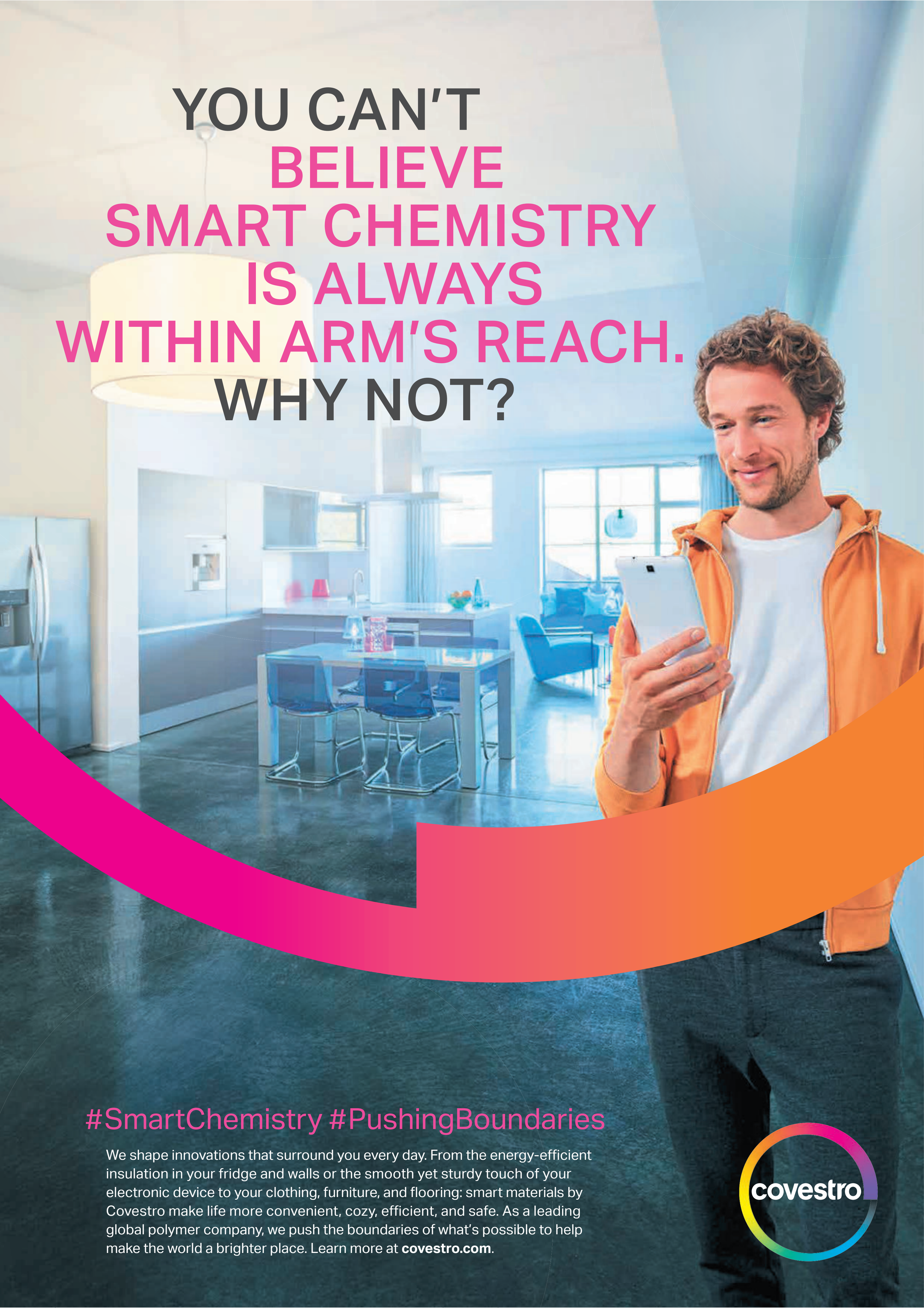
Chair: *Sabrina Disch, Cologne*

02.20 p.m.
L02.07
Soft quasicrystals optimize sphere packing
S. Förster, Jülich/DE , M. Dulle, Jülich/DE, T. Jurczyk, Jülich/DE, T. Gruhn, Bayreuth/DE

02.40 p.m.
L02.08
Assembling Nanocrystals into Hybrid Functional Gel Structures by Means of Multivalent Cations
D. Zámbó, Hannover/DE, A. Schlosser, Hannover/DE, J. Schlenkrich, Hannover/DE, P. Rusch, Hannover/DE, R. T. Graf, Hannover/DE, F. Lübkemann, Hannover/DE, A. Feldhoff, Hannover/DE, N. C. Bigall, Hannover/DE

03.00 p.m.
L02.09
Controlling Properties of Nanoparticle-based Networks via their Microstructure
P. Rusch, Hannover/DE, B. Schremmer, Hannover/DE, N. C. Bigall, Hannover/DE

03.20 p.m.
L02.10
Keynote Lecture
The micromechanics of shear thickening fluids and their application as protective materials for medical professionals, first responders, atheletes, and astronauts.
N. Wagner, Newark/US


YOU CAN'T
BELIEVE
SMART CHEMISTRY
IS ALWAYS
WITHIN ARM'S REACH.
WHY NOT?
covestro

KEY TOPIC: Multi-Scale Modelling

virtual room S02

Chair: *Michael Vogel, Darmstadt*

02.20 p.m.
L01.07
Keynote Lecture
Introducing memory in coarse-grained molecular simulations
N. F. A. van der Vegt, Darmstadt/DE

03.00 p.m.
L01.08
Probability theory of active suspensions
B. Deußen, Darmstadt/DE, M. Oberlack, Darmstadt/DE, Y. Wang, Darmstadt/DE

03.20 p.m.
L01.09
Systematic derivation of hydrodynamic equations for viscoelastic phase separation
B. Dünweg, Mainz/DE , D. Spiller, Mainz/DE, A. Brunk, Mainz/DE, M. Lukacova-Medvidova, Mainz/DE, O. Habrich, Darmstadt/DE, H. Egger, Darmstadt/DE

03.40 p.m.
L01.10
Iterative integral equation methods for structural coarse-graining
M. P. Bernhardt, Darmstadt/DE, M. Hanke, Mainz/DE, N. F. A. van der Vegt, Darmstadt/DE

Reaction Dynamics and Kinetics

virtual room S03

Chair: *Bernd Rathke, Bremen*

02.20 p.m.
L06.09
Observation and Mechanism of N_2 Cleavage by a Tantalum Cluster under Cryo Conditions
D. V. Fries, Kaiserslautern/DE, M. P. Klein, Kaiserslautern/DE, A. Steiner, Kaiserslautern/DE, M. H. Prosenc, Kaiserslautern/DE, G. Niedner-Schatteburg, Kaiserslautern/DE

02.40 p.m.
L06.10
Mechanistic Studies on a Deracemization Reaction via a Triplet 1,3-Diradical Induced by Energy Transfer from a Chiral Sensitizer
R. J. Kutta, Regensburg/DE, X. Li, München/DE, C. Jandl, München/DE, A. Bauer, München/DE, T. Bach, München/DE, P. Nuernberger, Regensburg/DE

03.00 p.m.
L06.11
Temperature-dependent trapping probability measurements of n-butane on ionic liquid surfaces using molecular beam techniques
L. Winter, Erlangen/DE, R. G. Bhuin, Erlangen/DE, M. Lexow, Erlangen/DE, F. Maier, Erlangen/DE, H.-P. Steinrück, Erlangen/DE

03.20 p.m.
L06.12
An experimentally validated neural-network potential energy surface for H-atom on free-standing graphene in full dimensionality
S. Wille, Göttingen/DE, H. Jiang, Göttingen/DE, O. Bünermann, Göttingen/DE, A. M. Wodtke, Göttingen/DE, J. Behler, Göttingen/DE, A. Kandratsenka, Göttingen/DE

03.40 p.m.
L06.13
Physico-chemical exploration of pioneering photography and electroplating reproduction around 1840
W. Kautek, Wien/AT, V. Ljubić Tobisch, Wien/AT

Industrial Topics

virtual room S04

Chair: *Patrick Nuernberger, Regensburg*

02.20 p.m. **Streak-based Measurement Systems for Transient Absorption and Fluorescence Lifetimes**
F. Brandl, Hamamatsu Photonics Deutschland GmbH

02.40 p.m. **EUV lithography as a corner stone of modern chip production**
L. Grimmelsmann, Carl Zeiss AG

03.00 p.m. **Warum McKinsey? – Mit Naturwissenschaften in die Topmanagement-Beratung**
M. Ketels, McKinsey & Company Inc.

03.20 p.m. **Drug development in the digital age – How can digital tools accelerate data-driven drug discovery?**
A. Steinbacher, Roche Diagnostics GmbH

03.40 p.m. **Fluorescence Upconversion Spectrometer**
M. Gutmann, LIOP-TEC GmbH

THE INDUSTRIAL TOPICS SESSION

Tuesday, May 11th, 2:20 – 4:00 pm

PRESENTERS

Hamamatsu Photonics Deutschland GmbH

Carl Zeiss AG

McKinsey & Company, Inc.

Roche Diagnostics GmbH

LIOP-TEC GmbH

DBG Award Winners

virtual room S05

Chair: *Jürgen Janek, Gießen*

02.20 p.m.
L11.01
Ewald-Wicke-Preis 2021
On the Optimum Binding Energy in Electrocatalysis
K. S. Exner, Essen/DE

02.40 p.m.
Paul-Bunge-Preis 2020
The History of Science is Thriving
S. Werrett, London/GB

03.00 p.m.
L11.02
Nernst-Haber-Bodenstein-Preis 2021
Photo-responsive conduction in nanoporous crystalline thin films
L. Heinke, Karlsruhe/DE

03.20 p.m.
Paul-Bunge-Preis 2021
Studying Scientific Instruments Today
L. C. Taub, Cambridge/GB

03.40 p.m.
L11.03
The Deutsche Forschungsgemeinschaft (DFG): Funding Opportunities for Early Career Researchers
W. Wachter, Deutsche Forschungsgemeinschaft

Spectroscopy

virtual room S06

Chair: *Alkwin Slenczka, Regensburg*

02.20 p.m.
L07.05
Infrared Spectroscopy of $CO_3^{\bullet-}(H_2O)_{1,2}$ and $CO_4^{\bullet-}(H_2O)_{1,2}$
C. van der Linde, Innsbruck/AT, M. G. Münst, Innsbruck/AT, M. Ončák, Innsbruck/AT, M. K. Beyer, Innsbruck/AT

02.40 p.m.
L07.06
Optical Spectrum of the Adamantane Radical Cation
P. B. Crandall, Berlin/DE, D. Müller , Berlin/DE, M. Förstel, Berlin/DE, J. Leroux, Berlin/DE, O. Dopfer, Berlin/DE

03.00 p.m.
L07.07
Photoelectron spectroscopy of BH_2 using synchrotron radiation and photoelectron/photoion coincidence (i^2PEPICO) spectroscopy
D. P. Mukhopadhyay, Würzburg/DE , D. Schleier, Würzburg/DE, I. Fischer, Würzburg/DE, J. -C. Loison, Bordeaux/FR, C. Alcaraz, Paris/FR, G .A. Garcia, Paris/FR

03.20 p.m.
L07.08
Heteronuclear long-range Rydberg molecules
M. Peper, Leipzig/DE , J. Deiglmayr, Leipzig/DE

03.40 p.m.
L07.09
Cryogenic Vibrational Spectroscopy – A Tool for Understanding Mechanisms in Organic Chemistry
K. Greis, Berlin/DE , C. Kirschbaum, Berlin/DE, S. Leichnitz, Potsdam/DE, G. von Helden, Berlin/DE, P. H. Seeberger, Potsdam/DE, K. Pagel, Berlin/DE

Tuesday, 11 May 2021, 04:00 – 06:00 p.m.

04:00 p.m.

POSTER SESSION


pco.dicam C1
pco.flim
pco.edge
pco.dimax
pco.panda

Wednesday, 12 May 2021, 08:30 a.m.

PLENARY LECTURE **virtual Audimax**

Chair: *Swetlana Schauermann, Kiel*

08.30 a.m. **IL4** **Multicomponent Aerogels from Colloidal Nanocrystals**
Nadja C. Bigall, Hannover/DE

Wednesday, 12 May 2021, 09:20 – 10:40 a.m.

KEY TOPIC: Physical Chemistry of Colloids **virtual room S01**

Chair: *Thomas Hellweg, Bielefeld*

09.20 a.m. **L02.11** ***Keynote Lecture***
Single Nanocrystal Arrays- Preparation and Spectroscopy
P. Mulvaney, Parkville/AU

10.20 a.m. **L02.12** **Magic number colloidal clusters**
N. Vogel, Erlangen/DE, J. Wang, Erlangen/DE, C. M. Fru, Erlangen/DE, T. Przybilla, Erlangen/DE, E. Spiecker, Erlangen/DE, M. Engel, Erlangen/DE

10.00 a.m. **L02.13** **The Road Not Taken – Icosahedral or Decahedral Symmetry in Spherical Confinement?**
J. Wang, Erlangen/DE, C. Fru Mbah, Erlangen/DE, S. Englisch, Erlangen/DE, P. Bommineni, Erlangen/DE, E. Spiecker, Erlangen/DE, N. Vogel, Erlangen/DE, M. Engel, Erlangen/DE

KEY TOPIC: Physical Chemistry of Colloids **virtual room S03**

Chair: *Stephan Förster, Jülich*

09.20 a.m. **L02.26** **Self-assembling of functionalized hematite nanospindles at the liquid-air interface**
F. A. F. Mees, Cologne/DE, S. Disch, Cologne/DE

09.40 a.m. **L02.27** **Tailoring of pore openings in gelatin-based hydrogel foams**
F. Dehli, Stuttgart/DE, A. Southan, Stuttgart/DE, W. Drenckhan, Straßburg/FR, C. Stubenrauch, Stuttgart/DE

10.00 a.m. **L02.28** **Inkjet Printing: Patterning of 3D Nanoparticle-Based Aerogel-Like Networks for Photoelectrochemical Applications**
F. Lübkemann, Hannover/DE, J.F. Miethe, Hannover/DE, D. Zámbó, Hannover/DE, R. Anselmann, Hanau/DE, P. Rusch, Hannover/DE, A. Schlosser, Hannover/DE, T. Kodanek, Hannover/DE, T. Heinemeyer, Hannover/DE, D. Natke, Hannover/DE, D. Zok, Hannover/DE, D. Dorfs, Hannover/DE, N. C. Bigall, Hannover/DE

10.20 a.m. **L02.29** **Electrochemical Switching of Block Copolymers at the Water-Oil Interface**
Q. Prasser, Freiberg/DE , F. A. Plamper, Freiberg/DE

KEY TOPIC: Multi-Scale Modelling

virtual room S02

Chair: *Lukas Stelzl, Mainz*

09.20 a.m.
L01.11
Constructing dynamic density functional theories for inhomogeneous polymer systems from microscopic simulations
F. Schmid, Mainz/DE, S. Mantha, California/US, S. Qi, Beihang/CN, B. Li, Mainz/DE

09.40 a.m.
L01.12
Developing and modelling organic membranes for photo-energy conversion
M. Presselt, Jena/DE

10.00 a.m.
L01.13
Keynote Lecture
Consistent representation of structural and dynamical properties from coarse-grained simulation models
J. F. Rudzinski, Mainz/DE

KEY TOPIC: Multi-Scale Modelling

virtual room S04

Chair: *Christoph Allolio, Prague*

09.20 a.m.
L01.26
Computational Investigation of the Soret Coefficient in the Context of Host/Ligand Binding
D. Markthaler, Stuttgart/DE, S. Mohankumar, Juelich/DE, S. Wiegand, Juelich/DE, N. Hansen, Stuttgart/DE

09.40 a.m.
L01.27
An efficient methodology for equilibrating confined and free-standing films of highly entangled polymer melts
H.-P. Hsu, Mainz/DE, K. Kremer, Mainz/DE

10.00 a.m.
L01.28
Hybrid simulations of shear-thinning polymer flows
L.Yelash, Mainz/DE, R. Datta, Mainz/DE, F. Kummer, Darmstadt/DE, M. Oberlack, Darmstadt/DE, M. Lukácová-Medvidová, Mainz/DE, P. Virnau, Mainz/DE

10.20 a.m.
L01.29
Can Soft Models Describe Polymer Knots?
K. Daoulas, Mainz/DE, J. Zhang, Mainz/DE, H. Meyer, Strasbourg/FR, P. Virnau, Mainz/DE

yPC Forum

virtual room S05

Chair: *yPC Team*

09.20 a.m.

L12

Chancengleichheit und Diversity in der Wissenschaft

Vereinbarkeit von Karriere und Familie
Prof. Dr. Stefanie Dehnen, Philipps Universität Marburg

Karriere in der Chemie mit Behinderung
Dr. Lukas Guggolz, Philipps Universität Marburg

Gender Equality in der Wissenschaft
Dr. Lisa Pecher, Wiley-VCH, Weinheim

mit anschließender Podiumsdiskussion

WEDNESDAY MORNING Parallel Sessions 1

Spectroscopy

virtual room S06

Chair: *Stefanie Tschierlei, Braunschweig*

09.20 a.m.
L07.10
2D hierarchical nanosheets with integrated Co-based HER-catalysts: An X-ray photoelectron and tip-enhanced Raman spectroscopy study
M. Küllmer, Jena/DE, M. Richard-Lacroix, Jena/DE, E. Hofmeister, Jena/DE, M. von Delius, Ulm/DE, V. Deckert, Jena/DE, A. Turchanin, Jena/DE

09.40 a.m.
L07.11
Surface properties of dendritic fibrous silica nanoparticles studied by wide-angle soft X-ray scattering
F. Gerke, Berlin/DE, B. Langer, Berlin/DE, B. Wassermann, Berlin/DE, A. Maity, Mumbai/IN, V. Polshettiwar, Mumbai/IN, E. Rühl, Berlin/DE

10.00 a.m.
L07.12
Femtosecond energy transfer in Fe(II)-Co(III) photocatalyst directly observed with X-ray emission spectroscopy
T.-K. Choi, Schenefeld/DE, M. Huber-Gedert, Paderborn/DE, M. Nowakowski, Paderborn/DE, A. Kertmen, Poznań/PL, J. Kubicki, Poznań/PL, M. Bauer, Paderborn/DE, W. Gawelda, Madrid/ES

10.20 a.m.
L07.13
Dinuclear Ir(III) Complex Exhibiting Unusually Slow Phosphorescence and Intersystem Crossing
R. Czerwieniec, Regensburg/DE, M. Z. Shafikov, Regensburg/DE

Wednesday, 12 May 2021, 10:40 – 11:05 a.m.

10.40 a.m. **COFFEE BREAK**

Wednesday, 12 May 2021, 11:05 – 12:45 p.m.

WEDNESDAY MORNING Parallel Sessions 2

KEY TOPIC: Physical Chemistry of Colloids

virtual room S01

Chair: *Tobias A. F. König, Dresden*

11.05 a.m.
L02.14
Interaction of Bio-Surfactants with Different Lipid Membranes
T. Hellweg, Bielefeld/DE

11.25 a.m.
L02.15
Innovative Cleaning Concept with Controlled Foams
T. Schad, Stuttgart/DE, N. Preisig, Stuttgart/DE, H. Piening, München/DE, D. Blunk, Köln/DE, W. Drenckhan, Strasbourg/FR, C. Stubenrauch, Stuttgart/DE

11.45 a.m.
L02.16
PNIPAM microgels at the air/water interface – from single interfaces to foams
M. Kühnhammer, Darmstadt/DE, R. von Klitzing, Darmstadt/DE

12.05 p.m.
L02.17
Keynote Lecture: Liesegang Prize
Giant vesicles: versatile colloids for unravelling biomembrane properties and for building artificial cells
R. Dimova, Potsdam/DE

KEY TOPIC: Physical Chemistry of Colloids

virtual room S03

Chair:	*Juliane Simmchen, Dresden*
11.05 a.m. **L02.30**	**Cooperative Ion-Solvent Dynamics in Organic Electrolytes Revealed by Diffusion NMR and Molecular Dynamics Simulations** M. Dvoyashkin, Leipzig/DE, M. Brehm, Halle (Saale)/DE
11.25 a.m. **L02.31**	**Large-Scale Fractionation of Colloidal Particles in Centrifugal Fields** A. Wittemann, Konstanz/DE, C. S. Plüisch, Konstanz/DE, R. Stuckert, Konstanz/DE
11.45 a.m. **L02.32**	**Mechanisms of Nucleation and Solid-Solid Phase Transitions in Triblock Janus Assemblies** H. Eslami, Darmstadt/DE, A. Gharibi, Boushehr/IR, F. Müller-Plathe, Darmstadt/DE
12.05 p.m. **L02.33**	**Revealing the surface chemistry on colloidal metallic nanoparticles by advanced ^{13}C and ^{15}N solid-state NMR techniques** T. Gutmann, Darmstadt/DE, N. Rothermel, Darmstadt/DE, V. Klimavičius, Vilnius/LT
12.25 p.m. **L02.34**	**Unbound ligands and entropy induce the bundling of ultrathin nanowires** S. Bettscheider, Saarbrücken/DE, B. Kuttich, Saarbrücken/DE, L. F. Engel, Saarbrücken/DE, L. González-García, Saarbrücken/DE, T. Kraus, Saarbrücken/DE

KEY TOPIC: Multi-Scale Modelling

virtual room S02

Chair:	*Robinson Cortes-Huerto, Mainz*
11.05 a.m. **L01.14**	***Keynote Lecture*** **Combining multiscale simulations with machine learning driven analysis to sample free energy landscapes of biomolecular systems** C. Peter, Konstanz/DE
11.45 a.m. **L01.15**	**Hierarchical atomic-resolution ensembles of disordered proteins and their condensates** L. S. Stelzl, Mainz/DE, L. M. Pietrek, Frankfurt am Main/DE, M. Zweckstetter, Göttingen/DE, G. Hummer, Frankfurt am Main/DE
12.05 p.m. **L01.16**	**Multiscale Modeling of a Drug-Delivery System Component** K. S. Exner, Essen/DE, A. Ivanova, Sofia/BG
12.25 p.m. **L01.17**	**Computational tools for automated rapid screening of fast ionic conductors** S. Adams, Singapore/SG

Theory and Data Science

virtual room S04

Chair:	*Michael Roemelt, Bochum*
11.05 a.m. **L08.01**	**A Fourth Generation High-Dimensional Neural Network Potentials Including Long-Range Charge Transfer** T. W. Ko, Göttingen/DE, J. A. Finkler, Basel/CH, S. Goedecker, Basel/CH, J. Behler, Göttingen/DE
11.25 a.m. **L08.02**	**Applications of machine learning in quantum simulations of hydrogen bond dynamics** A. Yachmenev, Hamburg/DE, Y. Saleh, Hamburg/DE, V. Sanjay, Hamburg/DE, J. Küpper, Hamburg/DE

11.45 a.m.
L08.03
Potential of Electrostatics-Finite Ion Size (PfEFIS) method: towards automatic ion diffusion network analysis in solids
N. E. R. Zimmermann, Hamburg/DE

12.05 p.m.
L08.04
Subsampling the core regions of a molecule in Variational Monte Carlo
J. Feldt, Paris/FR, R. Assaraf, Paris/FR

12.25 p.m.
L08.05
Deterministic quantum mechanics and chemical reactions: The success of the Maxwell-Boltzmann distribution
I. Frank, Hannover/DE

Agnes-Pockels-Session virtual room S05

Chair: *Jannika Lauth, Hannover; Klaus Boldt, Konstanz*

11.05 a.m.
Advanced Diffusion Studies of Active Enzymes and Nanosystems
J.-P. Günther. Stuttgart/DE

11.25 a.m.
From Flipped Molecules to Mid-Infrared Light Harvesting: Understanding the Vibrational Energy Flow Between CO Molecules on NaCl(100)
J. A. Lau, Göttingen/DE

11.45 a.m.
Metalloporphyrins: Revealing their molecular electronic structure and orbital-specific deexcitation processes experimentally
K. Schubert, Hamburg/DE

12.05 p.m.
Playing Minecraft with the „Voltammetric Duck“ - Theory of Cyclic Voltammetry at Macroporous Electrodes
T. Tichter, Berlin/DE

12.25 p.m.
Photodynamics Simulations Assisted by Machine Learning
Julia Westermayr, Wien/AT

Spectroscopy virtual room S06

Chair: *Roger Jan Kutta, Regensburg*

11.05 a.m.
L07.14
Evidence for Directed Electron Transfer in Flavin-modified Oligoprolines
J. Leier, Karlsruhe/DE, S. Wörner, Karlsruhe/DE, M. C. Michenfelder, Karlsruhe/DE, H. - A. Wagenknecht, Karlsruhe/DE, A. - N. Unterreiner, Karlsruhe/DE

11.25 a.m.
L07.15
Nitrogen-Release Pathways of a Carbenonitrene Precursor - Investigated by Matrix Isolation and Ultrafast Spectroscopy
N. Gessner, Regensburg/DE, J. Rowen, Bochum/DE, W. Sander, Bochum/DE, P. Nuernberger, Regensburg/DE

11.45 a.m.
L07.16
Hydrogen bonding in tetrathiatriyarylmethyl alcohol probed by ultrafast mid-infrared spectroscopy
P. Brünker, Bonn/DE , N. Fleck, Bonn/DE, O. Schiemann, Bonn/DE, J. Lindner, Bonn/DE, P. Vöhringer, Bonn/DE

12.05 p.m.
L07.17
Keynote Lecture
Femtosecond to millisecond dynamics of photoactive yellow protein revealed by the vibrational label –SCN
L. J. G. W. van Wilderen, Frankfurt am Main/DE, L. Blankenburg, Frankfurt am Main/DE, J. Bredenbeck, Frankfurt am Main/DE

Wednesday, 12 May 2021, 12:45 – 01:30 p.m.

12.45 p.m. **LUNCH BREAK**

Wednesday, 12 May 2021, 01:30 p.m.

PLENARY LECTURE

Chair: *Christine Peter, Konstanz*

13.30 p.m. **Physics-based machine learning for multiscale computer simulations**
IL5 T. Bereau, Amsterdam/NL

Wednesday, 12 May 2021, 02:20 – 04:00 p.m.

KEY TOPIC: Physical Chemistry of Colloids

virtual room S01

Chair: *Stephan V. Roth, Hamburg*

02.20 p.m. **Invertible Micelles from Double Anionic Block Copolyelectrolytes**
L02.18 K. Huber, Paderborn/DE, N. Carl, Grenoble/FR, S. Prévost, Grenoble/FR, R. Schweins, Grenoble/FR

02.40 p.m. **Influence of alcohol cosurfactants on structure and properties of SDS/PDADMAC PESCs.**
L02.19 O. Kuzminskaya, Berlin/DE, I. Hoffmann, Grenoble/FR, H. Choo, Berlin/DE, E. Benjowsky, Berlin/DE, D. Clemens, Berlin/DE, M. Gradzielski, Berlin/DE

03.00 p.m. **Phase behavior and flow properties of ultra-soft spheres**
L02.20 A. Scotti, Aachen/DE, W. Richtering, Aachen/DE

03.20 p.m. **Structured light-emitting metasurfaces based on confinement self-assembly**
L02.21 O. Aftenieva, Dresden/DE, T. König, Dresden/DE

03.40 p.m. **Probing Tailor-Mate Colloidal 2D Nanomaterials for Innovative Optoelectronics**
L02.22 J. Lauth, Hannover/DE, L. F. Klepzig, Hannover/DE, A. Niebur, Hannover/DE, A. Söll, Hannover/DE, L. Biesterfeld, Hannover/DE, O. Strolka, Hannover/DE, M. Romain, Hannover/DE

KEY TOPIC: Multi-Scale Modelling

virtual room S02

Chair: *Friederike Schmid, Mainz*

02.20 p.m. **Multiscale Reweighted Stochastic Embedding (MRSE): Deep Learning of Collective Variables for Enhanced Sampling**
L01.18 O. Valsson, Mainz/DE, J. Rydzewski, Toruń/PL

02.40 p.m. **Machine Learning in Computational Surface Science and Catalysis: Case Studies on Water and Metal–Oxide Interfaces**
L01.19 J. Paier, Berlin/DE

03.00 p.m.
L01.20
A machine learning potential for nucleotides in water
R. Martina, Mainz/DE, M. Sulpizi, Mainz/DE, A. Ferrarini, Padua/IT

03.20 p.m.
L01.21
Keynote Lecture
Four Generations of Neural Network Potentials
J. Behler, Göttingen/DE

Biophysical Chemistry and Biophotonics

virtual room S03

Chair: *Simone Techert, Hamburg*

02.20 p.m.
L03.01
Keynote Lecture
Time-resolved protein dynamics: Watching an enzyme at work using serial crystallography and photocaged compounds
H. Müller-Werkmeister, Potsdam/DE

03.00 p.m.
L03.02
Do Tyr/Trp redox pathways protect O_2-reducing S. Coelicolor laccase from oxidative damage?
P. Kielb, Potsdam/DE, H. B. Gray, Pasadena/US, J. R. Winkler, Pasadena/US

03.20 p.m.
L03.03
Isotopically Labelling the Anaerobic Pathways of E. coli: On-line Analysis by Advanced FTIR and Raman Spectroscop
G. D. Metcalfe, Sheffield/GB, T. W. Smith, Sheffield/GB, M. Hippler, Sheffield/GB

03.40 p.m.
L03.04
An Azidolipid Monolayer – Transitions, Miscibility, and UV Reactivity studied by Infrared Reflection Absorption Spectroscopy
C. Schwieger, Halle (Saale)/DE, M. Hoffmann, Halle (Saale)/DE, S. Drescher, Heidelberg/DE, C. Ihling, Halle (Saale)/DE, D. Hinderberger, Halle (Saale)/DE

Theory and Data Science

virtual room S04

Chair: *Martin Beyer, Innsbruck*

02.20 p.m.
L08.06
Keynote Lecture
Electronic Factors in the Isomerization of Donor-Acceptor Stenhouse Adducts Revealed by Ab Initio Electronic Structure Theory
M. Roemelt, Bochum/DE , M. Ugandi, Bochum/DE

03.00 p.m.
L08.07
Photochemistry in Bulk and on Surface: Co/MgO Nanocubes with Adsorbed O_2
M. Ončák, Innsbruck/AT, T. Schwab, Salzburg/AT, M. Niedermaier, Salzburg/AT, G. A. Zickler, Salzburg/AT, O. Diwald, Salzburg/AT

03.20 p.m.
L08.08
Do "Salty Chlathrate Hydrates" Exist? – A Theoretical Approach
S. Fritsch, Rostock/DE, D. Paschek, Rostock/DE, R. Ludwig, Rostock/DE

03.40 p.m.
L08.09
When Like-charged Ions Attract: The Influence of Hydroxyl Defects on the Size and Distribution of Cation Clusters in Ionic Liquids
J. Busch, Rostock/DE, J. Neumann, Rostock/DE, T. Niemann, Rostock/DE, D. Paschek, Rostock/DE, R. Ludwig, Rostock/DE, S. Gärtner, Didcot/GB, T. Youngs, Didcot/GB

WEDNESDAY AFTERNOON Parallel Sessions 1

Electrochemistry

virtual room S05

Chair: *Jan Philipp Hofmann, Darmstadt*

02.20 p.m.
L05.01
Charge attachment induced transport – Towards new paradigms in solid state electrochemistry
K. - M. Weitzel, Marburg/DE

02.40 p.m.
L05.02
The Effect of Ionic Defect Interactions on the Hydration of Yttrium-Doped Barium Zirconate
S. Eisele, Aachen/DE, S. Grieshammer, Aachen/DE, F. Draber, Aachen/DE, M. Martin, Aachen/DE

03.00 p.m.
L05.03
Thermodiffusion in doped ceria from molecular dynamics simulations
S. Grieshammer, Aachen/DE, G. E. Murch, Newcastle/AU

03.20 p.m.
L05.04
Charge carrier dynamics in semiconductor-metal hybrid nanostructures
J. Schlenkrich, Hannover/DE , D. Zámbó, Hannover/DE, A. Schlosser, Hannover/DE, M. Rosebrock, Hannover/DE, P. Rusch, Hannover/DE, N. C. Bigall, Hannover/DE

03.40 p.m.
L05.05
Tuning oxygen evolution activity as a function of composition: New mixed iridate-ruthenate layered oxides from $Na_2Ir_{1-x}Ru_yO_3$
N. M. Vargas-Barbosa, Münster/DE , S. Laha, Stuttgart/DE, S. Bette, Stuttgart/DE, R. Dinnebier, Stuttgart/DE, B. V. Lotsch, Stuttgart/DE

Spectroscopy

virtual room S06

Chair: *Ingo Fischer, Würzburg*

02.20 p.m.
L07.18
Real time observation of the photochemically induced formation of a transition metal nitrene complex
T. Unruh, Bonn/DE, H. V. Potthoff, Bonn/DE, J. Lindner, Bonn/DE, P. Vöhringer, Bonn/DE

02.40 p.m.
L07.19
Multi-spectroscopic investigations of the luminescence thermochromism of tetranuclear Cu(I)-complexes
P. Boden, Kaiserslautern/DE, P. Di Martino-Fumo, Kaiserslautern/DE, F. Rehak, Karlsruhe/DE, S. Steiger, Kaiserslautern/DE, J. Busch, Karlsruhe/DE, S. Bräse, Karlsruhe/DE, W. Klopper, Karlsruhe/DE, M. Gerhards, Kaiserslautern/DE

03.00 p.m.
L07.20
High Resolution Spectroscopy of Cyano-oxirane (c-C_2H_3OCN)
K. Keppler, Zürich/CH, S. Albert, Zürich/CH, Z. Chen, Lanzhou/CN, P. Lerch, Villingen/CH, C. Manca Tanner, Zürich/CH, M. Quack, Zürich/CH, J. Stohner, Wädenswil/CH

03.20 p.m.
L07.21
Quarantined (CC-stretched) Formic Acid: Molecular Work-Out in (Self) Isolation
K. A. E. Meyer, Göttingen/DE

03.40 p.m.
L07.22
How ester groups assist in the folding of linear alkyl chains – a combined Raman and quantum chemistry approach
M. Gawrilow, Göttingen/DE, M. Suhm, Göttingen/DE

Wednesday, 12 May 2021, 04:00 – 04:15 p.m.

04.00 p.m. **COFFEE BREAK**

Wednesday, 12 May 2021, 04:15 – 05:35 p.m.

KEY TOPIC: Physical Chemistry of Colloids

virtual room S01

Chair:	*Michael Gradzielski, Berlin*
04.15 p.m. **L02.23**	**Depolarized dynamic light scattering of gold nanorods decorated with thermoresponsive polymer ligands** M. Karg, Düsseldorf/DE
04.35 p.m. **L02.24**	**Active matter – implementing smart functionalities into colloids** J. Simmchen, Dresden/DE, S. Heckel , Dresden/DE, L. Wang, Dresden/DE, L. Niese, Dresden/DE
04.55 p.m. **L02.25**	***Keynote Lecture: Ostwald Prize*** **Progress in understanding wetting phenomena** H. - J. Butt, Mainz/DE

KEY TOPIC: Multi-Scale Modelling

virtual room S02

Chair:	*Dominik Horinek, Regensburg*
04.15 p.m. **L01.22**	**Multiscale Approach to Biomembrane Remodeling by Adsorbates** C. Allolio, Prague/CZ, V. Kubáč, Prague/CZ, D. Harries, Jerusalem/IL
04.35 p.m. **L01.23**	**Adversarial Reverse Mapping of Equilibrated Condensed-Phase Molecular Structures** M. Stieffenhofer, Mainz/DE, M. Wand, Mainz/DE, T. Bereau, Amsterdam/NL
04.55 p.m. **L01.24**	**Transition Between Abnormal and Normal Bipolar Resistive Switching** C. Ader, Aachen/DE, M. Martin, Aachen/DE
05.15 p.m. **L01.25**	**Coarse-grained MD simulations of nanoplastic particles interacting with a non-polar environment in aqueous solution** L. F. Dettmann, Rostock/DE, A. A. Ahmed, Rostock/DE, O. Kühn, Rostock/DE

Biophysical Chemistry and Biophotonics

virtual room S03

Chair:	*Bernd Herzog, Grenzach-Wyhlen*
04.15 p.m. **L03.05**	**Effect of pH on pyruvic acid in bulk and at the air/liquid interface** V. Wank, Wien/AT, J. Cyran, Mainz/DE, M. Bonn, Mainz/DE, E. H. G. Backus, Wien/AT
04.35 p.m. **L03.06**	**Exfoliated Silicate Nanosheets as Novel Near-Infrared Fluorophores for (Bio)Photonics** G. Selvaggio, Bochum/DE, M. Weitzel, Göttingen/DE, N. Oleksiievets, Göttingen/DE, R. Nißler, Bochum/DE, V. Karius, Göttingen/DE, R. Tsukanov, Göttingen/DE, S. Kruss, Bochum/DE
04.55 p.m. **L03.07**	**Electrostatics in Antibacterial Resistance: Active Site Electric Fields as the Basis for Catalysis in TEM β-Lactamases** J. Kozuch, Stanford/US, S. H. Schneider, Stanford/US, S. G. Boxer, Stanford/US
05.15 p.m. **L03.08**	**Quantified Efficiency of Membrane Leakage Events** M. Hoernke, Freiburg i.Br./DE, S. Braun, Freiburg i.Br./DE, S. Shi, Freiburg i.Br./DE

Deutsche
Forschungsgemeinschaft

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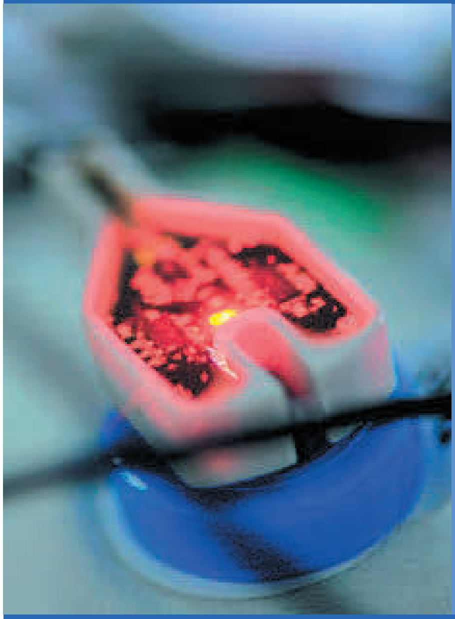

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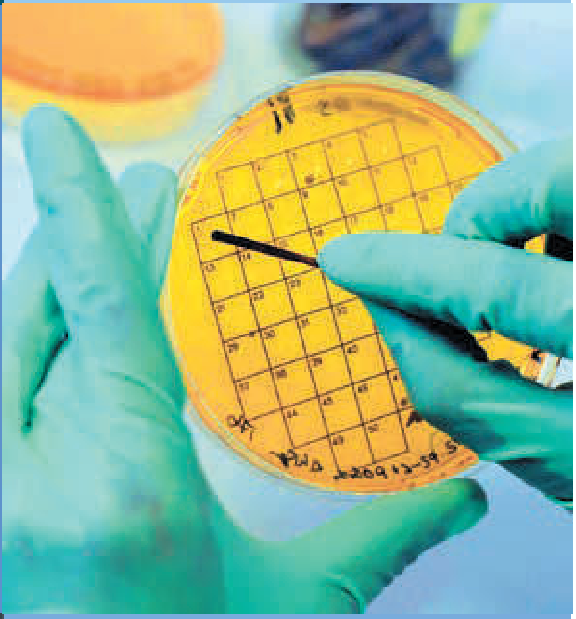

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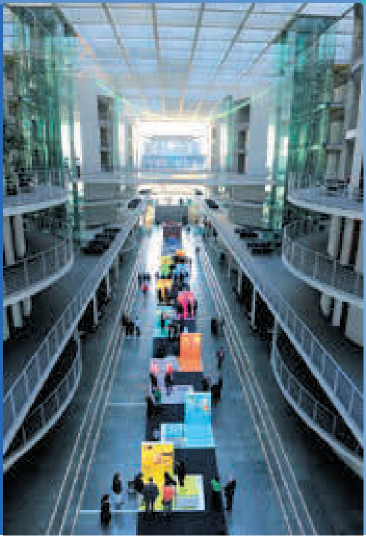

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Theory and Data Science

virtual room S04

Chair: *Jan-Michael Mewes, Bonn*

04.15 p.m.
L08.10
Efficient and Accurate Nonadiabatic Molecular Dynamics Simulations of S_1-S_0 Transitions within Time-Dependent Density Functional Theory
L. D. M. Peters, Munich/DE, J. Kussmann, Munich/DE, C. Ochsenfeld, Munich/DE

04.35 p.m.
L08.11
Importance of the random force for molecular dynamics simulations with electronic friction
N. Hertl, Göttingen/DE, O. Galparsoro, Göttingen/DE, R. Martin-Barrios, Talence/FR, P. Larregaray, Talence/FR, A. Kandratsenka, Göttingen/DE, A. M. Wodtke, Göttingen/DE

04.55 p.m.
L08.12
Development of a Force Field for Cellulose in Aqueous 1-Ethyl-3-methylimidazolium Acetate
E. Roos, Halle (Saale)/DE, D. Sebastiani, Halle (Saale)/DE, M. Brehm, Halle (Saale)/DE

05.15 p.m.
L08.13
Influence of PO_uN_{4-u}-structural units in LIPON on the formation and transport of Li-vacancies: A DFT study
P. Henkel, Gießen/DE, D. Mollenhauer, Gießen/DE

Electrochemistry

virtual room S05

Chair: *Nella Vargas-Barbosa, Jülich*

04.15 p.m.
L05.06
Keynote Lecture
Controlling electrocatalytic selectivity by ionic liquids: Electrooxidation of 2,3-butanediol on Pt(111) electrodes modified by [C_2C_1Im][OTf]
O. Brummel, Erlangen/DE, T. Yang, Shanghai/CN, L. Fromm, Erlangen/DE, Z. Liu, Shanghai/CN, A. Görling, Erlangen/DE, P. Wasserscheid, Erlangen/DE, O. Kasian, Erlangen/DE, J. Libuda, Erlangen/DE

04.55 p.m.
L05.07
Electrodeposition of Sn and Fe-Sn alloys with novel green electrolyte systems
S. Mrkonjić Zajkoska, Hirtenberg/AT, S. Hansal, Hirtenberg/AT, R. Mann, Hirtenberg/AT, W. E. G. Hansal, Hirtenberg/AT, W. Kautek, Wien/AT

05.15 p.m.
L05.08
In-situ high-flux X-ray multiscale network studies for developing the next generation of sustainable photovoltaics with high efficiency
E. Erbes, Hamburg/DE, N. Biswas, Hamburg/DE, K. Goordeyeva, Stockholm/SE, D. Söderberg, Stockholm/SE, S. V. Roth, Hamburg/DE, S. Techert, Hamburg/DE

Spectroscopy

virtual room S06

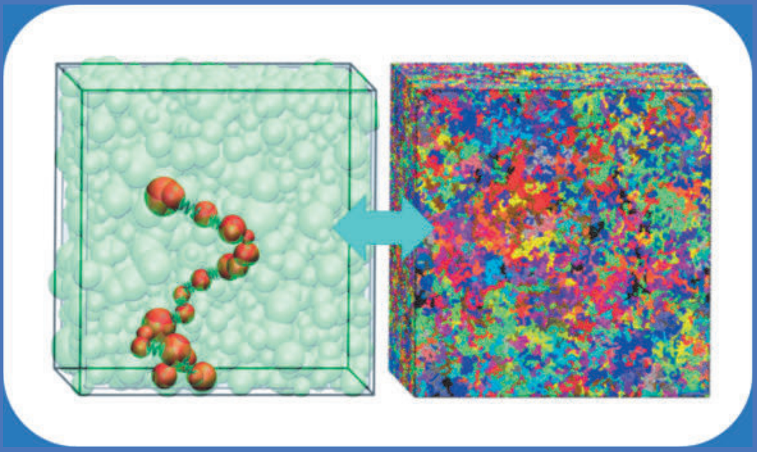
Chair: *Karl-Michael Weitzel, Marburg*

04.15 p.m. **L07.23**	**Following Surface Reactions Along a Flow Channel** P. Ober, Mainz/DE , E. H. G. Backus, Vienna/AT, M. Bonn, Mainz/DE
04.35 p.m. **L07.24**	**Water adsorption at low temperatures on clean and Pt-covered silicon surfaces** D. Moritz, Darmstadt/DE, W. Calvet, Darmstadt/DE, B. Kaiser, Darmstadt/DE, J. P. Hofmann, Darmstadt/DE, W. Jaegermann, Darmstadt/DE
04.55 p.m. **L07.25**	**Influence of the surface ligands on charge-carrier localization and trapping in dot-in-rod nanostructures** M. Wächtler, Jena/DE, B. Liu, Jena/DE, M. Micheel, Jena/DE
05.15 p.m. **L07.26**	**Interfacial Premelting of Ice in Nano Composite Materials** M. M. Mezger, Mainz/DE , H. Li, Stockholm/SE

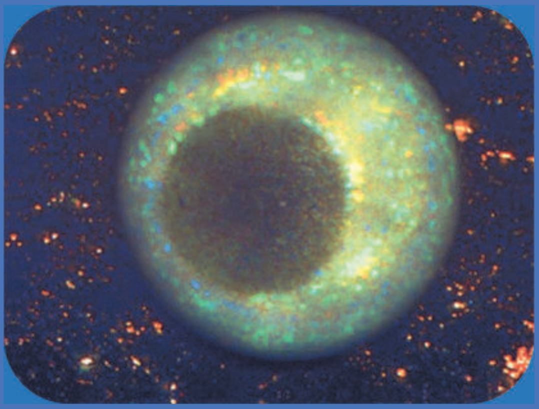
Wednesday, 12 May 2021, 05:40 – 06:00 p.m.

05:40 p.m. **AWARD CEREMONY AND CLOSING SESSION**


Ni
Cu
Pd
Ag
Pt
Au



LECTURES BY TOPIC



INVITED LECTURES: OPENING TALK AND PLENARY TALKS

IL1	**ENTROPY, COLLOIDS AND COVID19** D. Frenkel, Cambridge/Vereinigtes Königreich
IL2	**Physical Chemistry of Drying Droplets** C. Bain, Durham/Vereinigtes Königreich
IL3	**Towards Inverse Design of Soft Materials: Crystals, Quasi Crystals, Liquid Crystals** M. Dijkstra, Utrecht/Niederlande
IL4	**Multicomponent Aerogels from Colloidal Nanocrystals** Nadja C. Bigall, Hannover/Deutschland
IL5	**Physics-based machine learning for multiscale computer simulations** T. Bereau, Amsterdam/Niederlande

KEY TOPIC 01: Multi-Scale Modelling

L01.01 **Force probe simulations using an adaptive resolution scheme**
G. Diezemann, Mainz/Deutschland, M. Oestereich, Mainz/DE, J. Gauss, Mainz/DE

L01.02 **Ion Conductivity Simulations in Nanostructured Materials with First-Principles Resolution**
D. Sebastiani, Halle/Deutschland, C. Dressler, Halle/DE

L01.03 **Atomistic simulations of catalytic confined environments from supramolecular systems to biomass conversion**
G. Piccini, Lugano/Schweiz

L01.04 **MD Simulations with Near MP2 Accuracy - Adsorption in Zeolites**
F. Berger, Berlin/Deutschland, M. Rybicki, Berlin/DE, J. Sauer, Berlin/DE

L01.05 **Conformational changes as driving force for phase recognition**
S. Knippenberg, Hasselt/Belgien, Königreich, S. Osella, Warsaw/PL

L01.06 **Challenges in Biopharmaceutical Development: Modelling at Different Length Scales**
J. Smiatek, Stuttgart/Deutschland

L01.07 **Introducing memory in coarse-grained molecular simulations**
N. F. A. van der Vegt, Darmstadt/Deutschland,

L01.08 **Probability theory of active suspensions**
B. Deußen, Darmstadt/Deutschland, M. Oberlack, Darmstadt/DE, Y. Wang, Darmstadt/DE

L01.09 **Systematic derivation of hydrodynamic equations for viscoelastic phase separation**
B. Dünweg, Mainz/Deutschland, D. Spiller, Mainz/DE, A. Brunk, Mainz/DE, M. Lukacova-Medvidova, Mainz/DE, O. Habrich, Darmstadt/DE, H. Egger, Darmstadt/DE

L01.10 **Iterative integral equation methods for structural coarse-graining**
M. P. Bernhardt, Darmstadt/Deutschland, M. Hanke, Mainz/DE, N. F. A. van der Vegt, Darmstadt/DE

L01.11 **Constructing dynamic density functional theories for inhomogeneous polymer systems from microscopic simulations**
F. Schmid, Mainz/Deutschland, S. Mantha, California/US, S. Qi, Beihang/CN, B. Li, Mainz/DE

L01.12 **Developing and modelling organic membranes for photo-energy conversion**
M. Presselt, Jena/Deutschland,

L01.13 **Consistent representation of structural and dynamical properties from coarse-grained simulation models**
J. F. Rudzinski, Mainz/Deutschland

L01.14 **Combining multiscale simulations with machine learning driven analysis to sample free energy landscapes of biomolecular systems**
C. Peter, Konstanz/Deutschland

L01.15 **Hierarchical atomic-resolution ensembles of disordered proteins and their condensates**
L. S. Stelzl, Mainz/Deutschland, L. M. Pietrek, Frankfurt am Main/DE, M. Zweckstetter, Göttingen/DE, G. Hummer, Frankfurt am Main/DE

L01.16 **Multiscale Modeling of a Drug-Delivery System Component**
K. S. Exner, Essen/Deutschland, A. Ivanova, Sofia/BG

L01.17 **Computational tools for automated rapid screening of fast ionic conductors**
S. Adams, Singapore/Singapur

L01.18 **Multiscale Reweighted Stochastic Embedding (MRSE): Deep Learning of Collective Variables for Enhanced Sampling**
O. Valsson, Mainz/Deutschland, J. Rydzewski, Toruń/PL

L01.19 **Machine Learning in Computational Surface Science and Catalysis: Case Studies on Water and Metal–Oxide Interfaces**
J. Paier, Berlin/Deutschland,

L01.20 **A machine learning potential for nucleotides in water**
R. Martina, Mainz/Deutschland, M. Sulpizi, Mainz/DE, A. Ferrarini, Padua/IT

L01.21 **Four Generations of Neural Network Potentials**
J. Behler, Göttingen/Deutschland

L01.22 **Multiscale Approach to Biomembrane Remodeling by Adsorbates**
C. Allolio, Prague/Tschechische Republik, V. Kubáč, Prague/CZ, D. Harries, Jerusalem/IL

L01.23 **Adversarial Reverse Mapping of Equilibrated Condensed-Phase Molecular Structures**
M. Stieffenhofer, Mainz/Deutschland, M. Wand, Mainz/DE, T. Bereau, Amsterdam/NL

L01.24 **Transition Between Abnormal and Normal Bipolar Resistive Switching**
C. Ader, Aachen/Deutschland, M. Martin, Aachen/DE

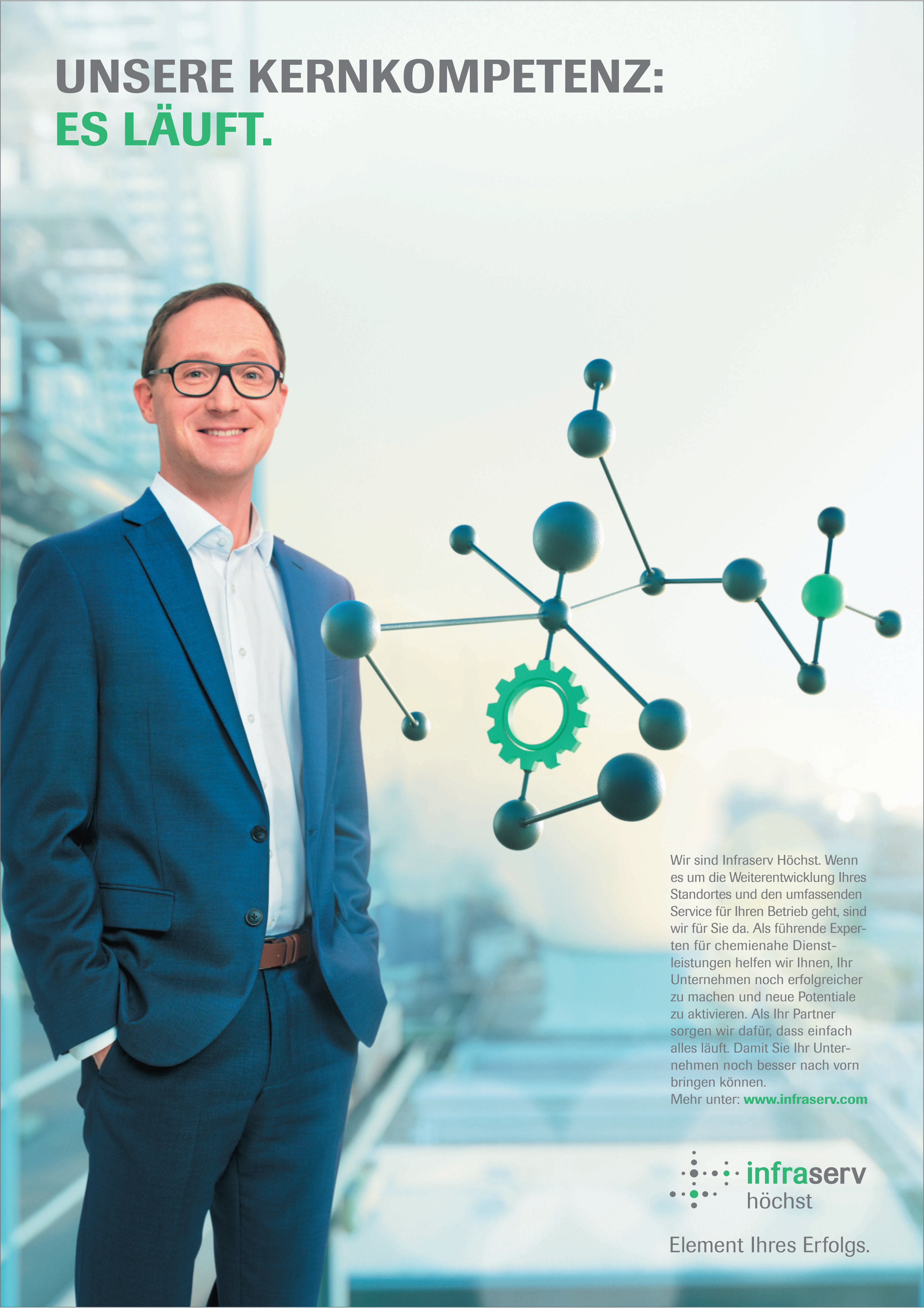
L01.25 **Coarse-grained MD simulations of nanoplastic particles interacting with a non-polar environment in aqueous solution**
L. F. Dettmann, Rostock/Deutschland, A. A. Ahmed, Rostock/DE, O. Kühn, Rostock/DE

L01.26 **Computational Investigation of the Soret Coefficient in the Context of Host/Ligand Binding**
D. Markthaler, Stuttgart/Deutschland, S. Mohankumar, Juelich/DE, S. Wiegand, Juelich/DE, N. Hansen, Stuttgart/DE

L01.27 **An efficient methodology for equilibrating confined and free-standing films of highly entangled polymer melts**
H.-P. Hsu, Mainz/Deutschland, K. Kremer, Mainz/DE

L01.28 **Hybrid simulations of shear-thinning polymer flows**
L. Yelash, Mainz/Deutschland, R. Datta, Mainz/DE, F. Kummer, Darmstadt/DE, M. Oberlack, Darmstadt/DE, M. Lukácová-Medvidová, Mainz/DE, P. Virnau, Mainz/DE

L01.29 **Can Soft Models Describe Polymer Knots?**
K. Daoulas, Mainz/Deutschland, J. Zhang, Mainz/DE, H. Meyer, Strasbourg/FR, P. Virnau, Mainz/DE



KEY TOPIC 02: Physical Chemistry of Colloids

L02.01 **Field Dependence of Magnetic Disorder in Nanoparticles**
S. Disch, Köln/Deutschland, D. Zákutná, Köln/DE, D. Honecker, Luxembourg/LU

L02.02 **Colloidal FeAu core-shell nanoparticles by laser ablation synthesis**
C. Rehbock, Essen/Deutschland, S. Barcikowski, Essen/DE

L02.03 **Functional optical surfaces by colloidal self-assembly**
T. A. F. König, Dresden/Deutschland

L02.04 **Surfactants and polymers active at interfaces: Examples of industrial Colloid and Interface Science**
J. Venzmer, Essen/Deutschland

L02.05 **Luminescent Europium Doped Yttrium Oxide Nano Discs**
J. Petry, Hamburg/Deutschland, R. Komban, Hamburg/DE, C. Gimmler, Hamburg/DE, H. Weller, Hamburg/DE

L02.06 **Solubility of proteins from extended molecular DLVO theory**
M. Kozlowska, Eggenstein-Leopoldshafen/Deutschland, S. Pusara, Eggenstein-Leopoldshafen/DE, W. Wenzel, Eggenstein-Leopoldshafen/DE

L02.07 **Soft quasicrystals optimize sphere packing**
S. Förster, Jülich/Deutschland, M. Dulle, Jülich/DE, T. Jurczyk, Jülich/DE, T. Gruhn, Bayreuth/DE

L02.08 **Assembling Nanocrystals into Hybrid Functional Gel Structures by Means of Multivalent Cations**
D. Zámbó, Hannover/Deutschland, A. Schlosser, Hannover/DE, J. Schlenkrich, Hannover/DE, P. Rusch, Hannover/DE, R. T. Graf, Hannover/DE, F. Lübkemann, Hannover/DE, A. Feldhoff, Hannover/DE, N. C. Bigall, Hannover/DE

L02.09 **Controlling Properties of Nanoparticle-based Networks via their Microstructure**
P. Rusch, Hannover/Deutschland, B. Schremmer, Hannover/DE, N. C. Bigall, Hannover/DE

L02.10 **The micromechanics of shear thickening fluids and their application as protective materials for medical professionals, first responders, atheletes, and astronauts.**
N. Wagner, Newark/USA

L02.11 **Single Nanocrystal Arrays- Preparation and Spectroscopy**
P. Mulvaney, Parkville/Australien

L02.12 **Magic number colloidal clusters**
N. Vogel, Erlangen/Deutschland, J. Wang, Erlangen/DE, C. M. Fru, Erlangen/DE, T. Przybilla, Erlangen/DE, E. Spiecker, Erlangen/DE, M. Engel, Erlangen/DE

L02.13 **The Road Not Taken – Icosahedral or Decahedral Symmetry in Spherical Confinement?**
J. Wang, Erlangen/Deutschland, C. Fru Mbah, Erlangen/DE, S. Englisch, Erlangen/DE, P. Bommineni, Erlangen/DE, E. Spiecker, Erlangen/DE, N. Vogel, Erlangen/DE, M. Engel, Erlangen/DE

L02.14 **Interaction of Bio-Surfactants with Different Lipid Membranes**
T. Hellweg, Bielefeld/Deutschland

L02.15 **Innovative Cleaning Concept with Controlled Foams**
T. Schad, Stuttgart/Deutschland, N. Preisig, Stuttgart/DE, H. Piening, München/DE, D. Blunk, Köln/DE, W. Drenckhan, Strasbourg/FR, C. Stubenrauch, Stuttgart/DE

L02.16 **PNIPAM microgels at the air / water interface – from single interfaces to foams**
M. Kühnhammer, Darmstadt/Deutschland, R. von Klitzing, Darmstadt/DE

L02.17 **Giant vesicles: versatile colloids for unravelling biomembrane properties and for building artificial cells**
R. Dimova, Potsdam/Deutschland

L02.18 **Invertible Micelles from Double Anionic Block Copolyelectrolytes**
K. Huber, Paderborn/Deutschland, N. Carl, Grenoble/FR, S. Prévost, Grenoble/FR, R. Schweins, Grenoble/FR

L02.19 **Influence of alcohol cosurfactants on structure and properties of SDS/PDADMAC PESCs.**
O. Kuzminskaya, Berlin/Deutschland, I. Hoffmann, Grenoble/FR, H. Choo, Berlin/DE, E. Benjowsky, Berlin/DE, D. Clemens, Berlin/DE, M. Gradzielski, Berlin/DE

L02.20 **Phase behavior and flow properties of ultra-soft spheres**
A. Scotti, Aachen/Deutschland, W. Richtering, Aachen/DE

L02.21 **Structured light-emitting metasurfaces based on confinement self-assembly**
O. Aftenieva, Dresden/Deutschland, T. König, Dresden/DE

L02.22 **Probing Tailor-Mate Colloidal 2D Nanomaterials for Innovative Optoelectronics**
J. Lauth, Hannover/Deutschland, L. F. Klepzig, Hannover/DE, A. Niebur, Hannover/DE, A. Söll, Hannover/DE, L. Biesterfeld, Hannover/DE, O. Strolka, Hannover/DE, M. Romain, Hannover/DE

L02.23 **Depolarized dynamic light scattering of gold nanorods decorated with thermoresponsive polymer ligands**
M. Karg, Düsseldorf/Deutschland

L02.24 **Active matter – implementing smart functionalities into colloids**
J. Simmchen, Dresden/Deutschland, S. Heckel , Dresden/DE, L. Wang, Dresden/DE, L. Niese, Dresden/DE

L02.25 **Progress in understanding wetting phenomena**
H. - J. Butt, Mainz/Deutschland

L02.26 **Self-assembling of functionalized hematite nanospindles at the liquid-air interface**
F. A. F. Mees, Cologne/Deutschland, S. Disch, Cologne/DE

L02.27 **Tailoring of pore openings in gelatin-based hydrogel foams**
F. Dehli, Stuttgart/Deutschland, A. Southan, Stuttgart/DE, W. Drenckhan, Straßburg/FR, C. Stubenrauch, Stuttgart/DE

L02.28 **Inkjet Printing: Patterning of 3D Nanoparticle-Based Aerogel-Like Networks for Photoelectrochemical Applications**
F. Lübkemann, Hannover/Deutschland, J. F. Miethe, Hannover/DE, D. Zámbó, Hannover/DE, R. Anselmann, Hanau/DE, P. Rusch, Hannover/DE, A. Schlosser, Hannover/DE, T. Kodanek, Hannover/DE, T. Heinemeyer, Hannover/DE, D. Natke, Hannover/DE, D. Zok, Hannover/DE, D. Dorfs, Hannover/DE, N. C. Bigall, Hannover/DE

L02.29 **Electrochemical Switching of Block Copolymers at the Water-Oil Interface**
Q. Prasser, Freiberg/Deutschland, F. A. Plamper, Freiberg/DE

L02.30 **Cooperative Ion-Solvent Dynamics in Organic Electrolytes Revealed by Diffusion NMR and Molecular Dynamics Simulations**
M. Dvoyashkin, Leipzig/Deutschland, M. Brehm, Halle (Saale)/DE

L02.31 **Large-Scale Fractionation of Colloidal Particles in Centrifugal Fields**
A. Wittemann, Konstanz/Deutschland, C. S. Plüisch, Konstanz/DE, R. Stuckert, Konstanz/DE

L02.32 **Mechanisms of Nucleation and Solid-Solid Phase Transitions in Triblock Janus Assemblies**
H. Eslami, Darmstadt/Deutschland, A. Gharibi, Boushehr/IR, F. Müller-Plathe, Darmstadt/DE

L02.33 **Revealing the surface chemistry on colloidal metallic nanoparticles by advanced 13C and 15N solid-state NMR techniques**
T. Gutmann, Darmstadt/Deutschland, N. Rothermel, Darmstadt/DE, V. Klimavičius, Vilnius/LT

L02.34 **Unbound ligands and entropy induce the bundling of ultrathin nanowires**
S. Bettscheider, Saarbrücken/Deutschland, B. Kuttich, Saarbrücken/DE, L. F. Engel, Saarbrücken/DE, L. González-García, Saarbrücken/DE, T. Kraus, Saarbrücken/DE

TOPIC 03: Biophysical Chemistry and Biophotonics

L03.01 **Time-resolved protein dynamics: Watching an enzyme at work using serial crystallography and photocaged compounds**
H. Müller-Werkmeister, Potsdam - Golm/Deutschland,

L03.02 **Do Tyr/Trp redox pathways protect O_2-reducing S. Coelicolor laccase from oxidative damage?**
P. Kielb, Potsdam/Deutschland, H. B. Gray, Pasadena/USA, J. R. Winkler, Pasadena/USA

L03.03 **Isotopically Labelling the Anaerobic Pathways of E. coli: On-line Analysis by Advanced FTIR and Raman Spectroscopy**
G. D. Metcalfe, Sheffield/Vereinigtes Königreich, T. W. Smith, Sheffield/GB, M. Hippler, Sheffield/GB

L03.04 **An Azidolipid Monolayer – Transitions, Miscibility, and UV Reactivity studied by Infrared Reflection Absorption Spectroscopy**
C. Schwieger, Halle (Saale)/Deutschland, M. Hoffmann, Halle (Saale)/DE, S. Drescher, Heidelberg/DE, C. Ihling, Halle (Saale)/DE, D. Hinderberger, Halle (Saale)/DE

L03.05 **Effect of pH on pyruvic acid in bulk and at the air/liquid interface**
V. Wank, Wien/Österreich, J. Cyran, Mainz/DE, M. Bonn, Mainz/DE, E. H. G. Backus, Wien/AT

L03.06 **Exfoliated Silicate Nanosheets as Novel Near-Infrared Fluorophores for (Bio)Photonics**
G. Selvaggio, Bochum/Deutschland, M. Weitzel, Göttingen/DE, N. Oleksiievets, Göttingen/DE, R. Nißler, Bochum/DE, V. Karius, Göttingen/DE, R. Tsukanov, Göttingen/DE, S. Kruss, Bochum/DE

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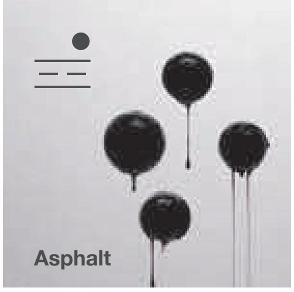
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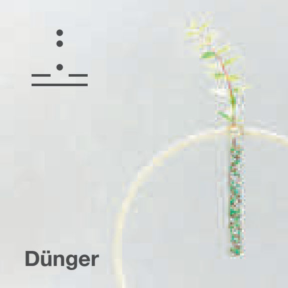
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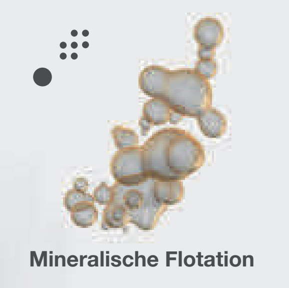
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L03.07 **Electrostatics in Antibacterial Resistance: Active Site Electric Fields as the Basis for Catalysis in TEM β-Lactamases**
J. Kozuch, Stanford/USA, S. H. Schneider, Stanford/USA, S. G. Boxer, Stanford/USA

L03.08 **Quantified Efficiency of Membrane Leakage Events**
M. Hoernke, Freiburg i.Br./Deutschland, S. Braun, Freiburg i.Br./DE, S. Shi, Freiburg i.Br./DE

TOPIC 04: Catalysis

L04.01 **Operando ambient pressure HAXPES studies of Cu/ZnO(10-14) and Cu/ZnO(000-1) model catalysts for methanol synthesis**
H. Noei, Hamburg/Deutschland, R. Gleißner, Hamburg/DE, M. Wagtsaffe, Hamburg/DE, C. Goodwin, Stockholm/SE, M. Soldemo, Stockholm/SE, M. Shipilin, Stockholm/SE, P. Lömker, Hamburg/DE, C. Schlueter, Hamburg/DE, P. Amann, Stockholm/SE, A. Nilsson, Stockholm/SE, A. Stierle, Hamburg/DE

L04.02 **TiO_2 and $BaTiO_3$ nanoparticles: gas phase functionalization and separation of photogenerated charges**
E. Neige, Salzburg/Österreich, T. Schwab, Salzburg/AT, G. Zickler, Salzburg/AT, O. Diwald, Salzburg/AT

L04.03 **Electron Transfer in mixed Oxide-Oxide Model Catalysis: Impact of Ti^{3+} on the (Photo-)Chemistry of Methanol at Tungsten Oxide Clusters deposited on Rutile TiO_2**
L. Mohrhusen, Oldenburg/Deutschland, J. Kräuter, Oldenburg/DE, M. Grebien, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE

L04.04 **Consecutive photoinduced electron transfer (conPET): The mechanism of the photocatalyst rhodamine-6G.**
S. Bergwinkl, Regensburg/Deutschland, F. Brandl, Regensburg/DE, C. Allacher, Regensburg/DE, B. Dick, Regensburg/DE

L04.05 **New insight into the mechanism of CO oxidation and water-gas shift reaction over Au catalysts using operando spectroscopies**
C. Hess, Darmstadt/Deutschland, M. Ziemba, Darmstadt/DE, J. Weyel, Darmstadt/DE

L04.06 **How Does an Ionic Liquid Adsorb on a Pt(111) Surface? A Combined Study by Infrared Reflection Absorption Spectroscopy and Density Functional Theory Calculations**
C. Hohner, Erlangen/Deutschland, G. Fickenscher, Erlangen/DE, L. Fromm, Erlangen/DE, A. Görling, Erlangen/DE, J. Libuda, Erlangen/DE

L04.07 **Ligand-Induced Heterogeneous Catalysis: Selective Hydrogenation of Acrolein on Ligand-Modified Pd(111)**
C. Schröder, Kiel/Deutschland, M. C. Schmidt, Kiel/DE, P. Haugg, Kiel/DE, A. -K. Baumann, Kiel/DE, S. Schauermann, Kiel/DE

TOPIC 05: Electrochemistry

L05.01 **Charge attachment induced transport - Towards new paradigms in solid state electrochemistry**
K. - M. Weitzel, Marburg/Deutschland

L05.02 **The Effect of Ionic Defect Interactions on the Hydration of Yttrium-Doped Barium Zirconate**
S. Eisele, Aachen/Deutschland, S. Grieshammer, Aachen/DE, F. Draber, Aachen/DE, M. Martin, Aachen/DE

L05.03 **Thermodiffusion in doped ceria from molecular dynamics simulations**
S. Grieshammer, Aachen/Deutschland, G. E. Murch, Newcastle/AU

L05.04 **Charge carrier dynamics in semiconductor-metal hybrid nanostructures**
J. Schlenkrich, Hannover/Deutschland, D. Zámbó, Hannover/DE, A. Schlosser, Hannover/DE, M. Rosebrock, Hannover/DE, P. Rusch, Hannover/DE, N. C. Bigall, Hannover/DE

L05.05 **Tuning oxygen evolution activity as a function of composition: New mixed iridate-ruthenate layered oxides from Na2Ir1-xRuyO3**
N. M. Vargas-Barbosa, Münster/Deutschland, S. Laha, Stuttgart/DE, S. Bette, Stuttgart/DE, R. Dinnebier, Stuttgart/DE, B. V. Lotsch, Stuttgart/DE

L05.06 **Controlling electrocatalytic selectivity by ionic liquids: Electrooxidation of 2,3-butanediol on Pt(111) electrodes modified by [C2C1Im][OTf]**
O. Brummel, Erlangen/Deutschland, T. Yang, Shanghai/CN, L. Fromm, Erlangen/DE, Z. Liu, Shanghai/CN, A. Görling, Erlangen/DE, P. Wasserscheid, Erlangen/DE, O. Kasian, Erlangen/DE, J. Libuda, Erlangen/DE

L05.07 **Electrodeposition of Sn and Fe-Sn alloys with novel green electrolyte systems**
S. Mrkonjić Zajkoska, Hirtenberg/Österreich, S. Hansal, Hirtenberg/AT, R. Mann, Hirtenberg/AT, W. E. G. Hansal, Hirtenberg/AT, W. Kautek, Wien/AT

L05.08 **In-situ high-flux X-ray multiscale network studies for developing the next generation of sustainable photovoltaics with high efficiency**
E. Erbes, Hamburg/Deutschland, N. Biswas, Hamburg/DE, K. Goordeyeva, Stockholm/SE, D. Söderberg, Stockholm/SE, S. V. Roth, Hamburg/DE, S. Techert, Hamburg/DE

TOPIC 06: Reaction Kinetics and Dynamics

L06.01 **Hydrogen-Bonded Ion Pair in Excited-State Proton Transfer**
A. Grandjean, Saarbrücken/Deutschland, J. L. Pérez Lustres, Berlin/DE, S. Muth, Regensburg/DE, D. Maus, Saarbrücken/DE, G. Jung, Saarbrücken/DE

L06.02 **Monitoring the photochemistry of a formazan over 12 orders of magnitude in time**
S. Wortmann, Regensburg/Deutschland, R. J. Kutta, Regensburg/DE, P. Nuernberger, Regensburg/DE

L06.03 **Unraveling the photo-induced dynamics of N^6,N^6-dimethyladenine by time-resolved spectroscopy and ab initio calculations**
R. Holtmann, Kiel/Deutschland, V. Lukaszczuk, Kiel/DE, F. Temps, Kiel/DE

L06.04 **Why substitution matters - temperature dependency of excited states of Ru(II) complexes**
M.-A. Schmid, Braunschweig/Deutschland, R. Nau, Ulm/DE, S. Amthor, Ulm/DE, S. Rau, Ulm/DE, S. Tschierlei, Braunschweig/DE

L06.05 **Estimating the Octane Number via a 2-Zone-Cylinder-Model**
S. Schlichting, Stuttgart/Deutschland, T. Methling, Stuttgart/DE, C. Janzer, Stuttgart/DE, U. Riedel, Cottbus/DE, M. Köhler, Stuttgart/DE

L06.06 **Nucleation enhancement of weakly-bound species: A molecular love story of CO2 and Toluene**
J. Krohn, Zürich/Schweiz, C. Li, Shanghai/CN, M. Lippe, Zürich/CH, R. Signorell, Zürich/CH

L06.07 **Acceleration of Mannich reaction in electrospray droplets**
M. Zühlke, Potsdam/Deutschland, J. A. Koenig, Potsdam/DE, C. Prüfert, Potsdam/DE, D. Riebe, Potsdam/DE, T. Beitz, Potsdam/DE, H.-G. Löhmannsröben, Potsdam/DE

L06.08 **Mechanisms for Regioselective Synthesis of Anisotropic Nano-Heterostructures**
D. Fischli, Konstanz/Deutschland, F. Enders, Konstanz/DE, S. Sutter, Konstanz/DE, R. Köser, Konstanz/DE, S. Monter, Konstanz/DE, K. Boldt, Konstanz/DE

L06.09 **Observation and Mechanism of N2 Cleavage by a Tantalum Cluster under Cryo Conditions**
D. V. Fries, Kaiserslautern/Deutschland, M. P. Klein, Kaiserslautern/DE, A. Steiner, Kaiserslautern/DE, M. H. Prosenc, Kaiserslautern/DE, G. Niedner-Schatteburg, Kaiserslautern/DE

L06.10 **Mechanistic Studies on a Deracemization Reaction via a Triplet 1,3-Diradical Induced by Energy Transfer from a Chiral Sensitizer**
R. J. Kutta, Regensburg/Deutschland, X. Li, München/DE, C. Jandl, München/DE, A. Bauer, München/DE, T. Bach, München/DE, P. Nuernberger, Regensburg/DE

L06.11 **Temperature-dependent trapping probability measurements of n-butane on ionic liquid surfaces using molecular beam techniques**
L. Winter, Erlangen/Deutschland, R. G. Bhuin, Erlangen/DE, M. Lexow, Erlangen/DE, F. Maier, Erlangen/DE, H.-P. Steinrück, Erlangen/DE

L06.12 **An experimentally validated neural-network potential energy surface for H-atom on free-standing graphene in full dimensionality**
S. Wille, Göttingen/Deutschland, H. Jiang, Göttingen/DE, O. Bünermann, Göttingen/DE, A. M. Wodtke, Göttingen/DE, J. Behler, Göttingen/DE, A. Kandratsenka, Göttingen/DE

L06.13 **Physico-chemical exploration of pioneering photography and electroplating reproduction around 1840**
W. Kautek, Wien/Österreich, V. Ljubić Tobisch, Wien/AT

TOPIC 07: Spectroscopy

L07.01 **Rotational and translational motion in ionic liquids by means of high field and field cycling NMR relaxometry**
A. Strate, Rostock/Deutschland, N. Nübler, Rostock/DE, L. Kuban, Rostock/DE, T. van Alphen, Rostock/DE, R. Ludwig, Rostock/DE

L07.02 **Microwave Study of Mono-Cholorobenzaldehydes**
M. M. Dohmen, Göttingen/Deutschland, S. Arnold, Hartsville/US, J. Garrett, Hartsville/US, P. Pinacho, Hamburg/DE, M. Schnell, Hamburg/DE, G. Brown, Hartsville/US, D. A. Obenchain, Göttingen/DE

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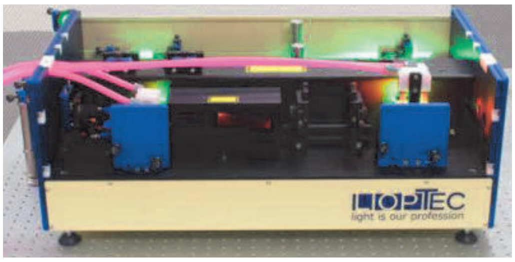

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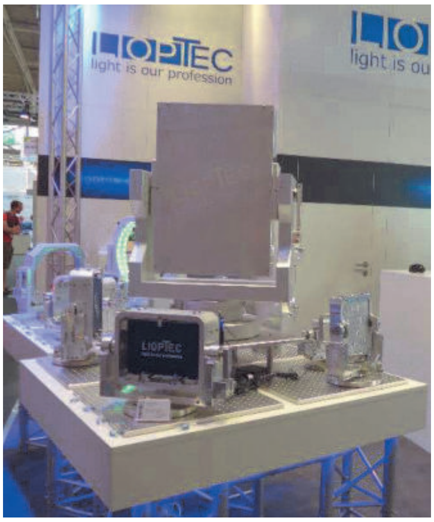

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L07.03 **Docking preference and geometry of 1-naphthol complexes revealed by rotational spectroscopy**
D. A. Obenchain, Göttingen/Deutschland, M. M. Quesada-Moreno, Hamburg/DE, R. T. Saragi, Valladolid/ES, A. Lesarri, Valladolid/ES, M. Schnell, Hamburg/DE

L07.04 **Stark-spectroscopic investigations of large organic molecules and their clusters with water in superfluid helium nanodroplets**
J. Fischer, Regensburg/Deutschland, F. Schlaghaufer, Regensburg/DE, A. Slenczka, Regensburg/DE

L07.05 **Infrared Spectroscopy of $CO_3^{\bullet-}(H_2O)_{1,2}$ and $CO_4^{\bullet-}(H_2O)_{1,2}$**
C. van der Linde, Innsbruck/Österreich, M. G. Münst, Innsbruck/AT, M. Ončák, Innsbruck/AT, M. K. Beyer, Innsbruck/AT

L07.06 **Optical Spectrum of the Adamantane Radical Cation**
P. B. Crandall, Berlin/Deutschland, D. Müller , Berlin/DE, M. Förstel, Berlin/DE, J. Leroux, Berlin/DE, O. Dopfer, Berlin/DE

L07.07 **Photoelectron spectroscopy of BH2 using synchrotron radiation and photoelectron/photoion coincidence (i2PEPICO) spectroscopy**
D. P. Mukhopadhyay, Würzburg/Deutschland, D. Schleier, Würzburg/DE, I. Fischer, Würzburg/DE, J. -C. Loison, Bordeaux/FR, C. Alcaraz, Paris/FR, G .A. Garcia, Paris/FR

L07.08 **Heteronuclear long-range Rydberg molecules**
M. Peper, Leipzig/Deutschland, J. Deiglmayr, Leipzig/DE

L07.09 **Cryogenic Vibrational Spectroscopy – A Tool for Understanding Mechanisms in Organic Chemistry**
K. Greis, Berlin/Deutschland, C. Kirschbaum, Berlin/DE, S. Leichnitz, Potsdam/DE, G. von Helden, Berlin/DE, P. H. Seeberger, Potsdam/DE, K. Pagel, Berlin/DE

L07.10 **2D hierarchical nanosheets with integrated Co-based HER-catalysts: An X-ray photoelectron and tip-enhanced Raman spectroscopy study**
M. Küllmer, Jena/Deutschland, M. Richard-Lacroix, Jena/DE, C. Tontsch, Ulm/DE, M. von Delius, Ulm/DE, V. Deckert, Jena/DE, A. Turchanin, Jena/DE

L07.11 **Surface properties of dendritic fibrous silica nanoparticles studied by wide-angle soft X-ray scattering**
F. Gerke, Berlin/Deutschland, B. Langer, Berlin/DE, B. Wassermann, Berlin/DE, A. Maity, Mumbai/IN, V. Polshettiwar, Mumbai/IN, E. Rühl, Berlin/DE

L07.12 **Femtosecond energy transfer in Fe(II)-Co(III) photocatalyst directly observed with X-ray emission spectroscopy**
T.-K. Choi, Schenefeld/Deutschland, M. Huber-Gedert, Paderborn/DE, M. Nowakowski, Paderborn/DE, A. Kertmen, Poznań/PL, J. Kubicki, Poznań/PL, M. Bauer, Paderborn/DE, W. Gawelda, Madrid/ES

L07.13 **Dinuclear Ir(III) Complex Exhibiting Unusually Slow Phosphorescence and Intersystem Crossing**
R. Czerwieniec, Regensburg/Deutschland, M. Z. Shafikov, Regensburg/DE

L07.14 **Evidence for Directed Electron Transfer in Flavin-modified Oligoprolines**
J. Leier, Karlsruhe/Deutschland, S. Wörner, Karlsruhe/DE, M. C. Michenfelder, Karlsruhe/DE, H. - A. Wagenknecht, Karlsruhe/DE, A. - N. Unterreiner, Karlsruhe/DE

L07.15 **Nitrogen-Release Pathways of a Carbenonitrene Precursor - Investigated by Matrix Isolation and Ultrafast Spectroscopy**
N. Gessner, Regensburg/Deutschland, J. Rowen, Bochum/DE, W. Sander, Bochum/DE, P. Nuernberger, Regensburg/DE

L07.16 **Hydrogen bonding in tetrathiatriyarylmethyl alcohol probed by ultrafast mid-infrared spectroscopy**
P. Brünker, Bonn/Deutschland, N. Fleck, Bonn/DE, O. Schiemann, Bonn/DE, J. Lindner, Bonn/DE, P. Vöhringer, Bonn/DE

L07.17 **Femtosecond to millisecond dynamics of photoactive yellow protein revealed by the vibrational label –SCN**
L. J. G. W. van Wilderen, Frankfurt am Main/Deutschland, L. Blankenburg, Frankfurt am Main/DE, J. Bredenbeck, Frankfurt am Main/DE

L07.18 **Real time observation of the photochemically induced formation of a transition metal nitrene complex**
T. Unruh, Bonn/Deutschland, H. V. Potthoff, Bonn/DE, J. Lindner, Bonn/DE, P. Vöhringer, Bonn/DE

L07.19 **Multi-spectroscopic investigations of the luminescence thermochromism of tetranuclear Cu(I)-complexes**
P. Boden, Kaiserslautern/Deutschland, P. Di Martino-Fumo, Kaiserslautern/DE, F. Rehak, Karlsruhe/DE, S. Steiger, Kaiserslautern/DE, J. Busch, Karlsruhe/DE, S. Bräse, Karlsruhe/DE, W. Klopper, Karlsruhe/DE, M. Gerhards, Kaiserslautern/DE

L07.20 **High Resolution Spectroscopy of Cyano-oxirane (c-C2H3OCN)**
K. Keppler, Zürich/Schweiz, S. Albert, Zürich/CH, Z. Chen, Lanzhou/CN, P. Lerch, Villingen/CH, C. Manca Tanner, Zürich/CH, M. Quack, Zürich/CH, J. Stohner, Wädenswil/CH

L07.21 **Quarantined (CC-stretched) Formic Acid: Molecular Work-Out in (Self) Isolation**
K. A. E. Meyer, Göttingen/Deutschland,

L07.22 **How ester groups assist in the folding of linear alkyl chains – a combined Raman and quantum chemistry approach**
M. Gawrilow, Göttingen/Deutschland, M. Suhm, Göttingen/DE

L07.23 **Following Surface Reactions Along a Flow Channel**
P. Ober, Mainz/Deutschland, E. H. G. Backus, Vienna/AT, M. Bonn, Mainz/DE

L07.24 **Water adsorption at low temperatures on clean and Pt-covered silicon surfaces**
D. Moritz, Darmstadt/Deutschland, W. Calvet, Darmstadt/DE, B. Kaiser, Darmstadt/DE, J. P. Hofmann, Darmstadt/DE, W. Jaegermann, Darmstadt/DE

L07.25 **Influence of the surface ligands on charge-carrier localization and trapping in dot-in-rod nanostructures**
M. Wächtler, Jena/Deutschland, B. Liu, Jena/DE, M. Micheel, Jena/DE

L07.26 **Interfacial Premelting of Ice in Nano Composite Materials**
M. M. Mezger, Mainz/Deutschland, H. Li, Stockholm/SE

TOPIC 08: Theory and Data Science

L08.01 **A Fourth Generation High-Dimensional Neural Network Potentials Including Long-Range Charge Transfer**
T. W. Ko, Göttingen/Deutschland, J. A. Finkler, Basel/CH, S. Goedecker, Basel/CH, J. Behler, Göttingen/DE

L08.02 **Applications of machine learning in quantum simulations of hydrogen bond dynamics**
A. Yachmenev, Hamburg/Deutschland, Y. Saleh, Hamburg/DE, V. Sanjay, Hamburg/DE, J. Küpper, Hamburg/DE

L08.03 **Potential of Electrostatics-Finite Ion Size (PfEFIS) method: towards automatic ion diffusion network analysis in solids**
N. E. R. Zimmermann, Hamburg/Deutschland,

L08.04 **Subsampling the core regions of a molecule in Variational Monte Carlo**
J. Feldt, Paris/Frankreich, R. Assaraf, Paris/FR

L08.05 **Deterministic quantum mechanics and chemical reactions: The success of the Maxwell-Boltzmann distribution**
I. Frank, Hannover/Deutschland,

L08.06 **Electronic Factors in the Isomerization of Donor-Acceptor Stenhouse Adducts Revealed by Ab Initio Electronic Structure Theory**
M. Roemelt, Bochum/Deutschland, M. Ugandi, Bochum/DE

L08.07 **Photochemistry in Bulk and on Surface: Co/MgO Nanocubes with Adsorbed O2**
M. Ončák, Innsbruck/Österreich, T. Schwab, Salzburg/AT, M. Niedermaier, Salzburg/AT, G. A. Zickler, Salzburg/AT, O. Diwald, Salzburg/AT

L08.08 **Do “Salty Chlathrate Hydrates” Exist?- A Theoretical Approach**
S. Fritsch, Rostock/Deutschland, D. Paschek, Rostock/DE, R. Ludwig, Rostock/DE

L08.09 **When Like-charged Ions Attract: The Influence of Hydroxyl Defects on the Size and Distribution of Cation Clusters in Ionic Liquids**
J. Busch, Rostock/Deutschland, J. Neumann, Rostock/DE, T. Niemann, Rostock/DE, D. Paschek, Rostock/DE, R. Ludwig, Rostock/DE, S. Gärtner, Didcot/GB, T. Youngs, Didcot/GB

L08.10 **Efficient and Accurate Nonadiabatic Molecular Dynamics Simulations of S1-S0 Transitions within Time-Dependent Density Functional Theory**
L. D. M. Peters, Munich/Deutschland, J. Kussmann, Munich/DE, C. Ochsenfeld, Munich/DE

L08.11 **Importance of the random force for molecular dynamics simulationswith electronic friction.**
N. Hertl, Göttingen/Deutschland, O. Galparsoro, Göttingen/DE, R. Martin-Barrios, Talence/FR, P. Larregaray, Talence/FR, A. Kandratsenka, Göttingen/DE, A. M. Wodtke, Göttingen/DE

L08.12 **Development of a Force Field for Cellulose in Aqueous 1-Ethyl-3-methylimidazolium Acetate**
E. Roos, Halle (Saale)/Deutschland, D. Sebastiani, Halle (Saale)/DE, M. Brehm, Halle (Saale)/DE

L08.13 **Influence of POuN4-u-structural units in LIPON on the formation and transport of Li-vacancies: A DFT study**
P. Henkel, Gießen/Deutschland, D. Mollenhauer, Gießen/DE


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TOPIC 09: Thermodynamics

L09.01 **Liquid Thermodynamics from First Principles: Accurate Gibbs Energies Through Integration of Scaled DFT Forces**
J. -M. Mewes, Bonn/Deutschland

L09.02 **Role and activity of Fe3+ and In3+ impurities on coarsening and functional properties in MgO nanoparticle derived ceramics**
K. Aicher, Salzburg/Österreich, T. Schwab, Salzburg/AT, M. Niedermaier, Salzburg/AT, G. Zickler, Salzburg/AT, M. Reissner, Wien/AT, O. Diwald, Salzburg/AT

L09.03 **Polyelectrolyte conformation and dynamics in solution measured by rheology and pulsed field gradient NMR**
C. G. Lopez, Aachen/Deutschland, W. Richtering, Aachen/DE, J. Linders, Essen/DE, C. Mayer, Essen/DE

L09.04 **Molecular self-assembly and boronate ester synthesis at the liquid-solid interface, a STM study**
N. Herrmann, Leuven/Belgien, N. Bilbao, Leuven/BE, K. S. Mali, Leuven/BE, X. Feng, Dresden/DE, S. De Feyter, Leuven/BE

TOPIC 10: Transport and Storage

L10.01 **Carbon Nanomembranes from Alkanethiol Monolayers**
R. Dalpke, Bielefeld/Deutschland, N. Biere, Bielefeld/DE, D. Emmrich, Bielefeld/DE, F. Paneff, Bielefeld/DE, D. Naberezhnyi, Bielefeld/DE, I. Ennen, Bielefeld/DE, M. Westphal, Bielefeld/DE, A. Beyer, Bielefeld/DE, P. Dementyev, Bielefeld/DE, A. Hütten, Bielefeld/DE, D. Anselmetti, Bielefeld/DE, A. Gölzhäuser, Bielefeld/DE

L10.02 **Investigation of a redox mass for rechargeable oxide batteries: $(Fe_{1-x}Mn_x)_yO_z$ with a $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ scaffold**
D. Görtz, Aachen/Deutschland, M. Schroeder, Aachen/DE

L10.03 **The Intrinsic Structural Resistance of a Grain Boundary to Transverse Ionic Conduction**
A. R. Genreith-Schriever, Cambridge/Vereinigtes Königreich

L10.04 **Discrete Modeling of Space Charge Zones in Solids**
C. Xiao, Stuttgart/Deutschland, C. C. Chen, Stuttgart/DE, R. Usiskin, Stuttgart/DE, J. Maier, Stuttgart/DE

L10.05 **The effect of long-range order on charge transport in self-assembled nanocrystal and nanocluster superlattices**
A. Maier, Tübingen/Deutschland, N. Mukharamova, Hamburg/DE, I. Vartanyants, Hamburg/DE, F. Fetzer, Tübingen/DE, M. Hodas, Tübingen/DE, O. Geladari, Tübingen/DE, P. Frech, Tübingen/DE, K. Braun, Tübingen/DE, M. Fleischer, Tübingen/DE, F. Schreiber, Tübingen/DE, A. Schnepf, Tübingen/DE, M. Scheele, Tübingen/DE, D. Lapkin, Hamburg/DE, N. Mukharamova, Hamburg/DE, I. Vartanyants, Hamburg/DE

L10.06 **Combined experimental and theoretical study of Li(1-x)FePO4 as a function of the state of lithiation**
J. Schepp, Marburg/Deutschland, L. Janin, Marburg/DE, S. Adams, Singapore/SG, K.-M. Weitzel, Marburg/DE

L10.07 **Cation Exchange Reactions on Semiconductor Nanoparticle Gel Networks**
S. Getschmann, Hannover/Deutschland, F. Lübkemann, Hannover/DE, P. Rusch, Hannover/DE, B. Schremmer, Hannover/DE, M. Rosebrock, Hannover/DE, D. Müller, Hannover/DE, N. C. Bigall, Hannover/DE

TOPIC 11: Award Winners Tuesday, 11 May 2021, 02:20 – 04:00 p.m. virtual room S05

L11.01 *Ewald-Wicke-Preis 2021*
On the Optimum Binding Energy in Electrocatalysis
K. S. Exner, Essen/Deutschland

Paul-Bunge-Preis 2020
The History of Science is Thriving
S. Werrett, London/GB

L11.02 *Nernst-Haber-Bodenstein-Preis 2021*
Photo-responsive conduction in nanoporous crystalline thin films
L. Heinke, Karlsruhe/Deutschland

Paul-Bunge-Preis 2021
Studying Scientific Instruments Today
L. C. Taub, Cambridge/GB

L11.03 **The Deutsche Forschungsgemeinschaft (DFG):**
Funding Opportunities for Early Career Researchers
W. Wachter, Deutsche Forschungsgemeinschaft

TOPIC 12: yPC Forum Wednesday, 12 May 2021, 09:20 – 10:40 a.m. virtual room S05

L12 **Chancengleichheit und Diversity in der Wissenschaft**

Vereinbarkeit von Karriere und Familie
Prof. Dr. Stefanie Dehnen, Philipps Universität Marburg

Karriere in der Chemie mit Behinderung
Dr. Lukas Guggolz, Philipps Universität Marburg

Gender Equality in der Wissenschaft
Dr. Lisa Pecher, Wiley-VCH, Weinheim

mit anschließender Podiumsdiskussion

TOPIC 13: Agnes Pockels-Session Wed., 12 May, 11:05 – 12:45 p.m. virtual room S05

Advanced Diffusion Studies of Active Enzymes and Nanosystems
J.-P. Günther. Stuttgart/DE

From Flipped Molecules to Mid-Infrared Light Harvesting: Understanding the Vibrational Energy Flow Between CO Molecules on NaCl(100)
J. A. Lau, Göttingen/DE

Me**talloporphyrins: Revealing their molecular electronic structure and orbital-specific deexcitation processes experimentally**
K. Schubert, Hamburg/DE

Playing Minecraft with the „Voltammetric Duck“ - Theory of Cyclic Voltammetry at Macroporous Electrodes
T. Tichter, Berlin/DE

Photodynamics Simulations Assisted by Machine Learning
Julia Westermayr, Wien/AT

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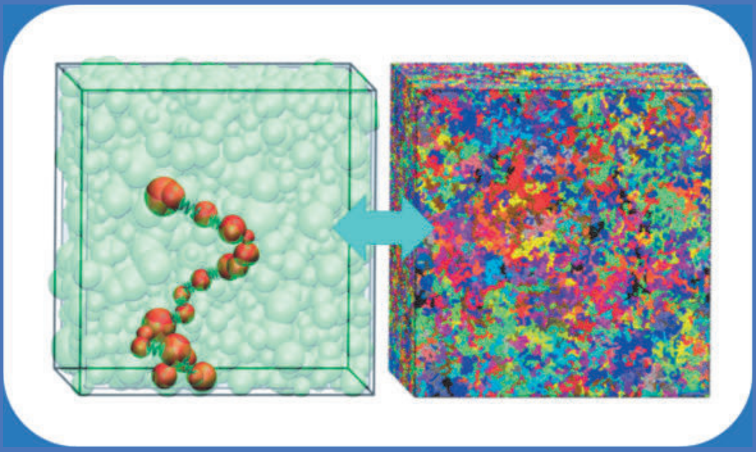

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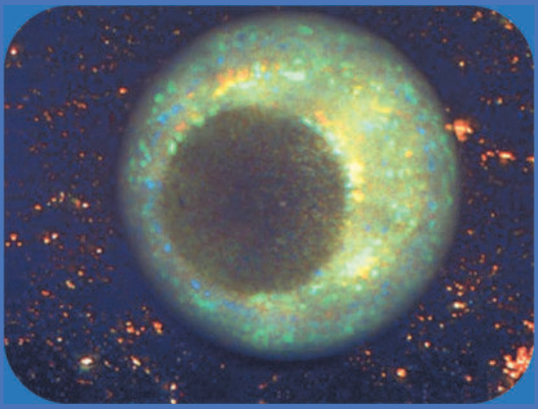


KEY TOPIC 01: Multi-Scale Modelling

P01.01	**Gas-phase charge distribution of nanoparticles generated by IR-MALDI** C. Prüfert, Potsdam/Deutschland, T. Beitz, Potsdam/DE, H.-G. Löhmannsröben, Potsdam/DE
P01.02	**Interpretable Embeddings from Molecular Simulations using Gaussian Mixture Variational Autoencoders** Y. Bozkurt Varolgünes, Mainz/Deutschland, T. Bereau, Amsterdam/NL, J. F. Rudzinski, Mainz/DE
P01.03	**Data driven characterization of Free Energy Landscapes for syndiotactic Polystyrene** A. Banerjee, Mainz/Deutschland
P01.04	**Effect of Steric Hindrance on the Self-Assembly of Crystallized Polymer Bundles** F. Tomazic, Erlangen/Deutschland, M. Engel, Erlangen/DE
P01.05	**Near-infrared plasmon-exciton interactions in colloidal nanostructures** N. Metzkow, Dresden/Deutschland, H. Decker, Dresden/DE, A. Eychmüller, Dresden/DE, V. Lesnyak, Dresden/DE
P01.06	**Quantifying soft degrees of freedom in volatile organic compounds: insight from quantum chemistry and focused single molecule experiments** R. Dahmani, Tunis/Tunesien, H. Sun, Aachen/DE, H. Mouhib, Marne-la-Vallée/FR
P01.07	**Ionic Liquids As A Fluoride Ion Source** A. Gaur, Bengaluru/Indien, N. V. S. Avula, Bangalore/IN, S. Balasubramanian, Bangalore/IN
P01.08	**Backbone modification via deamidation: An unconventional route to the thermostability of enzyme** S. Das, Bangalore/Indien, A. Dongre, Bangalore/IN, A. Bellure, Bangalore/IN, S. Kumar, Bangalore/IN, A. Chandra, Bangalore/IN, T. Karmakar, Bangalore/IN, P. Balaram, Bangalore/IN, S. Balasubramanian, Bangalore/IN, H. Balaram, Bangalore/IN
P01.09	**Thermodynamic Driving Forces of Guest Confinement in a Photoswitchable Cage** S. Juber, Bochum/Deutschland, S. Wingbermühle, Bochum/DE, P. Nuernberger, Regensburg/DE, G. Clever, Dortmund/DE, L. Schäfer, Bochum/DE
P01.10	**Theoretical structure modelling of molecular clustermaterials considering small model systems** S. Schwan, Giessen/Deutschland, D. Mollenhauer, Giessen/DE
P01.11	**Ab initio study of migration in NASICON NaZr2(PO4)3** J. Schuett, Aachen/Deutschland, S. Neitzel-Grieshammer, Aachen/DE
P01.12	**Mesoscopic Simulations of Crystallinity in Polymers: Partially Ordered Morphologies** E. L. Wood, Mainz/Deutschland, C. Greco, Mainz/DE, K. Kremer, Mainz/DE, K. Ch. Daoulas, Mainz/DE
P01.13	**From Oxidation States to Phase Transitions: Predictions of High-Dimensional Neural Networks** M. Eckhoff, Göttingen/Deutschland, K. N. Lausch, Göttingen/DE, P. E. Blöchl, Clausthal/DE, J. Behler, Göttingen/DE

P01.14 **Multi-Scale Modelling Approach for the Emulsion Polymerization Process of Styrene**
K. Brandl, Clausthal-Zellerfeld/Deutschland, M. Drache, Clausthal-Zellerfeld/DE, S. Beuermann, Clausthal-Zellerfeld/DE

P01.15 **Solubility predictor of Hepatitis B (HBV) virus core proteins as a function of C-terminal length**
S. Pusara, Eggenstein-Leopoldshafen/Deutschland, M. Kozlowska, Eggenstein-Leopoldshafen/DE, W. Wenzel, Eggenstein-Leopoldshafen/DE

P01.16 **Computer simulations on the molecular origin of shear thinning in poymer melts**
R. Datta, Mainz/Deutschland, F. Schmid, Mainz/DE, M. Lukacova, Mainz/DE, P. Virnau, Mainz/DE

P01.18 **Molecular dynamics simulation of surfactant−stabilized hexadecane−water interface upon cooling**
S. Tsibranska, Sofia/Bulgarien, A. Ivanova, Sofia/BG, S. Tcholakova, Sofia/BG, N. Denkov, Sofia/BG

P01.19 **MODELLING ROTATOR PHASES OF ALKANE-CONTAINING SYSTEMS**
S. Iliev, Sofia/Bulgarien, A. Ivanova, Sofia/BG, S. Tcholakova, Sofia/BG, N. Denkov, Sofia/BG

P01.21 **INTRODUCING MEMORY IN COARSE-GRAINED MOLECULAR SIMULATIONS**
V. Klippenstein, Darmstadt/Deutschland, N. F. A. van der Vegt, Darmstadt/DE

P01.22 **Combined experimental-simulation study of the role of pH in the synthesis and growth of gold nanoparticles using L-Asparagine**
L. A. Baptista, Mainz/Deutschland, R. Baez-Cruz, Mainz/DE, S. Ntim, Mainz/DE, P. Manidurai, Concepcion/CL, S. Espinoza, Prague/CZ, C. Ramanan, Mainz/DE, R. Cortes-Huerto, Mainz/DE, M. Sulpizi, Mainz/DE

P01.23 **Effects of shear flow on metal-confined ionic liquid**
S. Ntim, Mainz/Deutschland, M. Sulpizi, Mainz/DE

KEY TOPIC 02: Physical Chemistry of Colloids

P02.01 **Magnetic deflection of neutral sodium-doped ammonia clusters**
J. Barnes, Zurich/Schweiz, M. Beck, Zurich/CH, B. L. Yoder, Zurich/CH, S. Hartweg, Zurich/CH, R. Signorell, Zurich/CH, A. Luski, Rehovot/IL, E. Narevicius, Rehovot/IL, J. Narevicius, Rehovot/IL

P02.02 **Influence of nanoparticle fillers on the molecular mobility in ionic-liquid-based gel polymer electrolytes**
C. Schmidt, Paderborn/Deutschland, W. Keil, Paderborn/DE, M. Siebrecht, Paderborn/DE, M. K. Vyas, Delhi/IN, A. Chandra, Delhi/IN

P02.03 **Separation of Small Diameter SWCNTs in 1 – 3 Steps with Aqueous Two Phase Extraction**
B. S. Flavel, Karlsruhe/Deutschland, H. Li, Karlsruhe/DE, G. Gordeev, Berlin/DE, S. Reich, Berlin/DE, O. Garrity, Berlin/DE

P02.05 **Analysis of the Sedimentation Behavior of Colloidal Semiconductor**
E. Peters, Konstanz/Deutschland, K. Boldt, Konstanz/DE

P02.06 **Influence of Mg-doping in ZnO Photoanodes on their Characteristics in Dye-Sensitized Solar Cells**
A. Ringleb, Giessen/Deutschland, R. Ruess, Giessen/DE, N. Hofeditz, Marburg/DE, W. Heimbrodt, Marburg/DE, T. Yoshida, Yonezawa/JP, D. Schlettwein, Giessen/DE

P02.07 **Stimuli-Responsive Behavior of PNiPAm Microgels under Interfacial Confinement**
J. Harrer, Erlangen/Deutschland, M. Rey, Erlangen/DE, S. Ciarella, Eindhoven/NL, H. Löwen, Düsseldorf/DE, L. Janssen, Eindhoven/NL, N. Vogel, Erlangen/DE

P02.08 **Influence of Polymer Additives During Spin-Coating of WO3 Thin Films on their Spectroelectrochemical Performance**
T. H. Q. Nguyen, Giessen/Deutschland, F. Eberheim, Giessen/DE, S. Göbel, Giessen/DE, L. Gümbel, Giessen/DE, P. Cop, Giessen/DE, M. Eckert, Giessen/DE, T. P. Schneider, Giessen/DE, B. M. Smarsly, Giessen/DE, D. Schlettwein, Giessen/DE

P02.09 **Radiation damage and protection in microsolvated biomolecules**
M. Johny, Hamburg/Deutschland, S. Trippel, Hamburg/DE, J. Küpper, Hamburg/DE

P02.10 **Synthesis and structure formation of colloidal dumbbells**
R. Stuckert, Konstanz/Deutschland, A. Wittemann, Konstanz/DE

P02.11 **Synthesis and Characterisation of NIR photoluminsecent Aerogels**
D. Pluta, Hannover/Deutschland, P. Rusch, Hannover/DE, D. Zámbó, Hannover/DE, F. Lübkemann, Hannover/DE, D. Dorfs, Hannover/DE, N. C. Bigall, Hannover/DE

P02.12 **Foam-Analogue Nanostructure of a Water-Rich L3-Phase**
P. Menold, Stuttgart/Deutschland, N. Preisig, Stuttgart/DE, C. Stubenrauch, Stuttgart/DE, R. Strey, Köln/DE

P02.13 **Composition Dependent Optical Properties of Cu-Zn-In-Se Nanocrystals Synthesized via Cation Exchange**
A. Bora, Dresden/Deutschland, J. F. L Lox, Dresden/DE, N. Weiß, Dresden/DE, N. Gaponik, Dresden/DE, V. Lesnyak, Dresden/DE

P02.14 **Mechanosynthesis of polymer-stabilized lead bromide perovskites: insight into the formation and phase conversion of nanoparticles**
G. Jiang, Dresden/Deutschland, O. Erdem, Ankara/TR, H. V. Demir, Ankara/TR, N. Gaponik, Dresden/DE

P02.15 **Spectroscopic Investigation of the Electron Transfer between Inorganic Semiconductor Nanoparticles and Redoxactive Organic Molecules**
M. Micheel, Jena/Deutschland, M. Wächtler, Jena/DE

P02.16 **Microscopic modeling of entropic effects in protein transport through membrane proteins and in colloid-polymer solutions**
M. Castellano, Freiburg/Deutschland, T. Koslowski, Freiburg/DE

P02.17 **Structure and rheology of wormlike micelles**
B. von Lospichl, Berlin/Deutschland, H. Winter, Amherst/US, L. Noirez, Saclay/FR, N. Martin, Saclay/FR, M. Gradzielski, Berlin/DE

P02.18 **Delayed settling and sedimentation of bidisperse polymer suspensions in aqueous polymer solutions**
T. Sobisch, Berlin/Deutschland, D. Lerche, Berlin/DE, U. Schuldt, Berlin/DE

P02.19 **Quantitative Determination of Polymer Grafting Density on Colloidal Particles by Energy-Filtered Transmission Electron Microscopy**
S. Vazirieh Lenjani, Dresden/Deutschland, C. Rossner, Dresden/DE

P02.20 **The aggregation behaviour of hydrophobically modified thermo-responsive block-polymers in solution**
A. Prause, Berlin/Deutschland, M. Hechenbichler, Potsdam/DE, B. von Lospichl, Berlin/DE, A. Laschewsky, Potsdam/DE, M. Gradzielski, Berlin/DE

P02.21 **Synthesis and Characterization of Gold Nanocubes: An Investigation on Organic Ligand Exchange**
I. Maack, Oldenburg/Deutschland, M. Osmić, Oldenburg/DE, L. Mohrhusen, Oldenburg/DE, P. Buhani, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE

P02.22 **Investigation of the Influence of High-Energy Laser Pulses on Colloidally Dispersed Nanoparticles**
D. Kranz, Hannover/Deutschland, F. Lübkemann, Hannover/DE, R. Himstedt, Hannover/DE, D. Dorfs, Hannover/DE

P02.23 **Investigation of Colloidal Nanoparticles with Metal-Insulator Transition**
P. Bessel, Hannover/Deutschland, R. Himstedt, Hannover/DE, P. Rusch, Hannover/DE, D. Dorfs, Hannover/DE

P02.24 **Sensing with chirality pure near infrared fluorescent carbon nanotubes**
R. Nißler, Göttingen/Deutschland, L. Kurth, Göttingen/DE, H. Li, Karlsruhe/DE, A. Spreinat, Göttingen/DE, I. Kuhlemann, Göttingen/DE, B. Flavel, Karlsruhe/DE, S. Kruss, Göttingen/DE

P02.25 **Phase transitions in interfacial assemblies of microgels**
M. Rey, Edinburgh/Vereinigtes Königreich

P02.26 **Perfluorocarbons suppress efficiently coalescence in foams**
K. Steck, Strasbourg/Frankreich, P. Kekicheff, Strasbourg/FR, P. Muller, Strasbourg/FR, S. Andrieux, Strasbourg/FR, C. Stubenrauch, Stuttgart/DE, W. Drenckhan, Strasbourg/FR

P02.27 **Drainage and Stability of Solidifying Hydrogel Films**
S. Andrieux, Strasbourg/Frankreich, M. Patil, Strasbourg/FR, R. Bollache, Strasbourg/FR, A. Hourlier-Fargette, Strasbourg/FR, W. Drenckhan, Strasbourg/FR

P02.28 **2D assembly of CdSe nanoplatelets for application in electronic devices**
H. Decker, Dresden/Deutschland, V. Lesnyak, Dresden/DE, A. Eychmüller, Dresden/DE, N. Metzkow, Dresden/DE

P02.29 **NADES-based Surfactant-Free Microemulsions for Solubilization and Extraction of Curcumin from Curcuma Longa**
V. Huber, Regensburg/Deutschland, L. Muller, Regensburg/DE, P. Degot, Regensburg/DE, D. Touraud, Regensburg/DE, W. Kunz, Regensburg/DE

P02.30 **An aqueous route for the synthesis of In_2O_3 aerogels**
F. Thibaud, Dresden/Deutschland, L. Thoni, Dresden/DE, A. Eychmüller, Dresden/DE

P02.31 **Core-shell latexes for tailored wetting properties**
S. V. Roth, Hamburg/Deutschland, C. J. Brett, Hamburg/DE, J. Engström, Stockholm/SE, V. Körstgens, München/DE, P. Müller-Buschbaum, München/DE, E. Malmström, Stockholm/SE

P02.32 **Annealing of polymer colloids on CNF**
C. Harder, Hamburg/Deutschland, M. Betker, Hamburg/DE, A. E. Alexakis, Stockholm/SE, C. J. Brett, Hamburg/DE, A. Chumakov, Hamburg/DE, M. Gensch, Hamburg/DE, M. Schwartzkopf, Hamburg/DE, L. D. Söderberg, Stockholm/SE, E. Malmström, Stockholm/SE, P. Müller-Buschbaum, Garching/DE, S. V. Roth, Hamburg/DE

P02.33 **Ionic Liquids $[M^{3+}][A^{-}]_3$ with three-valent cations and their possible use to easily separate rare earth metals**
M. Rothe, Regensburg/Deutschland, M. Tress, Leipzig/DE, W. Kunz, Regensburg/DE

P02.34 **Influence of aromatic additives on the phase transition behaviour of thermoresponsive Poly(N-isopropylacrylamide) microgels with different cross-linker densities**
D. Schlattmann, Münster/Deutschland,

P02.35 **Photoelectrochemical investigation of CdSe/CdS core/shell nanoparticles and their three-dimensional assembly**
J. G. Eckert, Hannover/Deutschland, A. Schlosser, Hannover/DE, F. Lübkemann, Hannover/DE, B. Schremmer, Hannover/DE, C. Wesemann, Hannover/DE, R. Graf, Hannover/DE, P. Rusch, Hannover/DE, D. Dorfs, Hannover/DE, N. C. Bigall, Hannover/DE

P02.36 **New Insights in Sunscreen UV-Absorber Solubility - Crystallization Kinetics and Synergistic Effects in Oil Mixtures**
Bernd Herzog, Grenzach-Wyhlen/Deutschland, Ansgar Schäfer, Ludwigshafen/DE, Myriam Sohn, Grenzach-Wyhlen/DE, Jochen Giesinger, Grenzach-Wyhlen/DE

P02.37 **Insights into the Synthesis of Colloidal 2D PbSe Nanoplatelets with Tuneable Optoelectronic Properties**
L. Biesterfeld, Hanover/Deutschland, L. F. Klepzig, Hanover/DE, M. Romain, Hanover/DE, A. Schlosser, Hanover/DE, A. Niebur, Hanover/DE, J. Hübner, Hanover/DE, J. Lauth, Hanover/DE

P02.38 **Investigating the surface charge of microplastic particles with Colloidal Probe-Atomic Force Microscopy**
T. Witzmann, Dresden/Deutschland, A. Fery, Dresden/DE

P02.39 **Colloidal 2D PbSe Nanoplatelets with Tuneable Photoluminescence and High Quantum Yield**
L. F. Klepzig, Hannover/Deutschland, L. Biesterfeld, Hannover/DE, M. Romain, Hannover/DE, A. Schlosser, Hannover/DE, N. C. Bigall, Hannover/DE, J. Hübner, Hannover/DE, J. Lauth, Hannover/DE

P02.40 **Structural and Thermodynamic Characterisation of Nonionic Surfactants Systematically Modified by CO2 Incorporation in their Head Group**
R. Marschall, Berlin/Deutschland, M. Gradzielski, Berlin/DE, V. J. Spiering, Berlin/DE

P02.41 **Colloidal synthesis methods for ultrathin metallic and semiconducting 2D MoS_2 and WS_2 nanosheets**
A. Niebur, Hannover/Deutschland, A. Söll, Hannover/DE, O. Strolka, Hannover/DE, A. Hannebauer, Hannover/DE, D. Hennig, Hannover/DE, L. Harms, Oldenburg/DE, A. Schlosser, Hannover/DE, A. Frauendorf, Hannover/DE, A. Feldhoff, Hannover/DE, J. Hübner, Hannover/DE, J. Lauth, Hannover/DE

P02.42 **Adsorption of Proteins from Human Saliva to Self-Assembled Monolayers Varying in Charge and Wettability**
R. Müller, Regensburg/Deutschland, J. Lehnfeld, Regensburg/DE, S. Ruhl, Buffalo, NY/USA

P02.43 **Cellulose model surfaces as an approach to study the interaction between fibers and additives in paper**
C. Lux, Darmstadt/Deutschland, T. Tilger, Darmstadt/DE, O. Soltwedel, Darmstadt/DE, R. von Klitzing , Darmstadt/DE

P02.44 **Designing Pickering Emulsions for Hydroformylation: From nanoscale particles over microscale droplets to macroscale processes**
S. Stock, Darmstadt/Deutschland, A. Schlander, Darmstadt/DE, M. Kempin, Berlin/DE, K. Spanheimer, Berlin/DE, A. Weber, Berlin/DE, R. Schomäcker, Berlin/DE, A. Drews, Berlin/DE, M. Gallei, Saarbrücken/DE, R. von Klitzing, Darmstadt/DE

P02.45 **Experimental and theoretical investigations of $CuInS_2$ - carbon nanotube composites**
D. Voigt, Steinfurt/Deutschland, M. Bredol, Steinfurt/DE

P02.46 **Composite Formation of Gold Nanoparticles and Polymer Brushes**
P. Ritzert, Darmstadt/Deutschland, R. von Klitzing, Darmstadt/DE

P02.47 **Quantum dot layers for high-order harmonic generation**
R. Baruah, Jena/Deutschland, H. N. Gopalakrishna, Jena/DE, V. Korolev, Jena/DE, J. Hniopek, Jena/DE, M. Schmitt, Jena/DE, J. Popp, Jena/DE, D. Kartashov, Jena/DE, M. Wächtler, Jena/DE

P02.48 **Examination of the growth mechanism of Sb_2S_3 nanoparticles via hot-injection method**
M. Joschko, Darmstadt/Deutschland, F. Y. Fotue Wafo, Darmstadt/DE, C. Gille, Darmstadt/DE, D. Kisić, Belgrade/RS, I. L. Validžić, Belgrade/RS, C. Graf, Darmstadt/DE

TOPIC 03: Biophysical Chemistry and Biophotonics

P03.01 **Quantum Chemical Analysis of Nitrate Doped Sodium Chloride Clusters and Comparison with Experimental Absorption Cross Sections**
L. Grünewald, Innsbruck/Österreich, N. K. Bersenkowitsch, Innsbruck/AT, C. van der Linde, Innsbruck/AT, M. K. Beyer, Innsbruck/AT, M. Ončák, Innsbruck/AT

P03.02 **Morphology of Regular and Irregular Hydrogel using X-ray Scattering Method**
N. Biswas, Hamburg/Deutschland, M. Osterhoff, Göttingen/DE, J. Soltau, Göttingen/DE, S. C. Ng, Göttingen/DE, D. Görlich, Göttingen/DE, S. Techert, Hamburg/DE

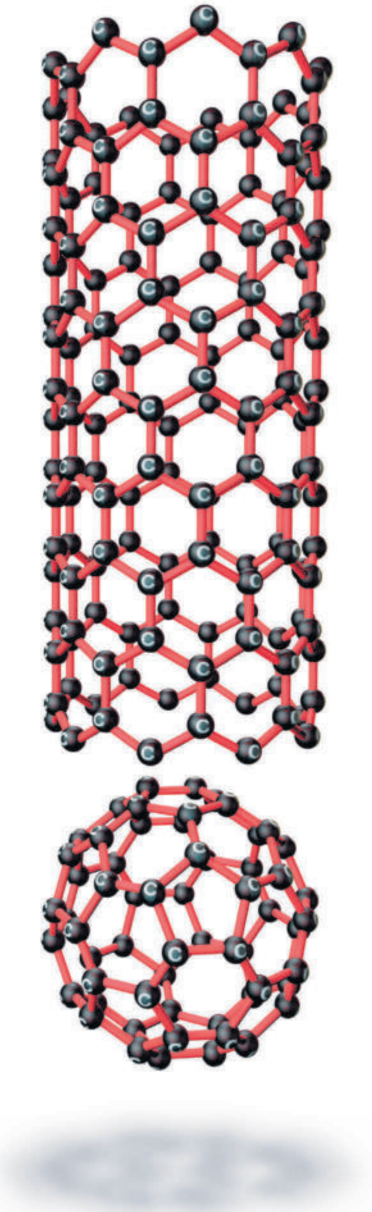
P03.03 **How Hofmeister series influence the thermodiffusion of potassium salts in water?**
S. Mohanakumar, Jülich/Deutschland, J. Luettmer-Strathmann, Ohio/US, S. Wiegand, Jülich/DE

P03.04 **Creating and controlling cryogenically-cooled beams of shock-frozen, isolated, biological and artificial nanoparticles**
A. Samanta, Hamburg/Deutschland, A. Estillore, Hamburg/DE, M. Amin, Hamburg/DE, L. Worbs, Hamburg/DE, J. Lübke, Hamburg/DE, N. Roth, Hamburg/DE, J. Küpper, Hamburg/DE

P03.05 **Selection and control of (bio)nanoparticles with electric fields**
J. Lübke, Hamburg/Deutschland, L. Worbs, Hamburg/DE, N. Roth, Hamburg/DE, A. Estillore, Hamburg/DE, A. K. Samanta, Hamburg/DE, J. Küpper, Hamburg/DE

P03.06 **Albumin Displacement at the Air/Water Interface by Polysorbate**
P. Garidel, Halle/Biberach/Deutschland, M. Rabe, Düsseldorf/DE, A. Kerth, Halle/Saale/DE, A. Blume, Halle/Saale/DE

P03.07 **Switchable Nanostructures of piezoelectric Polyamide 11**
M. La Rosa, Oldenburg/Deutschland, K. Al-Shamery, Oldenburg/DE



P03.08 **Colors in nature: a Science Project Day in High Schools**
E. Deniz, Oldenburg/Deutschland, M. La Rosa, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE

P03.09 **Polysorbate photooxidation and the impact on protein stability**
E. Hipper, Halle (Saale)/Deutschland, W. Kaiser, Biberach an der Riß/DE, D. Hinderberger, Halle (Saale)/DE, P. Garidel, Halle (Saale)/DE

P03.10 **Conformation and orientation of LKα14 in water/ethanol mixtures**
R. Gudbrandsdottir, Regensburg/Deutschland, D. Horinek, Regensburg/DE

P03.11 **ATP-peptide interactions studied by MD**
T.-M. Do, Regensburg/Deutschland, D. Horinek, Regensburg/DE

P03.12 **Remote near infrared identification of pathogens with multiplexed nanosensors**
R. Nißler, Göttingen/Deutschland, O. Bader, Göttingen/DE, M. Dohmen, Göttingen/DE, S. G. Walter, Köln/DE, C. Noll, Göttingen/DE, G. Selvaggio, Göttingen/DE, U. Groß, Göttingen/DE, S. Kruss, Göttingen/DE

P03.14 **Crystalline materials based on novel T. maritima encapsulin variants**
M. Rütten, Hamburg/Deutschland, T. Beck, Hamburg/DE

P03.16 **Development of thermophoretic µ-device for measuring Soret coefficient**
N. Lee, Juelich/Deutschland, S. Wiegand, Juelich/DE

P03.17 **CNF thin films as sustainable carrier material and their role in layered systems**
M. Betker, Hamburg/Deutschland, C. Harder, Hamburg/DE, M. Gensch, Hamburg/DE, M. Schwartzkopf, Hamburg/DE, C. Brett, Stockholm/SE, A. Chumakov, Hamburg/DE, Q. Chen, Hamburg/DE, L. D. Söderberg, Stockholm/SE, S. V. Roth, Hamburg/DE

P03.18 **Silver nanospheres and nanostars for surface-enhanced Raman spectroscopy in the biosciences**
M. Aldoghaim, Sheffield/Vereinigtes Königreich, M. Hippler, Sheffield/GB

P03.19 **Long-path FTIR and CERS Raman Analysis of Volatiles Produced in the Respiration and Fermentation of Bananas**
M. Alrasheedi, Sheffield/Vereinigtes Königreich, M. Hippler, Sheffield/GB

P03.20 **An Atomistic View of Solvent-Free Protein Liquids: The Case of Lipase A**
S. Behera, Bangalore/Indien, S. Das, Bangalore/IN, S. Balasubramanian, Bangalore/IN

P03.21 **Low-energy electron interactions with 5-aminoimidazole-4-carboxamide**
J. Pereirda da Silva, Caparica/Portugal, K. Ebel, Potsdam/DE, J. Olszewski, Potsdam/DE, J. Glatzel, Potsdam/DE, F. Ferreira da Silva, Caparica/PT, I. Bald, Potsdam/DE

P03.22 **Testing the Limitations of MD Force Fields for the Quantification of Local Electric Fields Using the Vibrational Stark Effect in Solution: Penicillin G as a Test Case**
J. Kozuch, Stanford/USA, S. H. Schneider, Stanford/USA, C. Zheng, Stanford/USA, Z. Ji, Stanford/USA, R. T. Bradshaw, London/GB, S. G. Boxer, Stanford/USA

TOPIC 04: Catalysis

P04.01 **InPd/Indiumoxide Aerogels for Methanol Steam Reforming**
L. Thoni, Dresden/Deutschland, N. Köwitsch, Chemnitz/DE, A. Eychmüller, Dresden/DE, M. Armbrüster, Chemnitz/DE

P04.02 **Nanoparticle substrate interactions: thermal treatment of gold nanoparticle arrays on different silicon-based substrates.**
A. Nagel, Potsdam/Deutschland, C. Pacholski, Potsdam/DE

P04.03 **The effect of atomic steps and oxygen coverage on the desorption rates of NH_3 and NO from Pd(111) surface**
S. Hoerandl, Goettingen/Deutschland, D. Borodin, Goettingen/DE, J. Fingerhut, Goettingen/DE, M. Schwarzer, Goettingen/DE, T. N. Kitsopoulos, Goettingen/DE, A. M. Wodtke, Goettingen/DE

P04.04 **Catalytic performance studies of Amine-stabilzed and Ligand-free Platinum Nanoparticles supported on Titania**
N. Brinkmann, Oldenburg/Deutschland, M. Siemer, Oldenburg/DE, J. Kräuter, Oldenburg/DE, A. Damps, Oldenburg/DE, F. Rößner, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE

P04.05 **Generating defects in titania under ambient pressure and UHV for (photo-)catalysis**
M. Grebien, Oldenburg/Deutschland, L. Mohrhusen, Oldenburg/DE, J. Kräuter, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE

P04.06 **Desorption of Alcohols from Rutile TiO_2 – Comparative Testing of Analysis Methods for Thermal Desorption Spectroscopy**
N. Kruse, Oldenburg/Deutschland, L. Mohrhusen, Oldenburg/DE, M. Osmic, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE

P04.07 **Selective Oxygen Functionalization of the h-BN/Rh(111) Nanomesh**
E. M. Freiberger, Erlangen/Deutschland, F. Späth, Erlangen/DE, F. Düll, Erlangen/DE, P. Bachmann, Erlangen/DE, U. Bauer, Erlangen/DE, J. Steinhauer, Erlangen/DE, H.-P. Steinrück, Erlangen/DE, C. Papp, Erlangen/DE

P04.08 **Reactivity and Passivation of Fe Nanoclusters on h-BN/Rh(111)**
N. J. Waleska, Erlangen/Deutschland, F. Düll, Erlangen/DE, P. Bachmann, Erlangen/DE, F. Hemauer, Erlangen/DE, J. Steinhauer, Erlangen/DE, H. - P. Steinrück, Erlangen/DE, C. Papp, Erlangen/DE

P04.09 **Keto-enol tautomerization as a first step in hydrogenation of carbonyl compounds**
M. C. Schmidt, Kiel/Deutschland, S. Attia, Kiel/DE, A. Baumann, Kiel/DE, C. Schröder, Kiel/DE, S. Schauermann, Kiel/DE

P04.10 **Influence of Lewis acidity of promoting metal oxides on the gas-phase hydrogenation of nitrobenzene**
N. H. Mohrbach, Bochum/Deutschland, J. Schulwitz, Bochum/DE, S. Lechler, Bochum/DE, P. Schwiderowski, Bochum/DE, W. Xia, Bochum/DE, B. Peng, Bochum/DE, M. Muhler, Bochum/DE

P04.11 **Model catalysis with SCILLs: How does the ionic liquid layer change adsorption, desorption and surface reaction?**
R. Eschenbacher, Erlangen/Deutschland, C. Schuschke, Erlangen/DE, D. Blaumeiser, Erlangen/DE, S. Schötz, Erlangen/DE, T. Bauer, Erlangen/DE, J. Libuda, Erlangen/DE

P04.12 **Operando Fischer-Tropsch synthesis on Fe_3O_4(111) using HAXPES**
H. Noei, Hamburg/Deutschland, M. Wagstaffe, M. Creutzburg, Hamburg/DE, P. Amann, Stockholm/SE, C. Goodwin, Stockholm/SE, M. Soldemo, Stockholm/SE, M. Shipilin, Stockholm/SE, P. Lömker, Hamburg/DE, C. Schlueter, Hamburg/DE, S. Kulkarni, T. F. Keller, A. Nilsson, Stockholm/SE, G. Vonbun-Feldbauer, Hamburg/DE, Andreas Stierle, Hamburg/DE

P04.13 **Water at the interface with the photocatalyst Strontium Titanate**
M. Buessler, Wien/Österreich, S. Maruyama, Tohoku/JP, H. Onishi, Kobe/JP, S. Sunsh, Mainz/DE, E. H. G. Backus, Wien/AT

P04.14 **Reactivity of Molybdenum Sulfide Clusters**
J. C. Hartmann, Natters/Österreich, M. Plattner, Innsbruck/AT, M. Ončák , Innsbruck/AT, A. Baloglou, Innsbruck/AT, C. van der Linde, Innsbruck/AT, M. K. Beyer, Innsbruck/AT

P04.16 **Atomically defined model electrocatalysts: Morphological and Chemical Analysis of Pt/Co_3O_4**
L. Fusek, Prague/Tschechische Republik, M. Kastenmeier, Erlangen/DE, M. Ronovský, Prague/CZ, T. Skála, Prague/CZ, N. Tsud, Prague/CZ, J. Mysliveček, Prague/CZ, V. Johánek, Prague/CZ, Y. Lykhach, Erlangen/DE, O. Brummel, Erlangen/DE, J. Libuda, Erlangen/DE

TOPIC 05: Electrochemistry

P05.01 **Tuneable Distance of Nanoplatelets in Semiconductor Nanoplatelet/Polymer Hybrid Structures**
R. T. Graf, Hannover/Deutschland, A. Schlosser, Hannover/DE, P. Rusch, Hannover/DE, D. Zambó, Hannover/DE, N. C. Bigall, Hannover/DE

P05.02 **Role of Li Adsorption and Intercalation in the MoS2 Catalyzed Hydrogen Evolution Reaction**
J. P. Hofmann, Darmstadt/Deutschland, L. Wu, Eindhoven/NL, N. Y. Dzade, Utrecht/NL, N. H. De Leeuw, Utrecht/NL, E. J. M. Hensen, Eindhoven/NL

P05.03 **Modeling Aqueous Zinc-Ion Batteries: The Influence of Electrolyte Speciation on Cell Performance**
N. Borchers, Ulm/Deutschland, B. Horstmann, Ulm/DE

P05.04 **ToF-SIMS and XPS Characterization of Lithium Metal Surfaces**
S.-K. Otto, Gießen/Deutschland, Y. Moryson, Gießen/DE, T. Fuchs, Gießen/DE, A. Henss, Gießen/DE, J. Janek, Gießen/DE

P05.05 **MOCASSIN: A Monte Carlo Interface for Solid State Ionics**
S. Eisele, Aachen/Deutschland, S. Grieshammer, Aachen/DE

P05.06 **Numerical simulations of the Hebb-Wagner polarization method of perovskite-type oxides**
N. Ahr, Aachen/Deutschland, M. Martin, Aachen/DE

P05.07 **Model Studies in Electro-Synthesis: Structure Dependence of the Electrochemical Reduction of Acetone on Pt(hkl) Single Crystals**
E. Franz, Erlangen/Deutschland, M. Kastenmeier, Erlangen/DE, T. Yang, Erlangen/DE, F. Waidhas, Erlangen/DE, O. Brummel, Erlangen/DE, J. Libuda, Erlangen/DE

P05.08 **On the electronic properties of LiO_2 and its importance during the formation of $^1O_2$**
D. S. Pietruschka, Giessen/Deutschland, D. Mollenhauer, Giessen/DE

P05.09 **Strain effect on ionic conductivity in doped ceria: Experimental and computational insights**
S. Grieshammer, Aachen/Deutschland, G. F. Harrington, Fukuoka/JP, S. Kim, Boston/US, K. Sasaki, Fukuoka/JP, H. Tuller, Boston/US

P05.10 **First-principles study of thiophenyl benzenethiol as sulfur host material for Lithium-Sulfur batteries**
Y. Schütze, Berlin/Deutschland, V. G. Ruiz, Berlin/DE, A. Bande, Berlin/DE, J. Dzubiella, Freiburg/DE

P05.11 **Pd particles supported on ordered Co_3O_4(111): Particle size effects in electrochemical environment**
M. Kastenmeier, Erlangen/Deutschland, X. Deng, Erlangen/DE, T. Skála, Prague/CZ, N. Tsud, Prague/CZ, L. Fusek, Prague/CZ, V. Johanek, Prague/CZ, J. Myslivecek, Prague/CZ, Y. Lykhach, Erlangen/DE, O. Brummel, Erlangen/DE, J. Libuda, Erlangen/DE

TOPIC 06: Reaction Kinetics and Dynamics

P06.01 **Harvesting vibrational energy to promote orientational isomerization in CO/NaCl(100)**
J. A. Lau, Göttingen/Deutschland, L. Chen, Dalian/CN, A. Choudhury, Göttingen/DE, D. Schwarzer, Göttingen/DE, V. B. Verma, Boulder/US, A. M. Wodtke, Göttingen/DE

P06.02 **Experimental and theoretical studies on the kinetics of the $CH_3OCH_2OCH_3$ + OH reaction**
A. Wolf, Karlsruhe/Deutschland, F. Poschen, Karlsruhe/DE, M. Olzmann, Karlsruhe/DE

P06.03 **Lifetime of the Metastable Isomer of CO on NaCl(100)**
A. Choudhury, Göttingen/Deutschland, J. DeVine, Göttingen/DE, D. Schwarzer, Göttingen/DE, A. M. Wodtke, Göttingen/DE

P06.04 **Rotational and collision energy dependence of reactions in the HBr^+ + HCl/DCl system**
D. Plamper, Marburg/Deutschland, S. Schmidt, Marburg/DE, K.-M. Weitzel, Marburg/DE

P06.05 **Experimental and theoretical studies on the kinetics of the methyl formate + OH reaction**
T. M. Pazdera, Karlsruhe/Deutschland, C. Kühn, Karlsruhe/DE, M. Olzmann, Karlsruhe/DE

P06.06 **Pyrolytic reactions of methyl formate: Shock-tube studies and kinetic modeling**
J. Wenz, Karlsruhe/Deutschland, L. Golka, Karlsruhe/DE, T. M. Pazdera, Karlsruhe/DE, R. Gartmann, Karlsruhe/DE, D. Gratzfeld, Karlsruhe/DE, M. Olzmann, Karlsruhe/DE

P06.07 **Photogeneration and Dynamics of Selenyl Radicals in Solution**
C. Allacher, Regensburg/Deutschland, A. K. Dutta, Regensburg/DE, R. J. Kutta, Regensburg/DE, S. Park, Regensburg/DE, A. Breder, Regensburg/DE, P. Nuernberger, Regensburg/DE

P06.08 **Degradation Kinetics of Anionic and Cationic Dye Molecules under Nanosecond Lasepulse Induced Plasmonic Heating of Gold Nanoparticles**
M. Niemeyer, Hannover/Deutschland, R. Himstedt, Hannover/DE, P. Bessel, Hannover/DE, P. Rusch, Hannover/DE, B. Schremmer, Hannover/DE, D. Kranz, Hannover/DE, D. Dorfs, Hannover/DE, N. C. Bigall, Hannover/DE

P06.09 **Hydrogen Atom Transfer (HAT) between phenol and phenoxy-radical**
B. Dick, Regensburg/Deutschland, U. Faltermeier, Regensburg/DE

P06.10 **Conformationally selected polar cycloaddition reactions in the gas phase**
J. Wang, Hamburg/Deutschland, A. Kilaj, Basel/CH, L. Xu, Basel/CH, P. Stranak, Basel/CH, S. Willitsch, Basel/CH, J. Küpper, Hamburg/DE

P06.11 **Formic Acid Oxidation on Pd(111)**
J. Fingerhut, Göttingen/Deutschland, M. Schwarzer, Göttingen/DE, D. Borodin, Göttingen/DE, G. Skoulatakis, Göttingen/DE, T. N. Kitsopoulos, Heraklion/GR, A. M. Wodtke, Göttingen/DE

P06.12 **Hydrogen recombination on Pd(111): Effect of Subsurface Penetration**
M. Schwarzer, Göttingen/Deutschland, J. Fingerhut, Göttingen/DE, D. Borodin, Göttingen/DE, G. Skoulatakis, Göttingen/DE, T. N. Kitsopoulos, Heraklion/GR, A. M. Wodtke, Göttingen/DE

P06.13 **Cryo kinetics and IR spectroscopy of N_2 and H_2 interactions with size selected Iron and Ruthenium clusters**
A. Steiner, Kaiserslautern/Deutschland, S. Dillinger, Kaiserslautern/DE, M. P. Klein, Kaiserslautern/DE, D. V. Fries, Kaiserslautern/DE, P. B. Armentrout, Salt Lake City/US, G. Niedner-Schatteburg, Kaiserslautern/DE

P06.14 **Reaction Kinetics of CdSe Nanocrystal Intermediates**
M. Seybold, Konstanz/Deutschland, K. Boldt, Konstanz/DE

P06.15 **Plasmon induced hot-electron transfer on DNA-metal nanoparticle superlattices**
S. Kogikoski Junior, Potsdam/Deutschland, A. Dutta, Potsdam/DE, I. Bald, Potsdam/DE

P06.16 **Reductive Alkylation of s-SWNTs**
M. Wederhake, Würzburg/Deutschland, K. Müller, Würzburg/DE, L. Stumpf, Würzburg/DE, F. Schöppler, Würzburg/DE, T. Hertel, Würzburg/DE

P06.17 **Hydration stop of cementitious suspensions by three techniques**
P. A. Kißling, Hannover/Deutschland, D. Cotardo, Hannover/DE, T. von Bronk, Hannover/DE, L. Lohaus, Hannover/DE, M. Haist, Hannover/DE, N. C. Bigall, Hannover/DE

P06.18 **Investigation of photolabile protection groups as tools for time-resolved structural dynamics**
Y. Pfeifer, Potsdam/Deutschland, M. Přeček, Prague/CZ, M. Kloz, Prague/CZ, A. Picchiotti, Hamburg/DE, H. Müller-Werkmeister, Potsdam/DE

TOPIC 07: Spectroscopy

P07.01 **Controlling Microgel Deformation via Deposition Method and Surface Functionalization of Solid Supports**
P. Lenssen, Aachen/Deutschland, L. Hoppe Alvarez, Aachen/DE, A. A. Rudov, Moscow/RU, R. A. Gumerov, Moscow/RU, U. Simon, Aachen/DE, I. I. Potemkin, Moscow/RU, D. Wöll, Aachen/DE

P07.02 **Investigation of the Optical Properties of Nickelsulfide Nanoparticles**
C. Wesemann, Hannover/Deutschland, R. Himstedt, Hannover/DE, D. Dorfs, Hannover/DE, N. C. Bigall, Hannover/DE

P07.03 **Ultrafast Dynamics of RuII Polypyridyl Complexes by Mass Spectrometry and Fragmentation Spectroscopy in an Ion Trap**
R. Israil, Kaiserslautern/Deutschland, L. Schüssler, Kaiserslautern/DE, P. Hüttchen, Kaiserslautern/DE, W. R. Thiel, Kaiserslautern/DE, R. Diller, Kaiserslautern/DE, C. Riehn, Kaiserslautern/DE

P07.04 **The Optical Spectrum of Au_2+**
K. Pollow, Berlin/Deutschland, M. Förstel, Berlin/DE, T. Studemund, Berlin/DE, R. Mitric, Würzburg/DE, O. Dopfer, Berlin/DE

P07.05 **Investigation of alcohol-formic acid dimers and trimers**
S. M. Schweer, Göttingen/Deutschland, M. A. Suhm, Göttingen/DE

P07.07 **Lable-free detection of rapamycin in human skin**
G. Germer, Berlin/Deutschland, R. Flesch, Berlin/DE, T. Ohigashi, Okazaki/JP, H. Yuzawa, Okazaki/JP, F. Rancan, Berlin/DE, K. Rajes, Berlin/DE, F. Zabihi, Berlin/DE, R. Haag, Berlin/DE, A. Vogt, Berlin/DE, E. Rühl, Berlin/DE

P07.08 **Label free drug detection in 3D cancer models by atomic force microscope infrared-spectroscopy**
G. Germer, Berlin/Deutschland, L. Gronbach, Berlin/DE, L. Elsholz, Berlin/DE, J. García-Miller, Berlin/DE, P. Patoka, Berlin/DE, C. Zoschke, Berlin/DE, E. Rühl, Berlin/DE

P07.09 **UV-VIS-Spectroscopy of $CO_3^-(H_2O)_{1,2}$ and $CO_4^-(H_2O)_{0,1,2}$**
M. Salzburger, Innsbruck/Österreich, M. Ončák, Innsbruck/AT, C. van der Linde, Innsbruck/AT, M. K. Beyer, Innsbruck/AT

P07.10 **Photolytic Decarboxylation of Ferric EDTA by Time Resolved Infrared Spectroscopy**
M. Bauer, Bonn/Deutschland, P. Vöhringer, Bonn/DE

P07.11 **Dynamic Tuning of Giant Circular Dichroism in Templated Colloidal Assemblies**
P. T. Probst, Dresden/Deutschland, M. Mayer, Dresden/DE, V. Gupta, Erlangen/DE, A. M. Steiner, Dresden/DE, Z. Zhou, Dresden/DE, G. K. Auernhammer, Dresden/DE, T. A. F. König, Dresden/DE, A. Fery, Dresden/DE

P07.12 **Rotational and translational dynamics of hydroxyl-functionalized ionic liquids investigated by means of fast-field cycling NMR relaxometry**
T. van Alphen, Rostock/Deutschland, A. Strate, Rostock/DE, V. Overbeck, Rostock/DE, R. Ludwig, Rostock/DE

P07.13 **Combined IR/UV spectroscopic and quantum chemical studies on chromone/methanol aggregates - investigation of dispersion interactions**
P. Boden, Kaiserslautern/Deutschland, P. H. Strebert, Kaiserslautern/DE, M. Meta, Kaiserslautern/DE, M. Gerhards, Kaiserslautern/DE

P07.14 **Inhomogeneity of the intermolecular hydrogen-bond modes in aqueous salt solutions**
L. Vietze, Mainz/Deutschland, J. Hunger, Mainz/DE, M. Bonn, Mainz/DE, M. Grechko, Mainz/DE

P07.15 **Alkynyl- and phenyl-extended phenanthroline based Cu(I) photosensitizers and their photophysical properties**
F. Döttinger, Braunschweig/Deutschland, Y. Yang, Braunschweig/DE, M. - A. Schmid, Braunschweig/DE, S. Tschierlei, Braunschweig/DE, M. Karnahl, Stuttgart/DE

P07.16 **Studies on the photochemistry of $Co^{III}(EDTA)^-$**
J. Schmidt, Bonn/Deutschland, P. Vöhringer, Bonn/DE

P07.17 **Vibrational Spectroscopy to study Proton Mobility in Ionic Liquids**
S. Shehaj, Potsdam/Deutschland, P. Börstler, Potsdam/DE, A. Lange, Potsdam/DE, Y. Pfeifer, Potsdam/DE, A. Taubert, Potsdam/DE, H. Müller-Werkmeister, Potsdam/DE

P07.18 **Colloidal photonic crystal slabs for sensing and energy harvesting**
S. Sarkar, Dresden/Deutschland, T. A. F. König, Dresden/DE

P07.19 **Distribution of Core-Shell-Nanoparticles with Radial Gradient**
D. Gutzeit, Konstanz/Deutschland, K. Boldt, Konstanz/DE

P07.20 **Dispersion-Bound Isolated Dimers in the Gas Phase: Observation of the Shortest C–H···H–C Distance via Stimulated Raman Spectroscopy**
P. H. Strebert, Kaiserslautern/Deutschland, D. Maué, Kaiserslautern/DE, D. Bernhard, Kaiserslautern/DE, S. Rösel, Gießen/DE, P. R. Schreiner, Gießen/DE, M. Gerhards, Kaiserslautern/DE

P07.21 **The photophysics and photochemistry of phenol-ammonia and pyrrole-ammonia complexes**
S. Fuchs, Regensburg/Deutschland, B. Dick, Regensburg/DE

P07.22 **Multi-spectroscopic investigations of dinuclear copper(I) and silver(I) complexes**
S. Steiger, Kaiserslautern/Deutschland, P. Boden, Kaiserslautern/DE, P. Di Martino-Fumo, Kaiserslautern/DE, F. Rehak, Karlsruhe/DE, J. Busch, Karlsruhe/DE, S. Bräse, Karlsruhe/DE, W. Klopper, Karlsruhe/DE, M. Gerhards, Kaiserslautern/DE

P07.24 **Investigating dispersion-controlled ketone-solvent balances as experimental benchmarks**
C. Zimmermann, Göttingen/Deutschland, T. L. Fischer, Göttingen/DE, H. C. Gottschalk, Göttingen/DE, M. A. Suhm, Göttingen/DE

P07.25 **An efficient approach for hydrophobic-to-hydrophilic transition of oleate-capped upconversion nanoparticles**
C. Sun, Berlin/Deutschland, M. Gradzielski, Berlin/DE

P07.26 **Dehydrogenation Reactions of O-Heterocyclic LOHC Molecules**
F. Hemauer, Erlangen/Deutschland, P. Bachmann, Erlangen/DE, F. Düll, Erlangen/DE, J. Steinhauer, Erlangen/DE, H.-P. Steinrück, Erlangen/DE, C. Papp, Erlangen/DE

P07.27 **“Intra-ionic” or “Inter-ionic” hydrogen bonding in hydroxy-functionalized omnium halides: A combined X-ray, ATR-IR and quantum chemistry approach**
L. Al Sheakh, Rostock/Deutschland, T. Niemann, Rostock/DE, P. Stange, Rostock/DE, R. Ludwig, Rostock/DE

P07.28 **Intramolecular charge transfer in metal-photoacid-complexes**
S. Muth, Regensburg/Deutschland, M. Springborg, Saarbrücken/DE, G. Jung, Saarbrücken/DE

P07.29 **Quantification of Material Gradients in Core/Shell Nanocrystals**
K. Boldt, Konstanz/Deutschland, S. Bartlett, Didcot/GB, N. Kirkwood, Melbourne/AU, B. Johannessen, Melbourne/AU

P07.30 **Infrared Spectrum of the Adamantane+-Water Cation: Hydration-Induced C-H Bond Activation and Free Internal Water Rotation**
M. A. R. George, Berlin/Deutschland, M. Förstel, Berlin/DE, O. Dopfer, Berlin/DE

P07.31 **Optical spectra of small gold cluster cations**
M. Förstel, Berlin/Deutschland, K. Pollow, Berlin/DE, T. Studemund, Berlin/DE, R. Mitric, Würzburg/DE, O. Dopfer, Berlin/DE

P07.32 **Optical Spectra of SinO+ Cluster of Astrophysical Interest**
T. Studemund, Berlin/Deutschland, M. Förstel, Berlin/DE, L. Dahlhöff, Berlin/DE, K. Pollow, Berlin/DE, R. G. Radloff, Berlin/DE, O. Dopfer, Berlin/DE

P07.33 **Low-energy electron irradiation induced synthesis of molecular nanosheets: influence of the electron beam energy**
C. Neumann, Jena/Deutschland, R. A. Wilhelm, Vienna/AT, M. Küllmer, Jena/DE, A. Turchanin, Jena/DE

P07.34 **A BUNSEN project: Benchmarks Using a New Setup for FTIR-Jet Spectroscopy of Intermolecular Energy Balances**
T. L. Fischer, Göttingen/Deutschland, H. C. Gottschalk, Göttingen/DE, M. A. Suhm, Göttingen/DE

P07.35 **Photolytic Formation of Nitrile Imine in Solution by Femtosecond Spectroscopy**
S. Flesch, Bonn/Deutschland, P. Vöhringer, Bonn/DE

P07.36 **High resolution ro–vibrational analysis of molecules in doublet electronic states: The ν_1 fundamental of chlorine dioxide ($^{16}O^{35}Cl^{16}O$) in the X^2B_1 electronic ground state**
K. Berezkin, Braunschweig/Deutschland, O.N. Ulenikov, Tomsk/RU, E.S. Bekhtereva, Tomsk/RU, O.V. Gromova, Tomsk/RU, M. Quack, Zürich/CH, S. Bauerecker, Braunschweig/DE, C. Sydow, Braunschweig/DE

P07.37 **Chirality Recognition and Synchronisation: Complexes of 1-Phenylethanol and Phenylmethanol**
M. Lange, Göttingen/Deutschland, R. Medel, Göttingen/DE, M. A. Suhm, Göttingen/DE

P07.38 **Imaging Flexible Molecules in Supersonic Jet Expansions**
M. M. Dohmen, Göttingen/Deutschland, N. O. B. Lüttschwager, Göttingen/DE

P07.39 **Dinuclear Design of Iridium(III) Complexes to Afford Strong Enhancement of Phosphorescence Rate**
M. Z. Shafikov, Regensburg/Deutschland, V. N. Kozhevnikov, New Castle/GB, R. Daniels, New Castle/GB

P07.40 **Fragmentation of Isocyanic acid, HNCO, following core excitation and ionization**
M. Gerlach, Würzburg/Deutschland, F. Fantuzzi, Würzburg/DE, L. Wohlfart, Würzburg/DE, K. Kopp, Würzburg/DE, B. Engels, Würzburg/DE, J. Bozek, Gif-Sur-Yvette/FR, C. Nicolas, Gif-Sur-Yvette/FR, D. Mayer, Potsdam/DE, M. Gühr, Potsdam/DE, F. Holzmeier, Leuven/BE, I. Fischer, Würzburg/DE

P07.41 **Tuning the excited state landscape of zinc (II) compounds in solution – a comprehensive study**
J. Leier, Karlsruhe/Deutschland, R. Tabone, Karlsruhe/DE, D. Tungulin, Karlsruhe/DE, C. Bizzarri, Karlsruhe/DE, A. - N. Unterreiner, Karlsruhe/DE

P07.42 **Temperature-dependent decomposition reactions of O-containing LOHC contaminants on Pt(111)**
V. Schwaab, Erlangen/Deutschland, J. Steinhauer, Erlangen/DE, F. Hemauer, Erlangen/DE, E. M. Freiberger, Erlangen/DE, N. Waleska, Erlangen/DE, H. - P. Steinrück, Erlangen/DE, C. Papp, Erlangen/DE

P07.43 **Line shape investigations of the electronic origin of phthalocyanines, porphin and their water-clusters in the gas phase**
F. Schlaghaufer, Regensburg/Deutschland, J. Fischer, Regensburg/DE, A. Slenczka, Regensburg/DE

P07.44 **Photoelectron Circular Dichroism of anionic metal complexes**
J. Triptow, Berlin/Deutschland, G. Meijer, Berlin/DE, A. Fielicke, Berlin/DE

P07.45 **Exploring the Optical Properties of Small Cationic Silicon Carbides**
R. G. Radloff, Berlin/Deutschland, K. Pollow, Berlin/DE, T. Studemund, Berlin/DE, M. Förstel, Berlin/DE, O. Dopfer, Berlin/DE

P07.46 **The Frozen Density Embedding method in combination with Pair Natural Orbitals**
R. Treß, Bochum/Deutschland, C. Hättig, Bochum/DE, S. Höfener, Karlsruhe/DE

P07.47 **Mixed Semiconductor and Noble Metal Nanoparticle Gel-networks**
M. Rosebrock, Hannover/Deutschland, D. Zámbó, Hannover/DE, P. Rusch, Hannover/DE, D. Pluta, Hannover/DE, F. Steinbach, Hannover/DE, P. Bessel, Hannover/DE, A. Schlosser, Hannover/DE, A. Feldhoff, Hannover/DE, K. Hindricks, Hannover/DE, P. Behrens, Hannover/DE, D. Dorfs, Hannover/DE, N. C. Bigall, Hannover/DE

P07.48 **Dynamics of Photoinduced Guest Uptake and Release by a Photochromic Coordination Cage**
K. Artmann, Regensburg/Deutschland, R. Li, Dortmund/DE, S. Juber, Bochum/DE, L. Schaefer, Bochum/DE, G. Clever, Dortmund/DE, P. Nuernberger, Bochum/DE

P07.49 **Through Bonds or Contacts? Mapping Protein Vibrational Energy Transfer Using Non-canonical Amino Acids.**
J. G. Löffler, Frankfurt/Deutschland, E. Deniz, Frankfurt/DE, L. Valiño-Borau, Freiburg/DE, K. B. Eberl, Frankfurt/DE, A. Gulzar, Freiburg/DE, S. Wolf, Freiburg/DE, P. M. Durkin, Berlin/DE, R. Kaml, Berlin/DE, N. Budisa, Winnipeg/CA, G. Stock, Freiburg/DE, J. Bredenbeck, Frankfurt/DE

P07.50 **Proton Transfer of excited aminopyrene-based superphotoacids in sulfuric acid investigated by ultrafast time-resolved spectroscopy**
A. Lehner, Regensburg/Deutschland, R. J. Kutta, Regensburg/DE, D. Maus, Saarbrücken/DE, A. Grandjean, Saarbrücken/DE, G. Jung, Saarbrücken/DE, P. Nuernberger, Regensburg/DE

P07.51 **A systematic study on ^{14}N nuclear quadrupole coupling and its relation with aromatic and molecular properties**
P. Pinacho, Hamburg/Deutschland, D. A. Obenchain, Hamburg/DE, M. Schnell, Hamburg/DE

P07.52 **Time-resolved photoelectron spectroscopy of Bengal Rose Dianions in the Gas Phase**
A. Veenstra, Karlsruhe/Deutschland, J. Czekner, Karlsruhe/DE, A.-N. Unterreiner, Karlsruhe/DE, M. M. Kappes, Karlsruhe/DE

P07.53 **Structural characterization of large gas-phase molecular ions by Trapped Ion Mobility Spectrometry (TIMS) and DFT calculations**
E. K. Schneider, Karlsruhe/Deutschland, Christoph Schissler, Karlsruhe/DE, Patrick Weis, Karlsruhe/DE, Ananya Baksi, Karlsruhe/DE, Manfred M. Kappes, Karlsruhe/DE

TOPIC 08: Theory and Data Science

P08.01 **The Interplay of Ionic Liquid Phase Boundaries: Liquid-Liquid and Vapor-Liquid Equilibria of Imidazolium Triflate Ionic Liquids with n-Alkyl Alcohols**
B. Rathke, Bremen/Deutschland, A. Aykoc, Bremen/DE, M. Pfeiffer, Bremen/DE, S. Wagenfeld, Bremen/DE, M. Stuckenholz, Bremen/DE, J. Kiefer, Bremen/DE, W. Schröer, Bremen/DE

P08.02 **Liquid-Liquid Phase Behavior of Ternary Mixtures of n-Alkanes with Ethanol**
B. Rathke, Bremen/Deutschland, A. Ballhause, Bremen/DE, S. Wagenfeld, Bremen/DE, J. Kiefer, Bremen/DE

P08.03 **Determining the mean cluster size of a pulsed supersonic jet at high densities using Rayleigh scattering**
S. Fazli, Berlin/Deutschland, W. Christen, Berlin/DE

P08.04 **Proline isomerization regulates the phase behavior of elastin-like polypeptides in water**
Y. Zhao, Mainz/Deutschland, K. Kremer, Mainz/DE

P08.05 **On how the Morphology Affects Water Release of Porous Polystyrene**
M. Hamann, Strasbourg/Frankreich, A. Quell, Ludwigshafen am Rhein/DE, L. Koch, Stuttgart/DE, C. Stubenrauch, Stuttgart/DE

TOPIC 09: Thermodynamics

P09.01 **Dissemination of the SI units mole and kilogram: Impact of isotope enrichment on measurement uncertainty**
A. Pramann, Braunschweig/Deutschland, O. Rienitz, Braunschweig/DE

P09.02 **KMC Simulation of the Onsager Transport Coefficients of reduced Ceria**
J. P. Arnold, Aachen/Deutschland, S. Grieshammer, Aachen/DE, M. Martin, Aachen/DE

P09.03 **Diamondoids: Cluster Formation and Interaction with Water**
T. Gimm, Berlin/Deutschland, X. Wang, Berlin/DE, K. Palczynski, Berlin/DE, A. Bande, Berlin/DE, J. Dzubiella, Freiburg/DE

P09.04 **Studying clusters of hydroxyl-functionalised cations stabilised by cooperative hydrogen bonds**
J. K. Philipp, Rostock/Deutschland, R. Ludwig, Rostock/DE

P09.05 **First Principles Studies of Electrical Conductance and Thermopower Properties of π-Conjugated Organometallic Complexes in Single Molecule Junctions**
J. Jung, Giessen/Deutschland, T. Ohto, Osaka/JP, H. Tada, Osaka/JP, D. Mollenhauer, Giessen/DE

P09.06 **Automated Guidance for (Non-)Expert Users of Quantum Chemistry Software**
M. Mücke, Göttingen/Deutschland, J. Diedrich, Göttingen/DE, R. J. Hickman, Toronto, ON/CA, A. Aspuru-Guzik, Toronto, ON/CA, J. Proppe, Göttingen/DE

P09.07 **Self-assembled monolayers of para-aminobenzoic acid on V_2O_5 – a theoretical and experimental study**
F. Dietrich, Temuco/Chile, E. Cisternas, Temuco/CL, J. Fernandez, Santiago/CL, M. Flores, Santiago/CL

TOPIC 10: Transport and Storage

P10.01 **Hopping in High Concentration Electrolytes - Long Time Bulk and Single-Particle Signatures, Free Energy Barriers, and Structural Insights**
S. Mukherji, Bangalore/Indien, N. V. S. Avula, Bangalore/IN, R. Kumar, Bangalore/IN, S. Balasubramanian, Bangalore/IN

P10.02 **New Insights into the Transport of Electrolytes in Supercapacitors**
M. Dvoyashkin, Leipzig/Deutschland, L. Borchardt, Bochum/DE

P10.03 **The Li^+ ion site energy distribution in Lithium aluminum germanium phosphate**
J. Wiemer, Marburg/Deutschland, M. Schäfer, Marburg/DE, K.-M. Weitzel, Marburg/DE

P10.04 **Liquid and Vapor Permeation through Carbon Nanomembranes made from Terphenylthiol SAMs on Ag(111)**
H. L. Le, Bielefeld/Deutschland, M. Westphal, Bielefeld/DE, P. Dementyev, Bielefeld/DE, A. Gölzhäuser, Bielefeld/DE

P10.05 **Mass storage: from bulk to interfacial storage**
C. Xiao, Stuttgart/Deutschland, R. Usiskin, Stuttgart/DE, J. Maier, Stuttgart/DE

P10.06 **Alkali-Aluminium-Germanium-Phosphates - From ionic DC conductivity to thermal electropoling**
K. Rein, Marburg/Deutschland, M. Schäfer, Marburg/DE, K.-M. Weitzel, Marburg/DE

P10.07 **Direct assessment of ultralow Li^+ jump rates in single crystalline Li_3N by evolution-time resolved 7Li spin-alignment echo NMR**
B. Gadermaier, Graz/Österreich, K. Hogrefe, Graz/AT, P. Heitjans, Hannover/DE, H. M. R. Wilkening, Graz/AT

P10.08 **Li-ion dynamics in the micro and nano-crystalline form of the solid electrolyte Li_3YBr_6**
H. M. R. Wilkening, Graz/Österreich, M. Gombotz, Graz/AT

P10.09 **Influence of defects on ionic transport in $LiTaO_3$ - a study using EXAFS and positron annihilation lifetime spectroscopy**
B. Gadermaier, Graz/Österreich, L. Resch, Graz/AT, D. M. Pickup, Canterbury/GB, I. Hanghofer, Graz/AT, I. Hanzu, Graz/AT, P. Heitjans, Hannover/DE, W. Sprengel, Graz/AT, R. Würschum, Graz/AT, A. V. Chadwick, Canterbury/GB, H. M. R. Wilkening, Graz/AT

P10.10 **Ionic transport in the Ge-substituted argyrodite-type materials $Li_{6+x}Ge_xP_{1-x}S_5I$ ($x = 0–0.6$) as investigated by ^7Li and ^{31}P solid-state NMR spectroscopy and neutron powder diffraction**
K. Hogrefe, Graz/Österreich, N. Minafra, Münster/DE, W. G. Zeier, Münster/DE, H. M. R. Wilkening, Graz/AT

P10.11 **The role of association colloids on the oxidation of lipids: Polar paradox and stabilisation of vegetable oils and biofuels**
F. Kerkel, Regensburg/Deutschland, D. Brock, Burghausen/DE, D. Touraud, Regensburg/DE, W. Kunz, Regensburg/DE

Research Training Group 2620

Ion Pairs in
Re-Action

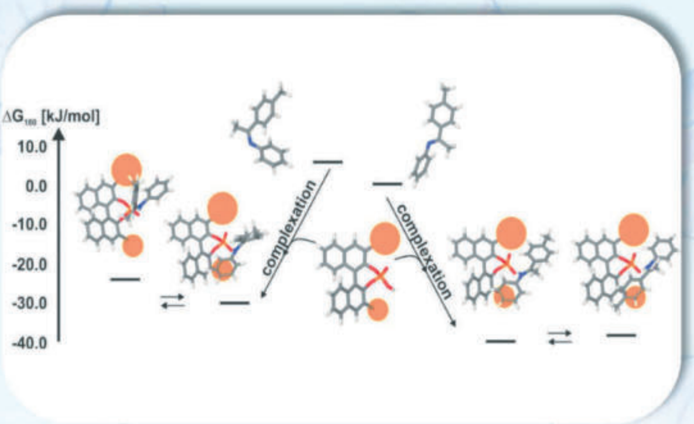
"Ion Pair Effects in Molecular Reactivity"

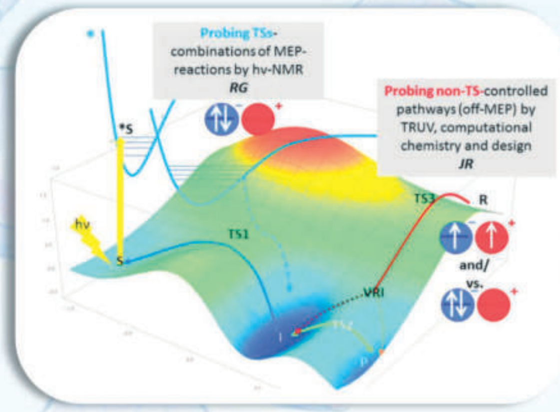
funded by DFG

The research programme is defined around the topic **Ion Pair Effects in Molecular Reactivity** and will allow to combine model systems, methods and perspectives from various chemical disciplines. The RTG will give students the opportunity of a highly qualifying scientific education at an internationally competitive level in an excellent research environment.

Spectroscopy and Structure Analysis

One goal of this RTG is to elucidate the structures and reaction mechanisms of ion pairs. Thus, characterizing and understanding intermediate structures is of great interest. A variety of spectroscopic methods from IR and UV/Vis ultrafast spectroscopy to advanced NMR provide insight into their structure and reactivity.



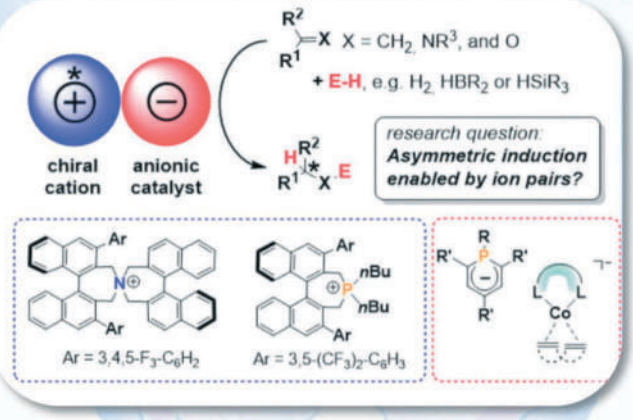


Computation & Simulation

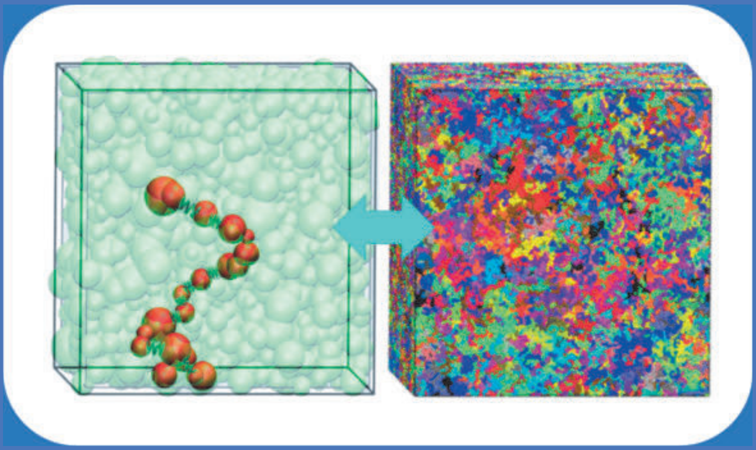
Ion pairs set significant challenges for theoreticians and experimentalists alike. Theoretical simulations and calculations are a vital part of understanding chemical transformations and thus the impact of spectroscopic data is maximized when theoretical prediction of spectra are available.

Synthesis and Catalysis

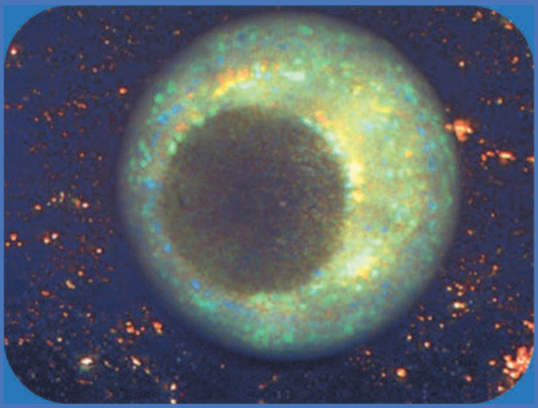
Ion pairs are omnipresent in chemistry and therefore provide a huge potential for synthesis and catalysis. The analysis of known as well as novel reaction types, which take advantage of ion pairs to enhance both reactivity and selectivity, is a key issue of the RTG. The obtained results will be used to develop new transformations.



https://www.uni-regensburg.de/chemistry-pharmacy/grk-2620/home/index.html



LECTURE ABSTRACTS



Entropy, colloids and COVID19

Daan Frenkel, Cambridge/UK
Prof Daan Frenkel, University of Cambridge, Lensfield Rd, Cambridge CB2 1EW, UK

Over the past 60 years, our view of entropy has changed.
I was taught that entropy was a measure of disorder. But, starting with the simulations of Alder and Wainwright, we now know that entropy is much more than that.

In my talk, I hope to describe some of the developments of our view on the role entropy on colloid science, ranging from entropic ordering to targeted drug delivery and genome recognition.

Physical Chemistry of Drying Droplets

C. D. Bain, Durham/UK

Prof. Dr. Colin Bain, Department of Chemistry, Durham University, Durham, DH1 3LE

Inkjet printing has great promise as a precision, digital manufacturing technology. To realise this potential, it is necessary to print uniform films of functional and structured materials on a range of substrates. Much progress has been made with the heuristic design of inks, but a detailed understanding of the physical chemistry of drying droplets – essential for predictive formulation of inks – is still being developed. One key challenge is the so-called 'coffee-ring effect' in which particles and solutes form a ring at the three-phase contact line during drying [1]. The small length scales (drop sizes < 50 μm) and time scales (drying times < 1 s) employed in high-speed precision manufacturing are a further challenge for experimental studies.

In this talk I will first describe two general strategies for overcoming the coffee-ring effect, one which uses a controlled sol-gel transition in laponite suspensions [2] and the second which exploits Marangoni effects in solvent blends [3].

I will then present a strategy for producing uniform layers of functional and structured particles by printing of emulsions [4] and discuss the physico-chemical challenges to the control of particle shape and structure.

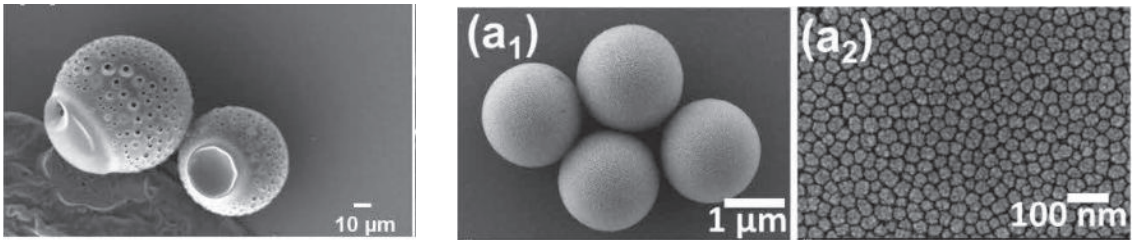


Figure 1 (left): Acorn-shaped particles form when Hamaker constant has the wrong sign; (right) Spheres of nanoparticles formed during droplet drying.

[1] R. D. Deegan et al. *Nature* **1997**, *389*, 827.

[2] E.L. Talbot et al. *ACS Applied Materials & Interfaces* **2014**, *6*, 9572.

[3] G. Hu et al. *Science Advances* **2020**, *6*, eaba5029.

[4] R. Deng et al. *ACS Applied Materials & Interfaces* **2019**, *11*, 40652.

Towards Inverse Design of Soft Materials: Crystals, Quasi Crystals, Liquid Crystals

M. Dijkstra, Utrecht, NL

Utrecht University, Debye Institute for Nanomaterials Science, Princetonplein 1,
3584 CC Utrecht, the Netherlands

In 1960, Feynman challenged us to think “from the bottom up” and to create new functional materials by directing and manipulating the arrangements of individual atoms ourselves. With recent advances in the synthesis of colloidal nanoparticles and the bottom-up fabrication of nanostructured materials using colloidal self-assembly, we are tantalizingly close to realizing this dream. In this talk, I will show using computer simulations how one can use hierarchical self-assembly to structure matter over multiple length scales, which enables an unprecedented control over the properties and functionalities of these nanomaterials. In addition, the fabrication of supraparticles [1-3] of these nanostructured materials allows for a subsequent self-assembly step.. The prediction and design of these structures remains an important challenge for nanomaterials science. I will present a method to predict which structures are stable assuming the shape and interactions between the constituent particles are known. I will show that particle shape alone can already give rise to a wide variety of structures such as crystals, plastic crystals, quasi crystals, and liquid crystals, which can be classified using machine learning techniques. Subsequently, I will show how one can reverse-engineer the particle interactions to stabilize crystals, liquid crystals, and even quasicrystals, which is the “holy grail” of materials design.

References

[1] B. de Nijs, S. Dussi, F. Smallenburg, J.D. Meeldijk, D.J. Groenendijk, L. Filion, A. Imhof, A. van Blaaderen, and M. Dijkstra, Nature Materials 14, 56-60 (2015).
[2] D. Wang, M. Hermes, R. Kotni, Y. Wu, N. Tasios, Y. Liu, B. de Nijs, E.B. van der Wee, C.B. Murray, M. Dijkstra, and A. van Blaaderen, Nature Communications 8, 2228 (2018).
[3] D. Wang, T. Dasgupta, E.B. van der Wee, D. Zanaga, T. Altantzis, Y. Wu, G.M. Coli, C.B. Murray, S. Bals, M. Dijkstra and A. van Blaaderen, Nature Physics 17, 128–134 (2021).

Multicomponent Aerogels from Colloidal Nanocrystals

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Assembling colloidal nanocrystals into macroscopic hydrogels and aerogels recently resulted in a new exciting material type. In such nanocrystal gel architectures, structure and properties can be controlled to a large extent. For example, when employing semiconductor nanocrystals as building blocks for such gels, macroscopic monoliths are yielded which either exhibit the properties of their nanoscopic building blocks, or which exhibit even new ones which are neither accessible with the nanoparticle building blocks nor with the corresponding bulk materials .

This means that finding routes for nano- micro- and macrostructuring of such macroscopic nanoarchitectures paves the way to synthesize materials with elaborate properties, e.g. consisting of several components, and in which the deliberate way of nano, micro and macro component distribution drastically influences the material properties. This is of interest for a broad application area ranging from photocatalysis and electrocatalysis to sensing, to name just a few.

In this talk, our recent efforts are discussed which concentrated on structuring of nanocrystal-based hydrogels and aerogels on the nanoscale, on the microscale and on the macroscale. All of these scales are crucial for controlling the final material properties: fine-tuning of the individual building blocks on the nanoscale by colloid-chemical routes, the network connections on the microscale, and the macroscale structure and shape of the eventual product.[1]

[1] Control over Structure and Properties in Nanocrystal Aerogels at the Nano-, Micro-, and Macroscale, Pascal Rusch, Dániel Zámbó, Nadja C. Bigall,
Acc. Chem. Res. 2020, 53, 10, 2414–2424,
https://doi.org/10.1021/acs.accounts.0c00463

Physics-based machine learning for multiscale computer simulations

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University of Amsterdam, Amsterdam, The Netherlands

Advanced statistical methods are rapidly impregnating many scientific fields, offering new perspectives on long-standing problems. When coupling machine learning (ML) to physical systems, many problems of interest display dauntingly large interpolation spaces, limiting their immediate application without undesired artefacts (e.g., extrapolation). The incorporation of physical information, such as conserved quantities, symmetries, and constraints, can play a decisive role in reducing the interpolation space. I will illustrate some of these aspects in the context of efficient kernel-based machine learning models for structure-based coarse-grained force fields that are both covariant and energy-conserving. Going back down the multiscale ladder, I will describe a backmapping strategy that learns the atomistic distribution of atoms conditional on the coarse-grained degrees of freedom. Our generative adversarial network is capable of accurately reproducing the Boltzmann distribution beyond pairwise statistics.

Force probe simulations using an adaptive resolution scheme

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Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz,
Germany

The mechanical properties and the force induced unfolding of soft matter systems like biomolecules can be investigated using force probe molecular dynamics (FPMD) simulations. In the most common protocol one end of the molecule is fixed in space and the other end is pulled apart with a constant velocity. In most FPMD simulations the pulling velocities are much higher than in experimental realizations of force spectroscopy. In order to match the time scales, in the past a number of coarse-graining (CG) techniques have been used to speed up FPMD simulations. However, some of the approaches that utilize simplified potentials lack atomistic resolution and this hampers a detailed analysis of, e.g., unfolding pathways. Therefore, mixed resolution schemes that treat the molecular complex under study with atomistic resolution and the solvent in a CG manner are promising candidates to further increase the efficacy of FPMD simulations. For this purpose we test the applicability of the adaptive resolution scheme (AdResS). Here, the solute and the neighboring solvent molecules are placed in a region where the interactions are treated in an all atom (AA) manner. For a CG description of the solvent molecules further apart we use the interaction potentials obtained from an iterative Boltzmann inversion CG procedure. The AA region and the CG region are separated by a hybrid region that allows to switch from atomistic to CG resolution. We present results from FPMD simulations using the AdResS methodology on a well-studied system, a dimer formed from mechanically interlocked calixarene capsules and compare the results with those from all-atom simulations. Since the system is driven out of equilibrium by the pulling process we investigate the dependence of the results on the size of the AA region. We find that for fast pulling a larger AA region is required. Our results show that multiscale simulations can be applied also in the strong non-equilibrium situations that the system experiences in FPMD simulations.

Ion Conductivity Simulations in Nanostructured Materials with First-Principles Resolution

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We present a three-level multiscale simulation concept for the calculation of light ion diffusion/conduction in disordered organic and inorganic materials. We combine quantum chemical calculations for elementary reactions between the ions and surrounding molecules with molecular dynamics simulations for the incorporation of local dynamical heterogeneities at the nanometer/nanosecond scale. Data from both levels are integrated in a stochastic propagation scheme that is applied to a structural model assembled from a large number of such nanometer sized building blocks. The approach allows for an atom-level resolution of ion dynamics with quantum chemical accuracy but with final length- and time-scales of micrometers and milliseconds.

As a proof-of-principle simulation, we have computed the proton conductivity of a slab of disordered polymer-coated CsH_2PO_4 nanocrystals and its dependency on the nano-porosity.

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Atomistic simulations of catalytic confined environments from supramolecular systems to biomass conversion

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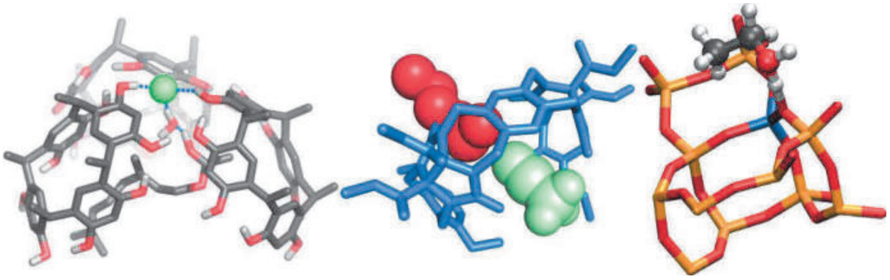
In recent years, new materials and processes opened the way to novel catalytic pathways. The main feature of these systems is the simultaneous presence of a liquid substrate/solvent solution confined in nanosized catalytic environments. These processes are highly relevant because they can potentially revolutionize industrial production for a more sustainable chemical industry, ranging from fine chemistry up to biomass conversion. Here, we report the study of two types of catalysis characterized by well-defined cavities hosting a limited number of solvent and substrate molecules: 1) organic reactions in hexameric calixarene nanocapsules[1] and molecular tweezers[2] and 2) liquid-phase biomass conversion over zeolites. Metadynamics simulations have been used in combination with recently developed methods for studying activated processes relevant to catalysis[5-7]. This allowed us understanding the complex dynamics of different catalytic reactions and shed light on the mechanistic aspects.



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MD Simulations with Near MP2 Accuracy - Adsorption in Zeolites

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Adsorption is a fundamental step in heterogeneous catalysis, which strongly affects the reaction kinetics and diffusion within the catalyst but inherently poses a *multi-scale problem*. While the behavior of adsorbates can only be properly described by approaches that sample for *long time scales*, e.g. Molecular Dynamic (MD) simulations, the chemically accurate description of explicit interactions between adsorbates and the host requires accuracy beyond force fields (FF) or density functional theory (DFT). To approach chemical accuracy, wavefunction methods, e.g. MP2, are required, which are limited to a small set of configurations (*short time scales*). Standard DFT calculations with empirical dispersion corrections predict adsorption enthalpies, which largely deviate from experiments.[1] FF calculations, which are commonly used, face parametrization and transferability problems.

We introduce a combined MP2:PBE+D2 MD approach that addresses the problems of standard DFT+dispersion calculations: i) empirical description of long-range dispersion interactions, ii) improper sampling of the configurational space with static calculations, and iii) harmonic partition functions. While the sampling of the configurational space is realized with MDs at PBE+D2 level (~200 ps, *long time scale*), the - anharmonicity including - enthalpies are based on fitted MP2:PBE+D2 energy surfaces.[2] MP2 corrections to the adsorption enthalpy are calculated for selected snapshots using an appropriate selection scheme that minimizes the number of expensive MP2:PBE+D2 calculations (*short time scale*). We calculate the MP2 correction according to a 2D linear fit of physically motivated structure parameters. These parameters provide an ansatz to calculate MP2 corrections for each step of the MD, effectively *combining the two scales*.

We illustrate this approach by calculating alkane adsorption enthalpies in zeolites with differing pore sizes (MFI, CHA, FAU) at varying temperatures and Brønsted acid site (BAS) densities, obtaining chemically accurate results compared to experimental data, and, importantly, we shed light on severe pitfalls that occur when calculating adsorption enthalpies using a standard approach, e.g. static calculations on ideal isolated BAS models at PBE+D2 level.

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Conformational changes as driving force for phase recognition

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Laurdan is one of the most used fluorescent probes for lipid membrane phase recognition. By means of Molecular Dynamics and hybrid Quantum Mechanics – Molecular Mechanics (QM/MM) calculations, we compare the position, orientation and optical properties of this probe embedded in dipalmitoyl-phosphatidylcholine (DPPC) solid gel (So), and dioleoylphosphatidylcholine (DOPC) liquid disordered (Ld) membranes at room temperature.

Laurdan can take two conformations, depending on whether the carbonyl oxygen points toward the β-position of the naphthalene core (Conf-I) or to the α-position (Conf-II) [1]. We observe that Conf-I has an elongated form in DPPC (So), whereas Conf-II takes an L-shape. Moreover, our results show that in DPPC (So) no intermixing between the conformations is present, whereas it has been seen in a fluid environment such as DOPC (Ld) [2, 3]. Despite Laurdan's wide use as a solvatochromic probe, little is known regarding its use as molecular rotor. We prove now that information on the probe's conformation can be obtained through the optical properties, ranging from one-photon absorption over two-photon absorption to the first hyperpolarizability. Fluorescence decay and anisotropy analyses are performed as well and stress the importance of Laurdan's conformational versatility. As a molecular rotor, Laurdan can be used to probe biochemical processes that change the lipid orders in cell membranes.

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Challenges in Biopharmaceutical Development: Modelling at Different Length Scales

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Biopharmaceutical processes for the production of biological drugs involve a large number of different unit operations. In addition to optimal settings for cell cultivation processes and the definition of suitable capturing and polishing steps, the development of a stable drug with a long shelf life is the main goal of every bioprocess. In the last few years, different modelling approaches have been introduced for a deeper understanding of the unit operations in order to reduce the experimental work and to shed light on the correlations between critical process parameters and critical quality attributes [1].

In this talk I will discuss the main principles of such approaches and their current applications. A special focus is on the use of atomistic models and quantum chemical methods in combination with machine learning algorithms to develop suitable drug formulations [2,3]. In addition, I will outline some challenges in combining salt ions and co-solute molecules for the stabilization of biotherapeutic proteins and the suppression of aggregation properties [4,5]. The beneficial combination of neural networks and mechanistic models for the study of cultivation processes will be highlighted in the last part of my talk.

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Introducing memory in coarse-grained molecular simulations

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Bottom-up methods for molecular coarse graining overestimate dynamic properties of the coarse-grained models they produce. This is commonly observed in standard molecular dynamics simulations and facilitates equilibration of structural and thermodynamic properties of complex systems. I will discuss recent efforts in deriving bottom-up coarse-grained molecular models for soft matter systems with improved dynamics. The approach is based on the application of Mori-Zwanzig theory using friction and noise terms obtained from a first principles approach with suitable assumptions.

Probability theory of active suspensions

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Active suspensions consist of a fluid, usually Newtonian, and of a large number of embedded active particles. The latter term describes rigid objects which exert a force onto the surrounding fluid and, hence, propel themselves through the suspension. Such conglomerates can be found in nature or as designed objects. For example, flocks of birds, swarming fish and bacteria colonies can be described as active suspensions. Our work is focused on microscopic active particles, e.g. colonies of *Escherichia coli*.

The movement pattern of active suspensions is sometimes described as *active turbulence*. However, the true nature of this behaviour is still unclear in particular as large-scale motion is observed way beyond the length-scale of the propelling particles. Due to the possible resemblance to hydrodynamic turbulence, we use an approach well-know in the field of single-phase turbulence. By introducing a probability density function (PDF) and its equations of motion, we obtain a description of the complete statistics of active suspensions. The equations of motion for the PDF constitute an infinite hierarchy of multi-point equations, where the equation for the k-point PDF depends on the $(k + 1)$- and $(k + 2)$-point PDF, exposing the famous closure problem of turbulence.

Based on the PDF equations, we will present two principal routes to obtain finite dimensional models for describing the motion of the suspension. The first method is to derive statistical moments and, thus, obtain equations of motion for such moments. Famous modelling approaches like the Reynolds Averaged Navier-Stokes (RANS) equation or the Eulerian spatial averaging theory can be obtained with this method. A disadvantage of this method is that information are lost as higher moments are no longer accessible.

The second method involves the calculation of symmetries of the infinite equations of motion and, in turn, derive group invariant solutions there off. In general, a symmetry of a differential equation is a transformation, which does not change the structure of said differential equation. Symmetries of differential equations mirror deep physical properties of the underlying problem, and, for some systems, the original differential equation can be retrieved there off. Even if this is not the case, group invariant modelling allows from a given set of symmetries to uniquely derive models with decisive properties cast into symmetries such as statistical information. Both routes will be presented including supporting statistical data from large-scale DNS of active suspensions.

Systematic derivation of hydrodynamic equations for viscoelastic phase separation

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We are interested in hydrodynamic two-fluid model equations for viscoelastic phase separation of polymer solutions. We present a novel derivation of a simple model that is directly rooted in the coarse-graining of a well-defined molecular model, such that all degrees of freedom have a clear and unambiguous molecular interpretation. By applying the GENERIC formalism we make sure that the model is consistent with both equilibrium and non-equilibrium thermodynamics. In particular, the Second Law of thermodynamics is strictly obeyed. The derivation proceeds in two steps: Firstly, we derive an extended model comprising two scalar and four vector fields, such that inertial dynamics of the macromolecules and of the relative motion of the two fluids is taken into account. In the second step, we eliminate these inertial contributions and, as a replacement, introduce phenomenological dissipative terms, based upon the principles of non-equilibrium thermodynamics. The final simplified model comprises the momentum conservation equation, which includes both interfacial and elastic stresses, a convection-diffusion equation where interfacial and elastic contributions occur as well, and a suitably convected relaxation equation for the end-to-end vector field. This approach differs from the usual derivation of rheological equations, because we consider here all degrees of freedom consistently on the same footing, and in the framework of the same formalism.

Iterative integral equation methods for structural coarse-graining

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Structural coarse-graining methods generate models of molecular systems which reproduce spacial distribution functions of a reference system. In this talk I will present novel Newton and Gauss-Newton methods for structural coarse-graining which are based on the Ornstein-Zernicke integral equation. While the established iterative Boltzmann inversion method converges very slowly and inverse Monte Carlo converges fast but needs time-consuming sampling of the Jacobian our new class of coare-graining methods approximates the Jacobian with integral equation theory. Its advantages are not only its performance, which we show to be better than the established methods, but we also demonstrate the integration of constraints on the potential updates. We have successfully extended the method to systems with internal degrees of freedom employing the reference interaction site model as a step towards general systems.

Constructing dynamic density functional theories for inhomogeneous polymer systems from microscopic simulations

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Computer simulations of the dynamical evolution of polymer systems can be very time consuming, especially if one wishes to study slow ordering and structure formation processes. One way to overcome this problem is to use dynamic density functional theories (DDFTs), i.e., coarse-grained models at the level of continuous density fields. Their static counterpart, the so-called self-consistent field (SCF) theory, is well established and has reached a level where it reproduces the static properties of inhomogeneous polymer systems at an almost quantitative level in many cases. In contrast, the predictions of dynamic density functional theories are usually far from accurate. Here we present a method to systematically construct DDFTs from microscopic simulation trajectories. The approach is tested by studying the ordering and disordering kinetics in diblock copolymer melts. The DDFT results are in very good agreement with simulation data for the corresponding fine-grained model. We will also show how to derive analytic expressions for the DDFT mobilities of linear multiblock polymers in the Rouse regime and apply them to study ordering processes in two-scale polymers.

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Developing and modelling organic membranes for photo-energy conversion

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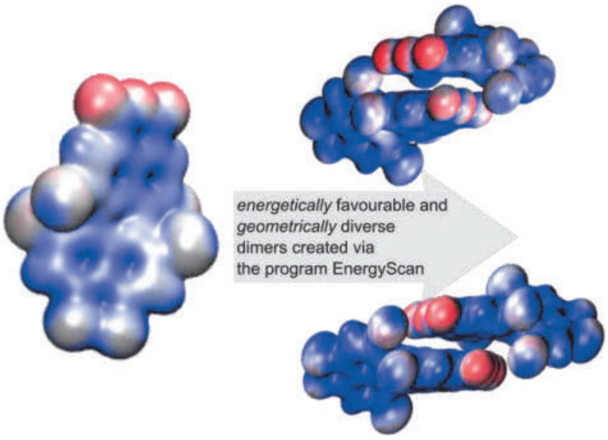

Employing amphiphilic dyes and interface assembly we produce quasi-two-dimensional membranes with controlled supramolecular structures and, hence, tailored optoelectronic properties. To identify supramolecular structures that give rise to measured membrane properties and to predict suitability of amphiphiles for achieving membranes with specific properties, we aim for modelling of molecular, supramolecular, to membrane properties. In the talk, recent experimental and theoretical[1] results on amphiphilic dye layers will be presented, with a focus on their relation. The properties of interest involve amphiphilicity, supramolecular structures[2], intermolecular binding energies[3], absorption and emission spectra[4, 5], frontier energy levels[6], fluorescence quantum yields[7], and charge carrier mobilities[1].

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Consistent representation of structural and dynamical properties from coarse-grained simulation models

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"Bottom-up" coarse-grained models retain chemical specificity by targeting the reproduction of properties from a higher-resolution reference model. These models are inherently limited by the molecular representation, set of interaction potentials, and parametrization method. These limitations often result in an inaccurate description of cross-correlations between coarse-grained degrees of freedom, complicating the stabilization of hierarchical structures in soft matter systems. Perhaps more troubling, reduced molecular friction and softer interaction potentials obscure the connection to the true dynamical properties of the system. In this talk, I will discuss the relationship between these two problems and introduce methodologies for characterizing and improving the dynamical properties generated by coarse-grained simulation models.

Combining multiscale simulations with machine learning driven analysis to sample free energy landscapes of biomolecular systems

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Simulations have become an important complement to experimental structural biological approaches since they provide a molecular-level view on structural ensembles and dynamics of conformational transitions or aggregation processes on ns to ms timescales. Multiscale simulations which combine atomistic and coarse grained simulation models can overcome size and time scale limitations of purely atomistic approaches while retaining chemical/biological specificity. In this context, linking the simulation scales and assessing and improving the inevitable shortcomings of the lower resolution models remains an ongoing effort. In combination with ever increasing computational power these approaches give access to unprecedented system sizes and simulation times and have led to a massive increase in the amount of data produced. Thus, processing and analyzing exceedingly large high-dimensional data sets has become one of the major challenges.

I will show examples how a multiscale simulation approach in combination with advanced analysis methods can be used to investigate and characterize the structural variability of biomolecular systems, in particular multidomain proteins and protein conjugates. Modern machine learning approaches are utilized to identify, compare, and classify relevant conformational states, to provide insights into the decisive features hidden in these high dimensional simulation data and to guide their interpretation with respect to experiments. Using efficient dimensionality reduction techniques we obtain low dimensional representations of the sampling which can be interpreted as conformational free energy landscapes. These low dimensional representations enable us to assess the consistency of the sampling in models at different levels of resolution, to go back and forth between the scales and ultimately to enhance and improve the sampling of the systems.

Hierarchical atomic-resolution ensembles of disordered proteins and their condensates

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Liquid-liquid phase separation of disordered proteins and the resulting biomolecular condensates are key in regulating the physical chemistry of cells. A detailed understanding of the structure and dynamics of disordered proteins in dilute and condensed states will help to understand how they shape cellular chemistry and elucidate their roles in health and disease. However, the inherent flexibility of disordered proteins and their condensates makes structural studies and their interpretation challenging. Atomistic molecular dynamics simulations could help to address this challenge, but the need for long simulations has stymied progress. Multi-scale approaches that reconstruct atomic-resolution representations from coarse-grained simulations provide one way forward. We adopt an alternative hierarchical approach[1], building on ideas from polymer science, combining a highly accurate description of local structures with efficient sampling of possible global structures and importantly retain atomic resolution at each step. Our atomic-resolution ensembles of the disordered proteins α-synuclein and tau agree well with small-angle X-ray scattering and NMR data. For tau we find that, pathogenic P301 mutations shift the ensemble towards locally more extended structures, which may be more aggregation prone. Our modeling also suggests that the aggregation-prone hexapeptide motifs sample extended structures as in fibrils. With the same hierarchical framework, we generate atomic-resolution models of tau condensates for direct structural analysis and large-scale simulations. In the condensates, dynamics is slowed downed, but tau remains highly flexible. With our hierarchical modeling of condensates of disordered proteins we can start to validate reconstructed atomic-resolution structures from coarse-grained and multi-scale simulations and develop these approaches further.

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Multiscale Modeling of a Drug-Delivery System Component

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Efficient drug delivery in the human organism requires the application of drug-delivery systems (DDS) that consist of several building blocks. Herein, we present a combination of molecular dynamics (MD) simulations and density functional theory (DFT) calculations to investigate a potential DDS component for the cytostatic doxorubicin (DOX), one of the widely used anthracycline chemotherapeutics due to its diverse activity against a wide range of tumors.[1] The DDS model consists, besides one drug molecule, of a thiolate-protected gold nanoparticle (Au-NP) and a specific drug-binding peptide (DBP) as carrier moieties.[2,3] The Au-NP and the DBP are covalently bound, and DOX is pre-adsorbed on a tryptophan residue (TRP) of the DBP, as obtained in a recent MD study.[4]

MD simulations in NPT ensemble at physiological conditions identify preferred adsorption configurations of the drug in the DDS component, the energetics of which is subsequently quantified by DFT calculations.[5] Surprisingly, it turns out that the task of the Au-NP is not limited to that of a carrier only, but it also contributes significantly to the stabilization of the drug. In the energetically most preferred adsorption state, DOX is intercalated between the Au-NP and a TRP residue of the peptide. In the energetically less favorable adsorption states, the drug is either intercalated between two TRP entities, non-specifically intercalated between the NP and the peptide, or stacked by a single TRP residue. The obtained results can be rationalized by the construction of a volcano plot, reminiscent of the catalysis and battery science communities,[6] and indicating a volcano-shaped trend of the drug stabilization energy in dependence of the drug distance to its nano carrier.

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Computational tools for automated high-throughput screening of fast ionic conductors

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Identifying new materials that combine high ionic conductivity with structural and electrochemical stability so far remains a slow trial and error search process. To rationally accelerate materials design and exploit the opportunities in the materials genome a dependable high-throughput screening of materials is required so that promising structures can be shortlisted for higher-level computational and experimental characterization. Here we report on the progress of our bond-valence site energy-based automated pathway analysis that provides rapid and simplified visualization of pathways [1,2]. Meaningful approximate predictions of ion transport pathways are achieved from crystal structure models within seconds to minutes (3 to 5 orders of magnitude faster than by DFT). Combined with a graphical user interface our software suite (that is available free for academic use from [2]) enables experimentalists to quickly identify candidate solid electrolyte materials. We also integrate this pre-screening into an automated workflow for subsequent DFT characterization [3]. Results are benchmarked against experimental and DFT results. Besides the migration barriers the approach now also comprises an AI-based dopant predictor focusing on bond-valence-based crystal chemical descriptors to assist experimentalists in exploring favourable substitutional doping strategies. The predictability of absolute room temperature conductivities from static energy landscape analysis, bond-valence based empirical MD simulations and ab initio molecular dynamics (AIMD) simulations will be compared. Several thiophosphate halides along the A_3PS_4-LiX (Cl, Br, I; A = Li, Na) tie line [4,5] the $A_x(MS_4)_y(M'S_4)_z$ phase space [5] or $LiTX_4$ compound series will be discussed as examples to illustrate under which circumstances the predictions from static BV calculations have to be complemented by dynamic simulations to capture the role of polyanion librations in promoting ion transport.

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Multiscale Reweighted Stochastic Embedding (MRSE): Deep Learning of Collective Variables for Enhanced Sampling

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We present a new machine learning method called multiscale reweighted stochastic embedding (MRSE) [1] for automatically constructing collective variables (CVs) to represent and drive the sampling of free energy landscapes in enhanced sampling simulations. The technique automatically finds CVs by learning a low-dimensional embedding of the high-dimensional feature space to the latent space via a deep neural network. Our work builds upon the popular t-distributed stochastic neighbor embedding approach [2]. We introduce several new aspects to stochastic neighbor embedding algorithms that makes MRSE especially suitable for enhanced sampling simulations: (1) a well-tempered landmark selection scheme; (2) a multiscale representation of the high-dimensional feature space; and (3) a reweighting procedure to account for biased training data. We show the performance of MRSE by applying it to several test systems.

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Machine Learning in Computational Surface Science and Catalysis: Case Studies on Water and Metal–Oxide Interfaces

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The goal of many computational physicists and chemists is the ability to bridge the gap between atomistic length scales of about a few multiples of an Ångström (Å), i. e., 10^{-10} m, and meso- or macroscopic length scales by virtue of simulations. The same applies to timescales. Machine learning techniques appear to bring this goal into reach. This work applies the recently published on-the-fly machine-learned force field techniques using a variant of the Gaussian approximation potentials combined with Bayesian regression and molecular dynamics as efficiently implemented in the Vienna ab initio simulation package, VASP [1,2]. The generation of these force fields follows active-learning schemes. We apply these force fields to simple oxides such as MgO and more complex reducible oxides such as iron oxide, examine their generalizability, and further increase complexity by studying water adsorption on these metal oxide surfaces [3]. We successfully examined surface properties of pristine and reconstructed MgO and Fe_3O_4 surfaces. However, the accurate description of water–oxide interfaces using machine-learned force fields, especially for iron oxides, remains a field offering plenty of research opportunities.

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A machine learning potential for nucleotides in water

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Recent experimental research [1] showed that nucleotides, under favorable conditions of temperature and concentration, can self-assemble into liquid crystals, forming columnar aggregates. It has been proposed that this ordered structure can favor the polymerization of long nucleotide chains, which is a fundamental step toward the so called “RNA world”. In this contribution, starting from *ab initio* molecular dynamics simulations, at the density functional theory level, an all-atom potential for nucleotides in water is proposed, which is based on an implicit neural network representation [2]. The potential stability and accuracy have been tested and its predictions on simple model systems are compared to the data generated both *ab initio* and using currently available empirical force fields for nucleic acids.

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Four Generations of Neural Network Potentials

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A lot of progress has been made in recent years in the development of machine learning (ML) potentials for atomistic simulations [1]. Neural network potentials (NNPs), which have been introduced more than two decades ago [2], are an important class of ML potentials. While the first generation of NNPs has been restricted to small molecules with only a few degrees of freedom, the second generation extended the applicability of ML potentials to high-dimensional systems containing thousands of atoms by constructing the total energy as a sum of environment-dependent atomic energies [3]. Long-range electrostatic interactions can be included in third-generation NNPs employing environment-dependent charges [4], but only recently limitations of this locality approximation could be overcome by the introduction of fourth-generation ML potentials [5], which are able to describe non-local charge transfer using a global charge equilibration step. In this talk an overview about the evolution of NNPs will be given along with typical applications in large-scale atomistic simulations.

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Multiscale Approach to Biomembrane Remodeling by Adsorbates

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The continuum description of lipid membranes via the Helfrich functional and its extensions is widely employed in the description of mesoscopic systems e.g. to describe fluid dynamics of red blood cells.[1] As its parameters directly refer to mesoscopic observables, the models can relatively easily be validated with available experimental data. The number of parameters is small and their interpretation is straightforward and suggestive. As a continuum model, it is computationally efficient and therefore enables fast, exploratory simulations.

One major problem in the application of this mesoscopic theory to membrane remodeling by proteins and other adsorbates is the *local* modification of membrane shape, lipid composition and elastic properties by adsorbates, such as proteins. For these applications, Helfrich theory has therefore been mostly supplanted by coarse-grained particle models. These models however, lack the advantages of the continuum theory and often have similar issues with specific interactions at the molecular level.

We address this problem by the direct incorporation of the molecular specificity into the local parametrization of the continuum model. For these purposes, we have developed methods to extract the local parameters from molecular simulations at atomic resolution.[2,3] Bridging the scales in this way we were able, to explain the lipid specificity of fusion of membrane fusion in presence of Ca^{2+} via a stalk-mechanism.[3,4] In order to generalize this approach to complex systems, we have developed a solver based on a quasi-G^1 continuous surface representation.[5,6] This approach is sufficiently flexible to accomodate contact deformations and lipid demixing phenomena and allows us to explore the origins of mesoscopic membrane deformations observed in Cryo-EM experiments.

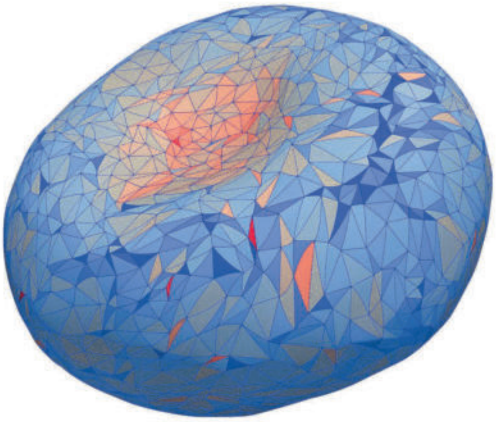

Fig. 1 Simulation Snapshot of Helfrich surface color coded with mean curvature.

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Adversarial Reverse Mapping of Equilibrated Condensed-Phase Molecular Structures

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A tight and consistent link between resolutions is crucial to further expand the impact of multiscale modeling for complex materials. We herein tackle the generation of condensed molecular structures as a refinement---backmapping---of a coarse-grained structure. Traditional schemes start from a rough coarse-to-fine mapping and perform further energy minimization and molecular dynamics simulations to equilibrate the system. In this study we introduce DeepBackmap: A deep neural network based approach to directly predict equilibrated molecular structures for condensed-phase systems. We use generative adversarial networks to learn the Boltzmann distribution from training data and realize reverse mapping by using the coarse-grained structure as a conditional input. We apply our method to a challenging condensed-phase polymeric system. We observe that the model trained in a melt has remarkable transferability to the crystalline phase. The combination of data-driven and physics-based aspects of our architecture help reach temperature transferability with only limited training data.

Transition Between Abnormal and Normal Bipolar Resistive Switching

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With today's increasing demand for powerful memory and storage devices, new technologies, such as memristor-based resistive switching materials, receive growing attention. [1-3] Due to the variety of materials and mechanisms, for example valence change, phase change or interphase switching, resistive switching is still not fully understood, even despite numerous studies and experiments. [3] In amorphous gallium oxide were for example two fundamentally different forms of current voltage curves observed experimentally, namely abnormal and normal bipolar resistive switching. [4,5]

With a simple drift diffusion model in our finite element simulations, we simulate the ionic movement on which the bulk switching, a type of valence switching, is based. Thereby, we can systematically investigate which parameters or material properties influence the switching behaviour in which way. Our simulations with experimental values for amorphous gallium oxide fit nicely to experimental results. Furthermore, we were able to observe and explain the transition between abnormal and normal bipolar resistive switching by changing the device's geometry.

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Coarse-grained MD simulations of nanoplastic particles interacting with a non-polar environment in aqueous solution

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Plastic waste in form of small particles is an emerging threat for marine and terrestrial ecosystems. Little is known about the fate and potential impacts of plastic nanoparticles in the environment. In this work, an attempt for understanding the molecular level interaction behavior between nanoplastics (NPs) and non-polar environments in aqueous solution is introduced. Here, NPs are simulated with different polymers, namely polyethylene oxide (PEO), polyethylene (PE), polypropylene (PP) and polystyrene (PS). On the other hand, carbon nanotubes (CNTs) are used to mimic non-polar environmental molecular systems. Moreover, hydrophobicity of CNTs is modified by introducing different hydrophobic and hydrophilic functional groups (alkane, phenyl, and carboxylic acid groups) into the inner surface of CNTs. The interaction of the modeled NPs with bare and modified CNTs in the presence of water is investigated via MARTINI force field based coarse-grained molecular dynamics simulations. The results show that hydrophobic polymers have a relatively strong affinity to CNTs, especially PE, which is connected to an increase of the contact area between polymers and CNTs. The hydrophobic functional groups introduced into CNTs increased the interaction between hydrophobic polymers and CNTs. This was observed as an attraction of hydrophobic polymers and reduction of their movement. In contrast, PEO showed the lowest affinity towards CNTs and was nearly not affected by functional groups. Therefore, one can expect that hydrophobic polymers have a higher tendency to accumulate at non-polar environmental molecular systems. The chemical nature of present functional groups plays a role in controlling this accumulation process.

Computational Investigation of the Soret Coefficient in the Context of Host/Ligand Binding

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The sensitivity of the thermophoretic properties of aqueous solutions of biomolecules towards complex formation can be related to the thermodynamic equilibrium constant or free energy change of the complexation process. To what extent the change in the Soret coefficient of the host molecule upon ligand binding (compared to the free host) can be attributed to changes in the hydration layer is a subject of current research [1,2]. Recently, an empirical correlation between the temperature dependence of the Soret coefficient (of the free host and the complex) and the corresponding octanol/water partition coefficient log P has been observed experimentally [1,2]. However, a detailed microscopic understanding of this correlation in terms of host/ligand/solvent interactions is still missing. In this work, we apply molecular dynamics (MD) simulations (non-equilibrium and equilibrium) combined with free energy calculations in oder to systematically study the influence of different thermodynamic parameters such as ligand concentration and the hydration properties of the involved molecular species on the respective Soret coefficient(s). Results for cyclodextrin systems which have been used as a model for protein receptors are compared with experimental data from infrared thermal diffusion forced Rayleigh scattering (IR-TDFRS) and calorimetric measurements.

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An efficient methodology for equilibrating confined and free-standing films of highly entangled polymer melts

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Understanding the interplay between the confinement and free surface effects, and the entanglement effect on the characteristics of chains and morphological properties of polymer films of highly entangled polymer melts is important due to their potential applications in real life from both theoretical and technological points of view. Equilibrating large polymer melts in confinement and with free surfaces by computer simulations is a challenge that requires high computational effort as well as the development of highly efficient algorithms. We approach this problem by first studying highly entangled large polymer melts confined between two walls with periodic boundary conditions in two directions parallel to the walls based on the soft-sphere coarse-grained (CG) model. Then we insert the microscopic details of the underlying bead-spring model. Tuning the interaction strength of wall potential, the monomer density of confined polymer melts in equilibrium is kept at the bulk density even near the walls. In a weak confining regime, the conformational properties of chains in the bulk melt are reproduced indicating that our confined polymer melts have reached their equilibrated state [1]. Switching to our recently developed CG model [2] to stabilize the system at zero pressure, we can switch off the wall potential and study free-standing polymer films or polymer films with one supporting substrate.

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Hybrid simulations of shear-thinning polymer flows

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Following the hybrid multiscale method approach we study macroscopic flows of polymer melts in confined geometry. The macroscopic dynamics of incompressible fluid is modelled by the continuity and momentum equations, which are solved by the Discontinuous Galerkin (dG) method. The constitutive model of the stress/strain-rate relation needed at the macroscopic solver level is constructed from the viscosity/shear-rate dependence obtained in Molecular Dynamics simulations of polymer chains. In our study we are interested in the influence of microscopic details of the molecular structure of polymers such as chain length and chain flexibility on responses in macroscopic flow.

Can Soft Models Describe Polymer Knots?

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Mesoscopic models enable computational studies of polymers on large length scales, thanks to potentials that are “soft”, i.e. comparable to thermal energy. However, they simplify local materials structure, which complicates the study of properties that are simultaneously affected by microscopic and mesoscopic features. Knotting behaviour is an intriguing example [1] of such multiscale properties. It concerns topological objects — knots — formed by polymer chains akin to macroscopic ropes. Our study investigates the applicability of mesoscopic models to the description of these objects.

We employ a mesoscopic model, representing polymers by worm-like chains. Non-bonded interactions are defined to deliberately create simplified local liquid structure. We parameterize the model to reproduce mesoscopic structure and conformations of melts described by a microscopic model. These microscopically resolved samples provide reliable reference data to check knotting behaviour in mesoscopic models.

We conclude [2] that soft models can describe knots only in those melts, where the characteristic length scale of polymer stiffness is substantially larger than the characteristic size of monomer-monomer excluded volume. We explain our findings using an existing free-energy model. [3],[4]

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Field Dependence of Magnetic Disorder in Nanoparticles

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Being intrinsic to nanomaterials, disorder effects crucially determine the magnetization properties such as the heating performance of magnetic nanoparticles (MNPs) [1-4]. However, despite the great technological relevance and fundamental importance, a key challenge in MNP research remains in the quantitative interpretation of spin disorder. The classical picture considers MNPs as a collinearly magnetized core with a shell of structurally and magnetically disordered surface spins.

We have recently shown that this static idea needs revision as inside MNPs the magnetization is more complex with a field-dependent magnetization process near the surface [5]. We have established a significant field induced growth of the integral moment by a magnetic ordering transition at the structurally disordered surface. Polarized small-angle neutron scattering (SANS) is one of the few techniques to investigate nanoscale magnetization with spatial resolution [6]. In our study, polarized SANS extends the traditional macroscopic magnetic characterization by revealing the local magnetization response and allowed us to quantitatively separate surface spin disorder from intra-particle disorder contributions. Finally, we have elucidated the intra-particle spin disorder energy, giving indirect insight into the structural defect profile in MNPs.

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Colloidal FeAu core-shell nanoparticles by laser ablation synthesis

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Bimetallic core-shell nanoparticles are highly interesting from a fundamental viewpoint as well as for biomedical imaging like MRI, especially when a core composed of a magnetic element is protected against oxidation and leaching by a noble metal shell. Chemical reduction synthesis enables the synthesis of these structures, however, mostly in multi-step and low yield procedures. In this work, we show that scalable laser ablation in liquids synthesis can fabricate bimetallic FeAu nanoparticles in a one-step process with an iron-rich core and a gold-rich shell and core-shell mass yields up to 99% [1]. Our experimental findings indicate that the core-shell formation is particularly favored in nanoparticles with diameters >10 nm and iron molar fractions >60%, which were confirmed by basic thermodynamic calculation [2]. In-depth characterization of the core-shell nanoparticles by advanced STEM/EDX methods revealed that atomic compositions and crystal structures of core and shell are equivalent to high-temperature phases found in the FeAu bulk phase diagram [3] and in situ heating experiment in TEM confirmed their metastability [4]. Based on these results we devised a formation mechanism for core-shell nanoparticles from non-equilibrium processes like laser ablation in liquids and pinpoint differences in melting temperature and surface energy as main driving forces. Finally, we show the transferability of these findings to other binary (AuCo) and ternary (AuCoFe) nanosystems.

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Functional optical surfaces by colloidal self-assembly

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For the next generation of photonic devices, a novel and cost-efficient approach is needed. This future development requires both tailored control over nanometer-sized building blocks on large area and a fundamental understanding of the strong as well as coherent coupling mechanisms [1]. Currently, practical demonstrations are scarce, and are limited in terms of how many devices may be fabricated in parallel. To realize fabrication on a larger scale, a synergy between optical surfaces and colloidal self-assembly will be leveraged. This requires, on the one hand, applying concepts from applied optics and, on the other hand, using pre-existing quantum emitter and plasmonic nanoparticle building blocks, which form an organized structure on large area by reducing their free energy [2, 3]. We discuss our recent achievements in finite-difference time-domain modelling, large area self-assembly of tailored building blocks as well as time and space resolved optical characterization to fabricate cost-efficient, programmable and up-scalable photonic devices [4].

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Surfactants and polymers active at interfaces: Examples of industrial Colloid&Interface Science

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Interfaces are everywhere, and the behavior of amphiphilic molecules at interfaces is crucial for our everyday life and most technical processes. There is, however, no direct link between molecular architecture of a (polymeric) surfactant and its application performance – the crucial connection is the physico-chemical behavior, i.e. phase behavior/miscibility/aggregation. One easy example: A strongly surface active molecule, e.g. a polyether-modified silicone can be a foam stabilizer – but only in a system in which it is soluble. In a different matrix, in which it is insoluble and forms droplets, the very same molecule will act as defoamer.

It will be demonstrated how physical chemistry can help to solve industrially relevant challenges. Examples will be formulation and deposition of silicone quats via a microemulsion, foam control in oil systems using polyether-modified silicones, and wetting of hydrophobic substrates by using superspreading and non-superspreading silicone surfactants.

Simple One Pot Synthesis of Luminescent Europium Doped Yttrium Oxide Y_2O_3:Eu Nano Discs

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Yttrium oxide (Y_2O_3) is considered to be one of the best host lattices for europium (Eu^{3+}) based red emitting phosphors because of its unit cell and photo-saturation properties. So, it is well known that the bulk Y_2O_3:Eu phosphor particles have more than 90% quantum efficiency. However, down scaling of this particles into nanoscale regime was found to be always difficult. Therefore, the development of an appropriate bottom-up method is needed. We present an improved nonhydrolytic solvent-based synthesis method for red emitting europium doped yttrium oxide nano discs. The as synthesized, monodisperse discs have a spherical shape and are made by a simple one-pot synthesis within a few hours. The synthesis shows good scalability and the size is tunable from 7 nm to 30 nm by varying the reaction conditions. A good dispersibility in organic solvents is given by high temperature coordinating solvents. The dispersed nanomaterial shows a bright red emission (607 nm) under UV excitation (273 nm). By X-ray diffractometry a distorted anisotropic cubic yttrium oxide phase was found giving rise to a distinct change in intensities of the red emission lines. A calcination temperature of 600 °C transformed the material into highly crystalline cubic yttrium oxide with a typical emission spectrum as known from bulk material.

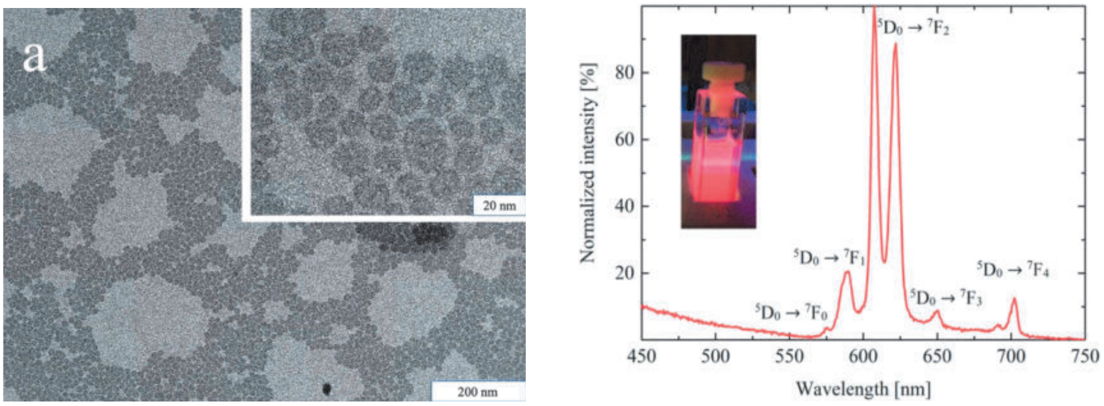

Figure 1: a) TEM images of the as synthesized nano discs. The spheric plates have a diameter of 13.8 nm +/- 3.7 nm and a thickness of approximately 2-3 nm. The PL emission spectrum shows a strong red emission at 607 nm and 622 nm upon host lattice excitation at 273 nm.

Solubility of proteins from extended molecular DLVO theory

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Assembly processes of proteins, including their aggregation, precipitation and crystallization, are steered by the interplay of various intermolecular interactions both of attractive and repulsive nature. They are highly important for many biotechnological processes, yet they are complex to be fully understood and *in silico* predicted. Among popular measures of the protein-protein interactions towards their crystallization behavior is the osmotic second virial coefficient, B_{22} [1]. It is often calculated from the potential of mean force (PMF) according to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [2]. However, pure DLVO accounts intermolecular forces between spherical particles, therefore, loses its predictive power for other geometries of interactive macromolecules. Alternatively, umbrella sampling MD simulations or Monte Carlo simulations with Martini coarse-graining (CG) were proposed, but these methods are computationally expensive and overestimate the PMF, therefore require fitting to experimental data.

In my talk, I will present an extended model and recently developed algorithm of calculation of B_{22} coefficient considering a specific shape of a molecule, enabling better *in silico* predictions of protein solubility without fitting to experimental data [3]. The model is based on the shape-based coarse-grained representation of the protein and the PMF derived from the extended DLVO theory. The new model was validated on the crystallization of well-studied proteins of different shapes and has shown a good agreement with experiments at different pH ranges and salt types. Further implementations enable construction of phase diagrams, resulting in acceleration of processing conditions of protein assembly and crystallization.

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Soft quasicrystals optimize sphere packing

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Quasicrystals exhibit by a peculiar state of order, which is fundamentally different from classical crystalline ordered states. Discovered in 1982 by Dan Shechtman for MnAl-alloys, they have since then been observed in more than 100 different binary and ternary metal alloys. Since 2004, non-metallic quasicrystals have been reported for colloidal systems including liquid crystals, block copolymers, nanoparticles and mesoporous silica. Although still rare, non-metallic quasicrystals are receiving increasing attention, because they allow extending the characteristic dimensions of quasicrystals from the Angstrom to the micrometer size range for optical and photonic applications.

Since the discovery of soft quasicrystals, it has become clear that quasicrystals are an ordered state that is widely found in matter. This raises the question about the origin of their stability, considering the very different types of matter they have been observed.

We demonstrate that soft quasicrystals form because of the existence of two intrinsic lengths scales and because at certain volume fractions sphere packing can be optimized by a short-range favorable geometry that does not allow long-range periodicity. This shown for quasicrystals formed by block copolymer micelles in water and in organic solvents, for polymer-coated nanoparticles, and for binary colloid mixtures. We calculate a phase diagram showing the stability regions of different quasicrystals and observe nearly quantitative agreement between calculated and experimentally observed stability regions. We show that all experimentally observed soft quasicrystals fall into two structure classes, and demonstrate a direct link between repulsive soft quasicrystals and attractive intermetallic quasicrystals by Boltzmann inversion of the interaction potential.

Assembling Nanocrystals into Hybrid Functional Gel Structures by Means of Multivalent Cations

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Assemblies built up from nanocrystal building blocks exhibit novel optical and electrical properties which enable extending the potential field of their applications. Additionally, the self-assembly process helps to overcome the disadvantages of the colloidally dispersed particles and provides a platform towards self-supported gel-like structures. The controlled synthesis procedures of cadmium chalcogenide semiconductor nanocrystals ensure the preparation of building blocks with well-defined size, shape, surface chemistry and ensemble properties. To merge the advantageous properties of both semiconductor and metal NCs, hybrid nanosystems have been synthesized *via* our novel approach to enhance the charge carrier separation upon illumination. These hybrid nanoparticle backbones open up new routes towards applications in the field of sensing. The preparation of 3D, interconnected gel structures from different nanocrystals has been performed based on the destabilizing of the semiconductor NCs and the simultaneous deposition of the metal domains. The present work shows routes towards voluminous, macroscopic assemblies consisting of interconnected CdSe/CdS, CdSe/CdTe, [1] metal and their hybrid nanoparticles by applying multivalent cations. [2] Beside the structural characteristics, the optical and photoelectrochemical properties of the assembled structures prove the enhanced charge carrier separation.

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Controlling Properties of Nanoparticle-based Networks via their Microstructure

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The generation of non-ordered, porous networks from nanocrystal building blocks presents a promising approach to manufacture macroscopic structures while retaining nanoscopic properties of the building blocks (optical properties, high surface area, *etc.*) Building on the assembly of these networks (often called gels) in recent years several methods have been proposed to further tune the structure and thereby the properties.[1] One such approach is the modification of the structure after its assembly opposed to the more traditional route of tuning the individual building blocks.

In this work we modify already connected nanocrystal-based gels with a thin silica shell resulting in core-shell network structure. It can be shown that this technique is suitable for mechanical reinforcement of these networks further broadening the range of potential applications.[2] By tuning of the synthesis sequence in combination with time-resolved photoluminescence spectroscopy we were furthermore able to selectively couple or decouple the individual building blocks giving additional insight into the optoelectronic processes within the network.[3]

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The micromechanics of shear thickening fluids and their application as protective materials for medical professionals, first responders, atheletes, and astronauts.

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Shear thickening colloidal and/or nanoparticle suspensions are commonly encountered in chemical and materials processing, and are also the basis of a technology platform for advanced, field responsive nanocomposites. In this presentation, I will review some of the experimental methods and key results concerning the micromechanics of colloidal suspension rheology. Micromechanics is the ability to predict the properties of complex systems from a colloidal or microscopic level description of the structure and forces. A fundamental understanding of colloidal suspension rheology and in particular, shear thickening, has been achieved through a combination of model system synthesis, rheological, rheo-optical and rheo-small angle neutron scattering (SANS) measurements, as well as simulation and theory (Colloidal Suspension Rheology Mewis and Wagner, Cambridge Univ. Press, 2012). The role of particle contact friction versus enhanced lubrication friction will be elucidated along with implications for formulation.

Shear thickening fluids (STFs) are novel field-responsive materials that can be engineered to be useful nanocomposites for enhanced ballistic and impact protection, puncture resistant medical gloves, energy absorbing materials for mitigating impacts and concussions, as well as in systems for mitigating puncture, micrometeoroid, and orbital debris threats in space applications. The development of commercial applications of STFs will be discussed. The rheological investigations and micromechanical modeling serve as a framework for the rational design of STF-based materials to meet specific performance requirements not easily achieved with more conventional materials. (Phys. Today, Oct. 2009, p. 27-32) I will illustrate some technological applications of STFs under commercial development, including use in astronaut protection and application in the Artemis Mission to the Moon as well as the Mission to Mars and the associated flight experiments on the International Space Station.

Single Nanocrystal Arrays- Preparation and Spectroscopy

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Nanotechnology is about using single nanoscale objects in devices and applications. Yet there are still few ways to reliably manipulate and position single nanocrystals with nanometre spatial resolution. In this talk, I will discuss the positioning of single nanocrystals into arrays using several different assembly methods. A key question is whether one can assemble nanocrystals using chemical forces or whether it is better to use applied fields to drive assembly. We show that electrophoresis (see Figure 1), the movement of particles in an applied DC electric field, is a valuable tool for single nanocrystal manipulation.

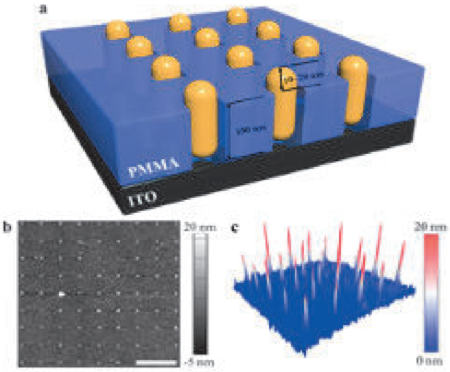

Figure 1. **Vertical gold nanorod assembly *via* EPD** (a) A schematic of the geometry of the vertically assembled gold nanorod array. (b) Atomic force microscopy image of part of a gold nanorod array showing 9 × 9 vertically oriented gold nanorods (scale bar: 10 μm). (c) 3D coloured map of the height profile extracted from the atomic force microscopy image. (Colour bar: Height).

Literature

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Magic number colloidal clusters

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Small particle clusters exhibit discrete behaviour as a result of the interplay between bulk crystallization and effect of interface that separates them from their surroundings. An example is the extraordinary high occurrence of clusters of certain sizes in the mass spectrum of small noble gas and metal clusters. These clusters are termed magic clusters for their superior thermodynamic stabilities.

Recently the study of particle clusters extended to the realm of colloids. The attractive force that holds together atoms is replaced by geometric confinement of weakly interacting colloids. Small numbers of colloids pack into clusters of various symmetries, whereas larger clusters favour icosahedral symmetry. An open question related to such colloidal clusters is whether they can also exhibit different thermodynamic stability depending on the number of their constituent building block, i.e., if the concept of magic cluster can be extended from the atomic scale to the scale of colloids.

We produce colloidal clusters of various sizes by confining colloids in emulsion droplets fabricated by microfluidics and find a large library of magic colloidal clusters with defined surface features [1]. With geometric modelling and electron tomography, we confirm that the structure of these colloidal clusters consist of closed shells of Mackay and anti-Mackay type. Free energy calculation show that these colloidal cluster exhibit superior thermodynamic stability in cases where the number of colloidal particles within the confinement affords closed shells. In contrast, if these numbers are not commensurate with a closed shell structure, the structures possess a higher free energy. Importantly, and differing from their atomic analogues, the occurrence of such magic number states is not driven by the mutual attraction of the individual building blocks. Instead, the thermodynamics in our colloidal system is entirely governed by entropy maximisation. In this presentation we combine experimental efforts with multiscale simulations and discuss the self-assembly of magic colloidal clusters, the kinetics behind the assembly mechanism, the resulting structures [2], and pathways to accommodate defects and excess particles [3].

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Nicolas Vogel, Free Energy Landscape of Colloidal Clusters in Spherical Confinement
ACS Nano 2019, 13, 8, 9005

The Road Not Taken – Icosahedral or Decahedral Symmetry in Spherical Confinement?

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Icosahedral or decahedral symmetries are frequently observed in nano- and micro-scale objects such as atomic clusters, supramolecular assemblies, nanoparticles and their superlattices. These five-fold multi-twinned structures, unfavorable in bulk, are often the free energy minimum configurations when the number of building blocks is finite. Despite their abundance, the competition between icosahedral and decahedral symmetry is not well understood. Here, we find icosahedral and decahedral colloidal clusters in spherical confinement consisting of up to 100,000 colloidal particles. Although free energy calculation indicates that both clusters are thermodynamically preferable in alternating regions of system sizes, decahedral clusters are disproportionally rare in simulation and experiment. We show that crystallization kinetics disfavors decahedral clusters under spherical curvature and the pathway towards decahedral symmetry is hindered at a surprisingly early stage during cluster formation.

Interaction of Bio-Surfactants with Different Lipid Membranes

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Saponins are plant derived bio-surfactants which exhibit an amphiphilic structure built of a hydrophobic steroidic or triterpenic backbone with a varying number of hydrophilic sugar chains. These molecules are part of the plant defence against bakteria and funghi. Most saponins have very strong biological effects are used in pharmacy. Examples are escin which regulates venous tension [1,2] and glycyrrhizin which has strong antiviral activity and is supposed to act e.g. against SARS-COV2. However, the interaction of saponins with biological membranes is still partly unclear and each saponin seems to have different effects at least quantitatively.

Therefore in this contribution the effect of the pure saponins escin [2] and glycyrrhizin on small unilamellar vesicles of DMPC, prepared by extrusion, is investigated mainly by different scattering methods in dependence on the saponin-amount and the temperature [3]. 1,2-Dimyristoyl-sn-glycero-3-phosphocholine (DMPC) belongs is a phospholipids and vesicles made of it act as a model membrane in the present work.

Model membranes consisting of DMPC mimic biological membranes quite well and allow to study effects of additives under different conditions, e.g. composition and temperature.

An incorporation of escin above a critical amount can be deduced from the investigated parameters, namely the thermal phase transition temperature and vesicle size parameters like the radius, membrane thickness and lipid head-to-head distance within one monolayer. At high escin amounts fianally lipid nanodiscs (bicelles) are formed. Moreover, saponins can interact with other pharmacologically relevant compounds [4].

Besides structural and thermodynamic data also neutron spin-echo (NSE) results will be presented [5]. NSE reveals the influence of the saponin on the bending elasticity of the DMPC model membranes which depends on the phase state of the lipid.

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Innovative Cleaning Concept with Controlled Foams

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The historical surfaces of artistic and cultural assets are often soiled as a result of either wear and tear or long-term exposure to environmental influences. Cleaning these is quite challenging. The project aims to develop new, innovative foam-based cleaning methods. By cleaning with foams, the amount of conventional detergents can be reduced by up to 90%. Current research shows that foamed detergents can clean far more efficiently than non-foamed ones [1]. By using the double syringe technique foams with varying liquid fractions but the same bubble sizes are produced [2]. To understand the role of foams within cleaning processes, cleaning tests have been performed in which foams with different stabilities and liquid fractions ε were applied to contaminated glass substrates (Figure 1). We found that unstable foams clean better than stable foams. Furthermore, three cleaning mechanisms were identified: (1) imbibition at low liquid fractions, (2) wiping, i.e. shifting of the contact line between oil, foam and glass, at all liquid fractions, and (3) drainage at high liquid fractions.

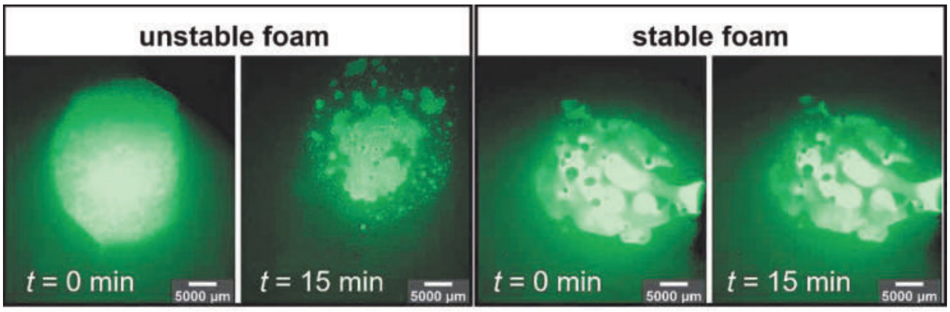

Figure 1: Pictures of the cleaning test with a stable and unstable foam on a glass substrate contaminated with fluorescent oil after foam application and after 12 min.

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PNIPAM microgels at the air / water interface – from single interfaces to foams

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Aqueous particle stabilized foams can be found in many technical applications and food products. In these systems the particles adsorb at the air-liquid interfaces of the foam and stabilize them. When altering the properties of the particles like their hydrophobicity, the properties of the produced foams can be changed. Typical particles are modified silica nanospheres, but also soft colloidal particles like proteins, especially in food-related systems [1].

Probing the internal structure of macroscopic liquid foams, like their film thickness, is very difficult with optical methods, since foams strongly scatter light in the visible range. To overcome this problem, small angle neutron scattering (SANS) can be used, as already demonstrated by Axelos *et al*. [2].

In this contribution microgel-stabilized foams are investigated. These foams are very stable at temperatures below the VPTT and can be destabilized on demand by increasing the temperature. The internal structure of these is investigated with SANS experiments, which allows for the determination of foam film thicknesses inside of the foam. In order to address the hierarchical structure of foams, the adsorption and structuring of PNIPAM microgels at the macroscopic air / water interface is also studied *via* Langmuir isotherms and *in situ* X-ray reflectivity. A relation is made between the structures on different length scales.

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Giant vesicles: versatile colloids for unravelling biomembrane properties and for building artificial cells

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Giant vesicles (5-100 µm in size, see Fig. 1) provide an exceptional colloidal system for the systematic study of basic properties of lipid and polymer membranes (Annu. Rev. Biophys. 48:93, 2019; “The giant vesicle book”, Eds. Dimova & Marques, CRC press, 2020). In this talk, we will introduce approaches and tools for assessing mechanical, rheological and electrical properties of membrane (including bending rigidity, spontaneous curvature, surface viscosity, capacitance, pore edge tension). Giant vesicles are also increasingly employed to unravel the mechanisms driving various biological processes and remodeling occurring at the level of the cell membrane. It is a common perception that membrane curvature is mainly generated by the activity of specific protein species. Here, we will demonstrate that it can be readily generated also by various asymmetries across the membrane, which plausibly represent a governing factor for defining shapes of membrane organelles (PNAS 115:5756, 2018; Nano Lett. 18:7816, 2018). In addition, the process of wetting of the membrane by molecularly-crowded aqueous phases will be discussed as a morphology-modulating element leading to a variety of shape transformations (PNAS 108:4731, 2011; ACS Nano 10:463, 2016). Finally, we will demonstrate the applicability of giant vesicles as a workbench for synthetic approaches to reconstitute growth and division in minimal artificial cells (Biophys. J. 116:79, 2019; Nature Commun. 11:905, 2020).

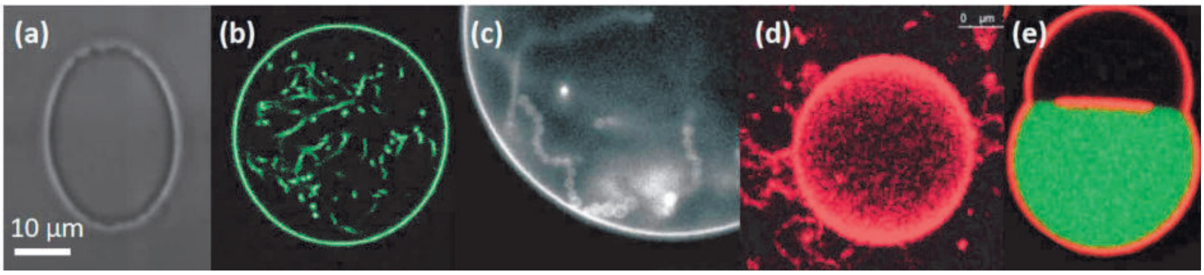

Figure 1: Giant vesicles exhibit morphological changes upon application of external stimuli such as (a) electric fields leading to elongation and poration, (b-d) compositional and buffer asymmetry resulting in (b) inward cylindrical, (c) necklace-like or (d) outward tubes, or (e) wetting by crowded aqueous droplets.

Invertible Micelles from Double Anionic Bock Copolyelectrolytes

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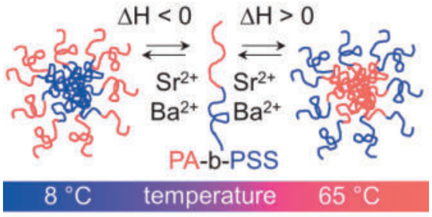
Anionic polyelectrolytes in water exhibit complex interaction patterns with a variety of metal cations. Two opposing trends establish a striking example: Whereas precipitation of sodium polyacrylate (PA) in the presence of alkaline earth cations is amplified with increasing temperature T, sodium polystyrene sulfonate (PSS) shows the opposite trend. [1] The present work combines these opposing trends in one polymer chain by preparing block copolyelectrolytes with a PA and a PSS block. Those block copolyelectrolytes form micelles in aqueous solution of M^{2+} (= Sr^{2+} or Ba^{2+}), which can be inverted: At T high enough, the tendency of PA to precipitate with M^{2+} induces an aggregation of PA blocks, leading to micelles with M^{2+}-PA cores. As T decreases, solubility of M^{2+}-PA increases and eventually the micelles disintegrate. Upon further lowering T, the solubility limit of M^{2+}-PSS is crossed and new micelles form, now with M^{2+}-PSS blocks in the micellar cores. This process could be deciphered by means of joint small angle neutron (SANS) and x-ray scattering (SAXS) and of isothermal titration calorimetry (ITC). [2] SANS based on deuterated PA-blocks in combination with contrast matching either probed a visible core or shell. ITC with homo polymers and block copolymers revealed an endothermic binding of M^{2+} to PA and an exothermic binding of the same cations to PSS. Tuning of the ratio of the block lengths and the composition in solution enabled us to reversibly form and invert the micelles, thus paving new routes to dual responsive delivery systems.



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Influence of alcohol cosurfactants on structure and properties of SDS/PDADMAC PESCs

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Upon mixing an ionic surfactant and an oppositely charged polyelectrolyte (PE) formation of complexes (PESCs) is induced.[1] Such systems are frequently applied in cosmetics, detergency and drug delivery.[2] The diversity of PESCs can be further expanded via addition of a third major component: a cosurfactant. In the current study the influence of long-, medium- and short-chain alcohols on SDS/PDADMAC (polydiallyldimethylammoniumchlorid) PESCs is investigated. Among all, n-dodecanol was in the spotlight as hydrolysis product of SDS. The remarkable effect of the cosurfactants on the formed PESCs was explicitly confirmed by the rheological measurements, showing pronounced and consistent increase by up to more than 3 orders of magnitude in the PESCs viscosity with increasing alcohol concentration. The internal structure of the formed complexes was elucidated in detail with contrast variation small angle neutron scattering (SANS) as wormlike aggregates, interconnected via PDADMAC chains.

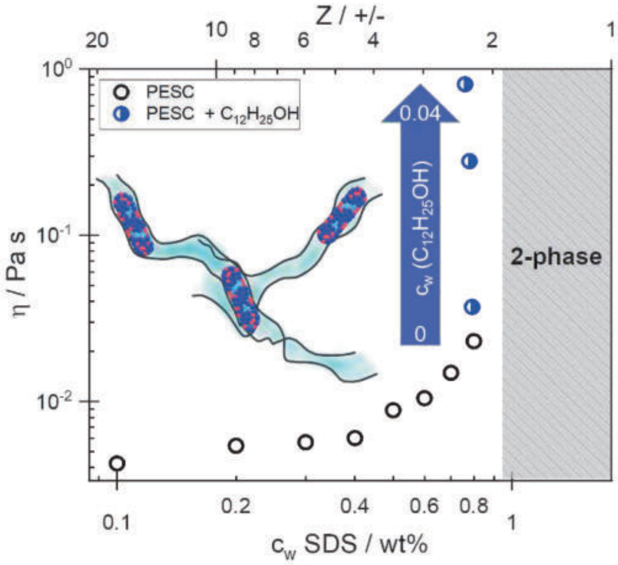

Figure 1. Wormlike PESC aggregates interconnected via PDADMAC chains: spike in viscosity is achieved through a small amount of added n-dodecanol cosurfactant.

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Phase behavior and flow properties of ultra-soft spheres

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In our recent publication we explored the phase behavior of super-soft spheres using solutions of ultra-low crosslinked poly(N -isopropylacrylamide) based microgels as a model system. For these microgels, the effects of the electric charges on their surfaces can be neglected and, therefore, only the role of softness on the phase behavior is investigated. The samples show a liquid-to-crystal transition at higher volume fraction with respect to both hard spheres and stiffer microgels. Furthermore, stable body centered cubic (bcc) crystals are observed in addition to the expected face centered cubic (fcc) crystals. Small-angle X-ray and neutron scattering with contrast variation allow the characterization of both the microgel-to-microgel distance, and the architecture of single microgels in crowded solutions. The measurements reveal that the stable bcc crystals depend on the interplay between the collapse and the interpenetration of the external shell of the ultra-low crosslinked microgels. Additionally, the flow properties of ultra-low crosslinked microgels shows a complex behavior in between the classic hard colloids and linear polymers also determined by the interplay between deswelling and interpenetration.

Structured light-emitting metasurfaces based on confinement self-assembly

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A robust printing technique, based on confining the colloidal solution between the structured template and the substrate, overcomes the challenge of assembling quantum emitters into nanometre-sized periodic structures on a centimeter scale. Such structured, light-emitting metasurfaces can be produced on various substrates, including conductive, semi-conductive or flexible, polymer supports. Combining these structures with a light-absorbing metallic counterpart by simple stacking at various angles results in a tunable Moiré pattern with strong lateral contrast and allows creating nanocavities for generating strong-coupling effects.[1] On the other hand, a combination with an identical emitter-based grating leads to a direct circular polarized photoluminescence, featuring a remarkably high degree of polarization without a need for any additional chiral template as an intermediary.[2] The suggested approach allows for reproducible, large-area manufacturing at reasonable costs and is of potential use for chiroptical sensors, photonic circuit applications, or preventing counterfeit.

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Probing Tailor-Made Colloidal 2D Nanomaterials for Innovative Optoelectronics

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Solution-processed two-dimensional (2D) semiconductors represent next generation materials for innovative optoelectronics including light and field effect transistors and near-infrared (NIR) emitting applications.[1, 2]

We use colloidal chemistry methods to synthetically tailor the optoelectronic properties (e.g. the band gap size) of 2D semiconductors of interest and probe the dynamics and characteristics of photoexcited states in the structures by ultrafast transient absorption spectroscopy.[2, 3, 4] For example, the strong quantum confinement in the thickness dimension of 2D semiconductors leads to increased exciton binding energies in the structures in comparison to their solid-state or spherical nanocrystal counterparts.[5]

Two material systems are addressed in this talk: efficient NIR emitters (1) and colloidal transition metal dichalcogenides (TMDCs) (2).

(1) 2D PbS and PbSe nanoplatelets exhibit narrow absorption and emission tunable over a wide range (700 – 1500 nm) with a high photoluminescence quantum yield of 35%, a value unprecedented at wavelengths close to the 2nd telecom window.

(2) Colloidal synthesis of ultrathin MoS_2 and WS_2 layers with either metallic or semiconducting character is shown. The formation of heterostructures has high potential for the efficient (photo-)generation and use of inter- and intralayer charge carriers and excitons.

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Depolarized dynamic light scattering of gold nanorods decorated with thermoresponsive polymer ligands

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Probing precisely the rotational and translational diffusion as well as the colloidal stability of rod shaped colloids is of significant fundamental interest with implications for many applications. Gold nanorods are ideal model systems for such anisotropic colloids. These can be synthesized with high precision in length and diameter with low polydispersity. Furthermore, the rod surface can be easily functionalized with polymer ligands employing for example thiol anchoring groups. This in turn allows for tailoring the surface properties and colloidal stability.

We synthesized gold nanorods with different dimensions and performed ligand exchange of the initial CTAB stabilizer by thermoresponsive polymer ligands composed of poly-N-isopropylacrylamide (PNIPAM). While we studied the size, shape and colloidal stability of the PNIPAM decorated rods by means of small angle X-ray scattering and transmission electron microscopy, the translational and rotational diffusion was investigated by depolarized dynamic light scattering following a recently published protocol.[1] We precisely determined the translational and rotational diffusion coefficients in a broad range of temperatures indirectly monitoring the conformational changes of the thermoresponsive ligands. The results are compared to theoretical predictions of diffusion coefficients for prolate spheroids.

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Active matter – implementing smart functionalities into colloids

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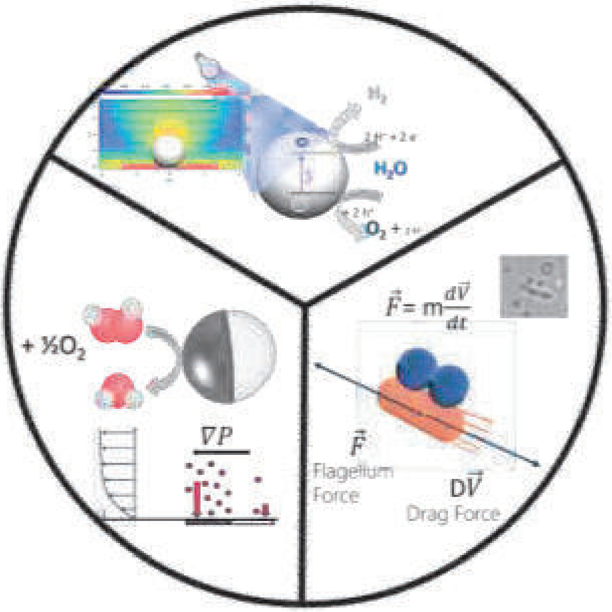
One of the most exciting new directions in colloidal soft matter is pushing colloids out of equilibrium, leading to self-propulsion.

A variety of different origins can be used to achieve energy dissipation in colloidal particles: catalytic reactions,[1] photocatalysis[2] or galvanic exchanges.[3] When energy is asymmetrically transferred between different forms, an active motility can be resulting. This property has been used to study different effects such as assembly,[2] apparent phototaxis,[4] but also used to tackle environmental problems: Through phoretic interactions our extremely fast photocatalytic particles can collect microplastics.[5]



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Progress in understanding wetting phenomena

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Although wetting phenomena have been studied for more than 200 years, many fundamental questions are not fully understood. For example, the speed of a water drop moving down an inclined plane cannot be predicted. Still significant progress has been made in the last decade, in particular with respect to dynamic wetting. The aim of the presentation is to draw attention to some new developments.

One new development is the increasing interest in contact angles hysteresis. Wetting phenomena are characterized by the contact angle, that is the angle between the solid/liquid and the liquid/air interfaces. In thermodynamic equilibrium this contact angle is related by the Young equation to the interfacial energies. Since Young’s equation is so simple and intuitive, it is widely used. Unfortunately, it is practically impossible to measure the equilibrium contact angle. When for example placing a drop on a surface its contact angle can assume a range of values depending of how the drop is placed. The range is limited by the advancing Θ_a and receding Θ_r contact angles; the difference is called contact angle hysteresis. Although contact angle hysteresis may appear as a nuisance, it is essential for our daily life because it provides friction to drops. Without contact angle hysteresis drops would slide off surfaces even at the smallest tilt angle. Many applications, such as coating, painting, flotation, would not be possible without contact angle hysteresis. Contact angle hysteresis is difficult to understand and quantify because it is caused by the nanoscopic or even atomic structure of the surfaces.

Self-assembling of functionalized hematite nanospindles at the liquid-air interface

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Nanoparticles with anisometric shape exhibit a reorientation behavior that can be directed by electric or magnetic fields or shear flow [1,2] and makes them relevant for technological applications such as nanoprobes or sensors [3]. In contrast to most elongated nanoparticles that are dominated by shape anisotropy, weakly ferromagnetic hematite nanospindles bear a strong magnetocrystalline anisotropy above the Morin transition (T_M = 263 K) and orient with their long axis perpendicular to an applied magnetic field [4,5]. This unique reorientation behavior entails the importance of fostering a precise understanding of the orientation and relaxation of hematite nanospindles in either free diffusion or at interfaces and also constrained by a magnetic field.

In this contribution, we will present our recent study of the self-organization of hematite nanospindles on the water-air interface. Self-organization at the liquid-air interface is advantageous compared to the self-assembly on static substrates because of the continuously possible rearrangement of the particles. After functionalization and phase-transfer of as-synthesized nanospindles into suitable organic solvents, the self-organization behavior was studied by Langmuir pressure-area isotherms. We observe a reproducible change of surface pressure with increasing particle area density that we attribute to a variation in particle arrangement. A reorientation from horizontal to vertical arrangement on the water surface can be speculated. Their exact orientation behavior will be accessible after Langmuir-Schäfer deposition on a solid substrate and subsequent structural analysis.

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Tailoring of pore openings in gelatin-based hydrogel foams

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Hydrogel foams based on gelatin are widely accepted as functional materials in the field of biomaterial science [1-2]. In order to generate tailor-made hydrogel foams for applications such as tissue engineering, the control over two key structural parameters, namely the pore diameter and the pore opening diameter, is crucial. This control can be achieved by using microfluidic bubbling for the generation of liquid foam templates. The pore diameters in hydrogel foams can easily be adjusted by varying the liquid flow rate or gas pressure during microfluidic bubbling [3,4]. However, tailoring the diameters of the pore openings still is a challenge. Here, two complimentary methods are used to adjust the diameters of the pore openings: (1) The addition of polymer solution to a pre-formed liquid foam composed of the same polymer solution. (2) The variation of the frequency of bubble formation during foam generation. With these methods, we could adjust the ratio of the pore opening diameter to the pore diameter d_p / D_p between 0.14 and 0.28 (Fig. 1). The obtained values were compared with theoretical predictions.

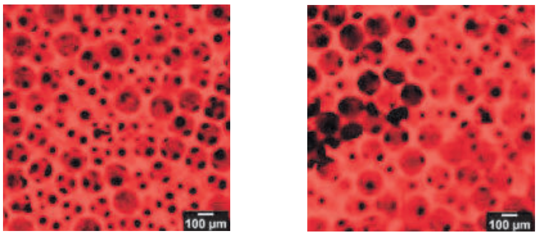

Fig. 1: Gelatin-based hydrogel foams with large (left) and small (right) pore opening diameters.

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Inkjet Printing: Patterning of 3D Nanoparticle-Based Aerogel-Like Networks for Photoelectrochemical Applications

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Inkjet printing is a common technique to deposit nanoparticles on different substrates and enables a lateral structuring. Moreover, the spotlight of current research is on the synthesis of nanoparticles with various shapes, sizes, and optical properties as well as on their assembly into three-dimensional structures commonly known as aerogels. Nowadays, the assembly of NPs into meso- or macrostructures is of high interest and the structures can be used in different fields, *e.g*. photocatalysis, catalysis and sensing. Here, the patterning of three-dimensional nanoparticle-based CdSe/CdS aerogel-like networks on conducting surfaces via inkjet printing of an aqueous nano-ink is presented.[1,2] The main focus of the presented work is on the implementation of the conventional nanoparticle-based gelation process in a commercial office printing system. By simultaneously printing the aqueous nano-ink and a destabilization agent, a aerogel-like network-coated electrode surface can be achieved, which enables the manufacturing of 3D nanoparticle-based network-coated (photo)electrodes for applications in (photo)electrochemistry. Additionally, the charge-carrier mobility within the printed three-dimensional semiconductor nanoparticle-based networks was investigated by spectroelectrochemical measurements.[2,3]

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Electrochemical Switching of Block Copolymers at the Water-Oil Interface

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Electro-responsive polymers have gained a significant interest in the current research due to promising properties for industry and technology, e. g. the ability to form micelles [1] and to release active molecules electrochemically [2]. We consider the aspect of the electrochemical stimulation of their interfacial activity and the behavior in the bulk phase. The block copolymer poly(ethylene oxide)$_{114}$-*b*-poly{[2-(methacryloyloxy)ethyl]-diisopropylmethylammonium chloride)$_{171}$, consisting of one non-ionic hydrophilic block and one polycationic block, was examined by emerging drop and light scattering experiments. Potassium hexacyanoferrates were electrochemically switched, which were able to convert the polyelectrolyte block from hydrophilic in presence of ferrocyanide $[Fe(CN)_6]^{4-}$ to an hydrophobic block in presence of ferricyanide $[Fe(CN)_6]^{3-}$. Micellization in the bulk phase and an effective decrease of the interfacial tension in presence of ferricyanides indicated a stronger complexation. Utilizing their electrochemical addressability, the ratio between ferro- and ferricyanide was electrochemically changed, tracing the interfacial tension in situ. While a chemical oxidation/reduction is feasible, also an electrochemical oxidation leads to a significant change in the interfacial tension. The corresponding reduction showed only a mild response under the same conditions. Atomic force microscopy of the interfacial structures transferred from the liquid-liquid Langmuir trough showed spherical particles matching in size the aggregates found in the bulk phase.

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Cooperative Ion-Solvent Dynamics in Organic Electrolytes Revealed by Diffusion NMR and Molecular Dynamics Simulations

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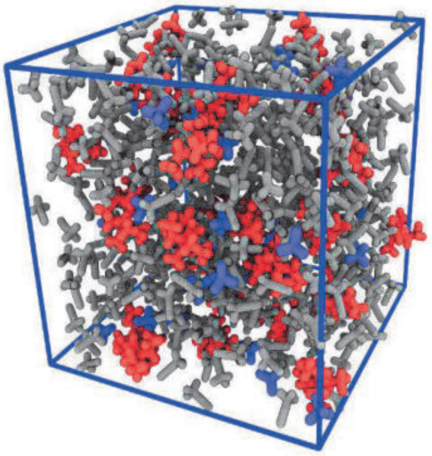

Fig. 1 Snapshot of the simulation cell with 1 M salt concentration (red: TEA^+ cations; blue: BF_4^- anions; grey: d-ACN solvent molecules).

The tetraethylammonium-tetrafluoroborate electrolyte solvated in acetonitrile ($TEA\text{-}BF_4$/ACN) is used in most commercial supercapacitors. Thus, the need for fundamental understanding of ions solvation- and diffusion mechanisms steadily increases [1]. Using combination of the pulsed filed gradient NMR and molecular dynamics simulations, we investigated diffusion processes of $TEA\text{-}BF_4$/ACN electrolyte (Fig. 1) in a broad range of temperatures and concentrations [1]. The experimentally obtained diffusivities show significant deviations from the predicted ones based on the known Stokes-Einstein relation (up to 2.5-fold). To rationalize this, we propose the model assuming partly-correlated motion of ions with their solvation shells. In turn, it allowed to quantify the shell rigidity, which is seen to decrease with increasing the electrolyte concentration. Finally, we share our critical vision and provide broader context with intention of making a small step forward in understanding the processes of ion mobility on a molecular level in one of the most promising area of energy storage.

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Large-Scale Fractionation of Colloidal Particles in Centrifugal Fields

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Density gradient centrifugation is an effective method for the isolation and purification of small particles. Hollow rotors capable of hosting density gradients replace the need for centrifuge tubes and therefore allow separations at large scales [1]. So far, zonal rotors have been used for biological separations ranging from the purification of whole cells down to serum proteins. We demonstrate that the high-resolution separation method opens up exciting perspectives apart from biology, namely in sorting mixtures of synthetic colloids [2]. Loading and unloading, while the rotor is spinning, avoids perturbations during acceleration and deceleration periods, and thus makes a vital contribution to sorting accuracy.

Nowadays one can synthesize colloidal particles in a wide variety of compositions and shapes. A prominent example for this are "colloidal molecules" or, generally speaking, defined assemblies of nanoparticles that can appear in varying aggregation numbers [3]. Fractionation of such multimodal colloids plays an essential role with regard to their organization into hierarchical organized superstructures such as films, mesocrystals and metamaterials. Zonal rotor centrifugation was found to be a scalable method of getting "colloidal molecules" properly sorted [2]. Separations were evaluated by differential centrifugal sedimentation, which provides high-resolution size distributions of the collected nanoparticle fractions. The performance achieved in relation to resolution, zone widths, sorting efficiencies and recovery rates clearly demonstrate that zonal rotor centrifugation provides an excellent solution to the fractionation of nanoparticle mixtures [2].

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Mechanisms of Nucleation and Solid-Solid Phase Transitions in Triblock Janus Assemblies

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A model, including chemical details of core nanoparticle as well as explicit surface charges and hydrophobic patches, of triblock Janus particles is employed to simulate nucleation and solid-solid phase transition in two dimensional layers. Explicit solvent and a substrate are included in the model and hydrodynamic and many-body interactions were taken into account within many-body dissipative particle dynamics simulation. In order not to impose a mechanism *a priori*, we performed free (unbiased) simulations, leaving the system the freedom to choose its own pathways.

In agreement with experiment and previous biased simulations, a two-step mechanism for the nucleation of a kagome lattice from solution was detected. However, a distinct feature of the present unbiased *vs.* biased simulations is that multiple nuclei emerge from solution, upon their growth aligned and misaligned facets at the grain boundaries are introduced into the system. Mismatch in the symmetry planes of neighbouring nuclei hinders the growth of less stable nuclei. Unification of such nuclei at the grain boundaries of misaligned facets obeys a two-step mechanism; melting of the smaller nuclei followed by subsequent nucleation of liquid-like particles at the interface of bigger neighboring nuclei. Besides, multiple postcritical nuclei are formed; the growth of some of which stops due to introduction of strain in the system. Such incomplete nucleation/growth mechanism is in complete agreement with recent experiments. The solid-solid (hexagonal-to-kagome) phase transition, at weak superheatings, obeys a two-step mechanism; a slower step (formation of a liquid droplet) followed by a faster step (nucleation of kagome from liquid droplet).

Revealing the surface chemistry on colloidal metallic nanoparticles by advanced ^{13}C and ^{15}N solid-state NMR techniques

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In the past years, colloidal nano-catalysts have become more and more attractive in chemical reactions as they close the gap between homogeneous catalysis of molecular complexes and heterogeneous catalysis on metal surfaces. They enable a large variety of surface reactions, such as the activation of ammonia under mild conditions or the oxidation of carbon monoxide at room temperature. While for many years colloidal particles are known and many studies concerning their reactivity towards bond activation have been published [1], details on their surface chemistry are still widely unexplored since surface techniques are mostly not applicable for these materials. Here, an analytical tool sensitive to the local coordination environment of the surface is required which is provided by solid-state NMR. [2]

The presentation will show how ^{13}C and ^{15}N solid-state NMR techniques can be used as a powerful approach to identify carbon and nitrogen containing surface species on colloidal metallic nanoparticles. As example, results on metallic ruthenium nanoparticles stabilized by bis-diphenylphosphinobutane (dppb) will be presented. After adsorption of NH_3 on these particles, hydrogen transfer is obtained to the surface which is a reversible process upon treatment of dihydrogen gas. The intermediary formed NH_2 species are shown to react with carbon monoxide in a subsequent reaction and form urea under mild conditions. [3]

Due to the low intrinsic sensitivity of the NMR technique, especially in case of small amounts of surface species that have to be detected the proposed approach may be limited. One technique to overcome sensitivity issues is Dynamic Nuclear Polarization (DNP) which uses the three order of magnitude higher electron-spin polarization and transfer it into nuclear spin polarization. [4,5] The second part of the presentation will show how ^{13}C solid-state NMR combined with DNP enhancement, can be used to monitor the carbon monoxide oxidation on alumina supported platinum nanoparticles where the formation of carbonate as side reaction is identified. [6]

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Unbound ligands and entropy induce the bundling of ultrathin nanowires

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Ultrathin gold nanowires with a metal core diameter of 1.6 nm and a shell of oleylamine ligands form stable colloidal dispersions. We studied the conditions under which such wires self-assemble into elongated bundles. Bundling is useful for the fabrication of electronic materials, composites, and applications in regenerative medicine. Dilution of the nanowire dispersions can induce bundling. We discuss the underlying mechanism and its entropic nature.

The non-polar oleylamine shell of ultrathin nanowires is thick enough to shield the cores's interaction, and one would expect stable dispersions in n-hexane or cyclohexane. Surprisingly, dilution with pure solvent destabilized such dispersion. The wires formed bundles with a regular, hexagonal cross-section. Molecular dynamics simulations and small-angle X-ray scattering show that the ligand shells of two neighboring nanowires in such bundles do not touch and that agglomeration is not driven by van der Waals forces. We find that bundling is entropic: linear solvent molecules or small amounts of unbound ligand align in direct proximity of the ligand shell. Nanowires can avoid the associated decrease in entropy by forming bundles and “share” aligned molecules.

Thermogravimetric data indicates that this entropic mechanism is only effective if the ligand shell is sufficiently sparse. Dilution with pure solvent shifts the chemical equilibrium and reduces the ligand density, thus enabling bundling. Dilution-induced bundling of nanowires can thus be explained as a combined effect of ligand desorption and depletion.

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Time-resolved protein dynamics: Watching an enzyme at work using serial crystallography and photocaged compounds

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Observing protein structural dynamics in proteins without intrinsic chromophores is difficult to achieve experimentally. Photocaged compounds are excellent tools to trigger and initiate irreversible reactions and make studies of chromophore-free proteins accessible [1].

Recent developments in time-resolved serial crystallography at XFELs and synchrotrons allow now to study irreversible protein dynamics during enzymatic reactions [2, 3]. With an experimental approach, hit-and-return (HARE) [4], the accessible timescale in single-shot pump-probe experiments can be extended to cover tens of milliseconds to hundreds of seconds, here applied to serial synchrotron crystallography (SSX). This timescale corresponds to typical enzymatic reactions.

Using HARE-SSX, we were able to follow the full reaction cycle of an enzyme, fluoroacetate dehalogenase, and captured 18 time points from 30 milliseconds to 30 seconds during the non-reversible turnover [5].

The experimental details reveal four catalytic turnovers and show the entire reaction mechanism, including the formation of the covalent intermediate and reveal the allosteric mechanism leading to the previously observed half-the-sites reactivity. Surprisingly, local water structure both on the protein surface and at the dimer interface shows a strong asymmetry between the subunits, revealing a “molecular phone wire” of water molecules, which seem to transmit the allosteric signal.

The HARE approach and use of photocaged compounds is promising for other pump-probe type experiments, like transient IR and 2D-IR spectroscopy, enabling detailed studies of protein dynamics on the millisecond to second scale.

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Do Tyr/Trp redox pathways protect O_2-reducing S. Coelicolor laccase from oxidative damage?

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O_2 reduction is one of the most important life-sustaining reactions in the biocatalysis field. The kinetically challenging task of reducing O_2 to H_2O requires the delivery of four electrons and four protons in a well-coordinated manner. The lack of electrons in the instance of 'catalytic action' might lead to the formation of highly reactive oxygen species (ROS), which at elevated levels are toxic to any biological environment. Although there has been substantial focus on the molecular mechanism of O_2 reactions at the enzymatic active site, it is necessary to expand the viewpoint to the redox role of the entire protein matrix in the context of protection against oxidative damage. In this respect, Gray and Winkler recently demonstrated the presence of redox-active Tyr and Trp chains in O_2-utilizing metalloenzymes, potentially providing conduits for transferring highly oxidizing holes away from protein active sites.[1] In the presented work, the hypothesis of the protective role of Tyr/Trp chains is explored on the example of *S. Coelicolor* laccase, in which the trinuclear center-proximal Tyr108 was shown to be involved in O_2 reduction by donating an electron during catalytic turnover. Accordingly, the Tyr/Trp redox pathways are identified, and their role in oxygen conversion is studied by means of molecular biology and absorbance spectroscopy.[2] Moreover, the incomplete O_2 reduction to ROS is more pronounced in the redox pathways-depleted enzyme suggesting the protective role of Tyr/Trp chains. However, the oxidative modifications of protein matrix are more prominent in the wild-type form than redox chains-depleted SLAC mutants, as evident from mass proteomics experiments, suggesting the catalytic role of Tyr/Trp chains.

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Isotopically Labelling the Anaerobic Pathways of *E. coli* : On-line Analysis by Advanced FTIR and Raman Spectroscopy

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Anaerobic pathways of *E. coli* are studied by a combination of spectroscopic analytical techniques for non-invasive, contactless, *in situ* monitoring, including FTIR spectroscopy with a long-path absorption White cell and cavity-enhanced Raman spectroscopy (CERS) for headspace analysis, as well as liquid phase Raman spectroscopy.

Spectroscopy is a method of choice since it does not require sample taking, can be used in closed systems, is real-time and *in situ*, and can distinguish isotopomers and isomers. FTIR spectroscopy is very useful for this task, in particular if sensitivity is enhanced by employing long path White cells. Many relevant gases in the biosciences cannot be detected by IR spectroscopy but require Raman spectroscopic detection. Since Raman scattering is weak, however, special enhancement is required for effective Raman monitoring of gases. We have developed in the past in Sheffield a new technique, based on CERS which achieves sub-ppmv detection limits and isotope resolution [1-3].

In this contribution, we report our progress in applying advanced spectroscopic techniques for online monitoring of *E. coli* metabolism. With liquid Raman spectroscopy, time-dependent concentrations of phosphate anions are obtained that can be used to calculate the pH *in situ* using a modified Henderson-Hasselbalch equation [4]. Isotope labelling of chemical species provides insight into pathways of *E. coli*, including fermentation and anaerobic respiration [5,6].

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An Azidolipid Monolayer – Transitions, Miscibility, and UV Reactivity studied by Infrared Reflection Absorption Spectroscopy

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We developed an azide-modified lipid with the potential to be used in photocrosslinking studies in lipid bilayers[1,2] or monolayers[3] with interaction partners, such as peptides or proteins. The UV-activatable lipid is a phosphatidylcholine (PC) and bears a terminal azide moiety in one of its hydrophobic tails (Azido-PC). Here, we present systematic monolayer studies of pure AzidoPC and its mixtures with the model lipid DPPC. Besides a thorough thermodynamic analysis with the Langmuir film balance technique, we performed infrared reflection-absorption spectroscopy (IRRAS) to get detailed insights in the organization of those (mixed) monolayers. Additionally, we applied high-resolution mass spectrometry (HRMS) to see effects of UV-irradiation on the lipids' chemical structure and organization. Our results suggest that in expanded monolayers of pure AzidoPC the azido-terminated chain folds back towards the air-water interface. Conversely, in condensed monolayers, the chains stretch and the azide moiety detaches from the interface. For future applications as UV-activatable dopant, we studied the miscibility of the azide-modified lipid with DPPC and found a sufficient miscibility over all investigated mixing ratios. Finally, we showed photo-dissociation of AzidoPC upon irradiation with UV light at 305 nm, leading to chemical crosslinking with adjacent monolayer lipids. This shows the potential of AzidoPC to be used as crosslinking agent within self-assembled lipid or lipid/protein layers.

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Effect of pH on pyruvic acid in bulk and at the air/liquid interface

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Pyruvic acid is an important intermediate in several metabolic relevant processes and also in the environment. Their acid/base behavior, especially at interfaces, is relevant for understanding the chemical interaction of organic matter in oceans and atmospheric aerosols, where reaction rates and product distributions change due to different pH conditions, e.g. chemical processing and molecule transport.

Here a surface-specific technique, sum frequency generation spectroscopy (SFG), has been used to determine the dissociation of pyruvic acid at the air/water interface. For comparison, infrared bulk measurements utilizing ATR spectroscopy were completed. The protonation state was determined by probing the vibrational signatures of the carboxylic acid groups. Phase resolved SFG spectroscopy was used to determine the orientation of the pyruvic molecules at the air/liquid surface.

We observe that pyruvic acid at the water interface is more alkaline than in the bulk, which indicates that the carboxylic acid group deprotonates at a higher pH value at the surface than in the bulk. The different protonation states can have an impact on the conformation and functioning of molecules on the aqueous surface and an influence on the environment and biologically relevant reaction processes.

Exfoliated Silicate Nanosheets as Novel Near-Infrared Fluorophores for (Bio)Photonics

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Imaging of complex (biological) samples in the near-infrared (NIR) range of the spectrum is beneficial due to reduced light scattering, absorption, phototoxicity and autofluorescence. However, there are only few near-infrared fluorescent materials known and suitable for biomedical applications.

Here, we exfoliated the layered silicates Egyptian Blue ($CaCuSi_4O_{10}$, EB), Han Blue ($BaCuSi_4O_{10}$, HB) and Han Purple ($BaCuSi_2O_6$, HP) that emit NIR fluorescence with a long excited state lifetime ($\tau \approx$ 10-100 µs). We use a mixed approach consisting of milling, tip sonication and centrifugation steps and gain nanosheets (NS), whose intense NIR fluorescence emission ($\lambda_{em} \approx$ 920-950 nm) is retained. EB-NS show no bleaching while displaying outstanding fluorescence intensity. Furthermore, we perform *in vivo* single-particle tracking and microrheology measurements in developing *Drosophila* embryos. Additionally, EB-NS can be successfully detected in plants by means of a low-cost stand-off detection setup. [1] EB-NS, HB-NS and HP-NS are also bright enough to be imaged through several cm of tissue phantoms. Finally, we demonstrate fluorescence lifetime imaging of all the mentioned NS on the microscopic and macroscopic level. [2]

In summary, we present a new route to NIR fluorescent nanosheets that promise high potential as novel NIR fluorophores for bioimaging and photonics.

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Electrostatics in Antibacterial Resistance: Active Site Electric Fields as the Basis for Catalysis in TEM β-Lactamases

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Bacterial resistance presents one of the major global public health threats of today's world. Although substantial efforts have been made to design more efficient antibiotics, the use and misuse of these drugs has led to the appearance of super-resistant bacteria. As such, providing new biophysical understanding to the processes of evolution is necessary to develop new antibacterial strategies. Towards this goal, we sought to provide insight into how evolution utilizes the concept of electrostatic catalysis[1] in TEM β-lactamases to shift its narrow spectrum penicillinase activity in TEM-1 towards extended spectrum activity in TEM-52, leading to the emergence of resistance against 3rd generation cephalosporin antibiotics. Using the concept of the vibrational Stark effect, we quantify the active site electric fields from the point of view of initial and final substrates, i.e., penicillin G and cefotaxime, and compare these results to a detailed mass spectrometry-based kinetic analysis and structural insights from molecular dynamics simulations. We observe that, like ketosteroid isomerase,[2] the prime example of electrostatic catalysis, the enzyme utilizes immense preorganized electric fields of up to -160 MV/cm for both substrates, which serves as the catalytic basis to fine tune substrate-dependent chemical re-positioning and active site fluctuations during evolution. These electric fields, thus, present a quantifiable, physical variable to understand broad spectrum β-lactamase activity as well as, in general, the evolvability, substrate promiscuity, and overall protein fitness landscape towards antibiotic resistance.

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Quantified Efficiency of Membrane Leakage Events

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In many therapeutic strategies like killing pathogenic microbes by antimicrobial peptides, drug delivery, endosomal escape, and in disease-related processes such as apoptosis, the membrane is permeabilized.

Our concept for quantifying the efficiency of individual membrane leakage events replaces less stringent descriptions of dye leakage. The concept is applicable to many types of leakage events including thinning, defects, (toroidal) pores, or channels.

We measure release and fluorescence lifetime of a self-quenching dye in vesicles of varying lipid composition. Apart from the dose-response, our analysis also quantifies the efficiency of individual leakage events. Additionally, cumulative leakage kinetics can indicate certain membrane permeabilization mechanisms. For example, applying our concept to different antimicrobial peptide analogues shows how the leakage mechanism and leakage efficiency of a given compound change with lipid composition. Thus, lipids play an important role for the selectivity of membrane permeabilization.

The concept for the quantitative description of leakage behavior and understanding of leakage mechanisms improves the comparability of model studies and microbiological findings, aids the design of experiments, and helps to improve membrane-active compounds.

Operando ambient pressure HAXPES studies of Cu/ZnO(10-14) and Cu/ZnO(000-1) model catalysts for methanol synthesis

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The vicinal ZnO(10-14) facet recently gained scientific interest for its high density of surface steps and outstanding stability [1]. It has the lowest formation energy in comparison with other mixed-terminated facets such as (10-10) or (11-20) and therefor can be expected to play a distinct role in $Cu/ZnO/Al_2O_3$ powder catalysts [2]. We investigate the growth and morphology of the Cu nano particles on the vicinal ZnO surface under UHV conditions. In initial growth stages Cu nanoparticles adapt the height oscillations of the underlying stepped substrate closely and form elongated islands upon further growth. High energy surface x-ray diffraction as well as scanning tunneling microscopy reveals that the particle orient their <111> direction parallel to the <0001> direction of the ZnO(10-14) substrate, resulting in a unique interface relationship. The Cu particles present large area facets of high index as accessible sites for catalytic reactions. Additionally, sintering of the particles is inhibited by the substrate steps induced anisotropic diffusion over the surface.

Ambient Pressure XPS studies reveal the higher abundance of reaction intermediates for Cu/ZnO(10-14) in comparison to the Cu/ZnO(000-1) system on the surface of these model catalysts. Switching from CO/H_2 over $CO/CO_2/H_2$ to CO_2/H_2 conditions and vice versa revealed complete reversibility.

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TiO_2 and $BaTiO_3$ nanoparticles: gas phase functionalization and separation of photogenerated charges

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Photocatalytic hydrogen production continues to be an attractive approach for the generation of a carbon-free energy source. However, the efficiency of the solar energy conversion process is mainly limited by the recombination of photogenerated electron-hole pairs in the photocatalytic material along with the back-reaction of the intermediate species.[1] It was shown that the use of a ferroelectric metal oxides in combination with photocatalytic materials components enhance the charge carrier lifetimes and promotes spatially selective photochemical reactions at the surface of the ferroelectric material.[2]

Here, we aim at an evaluation of charge separation properties of $BaTiO_3$ nanoparticles where ferroelectric polarization effects may enhance charge separation and, hence, diminish the recombination of photogenerated charges. For this reason, we compared vapor phase grown TiO_2 nanoparticles with $BaTiO_3$ nanoparticles from Flame Spray Pyrolysis with regard to light induced charge separation as investigated with Electron Paramagnetic Resonance (EPR) spectroscopy.[3] In a complementary synthesis approach we produced nanocomposites of titanium dioxide (TiO_2) nanoparticles that are coated with barium, barium oxide or a barium titanate phase. In addition to the structural analysis via X-ray diffraction (XRD), we analysed structure and composition of particles and particle interfaces between the different materials components with transmission electron microscopy (EDX/ TEM).

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Electron Transfer in mixed Oxide-Oxide Model Catalysis: Impact of Ti^{3+} on the (Photo-)Chemistry of Methanol at Tungsten Oxide Clusters deposited on Rutile TiO_2

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Due to its outstanding properties, titanium dioxide is a promising material for heterogenous (photo-) catalysis. Moreover, rutile TiO_2 can be partially reduced under the formation of point defects such as oxygen vacancies and Ti^{3+} interstitials.[1] Both are carriers of electronic charge, leading to a well controllable self-n-doping. This provokes a drastically increase in thermal and photochemical reactivity.[2-4]

By deposition of tungsten oxide clusters on rutile TiO_2 (110), we mimic a model oxide-oxide cocatalytic system. First, the electron transfer in such materials was investigated in an x-ray photoelectron spectroscopy (XPS) based study. In brief, the deposition of $(WO_3)_n$ clusters enables the accumulation and pinning of Ti^{3+} sites near the surface for highly reduced TiO_2 and additionally allows an increase of the surface Lewis acidity. We suggest the formation of partially anionic $[(WO_3)_n]^{z-}$ clusters by electron transfer from Ti^{3+} towards the clusters.[5]

We aim to obtain a systematic understanding of the role of such defects in thermal and photochemical reactions from temperature-programmed reaction (TPRS) studies under well-defined UHV conditions. In detail, we present the defect dependent population of different reaction pathways in the conversion of methanol under special consideration of the tungsten oxide cluster coverage. Particularly the deoxygenation reaction forming methane as well as the partial oxidation under production of formaldehyde turned out to be highly sensitive towards the presence of Ti^{3+}, $(WO_3)_n$ clusters and different species of oxygen.[2] In addition, the condensation route forming dimethyl ether as well as thermal and photostimulated C-C coupling reactions also appear as Ti^{3+} mediated processes.[6]

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Consecutive photoinduced electron transfer (conPET): The mechanism of the photocatalyst rhodamine-6G.

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The dye rhodamine-6G (R6G) can act as a photocatalyst via photoinduced electron transfer (PET). After electronic excitation with green light, R6G is reduced by an electron donor like DIPEA (diisopropylethylamin). The R6G radical has a reduction potential of ca. -0.9 V and can split phenyl iodide into iodine anions and phenyl radicals. In 2014, König et al. proposed a strategy, termed consecutive photoinduced electron transfer (conPET), that adds the energy of two photons for a photoreduction, using a photogenerated radical as an intermediate [1]. He showed that photoexcitation of the R6G radical at 420 nm splits aryl bromides into bromine anions and aryl radicals [2]. The required increase in reduction potential is attributed to the electronically excited R6G radical, according to the conPET idea.

We present a study of the mechanism of the formation and photoreactions of the R6G radical by using transient spectroscopy in the time range from femtoseconds to minutes in combination with quantum chemical calculations [3]. We conclude that one photon of 540 nm light produces two R6G radicals. The lifetime of the photoexcited radical of ca. 350 fs is too short to allow direct interaction with the substrate. We propose that this excited state spontaneously forms solvated electrons, which are captured by the substrate. In the absence of a substrate the solvated electrons recombine with R6G and recover the radical on a time scale of nanoseconds. A third time constant of ca. 10 ps is assigned to vibrational cooling of hot R6G and hot R6G radical.

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New insight into the mechanism of CO oxidation and water-gas shift reaction over Au catalysts using *operando* spectroscopies

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Gold deposited on reducible metal oxide supports such as ceria has attracted great attention due to its unique catalytic performance in redox reactions. The rational design of better catalysts crucially depends on the identification of the active sites as well as their dynamics under reaction conditions using *operando* spectroscopies.

Room temperature CO oxidation over low-loaded Au/CeO_2 catalysts has been studied in detail using *operando* IR spectroscopy supported by DFT calculations (DFT).[1] Using a combination of steady-state and transient IR spectroscopic techniques, the active sites are identified as single and pseudo-single gold sites on the ceria support forming $O_{lattice}$–Au^+–CO species, independent of the initial state of the catalyst. The reaction mechanism is further elucidated by the simultaneous detection of the active and the inhibiting (hydrogen carbonate, CO/CeO_2 species, while detailed analysis of transient spectra reveals the CO adsorption and reaction dynamics. Comparison between different ceria supports (sheets, nanorods, cubes) enables us to extract the facet-specific characteristics of the CO oxidation over Au/CeO_2 catalysts.[2]
Regarding the low temperature water–gas shift (WGS) reaction over noble metal/ceria catalysts two main reaction mechanisms are debated in the literature, i.e., the redox and associative mechanism. In both mechanisms the cleavage of O–H bonds has been considered to be a key step, but direct experimental evidence is scarce. We have employed *operando* Raman/UV-Vis spectroscopy, combined with isotope labelling and DFT, to elucidate the role of surface and bulk oxygen in the WGS reaction over Au/CeO_2 catalysts.[3,4] Our results are fully consistent with a redox mechanism, involving a reaction pathway for replenishment of surface oxygen ions O^{2-} from terminal O–H groups. We further demonstrate the effect of ceria faceting [(110), (100), (111)] on the WGS mechanism of Au/CeO_2 catalysts, highlighting the role of the support.[4]

Our results demonstrate the potential of combining *operando* spectroscopies to monitor the dynamics of single gold sites and facet-dependent support oxygen in Au/CeO_2 catalysts to provide new insight into the reaction mechanisms of the CO oxidation and WGS reaction.

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How Does an Ionic Liquid Adsorb on a Pt(111) Surface? A Combined Study by Infrared Reflection Absorption Spectroscopy and Density Functional Theory Calculations

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Recently, there has been a lot of interest in ionic liquid (IL) thin films due to their ability to modify the activity and selectivity of catalytic materials. In order to better understand the operation principles of such solid catalysts with ionic layers (SCILLs), surface science studies can provide detailed insights into the interaction of the IL with the catalytically active metal surface.

In this work, we have investigated the adsorption behavior of the IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf$_2$]) on Pt(111) combining experimental and theoretical studies. Under ultrahigh vacuum (UHV) conditions, [EMIM][NTf$_2$] was deposited on a Pt(111) single crystal surface by physical vapor deposition (PVD) at different surface temperatures (200 K, 300 K and 400 K). The adsorption process and the thermal behavior of the adsorbed species were monitored by in-situ infrared reflection absorption spectroscopy (IRAS). We observe the formation of a strongly bound monolayer, in which the [NTf$_2$]$^-$ interacts with the metal surface via the SO$_2$ groups. The cation [EMIM]$^+$ does not feature a specific adsorption geometry on the Pt(111) surface. In the more weakly bound IL multilayer, the preferential orientation of the ions is gradually lost.

To verify the adsorption geometries of [NTf$_2$]$^-$ on Pt(111) suggested on the basis of the experimental data, we conducted density functional theory (DFT) calculations. In total, we analyzed four different systems: (a) [EMIM][NTf$_2$] in gas phase, [NTf$_2$]$^-$ on (b) a small (4x4) and (c) a large (6x6) Pt(111) surface area (here Na$^+$ was used as a counterion) as well as (d) a single ion pair of [EMIM][NTf$_2$] on (6x6) Pt(111). The calculations showed indeed that the [NTf$_2$]$^-$ binds to the Pt(111) surface via its SO$_2$ groups. However, the surface area available and the number of surrounding cations affect the orientation of the two SO$_2$ groups and, thereby, the resulting IRA spectra.

Ligand-Induced Heterogeneous Catalysis: Selective Hydrogenation of Acrolein on Ligand-Modified Pd(111)

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One of the major challenges in heterogeneous catalysis is obtaining control over selectivity in multi-pathway transformations of hydrocarbons. Towards this goal, a new approach was recently introduced, which is based on employing catalytic surfaces functionalized with organic ligands. The intermolecular interactions between the reactants and the co-adsorbed ligand species were shown to be capable of promoting the desired reaction pathway. In our recent studies, on acrolein hydrogenation over Pd, almost 100% selectivity in the formation of the target product unsaturated alcohol propenol was detected, which arises from the presence of the oxopropyl-ligand species formed at the initial stages of reaction.[1]

In this contribution, we present a mechanistic study on hydrogenation of acrolein over ligand-modified Pd(111) surface. We employ a combination of spectroscopic and microscopic tools along with the molecular beam techniques to obtain detailed information on the mechanisms and kinetics of acrolein partial hydrogenation to propenol. Specifically, infrared reflection adsorption spectroscopy (IRAS) is employed to identify and follow the evolution of the surface species, including the pre-adsorbed ligands and the reaction intermediates, under the reaction conditions. Complementary, their spacial distribution on the catalytic surface is monitored by scanning tunneling microscopy (STM).

The induction period of the formation of propenol, which is typically observed for acrolein hydrogenation, can be significantly reduced by precovering the surface with allyl cyanide as a ligand. Spectroscopic observations suggest fast formation of the desired reaction intermediate – propenoxy-species – on the ligand-modified surface. Data on the reaction kinetics of acrolein hydrogenation and the spacial distribution of the allyl cyanide ligand under the catalytically relevant conditions will be reported.

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Charge attachment induced transport -
Towards new paradigms in solid state electrochemistry

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Modern applications in solid state electrochemistry, e.g. in the field of energy storage and conversion, involve the transport of charge carriers through surfaces or interfaces as a key aspect. Many of the electrochemical concepts for such transport in fact originate from the field of liquid state electrochemistry. The transfer of concepts from the liquid to the solid state causes some problems, which are addressed in this contribution [1]. Topics covered include i.) electrode potentials and half-cell potentials, ii.) charge carrier blocking and dielectric breakdown, and iii.) activities versus particle densities. Many of these topics can be addressed by the charge attachment induced transport (CAIT) technique developed in the authors group [2,3,4]. The discussion involves modifying some of the paradigms we became acquainted to in the liquid state.

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The Effect of Ionic Defect Interactions on the Hydration of Yttrium-Doped Barium Zirconate

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Acceptor doping of perovskite structured barium zirconate $\mathrm{BaZrO_3}$, e.g. with $\mathrm{Y_2O_3}$, leads to the formation of oxygen vacancies.

$$\mathrm{Y_2O_3} \xrightarrow{\mathrm{BaZrO_3}} 2\mathrm{Y'_{Zr}} + 3\mathrm{O_O^x} + \mathrm{V_O^{\cdot\cdot}}$$

Exposing the doped oxide $\mathrm{BaZr_{1-x}Y_xO_{3-0.5x}}$ (BZY) to a hydrating atmosphere at elevated temperatures introduces mobile protons into the system, which leads to high proton conductivity.

$$\mathrm{V_O^{\cdot\cdot}} + \mathrm{H_2O(g)} \leftrightharpoons \mathrm{O_O^x} + 2\mathrm{H_i^{\cdot}}$$

The degree of hydration is a function of water partial pressure and temperature. In most studies, the classical mass action law for non-interacting defects is applied to model the defect chemistry of this system. However, at high defect concentrations the interactions of defects play a crucial role. The present study focuses on the change in the free energy of hydration $\Delta\mathrm{F_{inter}}$ introduced by the defects. Combining a DFT derived interaction model with an MMC multistage sampling principle [1], we obtain $\Delta\mathrm{F_{inter}}$ which can be separated in the defect influence on the inner energy $\Delta\mathrm{U_{inter}}$ and configurational entropy $\Delta S_{\mathrm{inter}}$. Neglecting volume changes, the interaction dependent part of the equilibrium constant is deducible from $\Delta\mathrm{F_{inter}}$, yielding the quotient of activity coefficients for the mass action law. This enables an ab-initio correction of the relation between water partial pressure $\mathrm{p(H_2O)}$ and degree of hydration.

The results show very good agreement with experimental data, indicating that the non-ideal hydration of BZY can be explained by the ionic defect interactions.

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Thermodiffusion in doped ceria from molecular dynamics simulations

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Cerium oxide is a versatilely applicable ceramic, e.g. as high temperature coating material. Doped with trivalent oxides, such as gadolinium oxide, the material shows high oxygen ion conductivity exceeding that of commonly applied yttria-stabilized zirconia.

In this study, we estimate thermal and ionic conductivity of pure and doped cerium oxide by equilibrium molecular dynamics simulations based on widely applied empirical pair potentials and making use of the Green–Kubo formalism. The simulations show the limitations of most of the present potentials to accurately describe the thermal expansion, thermal conductivity and ionic conductivity at once.[1]

Based on our results we apply the Green–Kubo formalism for Gd-doped ceria to obtain the off-diagonal Onsager phenomenological coefficients which describe the coupling of the transport of mass and the transport of heat, also known as thermodiffusion or Soret-effect. We demonstrate that determination of this coupling is possible in solid oxides using molecular dynamics simulations.

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Charge carrier dynamics in semiconductor-metal hybrid nanostructures

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Semiconductor-metal hybrid systems on the nanoscale show an efficient charge carrier separation which makes these materials promising for photoelectrochemical applications (*e.g.* in the field of hydrogen evolution reaction). Separating an excited electron and hole in the semiconductor and the metal, respectively, enables further reactions of the charge carriers. The Fermi level with a position in between the valence band and conduction band of the semiconductor and the catalytic activity of the metal enable a good quantum efficiency for reactions with the excited electrons.

The use of nanoparticles is often limited to solution-based applications. Assembling these particles can lead to a solid macroscopic gel-like structure that broadens the possible applications. Upon assembly, novel properties can be obtained, nevertheless, the nanoscopic characteristics can be retained which makes the macroscopic structures advantageous.

Combining semiconducting and metallic nanomaterials to build up three-dimensional macroscopic assemblies leads to an efficient charge carrier separation when the contact between the two materials is given. This work shows the difference between mixed and on-grown semiconductor-metal hybrid nanostructures in structural and photoelectrochemical investigations. Furthermore, the influence of the distribution of the metal domains on the semiconducting structures has been investigated. [1]

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Tuning oxygen evolution activity as a function of composition: New iridate-ruthenate layered oxides from $Na_2Ir_{1-x}Ru_yO_3$

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We recently reported highly active exfoliated iridate and ruthenate nanosheets as stable electrocatalysts for the oxygen evolution reaction (OER) in acidic medium derived from the layered $K_{0.75}Na_{0.25}IrO_2$ and $NaRuO_2$ compounds.[1,2] The nanosheets are among the best performing catalysts both in terms of specific and mass activity, which may allow cost-effective electrode design at low noble metal catalyst loading for PEM. It was recently proposed that surface segregation can aid the design of stable noble metal oxides for the OER.[3] Here, we explore such an effect by characterizing the electrocatalytic acitivity and stability of mixed Ir-Ru layered oxides, $H_3NaIr_{2-2x}Ru_{2x}O_6$ ($0 \leq x \leq 1$). Starting from the parent compound Na_2RuO_3, we prepare solid-solutions of $Na_2Ir_{1-x}Ru_xO_3$, acid exchange them and then disperse them prior to drop-casting onto glassy carbon electrodes for characterization. In general, we observe a composition-dependent trend for the performance (overpotential at specific current densities) of the catalysts. Similarly, the stability of the catalysts is greatly affected by the composition. Our electrochemical characterization is complimented by electron microscopy, x-ray diffraction as well as ex-situ spectroscopic methods to truly assess the structure-property relationships of this class of materials.

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Controlling electrocatalytic selectivity by ionic liquids: Electrooxidation of 2,3-butanediol on Pt(111) electrodes modified by [C_2C_1Im][OTf]

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Recently it has been shown that ionic liquids (ILs) can be used to control selectivity in heterogeneously catalyzed processes.[1] Here, we aim to transfer this concept, denoted as SCILL (solid catalysts with ionic liquid layer) to electrocatalysis and electrosynthesis.

As a model reaction, we investigated the selective electrooxidation of 2,3-butanediol on Pt(111) electrodes in acidic environment. We modified the Pt surface using the IL 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [C_2C_1Im][OTf] dissolved in the aqueous electrolyte. On the IL-modified electrode, we studied the reaction mechanism by electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) in combination with density functional theory (DFT). We identified the reactant 2,3-butanediol and the potential selective oxidation products acetoin and diacetyl using specific IR bands which can be observed in-situ by EC-IRRAS. We demonstrate that in the absence of the IL the partial oxidation product acetoin is formed between 0.3 and 0.6 V_{RHE}. At higher potential acetoin further reacts to diacetyl. Additionally, traces of CO_2 are formed as byproduct, while no adsorbed CO is formed during the reaction. In the presence of the IL, however, the oxidation to diacetyl is suppressed even at potentials above 0.6 V_{RHE}. These results demonstrate that it is possible to modify the selectivity of an electrocatalyst by ionic liquids.

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Electrodeposition of Sn and Fe-Sn alloys with novel green electrolyte systems

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Fe-based alloys with Ni and Co are frequently used for magnetic recording heads, magnetic sensors, or actuators due to their ferromagnetic properties. However, Co is a critical raw material (European Commission), and a material of very high concern (ECHA). Elemental Ni is allergenic and cancerogeneous according to the European Chemical Agency (ECHA). Therefore, FeSn alloys have been studied as alternatives to FeNiCo alloys.

One of the main challenges in the Fe-Sn electrodeposition is the electrolyte stability due to the varying oxidations states of Fe and Sn. Environmentally friendly electrolytes [1-3] such as citrate-tartrate- chloride and methanesulfonic acid (MSA) were studied. As brightener served alkoxylated β-naphthol (ABN) instead the frequently used β-naphthol. The influence of ABN on the kinetics of the Sn deposition was investigated. The influence of the pH, the Sn to Fe metal ratio, and the presence of ABN on the stoichiometry and morphology of the electrodeposited Fe-Sn was studied. Besides β-Sn and $FeSn_2$, the ferromagnetic phase Fe_5Sn_3 was obtained. The mechanism of the Fe-Sn electrodeposition could be elucidated.

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In-situ high-flux X-ray multiscale network studies for developing the next generation of sustainable photovoltaics with high efficiency

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A crucial challenge in bio-inspired energy research is to develop a rationale for the synthesis and use of sustainable, bio-based materials optimized for energy harvesting, energy storage, or energy conversion [1]. Cellulose fibers have excellent mechanical strength, are thermally stable, are very lightweight, and have a very low surface roughness in thin films. Additionally, cellulose nanofibers (CNF) and carboxy-methylated CNF (CMC) are biocompatible and the amount of resources is vast. These attributes make cellulose a very promising precursor for the design of high-performance bio-based materials and nanocomposites. The pure cellulose with intercalated water forms a hydrogel but is not useful as material which primary functionality is transforming absorbed light into electrical energy, like in organic solar cells (OSC) [2]. The current study aims to investigate CNF and CMC doped with optical-light absorbing, electron transfer (ET) dyes. The use of small molecules in OSC is well known to increase the power conversion efficiency [3]. The idea is to combine the advantages of cellulose with the positive effect of small molecules. The structural and morphological integrity of the dyes under performance conditions were studied with time-resolved grazing incidence X-ray scattering (GISAXS) techniques [4] and photo-sensitization experiments. This analysis showed us the intercalation dynamics, distribution and function of pyrene-based photo-dopants within the hydrogel and whether these dopants alter the overall cellulose fiber structures [5].

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Hydrogen-Bonded Ion Pair in Excited-State Proton Transfer

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Despite intensive research of proton transfer and its mechanism in the last decades, studies addressing the solvent dependency of the elementary proton transfer step are scarce. In most of the investigated systems a change of the solvent is accompanied by a change of the proton acceptor. [1-3]

Here we present a stable hydrogen-bonded complex of a pyrene-based photoacid and a phosphine oxide, which allows to change the solvent, i.e. the surrounding dielectric continuum, without changing the proton acceptor itself. Therefore, it is possible to decouple and investigate the solvent dependency. Due to the increase of acidity upon electronic excitation of photoacids, the proton transfer to the phosphine oxide can be triggered with a photon. High fluorescence quantum yields allow to observe the different species via steady-state fluorescence spectroscopy.

We were able to single out the spectral form of the generated hydrogen-bonded ion pair (HBIP). This enabled a solvatochromism study based on Lippert-Mataga to identify a difference between complex and HBIP in their change of the permanent dipole moment upon excitation of ~3 Debye. [4] This implies a displacement of the elementary charge along the H-bond, which is in quantitative agreement with the assigned Eigen-Weller-Model.

In the near future, this probe system will be adapted to TIRF microscopy to investigate proton transfer reactions on a single-molecule level.

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Monitoring the photochemistry of a formazan over 12 orders of magnitude in time

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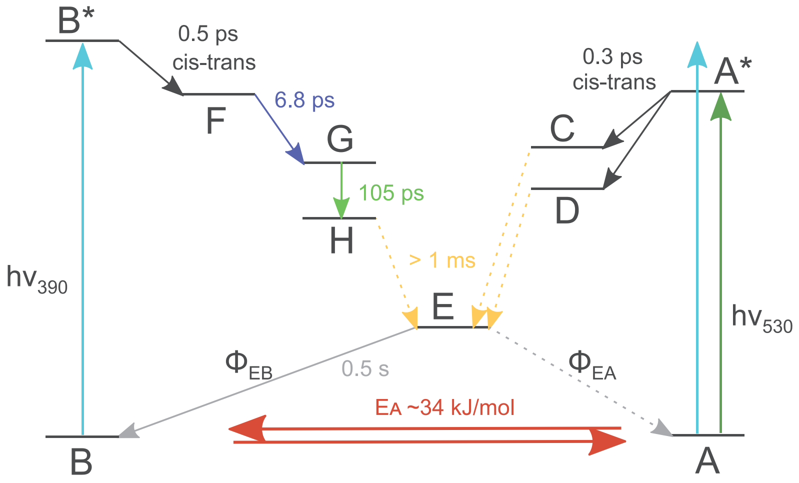
2,3,5-triphenyltetrazolium chloride (TTC) converts photochemically into phenylbenzo[c]tetrazolocinnolium chloride (PTC)[1] and 1,3,5-triphenyltetrazolium formazan (TPF)[2]. This photoreaction is used in so-called TTC assays indicating cellular respiration and cell growth.[3] While the photochemistry of the precursor TTC is well understood,[4,5,6] only little is known about its TPF analogue. TPF is stabilized by an intramolecular hydrogen bond (isomer A)[2] and switches photochemically (530 nm) *via* an E-Z isomerization into another TPF-stereosiomer (isomer B).[7] So far, two different mechanisms are discussed for this photoreaction.[8] We investigated this mechanism by time-resolved spectroscopy in dependence on temperature, excitation wavelength, and solvent environment, resolving several intermediates over a temporal range spanning 12 orders of magnitude along the reaction path. Quantum chemical calculation identified 11 possible stable isomers of which we could observe 8, and allowed an assignment of how these species are interconnected.



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Unraveling the photo-induced dynamics of *N*^{6},*N*^{6}-dimethyladenine by time-resolved spectroscopy and *ab initio* calculations

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N^6,*N*^{6}-dimethyladenine (DMAde) is a derivative of the nucleobase adenine. For DMAde methylation of the diamino group at the C6 position leads to very interesting and anomalous emission properties. Contrary to other nucleobases, DMAde exhibits dual fluorescence which is assumed to originate from two different excited-state species: the locally excited (LE) state and a twisted intramolecular charge transfer (TICT) state [1,2]. To ultimately identify the involved species as well as to untangle the underlying processes after photoexcitation, we used time-resolved vibrational absorption spectroscopy (TVAS) and fluorescence up-conversion (UPC). Aided by quantum chemical calculations, we obtained two minimum structures in the $S_1(\pi\pi^*)$ state which are separated by a shallow energy barrier of 0.05 eV. One structure, identified as LE structure, is characterized by C^2-puckering which is already known from adenine. In contrast, the global minimum structure shows a twist by ~ 60 ° of the NMe_2 group with respect to the purine frame and the C6 atom is strongly pyramidalized. In the UPC measurements, we observed the literature-known short-lived fluorescence of the LE structure. Owing to the structure sensitivity of TVAS, we detected the previously predicted TICT structure for the first time. Additionally, a novel excited-state species is identified and ascribed to a diffuse distribution of vibrationally hot structures with partial twisting of the NMe_2 group. With $\tau \approx 20$ ps, these pTICT structures either reach the TICT minimum in the S_1 state or return back to the ground state via fluorescence.

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Why substitution matters - temperature dependency of excited states of Ru(II) complexes

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Artificial photosynthesis, such as reduction of protons to hydrogen, is an increasing field of research over the last years.[1] Photosensitizers with stable long-lived excited states are a key for these reactions and the temperature influences the reaction as well as the emission lifetime of the corresponding excited states of the coordination compounds, and therefore, plays a role in catalysis. [2,3]

Looking at temperature dependent emission lifetimes of the well know $[Ru(bpy\text{-}R_2)_3]^{2+}$ complex, we noticed that simple changes in the ligand design resulted in significant stabilization of emission lifetime over broad temperature ranges (compare figure 1). To understand the behaviour electrochemical, steric and photophysical properties and solvent interaction of the complexes were investigated in detail. [4]

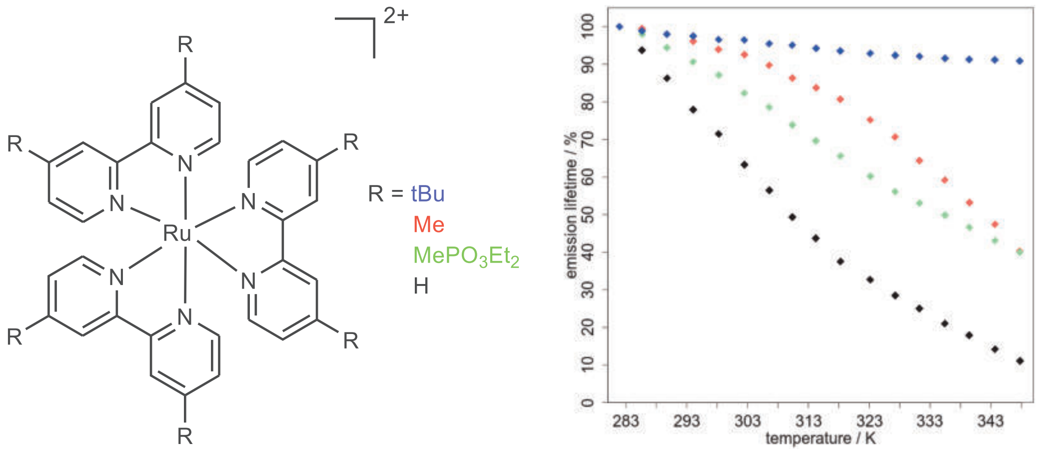

figure 1. Overview of the emission lifetimes vs. temperature in inert MeCN (right) of the $[Ru(bpy\text{-}R2)3]^{2+}$derivates (left).

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Estimating the Octane Number via a Numerical 2-Zone-Cylinder-Model

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Sustainably produced synthetic fuels offer great potential for reducing greenhouse gases in the transport sector, and the possibility of using existing infrastructures facilitates a quick implementation into the transportation system. Nevertheless, renewable fuels have to be economically competitive and comply with technical specifications. An assessment of their pollution behavior and performance enables the optimization process more efficiently.

An important indicator for the performance of fuels in IC engines is the octane number describing the resistance against self-ignition. The experimental, standardized procedure to derive the octane number is very cumbersome and cost-intensive, and efficient numerical methods for deriving the octane number are required.

This work focuses on the correlation between the octane number and the ignition delay times by the development of a simplified numerical 2-zone-cylinder model. It represents the combustion chamber by a burned and an unburned zone connected by a flame front, which is modeled by two chemical kinetic homogeneous reactors.

The model is designed to incorporate the boundary compression conditions of the experimental, standardized procedure. Premature ignitions in the unburned reactor define critical compression ratios of fuels or their octane number, respectively.

A first comparison of the results is in good agreement with experimental data and allows a priori estimations of octane numbers.

Nucleation enhancement of weakly-bound species: A molecular love story of CO_2 and Toluene

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Abstract

The transition of gases to condensed phases plays a critical role in aerosol formation, cloud physics, and a wide variety of industrial and biological processes. The initial stage of this transition, nucleation, involves the formation of stable clusters from single atoms or molecules. Although nucleation has been investigated by numerous experimental and theoretical studies, the observation and kinetic analysis of nucleation down to the molecular level remains challenging, especially for species that form weakly-bound molecular clusters in the nucleation process. Here we report studies on binary nucleation of CO_2 -toluene mixtures, via soft single photon vacuum-ultraviolet ionization coupled with time-of-flight mass spectrometry [1]. We retrieve the time evolution of cluster size distributions within a time window of up to ~150 μs and a resolution of ~2 μs. Cluster compositions are resolved by mass spectrometry, which allow us to perform in-depth studies of nucleation kinetics. For CO_2-toluene binary nucleation, we find evidence that the formation of transient, mixed clusters opens alternative nucleation pathways and thereby enhances the cluster formation rates of toluene significantly. Further, we explore the question whether these two species share a special relationship or if the nucleation enhancement of low vapor pressure substances by CO_2 is a more general phenomenon.

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Acceleration of Mannich reaction in electrospray droplets

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Batch reactions in large reaction vessels are still preferred in synthesis for most applications in the chemical industry. In recent years however, several groups started to systematically investigate reactions in confined spaces, such as thin films, electrospray (ES) droplets or upon microdroplet–microdroplet collisions. Reaction rates increased by orders of magnitude were found at high surface-to-volume ratios, mostly due to the partial solvation of the reagents at the interface. The acceleration depends strongly on the chemical composition of the reaction mixtures and the physical parameters, such as the reaction volumes as well as the chemical reaction itself.[1]

Here, a Mannich reaction was investigated. This reaction is mainly employed in many biosynthetic pathways.[2] The common batch synthesis requires high acid concentrations, and often toxic and/or expensive catalysts in order to achieve high product yields within a minimum of some hours reaction time.[3] In our work, the Mannich reaction solution was electrosprayed and the product species formation was observed on a millisecond time scale in a mass spectrometer (MS) for the first time. Chemical manipulations, such as the variation of the reactant ratio, the solvent composition and the initial concentration of the reaction, were performed to optimize the reaction conversion ratio. ES parameters were adapted to study physical influences on the acceleration of the reaction in detail. For example, higher distances between the ES source and the MS inlet lead to an increase of the droplet flight time and thus in longer reaction time. Lower sheath gas flow rates have the same effect, but additionally decrease the initial droplet size in the ES. Temperature variations along the flight path of the droplets influence their shrinkage rate and can thus have a positive or negative effect on the reaction conversion ratio.

A detailed understanding of the various parameters on reaction rate could lead to a better understanding of syntheses and a reduction of expensive and/or toxic catalysts.

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Mechanisms for Regioselective Synthesis of Anisotropic Nano-Heterostructures

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Regioselective synthesis of nano-heterostructures is a crucial field, because the resulting, anisotropic structures allow for directional charge carrier dynamics.[1] So far, their formation is often only described empirically. Herein we present mechanistic understanding of the synthesis of axial heterojunctions in semiconductor nanorods, in both the reaction and diffusion-controlled kinetic regimes. In particular, we discuss the role of nucleation intermediates and magic-size clusters (MSC) in regioselective nucleation and growth.

In the first example we show that preferential, rapid growth of CdS nanorods selectively in the [000-1] direction of CdSe nanorod seeds occurs in the presence of fibrillar coordination polymers (CP) that reversibly bind the nucleating monomer. The CP fibrils are monomer reservoirs that cause the formation of localized hot-spots of high monomer concentration rather than a homogeneous distribution of monomer in the reaction solution. The CP feed results in reaction-controlled growth at the most reactive crystal facet of the nanorod seeds, leading to high anisotropy and regioselectivity.[2] Conversely, suppression of the CP formation also suppresses 1-dimensional growth.

In the second example, growth of single semiconductor tips on one end of a nanorod can also be accomplished under limited monomer supply. We show that heterogeneous nucleation with high regioselectivity occurs only under the conditions that also favour the formation of long-lived MSCs.[3] This highlights that the crucial parameter is a sufficiently high kinetic barrier for homogeneous nucleation of nanoparticles.

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Observation and Mechanism of N_2 Cleavage by a Tantalum Cluster under Cryo Conditions

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Previously, DFT modeling predicted dissociative adsorption of the very first N_2 molecule when reacted with small Ta_n^+ clusters ($n \leq 4$).[1] Subsequent DFT studies focused on reverse catalysis modeling, namely on ammonia activation, by Ta_n^+ ($n = 2 – 10$) cluster complexes.[2]

In the present contribution we investigate the cryo N_2 activation by the model system Ta_4^+, as motivated by prior room temperature studies on Ta_2^+.[3] We combine kinetic and IR-PD spectroscopic cryo ion trap investigations with DFT modeling. Experimental results reveal peculiar details for the first and second adsorption kinetics, and the infrared signatures show no NN stretching bands in $[Ta_4(N_2)_1]^+$ and $[Ta_4(N_2)_2]^+$. This is consistent with cleavage of the first two adsorbed dinitrogen molecules and we unravel a multistep ***a****bove* ***e****dge-****a****cross* ***s****urface* (***AEAS***) mechanism for the cleavage of first and second N_2 adsorbates. Cleavage of the third N_2 ligand is kinetically hindered. We recognize that substoichiometric N_2 exposure allows for spontaneous activation by Ta_4^+, while higher N_2 exposure causes self-poisoning.

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Mechanistic Studies on a Deracemization Reaction via a Triplet 1,3-Diradical Induced by Energy Transfer from a Chiral Sensitizer

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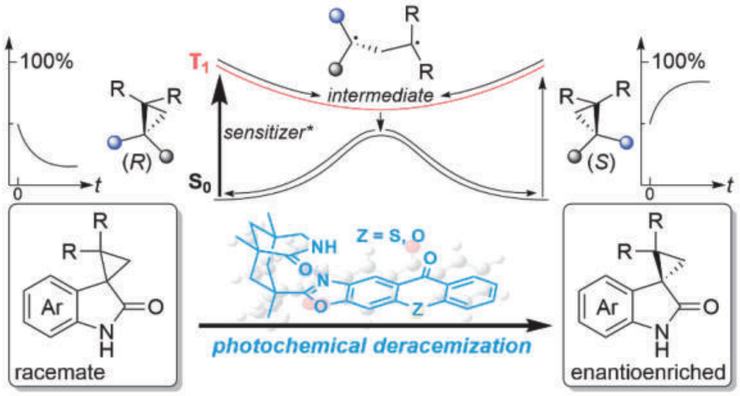
The photochemical deracemization[1] of spiro[cyclopropane-1,3'-indolin]-2'-ones (spirocyclopropyl oxindoles) was investigated by time-resolved spectroscopies and computational approaches. The corresponding 2,2-dichloro compound is configurationally labile upon direct irradiation at 350 nm and when sensitized by excited achiral thioxanthen-9-one exciting at 405 nm. The triplet 1,3-diradical intermediate generated in the latter reaction was transiently detected, and the mechanism of formation was elucidated as a triplet energy transfer. Charge transfer was excluded by complementary studies in the presence of a known electron donor substrate.



Deracemization is achieved by utilization of a chiral thioxanthone with a lactam hydrogen bonding site as a photosensitizer. Three mechanistic contributions were identified co-acting favorably for high enantioselectivity. First, the binding constants to the chiral thioxanthone differ by a factor of 3 for the minor and the major enantiomers. Second, the molecular distance is smaller by *ca.* 100 pm in the complex of the minor enantiomer, presumably promoting a more efficient energy transfer. Third, the lifetime of the intermediate 1,3-diradical exceeds the complex lifetime, facilitating a racemic deactivation back to the ground state.[2]

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Temperature-dependent trapping probability measurements of *n*-butane on ionic liquid surfaces using molecular beam techniques

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Ionic Liquids (ILs) are a class of compounds consisting only of cations and anions, which are usually liquid already below room temperature. Besides other applications, IL thin films are the key components in the catalytic concepts Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). These catalysts show improved behavior e.g. in hydrogenation reactions. In these processes, the phase transfer of hydrocarbons through the ionic liquid/gas interface plays a crucial role.

We have built a new ultra-high vacuum apparatus dedicated for the investigations of ILs with molecular beam techniques. It was used to study the first step of the interaction dynamics of *n*-butane on a series of alkylimidazolium ionic liquids with varying alkyl chain lengths[1] and anions[2] ([C_nC_1Im][X]). Based on the temperature-dependent behavior of the initial trapping probability at low temperatures, measured by the direct method of King and Wells, we found that the binding energy is dominated by the interaction with the alkyl chain of the cation, whereas the ionic headgroups contribute only weakly.

L.W., R.G.B, M.L. and H.-P.S. thank the European Research Council (ERC) for financial support of this research in the context of an Advanced Investigator Grant to H.-P.S (No. 693398-ILID).

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An experimentally validated neural-network potential energy surface for H-atom on free-standing graphene in full dimensionality

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Understanding the formation of covalent bonds due to atomic-scale motions and energy dissipation pathways involved is an ongoing challenge in the field of chemistry. Measurements performed in our group show a bimodal pattern of the translational energy loss distribution of hydrogen atoms scattered from graphene. [1]

The second generation reactive empirical bond order potential was fitted to ab initio electronic structure data obtained from embedded mean-field theory to generate a potential energy surface (PES). [2]
First-principles dynamics simulations using the provided PES were able to reproduce the bimodal feature of the energy loss spectrum and were in qualitative agreement with experimental results. But these investigations could not fully provide a detailed description of the scattering and sticking mechanisms.
Therefore, we developed a full-dimensional neural network PES [3] by fitting to the density functional data in order to further reduce the remaining errors by the fitting procedure of the PES underlying molecular dynamics simulations performed. We could show that our latest PES is in much better agreement with experimental results. [4]

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Physico-chemical exploration of pioneering photography and electrotyping reproduction around 1840

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A physico-chemical elucidation of the worldwide first photographic technology allowing manifold reproduction is presented. An etched daguerreotype manufactured around 1840 in Vienna, preserved by the Technisches Museum Wien, served as a case-example [1]. Surface analysis showed that the photographic process involved the formation of colloidal Ag nanoparticles (AgNPs) with sizes of 30-120nm with shell layers consisting of Ag_2O, Ag_2S, and some AgCl. The breakthrough photographic technique provided a hitherto unachieved high sensitivity due to various halogenide mixtures. The image development consisted in the reduction of the Ag halides by H_2SO_3 created by the hydrolysis of S_2Cl_2 leading to AgNPs adjacent to the latent image Ag nuclei. The fixation of the image was performed either by KCN or by $Na_2S_2O_3$. The investigated plate exhibits etched areas with Ag_2O conversion layers and no Cl or S. The technology of electrotyping was successfully applied for the reproduction of printing plates around 1840 in Vienna [2,3]. The first reproduction method for daguerreotypes invented by Joseph Berres in Vienna consisted in etching to enable printing. The gum arabic preferentially wetted the exposed AgNP regions so that unexposed areas could be etched by HNO_3. All these recent findings serve for the future technological elucidation of early photographs from the first half of the 19th century.

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Rotational and translational motion in ionic liquids by means of high field and field cycling NMR relaxometry

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Conventional high field (HF) and improved field cycling (FC) relaxometry are promising NMR techniques for studying rotational and translational dynamics in ionic liquids (ILs). The combined methods cover a frequency range from typically a few kHz up to hundreds of MHz for ^{1}H nuclei and thus allow spin-lattice relaxation time experiments over eleven orders of magnitude in frequency. In combination with specially synthesized ILs, that can be easily supercooled, we are able to study the spin-lattice relaxation time, T_1, as a function of resonance frequency, ν_0, over a broad frequency and temperature range.

In this work we focus on ionic liquids based on the 1-(4-Hydroxybutyl)-pyridinium cation. [1] Here, the OH groups that are involved in hydrogen bonding are far away from the center of mass. The reorientational correlation time of these molecular bond vectors OD, τ_{OD}, can be determined from HF deuteron NMR T_1 relaxation time experiments. Additionally, we have access to the overall tumbling of the cation, τ_{rot}, as well as to the translational diffusion coefficients, D_{trans}, from dipolar relaxation rates measured by FC relaxometry in a frequency range between 10 kHz and 42,6 MHz. Here, the challenge is to dissect the total relaxation rates of the nuclear magnetic relaxation dispersion (NMRD) profiles into intra- and intermolecular contributions. While we obtained translational diffusion coefficients from the intermolecular relaxation rates, the intramolecular part provides access to the rotational correlation times.

While it could be shown for trialkylammonium based ILs that both reorientational correlation times (τ_{ND} and τ_{rot}) nicely overlap and explain the same dynamics of the cation, [2] this should be completely different for 1-(4-Hydroxybutyl)-pyridinium based ionic liquids.

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Microwave Study of Mono-Cholorobenzaldehydes

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Rotational spectroscopy is a powerful tool for structure determination of gas-phase molecules due to its high accuracy. One can observe a hyperfine splitting of rotational transitions in the presence of a quadrupolar nucleus when the molecular rotation couples with the nuclear spin, which provides additional information about the local chemical environment. The method's sensitivity to the electronic field is useful for structure determination and cross-validation of predicted electric field gradients by quantum chemical calculations.

The series of mono-halogenated benzaldehyde containing fluorine has already been studied. [1, 2] We expand on the series by replacing fluorine with a quadrupolar halogen atom (I(Cl)= 3/2) and presenting broadband and cavity microwave spectroscopy results of ortho, meta, and para-chlorobenzaldehyde, where the chlorine nucleus can act as a local probe for changes between the different isomers. These studies serve as a baseline for future gas-phase complex studies involving chlorobenzaldehyde.

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Docking preference and geometry of 1-naphthol complexes revealed by rotational spectroscopy

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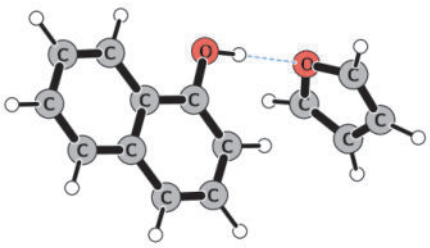
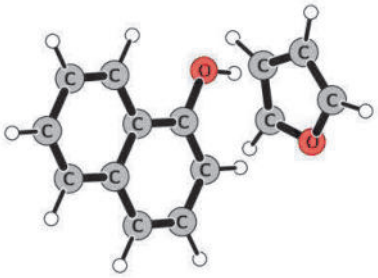
We examine the interplay of docking preference on 1-naphthol in van der Waals complexes with simple molecules. The advantage of 1-naphthol is that it allows two main docking sites, the first on the conjugated π-system of the fused rings and the second on the hydrogen bond donor site at the hydroxyl group. Initial complexes studied include furan, dimethylfuran, and thiophene. These three systems follow a similar structure of a heterocyclic, five-membered ring containing a chalcogen as the heteroatom, setting up a common structural motif to benchmark quantum chemical methods with experimental results. Later measurements were extended to benzene and carbon monoxide complexes. Current progress on the ethylene and acetylene complexes will also be discussed. We compare these results with recent literature reports of the dissociation energies and computational studies, where available.

The spectra for all the reported systems were recorded using a broadband microwave spectrometer in the 2-8 GHz frequency range in a cold, supersonic jet. From the spectroscopic constants of those complexes, an effective geometry has been determined for each. A combination of experiment and quantum chemical calculation results are used to determine each furan-docking site's relative abundances observed in the expansion. Additionally, we will discuss the role of equilibrium vs. ground state geometries in the results of complexes involving furan.



OH···O



OH···π

Stark-spectroscopic investigations of large organic molecules and their clusters with water in superfluid helium nanodroplets

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Prof. Dr. A. Slenczka, Regensburg/DE, University of Regensburg,
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Superfluid helium nanodroplets serve as a gentle and ultracold (T = 0.37 K) host system for molecular and atomic species as well as weakly bound (van der Waals) clusters [1]. Probing the dopant by means of electronic spectroscopy reveals information on the dopant species as well as on the helium environment and finally on the interplay between both. These features are subsumed under investigation of microsolvation, which becomes apparent in spectral features such as line splitting, the appearance of a phonon wing or helium induced shifts of electronic transitions.

Despite the vanishing viscosity of superfluid helium the spectral shape of the zero phonon line at the electronic origin of almost all molecules embedded into superfluid helium droplets does not reveal the band system of a free rotor [1]. According to previous investigations [2] helium induced inhomogeneous line broadening dominates the observed spectra. In order to decipher pure molecular and helium induced contributions we utilize electronic Stark-spectroscopy. Thereby, the Stark-field imprints anisotropy into the molecular ensemble as a result of hindering free rotation of the dopant, which effects the rotational band shape and, thus, becomes visible even when covered by inhomogeneous line broadening. We present electronic Stark-spectra of clusters consisting of a single chromophore like phthalocyanine or chloroaluminiumphthalocyanine and additional water molecules. The optical anisotropy as well as field induced spectral shifts are readily recognized in the Stark-spectra of these polar clusters. Those field induced features suffice to propose or exclude possible configurations of the clusters.

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Infrared Spectroscopy of $CO_3^{\bullet-}(H_2O)_{1,2}$ and $CO_4^{\bullet-}(H_2O)_{1,2}$

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The radical anions $CO_3^{\bullet-}(H_2O)_{1,2}$ and $CO_4^{\bullet-}(H_2O)_{1,2}$ are important ions in the atmosphere. A steady state fractional abundance of $CO_3^{\bullet-}$ and its hydrated counterpart $CO_3^{\bullet-}(H_2O)$ in the range of 0.3–2.3% of the total negative ion inventory is predicted in quantitative models with $CO_3^{\bullet-}(H_2O)$ dominating up to 11 km altitude [1]. The presence of $CO_3^{\bullet-}$ and $CO_3^{\bullet-}(H_2O)$ was confirmed in direct sampling of ions in the boreal forest [2]. The $CO_4^{\bullet-}$ ion is another radical anion that is derived from CO_2. Its fractional abundance in the atmosphere is about 0.01% [1]. The understanding of their spectroscopic properties and hydration structure are important task to understand their reactivity. The reactivity often depends strongly on the number of solvating water molecules [3].

The infrared spectra were measured in the C-O and O-H stretch region. The O-H stretch region exhibits broad spectra with additional maxima and shoulders beside the free O–H stretch frequency for all ions. The C–O stretching region showed clear maxima, but dissociation of $CO_3^{\bullet-}(H_2O)_{1,2}$ was surprisingly inefficient, probably due to radiative cooling. While $CO_3^{\bullet-}(H_2O)_{1,2}$ and $CO_4^{\bullet-}(H_2O)$ loose water upon dissociation, $CO_4^{\bullet-}(H_2O)_2$ exhibits a dissociation channel with loss of CO_2. All experimental infrared spectra are compared to calculated spectra within harmonic approximation and from analysis of molecular dynamics simulations. The comparison of experiment and theory clearly shows that multiple isomers contribute to the observed spectrum at finite temperatures.

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Optical Spectrum of the Adamantane Radical Cation

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Known for their stable structural and thermal properties, diamondoids and their radical cations are viable candidates as carriers for diffuse interstellar bands [1]. While previous diamondoid research has mainly focused on neutral molecules and their derivatives, little is known about their radical cations, which may form in interstellar environments by ionizing radiation [2]. We report the first experimental optical spectrum of the simplest diamondoid cation, the adamantane radical cation ($C_{10}H_{16}^+$), obtained via electronic photodissociation spectroscopy at 5 K between 310–1000 nm. The optical spectrum reveals a broad band spanning the range of 420–850 nm, assigned to the $D_2(^2E) \leftarrow D_0(^2A_1)$ transition using time-dependent density function theory calculations. Despite a vibrational temperature below 20 K, we observe no vibrational structure because of lifetime broadening and/or Franck-Condon congestion. A second band system originating at 345 nm that shows vibrational progressions is attributed to the overlapping $D_5(^2A_1)/D_6(^2E) \leftarrow D_0(^2A_1)$ transitions split by the Jahn-Teller effect. The lifetime deduced from the widths of these vibronic bands is ~30 fs. Comparison of the spectrum with known diffuse interstellar bands suggests that $C_{10}H_{16}^+$ is not likely to be a carrier. However, the strong absorption features in the UV to near IR show promise in the investigation of higher order diamondoids as potential candidates [3].

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Photoelectron spectroscopy of BH_2 using synchrotron radiation and photoelectron/photoion coincidence (i^2PEPICO) spectroscopy

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Determination of accurate ionization and appearance energies are always crucial for any reactive intermediate as it permits to derive accurate binding energies and standard heats of formation. Moreover, photoelectron spectra (PES) give valuable information regarding the nature of bonding, threshold for dissociative photoionization and cationic structure.

BH_2 is one of the simplest hydrides, a free radical with only seven electrons. Although Herzberg measured its first electronic spectrum almost fifty years back, its IE, as well as PES, was not measured yet [1]. As the photoionization leads to a linear cation from bent neutral molecule, recording of vibrationally resolved PES, as well as spectral simulation, are both challenging. In this study, we report the first recorded slow photoelectron spectrum (SPES) of BH_2 and precisely determined its IE as 8.12 ± 0.02 eV. BH_2 was generated in a flow-tube reactor from B_2H_6 by H-abstraction using fluorine atoms produced via F_2 microwave discharge. SPES with mass selectivity was recorded using i^2PEPICO spectrometer coupled with synchrotron radiation provided by SOLEIL beam line facility. Recorded SPES portrayed a long progression of bending vibration indicating large change of bond angle upon ionization. Spectral simulation is also done by calculating Franck-Condon (FC) factors between neutral and cationic states. Apart from that we also record SPES of BH from both $X^1\Sigma^+$ singlet and $a^3\Pi$ triplet state which allow us to first experimentally determined the singlet/triplet gap (ΔE_{ST}) of BH.

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Heteronuclear long-range Rydberg molecules

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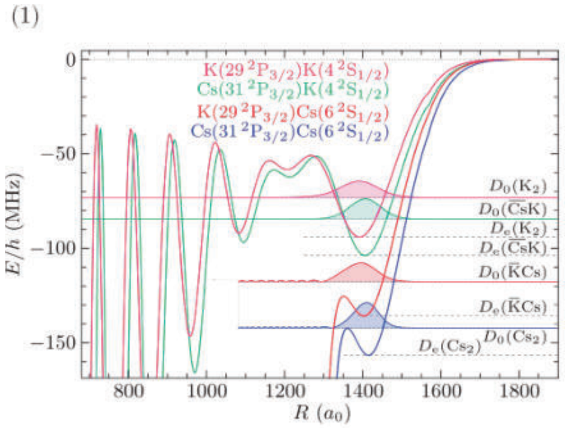
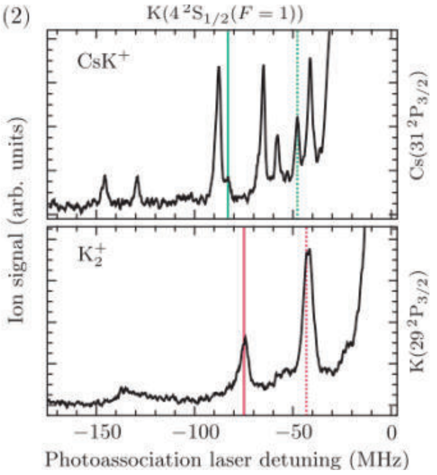
In this contribution, I will present recent results of the spectroscopy of heteronuclear long-range Rydberg molecules (LRMs) [1]. LRMs are bound states of a Rydberg atom and a ground-state atom located within the orbit of the Rydberg electron, with the binding originating from the Rydberg electron–ground-state atom scattering interaction [2]. These “exotic” molecular states have, *e.g.*, been proposed to serve as an intermediary state in the formation of ion-pair states and plasmas consisting of oppositely charged particles with equal mass [3] and for the creation of long-range multiparticle entanglement [4]. Spectroscopic and theoretical studies of LRMs yield, otherwise difficult to obtain, low-energy electron-atom scattering phase shifts [5]. However, the current theoretical tools used to model LRMs suffer from intrinsic difficulties. Isoelectronic substitution of the constituent atoms allows for a controlled variation of the binding (see potential energy curves of heteronuclear LRMs in Fig. 1). Photoassociation spectroscopy of heteronuclear LRMs (see Fig. 2) thus serves as a testbed for current and future ab-initio theoretical models.

(1)



(2)



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Cryogenic Vibrational Spectroscopy – A Tool for Understanding Mechanisms in Organic Chemistry

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Studying mechanisms in organic chemistry is often a tedious task. Even though there are various methods available to get indirect information on the mechanism, it is usually not possible to directly characterize short-lived intermediates involved in the reaction. To solve this issue, we generate the ions of interest via electrospray ionization and isolate them in the clean-room environment of a mass spectrometer. The ions are accumulated in an ion trap and subsequently picked up by superfluid helium droplets (0.4 K). The doped droplet beam then overlaps with an infrared beam produced by the Fritz Haber Institute free-electron laser. Resonant photons excite vibrational modes leading to the release of the ions from the droplets, detected by a time-of-flight detector, while the ion count plotted as a function of the photon wavenumber leads to an infrared spectrum. The highly resolved spectrum is diagnostic for the ions' structure leading in combination with computed spectra to unambiguous structural assignments.

A particularly challenging intermediate is the glycosyl cation – a reactive species that occurs during the chemical synthesis of sugars. Although it has been postulated that acyl protecting groups can interact with the charge in glycosyl cations to influence the stereoselectivity of the reaction, the ions exhibiting these effects were only characterized very recently. By using the above-described technique, we recently provided the first direct evidence for the participation of neighboring and remotely located protecting groups. The data was compared to results from synthesis, which showed that there is a clear correlation between the gas-phase structure and solution-phase chemistry. As a result, the outcome of glycosylation reactions can be predicted. In the future, the presented approach will be used to investigate further reactive intermediates in organic chemistry.

2D hierarchical nanosheets with integrated Co-based HER-catalysts: An X-ray photoelectron and tip-enhanced Raman spectroscopy study

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Hydrogen production by molecular photocatalysis is an important approach for the realization of renewable energy sources. In this respect, the implementation of cobalt-based molecular catalysts [1] in heterogeneous catalysis provides many advantages in comparison to well-established catalysts based on rare earth metals. Here we report on the integration of such catalysts into molecular nanosheets, which can simultaneously serve as two-dimensional (2D) matrix for catalyst immobilization and as a potential separation membrane for products of the photocatalytic reactions. The synthesized low-dimensional 0D/2D hybrids consist of amine carbon nanomembranes (NH_2-CNMs) with only 1 nm thickness [2] and of cobalt(III)(dimethylglyoxime) complexes [1] immobilized on their surface. We establish different synthetic pathways to engineer these nanostructures and characterize them employing X-ray photoelectron spectroscopy in combination with tip-enhanced Raman spectroscopy. Based on these complementary techniques we obtain a detailed picture of the chemical and structural properties of these novel molecular nanostructures on the millimeter down to the nanoscale. We show that this approach enables development and characterization of a variety of other systems with a mixed dimensionality for implementation in molecular photocatalysis.

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Surface properties of dendritic fibrous silica nanoparticles studied by wide-angle soft X-ray scattering

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Surface properties of dendritic fibrous silica nanoparticles (*d* = 200-800 nm) are studied using wide-angle X-ray scattering (WAXS) spectroscopy as well as photoionization in the soft X-ray regime. A beam of free silica nanoparticles is focused by an aerodynamic lens into the interaction region where it is crossed with the tunable, horizontally polarized soft X-rays (hν = 100-180 eV) emerging from the undulator beamline UE56/2-PGM2 at the BESSY II synchrotron radiation facility (Berlin, Germany). Elastically scattered X-rays are detected by a micro channelplate (MCP) detector behind a slit (0.8 mm width, 20 mm height) that is rotated horizontally around the scattering center at a distance of 50 mm. Measurements are performed in two different ways, (a) at a fixed scattering angle $\vartheta = 18°$ varying the photon energy, and (b) at a fixed photon energy of hν = 139 eV varying the scattering angle. Typical results from the latter method are compared in Fig. 1 for smooth silica nanospheres (a) and dendritic fibrous silica nanoparticles (b), where the scattering intensity is plotted on a log-log scale against the magnitude of the scattering vector $q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$. For the smooth sample (a) the scattering intensity follows the slope of -4, as predicted by Porod's law for bulk scattering. In contrast, the dendritic fibrous sample (b) shows a significantly different behavior. The slope is less steep and the q values follow a slope of -2.8, which is attributed to additional scattering contributions from the rough surface. Results from other fibrous nanoparticle samples of different size and fiber length and density will be discussed in detail.

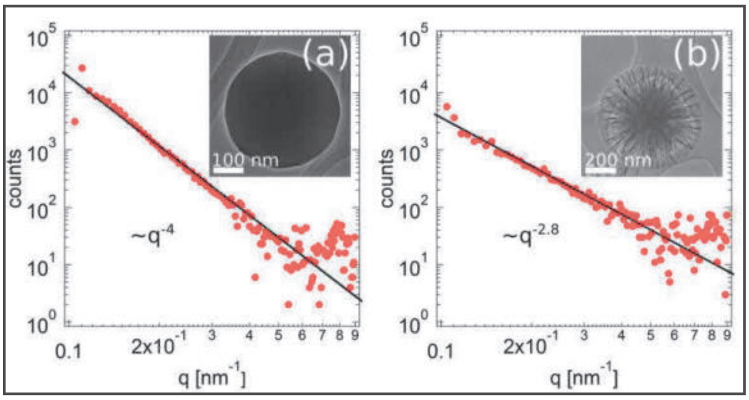

figure 1: X-ray scattering intensity at SiO_2 nanoparticles of different surface structure irradiated by soft X-ray radiation with photon energy E = 139 eV

Femtosecond energy transfer in Fe(II)-Co(III) photocatalyst directly observed with X-ray emission spectroscopy

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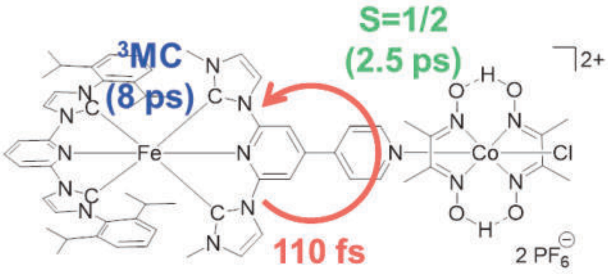

Modeling the bimetallic photocatalyst especially without any noble-metal element demands a clear understanding of how the incident photon energy transforms efficiently into useful chemical energy. An excited electron in the photoactive moiety could be transferred to the catalytic moiety, or activate it *via* an energy transfer, on the so-called ultrafast timescale.

Herein we show and discuss our recent results of femtosecond-resolved X-ray emission spectroscopy measurements on the Fe(II)-Co(III) photocatalyst at SACLA. Upon 515 nm photoexcitation, both Fe Kα_1 and Co Kα_1 transient emission signal kinetics revealed the same 110 fs arising time constant, indicating that both moieties are coupled. Subsequently, the 8 ps (^{3}MC; the triplet Metal-Centered state) and 2.5 ps (S=1/2; the doublet Co(II) excited state) decay dynamics appeared in the Fe Kα_1 and Co Kα_1 transient signal kinetics respectively, unveiling that the excited electron in the Metal-to-Ligand Charge Transfer (MLCT) state of the Fe(II) moiety spontaneously perturbed the Co(III) moiety by the energy transfer, letting an excessive electron from its dimethylglyoxime (dmgH) ligand be transferred on the Co(III) metal ion. The resulting Co(II) photoactivated complex leads to the twice faster photocatalytic proton reduction compared to the corresponding two-component system.

Dinuclear Ir(III) Complex Exhibiting Unusually Slow Phosphorescence and Intersystem Crossing

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Modulating the design of the ditopic ligand we obtained a new dinuclear Ir(III) complex **1** (Figure 1) which shows unusually slow $T_1 \rightarrow S_0$ phosphorescence accompanied by $S_1 \rightarrow S_0$ fluorescence. The latter indicates that intersystem crossing (ISC) depleting the S_1 state in favor of triplet manifold is also comparatively slow.

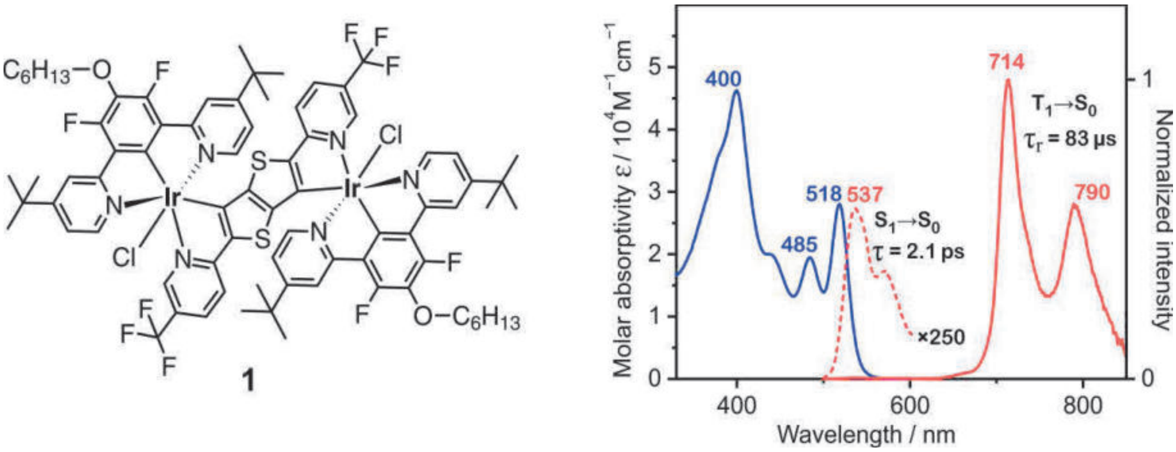

Figure 1. Chemical structure of a dinuclear Ir(III) complex **1** and its absorption (blue) and emission (red) spectra in CH_2Cl_2 solution

By means of transient absorption spectroscopy it was found that ISC from S_1 state occurs directly to T_1 state, $S_1 \rightarrow T_1$, with a comparatively large time constant of about 2.1 ps. On the basis of spectroscopic data and DFT calculations it was rationalized that the found photophysical properties of complex **1** are brought by the correlating effects of weak involvement of metal centers to the formation of states S_1 and T_1, and a comparatively large energy gap between the two, $\Delta E(S_1 – T_1)$. [1]

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Evidence for Directed Electron Transfer in Flavin-modified Oligoprolines

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Charge transfer in proteins over long distances has received increased attention due to its importance in biological systems. For example, electron transfer (ET) in redox-active systems is often explained by a series of hopping processes where flavin-modified amino acids are known as photoinducible electron acceptors. Flavin moieties can undergo ET directed from the electron donors such as tryptophan and tyrosine, which is important in the generation of the fully reduced flavin-states. [1] We previously reported on femtosecond absorption studies from the UV to the visible region of flavin-based oligoprolines with tryptophan as the electron donor to study the competitive photophysical pathway of directed and non-specific ET in flavins. [2]

In absence of tryptophan, the analyzed peptide had a dominant non-specific ET, forming an ion pair in agreement with reference [3]. In contrast, peptides with tryptophan showed a weak non-specific but intensified directed ET. Furthermore, we suggest that the directed ET can occur from the S1 state in contrast to the ion pair state, which is higher located in energy. [2]

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Nitrogen-Release Pathways of a Carbenonitrene Precursor Investigated by Matrix Isolation and Ultrafast Spectroscopy

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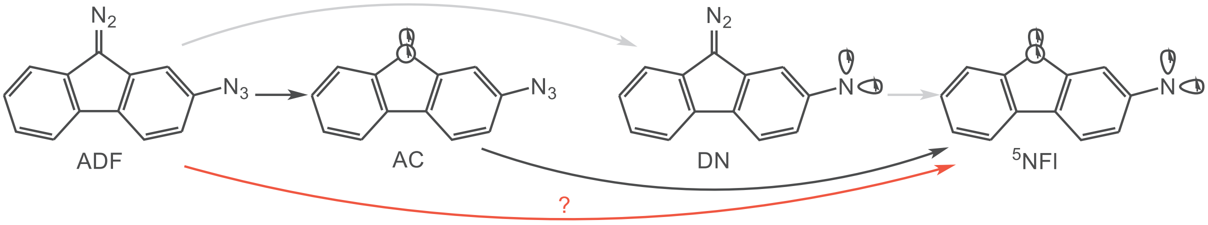
Illumination of 2-azido-9-diazofluorene (ADF) in an argon matrix led to the quintet carbenonitrene 2-nitreno-9-fluorenylidene (^{5}NFI), corroborating photocleavage of two N_2 molecules, one at the diazo (R-N_2) and one at the azido (R-N_3) functional group.



In order to investigate how the photocleavage proceeds, ultrafast transient absorption spectroscopy on ADF in acetonitrile is employed. Previous studies addressed related precursors comprising either solely the diazo or the azido group, i.e. the formation of the carbene 9-fluorenylidene [1] as well as of the nitrene 2-fluorenylnitrene [2], yielding a singlet-triplet-equilibrium [1] and a triplet [2], respectively. For ADF, we explore whether the diazo-nitrene (DN) or the azido-carbene (AC) is generated upon photoexcitation. In addition, the possibility of concerted or stepwise release of two N_2 molecules is discussed, as required to form ^{5}NFI observed in the cryogenic studies.

Transient spectra recorded in the visible and ultraviolet regime upon excitation at 270 nm or 310 nm show spectral features and lifetimes of intermediates consistent with the formation of both the azido-carbene and the diazo-nitrene species. This is identified by characteristic absorption features of the reactive intermediates arising on the picosecond time scale, complemented by steady-state spectra at cryogenic temperatures where these intermediates are stable for hours. Thus, after photoexcitation of ADF, two concurrent pathways for photocleavage of a single molecule of N_2 are accessible. For formation of the quintet carbenonitrene ^{5}NFI, our data indicates the necessity of a second electronic excitation.

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Hydrogen bonding in tetrathiatriarylmethyl alcohol probed by ultrafast mid-infrared spectroscopy

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Tetrathiatriarylmethyl radicals derived from the Finland trityl radical are one of the main classes of spin labels. They are commonly utilized in spin-sensitive techniques such as magnetic resonance imaging (MRI) or electron paramagnetic resonance (EPR) spectroscopy. EPR spectroscopy allows for distance measurements in proteins even under in-cell conditions. The synthesis of functionalized trityl radicals involves closed-shell molecules up until the final dehydroxylation and subsequent reduction of trityl alcohols. These precursors feature intramolecular O–H···S hydrogen bonds which are suspected to break and reform with another sulfur atom.

Ultrafast mid-infrared pump-probe spectra of the trityl alcohol were recorded. A sample solution was excited with laser pulses centered around 3337 cm^{-1} corresponding to the ν(O–H) fundamental frequency. Delayed probe pulses with frequencies between 3000 cm^{-1} and 3400 cm^{-1} give rise to a ground state bleaching and transient absorption signal. These signals are separated by a very large anharmonic red shift of ~270 cm^{-1}. Both signals fully decay with a lifetime of ~1.5 ps after excitation. Two-dimensional spectra provide signals that exhibit tilting dynamics. *Ab initio* calculations and Brownian Oscillator Simulations based on Kubo’s stochastic line shape theory provide the link to the real motion of the O–H oscillator of the trityl alcohol.

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Femtosecond to millisecond dynamics of photoactive yellow protein revealed by the vibrational label –SCN

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Protein dynamics can occur on timescales spanning many orders of magnitude. The photocycle of photoactive yellow protein (PYP) for example ranges from femtoseconds to a second [1]. Tracking fast dynamics on the amino-acid level in the solution phase is not feasible with NMR spectroscopy or X-ray scattering. One way of accessing local information is to use a vibrational label such as thiocyanate (SCN), which can be inserted at any desired amino acid location [2-3]. Local information is then provided by the label's vibrational properties, which change upon perturbations of the local electrostatic and structural surroundings [4-6].

Upon light absorption, PYP partially unfolds after the chromophore isomerized on a ps time scale. With transient fs-ms infrared spectroscopy on PYP mutants having an incorporated SCN, we can follow most part of the photocycle. The data reveal that the label itself hardly alters the photocycle, and that it only responds to changes in its local environment, which in turn depend on the structural unit in which it was placed. In the IR spectroscopy of unlabelled proteins, site resolution is typically only achieved for changes of the chromophore or of protonatable/H-bonded side chains, with the by far largest part of the protein contributing to a single broad band (such as the amide I band). Vibrational labels present a big improvement as careful selection of a labelled site can provide local structural information at almost any desired location, and may resolve new intermediates. This method can also assist in unravelling other systems like ligand docking in proteins or protein-protein interaction in near atomic detail.

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Real time observation of the photochemically induced formation of a transition metal nitrene complex

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Transition metal azides have recently attracted considerable attention as photochemical precursors for transition metal nitrenes or nitrides. The latter species feature interesting catalytic reactivities including chemical bond activation. [1, 2]
Here, we explore the multiscalar dynamics of Diazido[1,2-bis(diphenylphosphino)-ethane]nickel(II), (Ni(dppe)(N_3)$_2$), following ultraviolet (UV) excitation using a combination of femtosecond UV-pump-Infrared-probe (UV-IR) spectroscopy and step-scan Fourier-transform IR-spectroscopy. The UV-IR spectra exhibit a strong negative signal in the asymmetric azide stretching region due to depletion of the electronic ground state together with a broad redshifted absorption due to the excited state. The induced absorption dynamically narrows in 100 ps as a result of excited state cooling and ultimately evolves into a permanent transient absorption centered at 2040 cm^{-1}. In agreement with calculations based on density functional theory, this feature can be assigned to the formation of a nitrene complex Ni(dppe)(N_3)(N), which arises upon N_α-N_β bond cleavage and release of dinitrogen from one of the parent's photolabile azido ligands. A lower estimate of about 27 % for the primary quantum yield of this photolytic conversion could be obtained from the permanent N_3-bleaching signal. The majority of the complexes return to the electronic ground state with a time constant of 12 ps. To further corroborate our interpretation and to verify the intermediacy of a nitrene species brought about by photoexcitation, step-scan experiments in the presence of suitable quenchers were carried out, thus resolving the photo-induced reactivity of the transition metal nitrene intermediate.

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Multi-spectroscopic investigations of the luminescence thermochromism of tetranuclear Cu(I)-complexes

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In this contribution[1] a multi-spectroscopic approach is applied for the photophysical and structural characterization of OLED (organic light emitting diodes) relevant highly luminescent tetranuclear complexes with a Cu_4X_4 ($X^- = I^-, Br^-, Cl^-$) cluster core and two 6-MePyrPhos bridging ligands.

Static and time-resolved (time-correlated single photon counting) luminescence spectroscopy are used for the analysis of the electronic properties of the emissive excited states. Interestingly, temperature dependent measurements on solid samples (KBr pellets and neat films) in the range from 290 K down to 20 K revealed a pronounced luminescence thermochromism with a color change from orange-red to blue at low temperature, hence almost the entire visible electromagnetic spectrum is covered.

Time-resolved step-scan FTIR spectroscopy is used for the structural analysis of the luminescent excited states involved in this thermochromism and consists of the very first experimental approach with respect to this issue, to the best of our knowledge. The samples were electronically excited with the third harmonic of a Nd:YAG laser (355 nm, 100 Hz) and step-scan difference spectra of the long-lived (nanosecond and microsecond lifetimes) excited states were recorded. The measured spectra were interpreted by comparison with high-level quantum chemical calculations and revealed two excited triplet Cu_4X_4 cluster geometries with strongly differing copper-copper distances, depending on temperature. These huge structural changes correlate directly with the emission color and are the origin of the observed thermochromic behavior.

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High Resolution Spectroscopy of Cyano-oxirane (c-C_2H_3OCN)

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Oxiranecarbonitrile (cyano-oxirane, c-C_2H_3OCN) is of interest as a possible precursor molecule of evolution [1]. We have calculated parity violation in this molecule in view of possible experiments and biomolecular homochirality [2]. Its spectrum has been measured in the millimeter and submillimeter [3] and terahertz [4] regions. We have recorded its infrared spectrum (295K, resolution: 0.0011 cm^{-1}) using the Zurich Prototype ZP 2001 FTIR spectrometer [5]. Here we report results of the rovibrational analysis of two thousand transitions associated with the ν_{12} (915.3 cm^{-1}) and ν_{13} (848.2 cm^{-1}) bands. The analysis incorporated molecular parameters and ground state energies obtained from our work in the terahertz region [4], and was performed using a Watson Hamiltonian and the WANG program [6]. Simulations performed using the spectroscopic parameters obtained by a least squares analysis reproduce the observed spectrum well. The results are discussed as they pertain to astrophysical spectroscopic searches and the evolution of biomolecular homochirality [7].

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Quarantined (CC-stretched) Formic Acid: Molecular Work-Out in (Self) Isolation

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Vibrational spectra of small molecules effectively probe the underlying potential energy hypersurface, which can be tested when combined with accurate anharmonic calculations. Particularly suited for a performance test of quantum chemical gas phase calculations are spectra recorded in a supersonic expansion, as significant rotational cooling is achieved while the molecules or molecular clusters remain isolated in the gas phase. One of the smallest reference systems for such a study is the formic acid monomer with its *cis*-*trans*-torsional isomerism. New vibrational reference data on the stretching vibrations of the higher-energy *cis*-conformer of HCOOH (depicted in Fig. 1) were recently provided *via* a combination of Raman jet spectroscopy with thermal excitation [1] and the weights in this molecular work-out have been increased by extending it to the deuterated isotopologues, as illustrated in Fig. 1. [2]

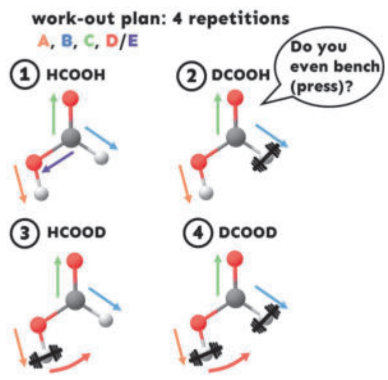

Fig 1: Molecular work-out of *cis*-formic acid. Adapted from Ref. [2], licensed under CC BY 3.0.

Another promising carboxylic acid for such a study is the smallest acetylenic acid, HCC-COOH, whose *cis*- and *trans*-rotamers will be discussed in this contribution and compared to those of formic acid. The advantage of this CC-stretched formic acid is the smaller *cis*-*trans*-energy difference yielding a higher *cis*-abundance in the expansion, but also the *trans*-rotamer and its dimers prove to be an insightful reference system for benchmarking.

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How ester groups assist in the folding of linear alkyl chains – a combined Raman and quantum chemistry approach

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When suspended in vacuum, linear alkanes assume a folded global minimum structure beyond a chain length $n = 17 \pm 1$,[1] largely driven by London dispersion forces. Raman spectroscopy in adiabatic gas expansions is highly suitable to study this conformational switch, which allows for benchmarking theoretical methods in terms of segment interaction and distortion within chain polymers.[2–4]

For quantifying conformational preferences not only wavenumbers, but also intensities are required. The usual approach of signal integration and comparison to calculated scattering cross sections is often hindered by spectral overlap due to rotational broadening. Here we propose a new approach for simulating rotational broadening of Raman spectra in supersonic expansions. This model is applied to explore linear alkyl esters in terms of folding motifs and conformational preference.

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Following Surface Reactions along a Flow Channel

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Whether in a river, in a reactor, or along an electrode – reactions at the interface of solids and flowing liquids are everywhere. A molecular picture of the interfacial reactions under flow conditions resolved across the interface is highly desirable, as it will improve our understanding of interfacial reactions under realistic (non-static) conditions. In this work, we used vibrational Sum Frequency Generation (v-SFG) Spectroscopy to track flow-induced dissolution position-resolved along mineral interfaces.

In v-SFG, infrared (IR) and visible laser pulses are overlapped in space and time at the interface of interest, generating sum-frequency light. This process is forbidden in centrosymmetric media such as bulk water. The symmetry-breaking that necessarily occurs at an interface makes v-SFG interface-specific. If the IR beam is resonant with the O-H stretch vibration of water molecules, the signal is strongly enhanced. Through the O-H stretch spectrum, the v-SFG spectrum reports back on the structure of the interfacial water. Moreover, electrostatic interactions between the dipole of the water molecules and the field of a charged mineral surface align the water molecules, resulting in a larger v-SFG signal. Therefore, the v-SFG intensity serves as a measure of the surface charge.[1,2]

Interfacial dissolution processes are promoted by macroscopic flow, which changes the surface charge and can, therefore, be studied by v-SFG water spectra.[3] We show that these dissolution processes vary dramatically with the distance from the inlet in the flow channel. These findings will impact the modeling of mineral dissolution and are relevant to other interfacial reactions under flow conditions such as in heterogeneous catalysis or electrochemistry.

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Water adsorption at low temperatures on clean and Pt-covered silicon surfaces

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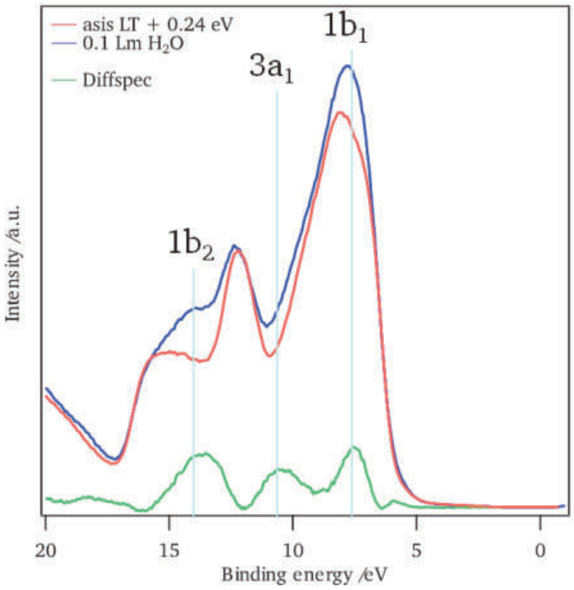
Hydrogen by photoelectrochemical (PEC) water splitting might play a key role for future energy storage systems. In the last decade, multijunction silicon photocathode devices could reach solar-to-hydrogen efficiencies of about 10%. However, the fundamental loss mechanisms along the device interfaces are still not fully understood and impede further efficiency improvement.

In order to address the charge transfer losses at the electrochemical interface, we focus on the semiconductor-electrolyte interface of single crystalline silicon to water. Specifically, the impact of different surface terminations and resulting surface defect concentrations is investigated.

For that purpose, water from the gas phase is stepwise adsorbed on the substrates at cryogenic temperatures. The interaction of water with the semiconductor surface is investigated with respect to chemical composition, charge transfer and electronic structure by X-ray photoemission spectroscopy (XPS) as well as monochromatic ultraviolet photoelectron spectroscopy (UPS).



Low temperature (LT) UP-Spectra of n-Si/SiO_2-substrate and with 0.1Lm H_2O on top. Differential spectrum indicates molecular adsorption.

In this study, different hydrogen and oxygen terminated surfaces are prepared. Furthermore, the impact of atomic Pt-clusters on the adsorption behavior is investigated. It is shown, that the electronic interaction of the adsorbed species strongly depends on the defect concentration at the surface. Furthermore, only in the presence of atomic platinum, clear indications for the H_2O dissociation are observed.

Influence of the surface ligands on charge-carrier localization and trapping in dot-in-rod nanostructures

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Colloidal semiconductor nanocrystals are extremely potent and versatile materials for light-harvesters for photovoltaics and photocatalysis. Colloidal nanocrystals can be regarded as inorganic-organic hybrids, since organic surface ligands are an essential part of the final structure, not only determining the dispersibility of the particles in non-polar or polar solvents, but also passivate surface trap states or even induce traps directly impacting, e.g. the photoluminescence quantum yield of the band gap emission or photon-to-hydrogen conversion efficiencies in assemblies for light-driven water splitting.

To collect detailed insight into the mechanisms behind these effects, we have studied the impact of the surface ligand on the intrinsic exciton relaxation and localization processes in CdSe@CdS dot-in-rod nanostructures by a combination of steady-state and time-resolved absorption and photoluminescence spectroscopy.[1] The ligands reported, which render the nanorods dispersible in water, can be classified by their anchoring groups (mono-thiols, di-thiols, and imines) and their hydrophilic segment (carboxylate, PEG, imines). Results obtained with these surface ligands are compared to the benchmark system with TOPO ligands, a phosphine oxide, in toluene. We show that the introduction of the widely used thiol ligands leads to a decreased hole localization in the CdSe core due to hole trapping at the surface. On the other hand, steric restrictions in dithiolates or ligands with bulky side chains decrease the surface coverage, and increase the density of electron trap states, impacting the recombination dynamics at the ns timescale. Imines (PEI) on the other hand can saturate and remove surface traps to a wide extent. Implications for catalysis are discussed.

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Interfacial Premelting of Ice in Nano Composite Materials

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At solid/ice interfaces, a premelting layer is formed at temperatures below the melting point of bulk water. This interfacial premelting layer in ice/clay nano composites was studied by quasi elastic neutron scattering and high energy X-ray diffraction. Using well defined and characterized ice/vermiculite, ice/kaolin, and ice/talc composite samples, this work bridges the gap between studies on single crystalline ice/solid model interfaces [1, 2] and naturally occurring soils and permafrost. Below the melting point of bulk water, the formation of liquid water was observed. The liquid fraction is gradually increasing with temperature. Quantitative analysis of the molten fraction reveals differences in the deviation from Antonow's rule relating the interfacial free energy between ice, water, and the clays [3]. The translational diffusion constants of the confined premelting water is strongly reduced compared to super cooled bulk water [4]. Adjacent to charged vermiculite the lowest water mobility was observed, followed by kaolin and the more hydrophobic talc. Results are explained by the intermolecular water interactions with different clay surfaces and interfacial segregation of the low-density liquid water (LDL) component.

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A Fourth-Generation High-Dimensional Neural Network Potential Including Non-Local Charge Transfer

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Machine learning potentials (MLPs) have become an important tool for performing reliable atomistic simulations [1], since they provide close-to first-principles accuracy while the computational costs are comparable to empirical force fields. To date, the majority of MLPs relies on the representation of energies and charges as a function of the local atomic environments. They are thus unable to capture global changes in the electronic structure due to long-range charge transfer and cannot describe systems in multiple charge states. Recently, non-local MLPs have been introduced to overcome these limitations [2]. Here we propose a fourth-generation high-dimensional neural network potential (4G-HDNNP) that is able to take global charge redistributions and the corresponding non-local effects into account [3]. We illustrate the improved accuracy of 4G-HDNNPs for several benchmark systems including molecular and periodic systems.

Literature:
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[3] T. W. Ko, J. A. Finkler, S. Goedecker, J. Behler, Nature Comm., accepted (2020). arXiv:2009.06484 (2020).

Applications of machine learning in quantum simulations of hydrogen bond dynamics

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Understanding interactions between organic molecules and water at a microscopic level is central to many chemical and virtually all biological processes. Experimental studies of microsolvated clusters provide important insights into the mechanism of solvation by looking at molecular complexes with water at specific binding sites. Here, accurate theoretical predictions of nuclear motion and tunneling dynamics are crucial for the development of improved experimental protocols, elucidation of acquired data, and unraveling of the underlying chemistry motifs.

The exponential scaling of the computational burden with the number of degrees of freedom, i.e., cluster size, renders the computational costs of existing variational methods unaffordable for clusters composed of more than two moieties. The development of new theoretical methods that employ machine learning offer a great promise in mitigating the exponential scaling of variational calculations.

We will present some of our recent applications of machine learning in quantum simulations of hydrogen-bonded complexes of indole and pyrrole with water. In particular, we will present new pool-based active learning approaches for reducing the costs of computing the multi-dimensional *ab initio* potential energy surfaces. We will also present our initial approach in using the spectral inference networks [1] for variational simulations of nuclear motion dynamics with many floppy degrees of freedom.

[1] D. Pfau, S. Petersen, A. Agarwal, D. G. T. Barrett, K. L. Stachenfeld, “Spectral Inference Networks: Unifying Deep and Spectral Learning”, *Seventh International Conference on Learning Representations (ICLR 2019)*, arXiv:1806.02215v3

Potential of Electrostatics-Finite Ion Size (PfEFIS) method: towards automatic ion diffusion network analysis in solids

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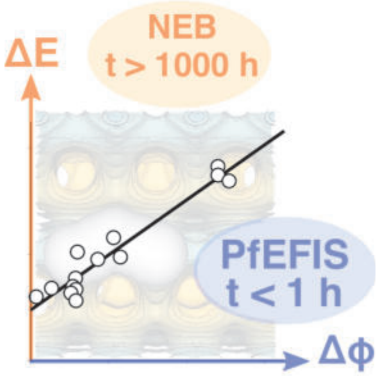
Finding new safe and ecological cathode materials for high-energy-density rechargeable batteries is an important challenge because the demand for lithium ion materials is dramatically increasing. Since experimental screenings are expensive and take a lot of time, computational screenings have become attractive alternatives. In this context, we have developed a method, the potential of electrostatics-finite ion size (PfEFIS) barrier estimation method, that can significantly (i.e., by a factor of 10,000) speed up the discovery process by efficiently estimating jump-diffusion barriers of ions in typical battery candidates [1].



The key idea of PfEFIS is to relax a chain of states in the field of the electrostatic potential that is averaged over a spherical volume using different finite size ion models. For magnesium–as an alternative to lithium–migrating in typical battery material candidates such as transition metal oxides, we find that the optimal model is a shell that is slightly larger than usual ion sizes found in literature [2]. This data-driven result parallels typical assumptions made in models based on Onsager's reaction field theory to quantitatively estimate electrostatic solvent effects. We believe that the method can potentially also be used to estimate proton and oxygen ion migration in solid materials, thus, facilitating computational screening studies for solid oxide fuel cells. Work is in progress to automatically identify ion insertion sites.

Literature:

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Subsampling the core regions of a molecule in Variational Monte Carlo

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Quantum Monte Carlo (QMC) methods use a stochastic approach to solve the Schrödinger equation. Their scaling with the system size considering the computational costs is very much favorable compared to deterministic quantum chemistry methods. A great flexibility in the choice of the wave function allows to efficiently treat both dynamical as well as static correlation which makes QMC methods for instance particularly useful for the description of excited states.

Different regions of space exhibit different time scales and contribute to a varying degree to the overall variance in a Variational Monte Carlo algorithm. This leads to large inefficiencies within a regular algorithm as the same computational effort is spend on all regions. We propose a Monte Carlo scheme which exploits that core regions are physically independent in a molecule to almost remove their high variance contribution to the numerical cost. The method relies on efficiently subsampling the core regions using independent sidewalks. The numerical overhead of this procedure as a function of the total number N of electrons is $O(N)$. It is negligible in comparison to the overall scaling $O(N^3)$ (due to the evaluation of determinants).

After eliminating the statistical fluctuations of the core regions the underlying information mainly from the valence region can be exploited to achieve an additional gain in computational time by optimizing the parameters of the main walk accordingly. Tests are presented on atoms, alkane chains and clusters of silicons which display a gain in numerical efficiency between one and two orders of magnitude for large N.

Deterministic quantum mechanics and chemical reactions: The success of the Maxwell-Boltzmann distribution

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The Born-Oppenheimer approximation can be replaced by a better approximation in a very simple way. The consideration starts from the notion that it is problematic to describe the nuclear motion and the electronic cloud in a similar way, hoping that the Schrödinger equation will generate meaningful results for both of these two completely different types of objects. As the result of the simulation of a chemical reaction one wants to obtain well localized nuclei which clearly define the product state, not a nuclear cloud extending over several Angstroms. The only consistent way to achieve this is by treating the motion of the nuclei classically right from the beginning. The immediate result is ab-initio molecular dynamics (AIMD). Movies of chemical reactions generated with AIMD show clearly that this approach is working well at normal energies. Tunnelling is electronic tunnelling in every case. Thermal reactions are explained by outliers of the classical Maxwell-Boltzmann velocity distribution. The development of this distribution is guaranteed in a molecular dynamics run as it is the most likely distribution. In the present study we use AIMD to investigate some critical cases, namely the ammonia inversion, black-body radiation, Bose-Einstein condensation, and superconductivity.

Electronic Factors in the Isomerization of Donor-Acceptor Stenhouse Adducts Revealed by *Ab Initio* Electronic Structure Theory

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In recent years, donor-acceptor Stenhouse adducts (DASAs) have gained a lot of attention as versatile visible-light photoswitches.[1, 2] This presentation will focus on a recent study of the photochemically and thermally induced isomerization of multiple first, second, and third generation DASAs by means of state-of-the-art *ab initio* electronic structure methods leading to new insight into multiple facets of the reaction mechanism.[3] On the basis of calculated ground and excited state potential energy surfaces as well as a thorough analysis of the wave function compositions, interesting features of the reaction mechanism have been deduced. For example, the closed form of second- and third-generation DASAs can be significantly stabilized by π–π interactions between the donor and acceptor termini when certain structural requirements are fulfilled. The central point of the presented work concerns the delicate balance between neutral and zwitterionic resonance structures that governs the relative barrier height for the crucial C_2–C_3 and C_3–C_4 bond rotations. Finally, a set of calculations on yet unreported derivatives highlights how this balance and hence the barrier heights can be tuned through variation of the donor-acceptor strength as well as the solvent polarity.

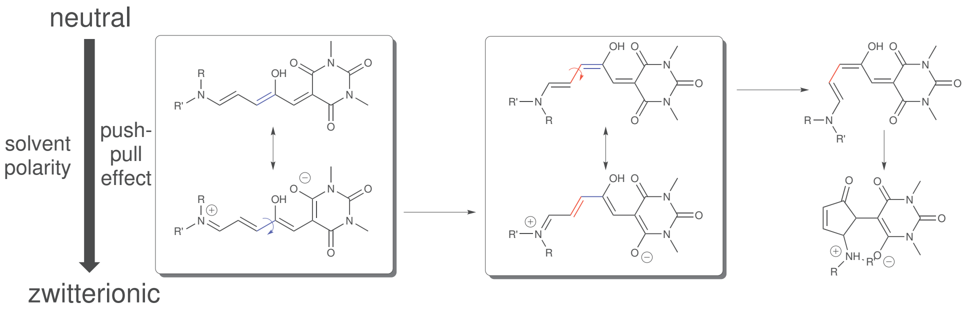

Figure1. Schematic representation of how electronic and environment effects influence the isomerization reaction of DASA photoswitches.

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Photochemistry in Bulk and on Surface:
Co/MgO Nanocubes with Adsorbed O_2

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Metal oxide nanoparticles can be used as basic elements for controlled functionalization and understanding of their properties is therefore crucial for nanotechnology; their characteristics can be moreover tuned by adding various impurities. Photochemistry of the particles can give us direct insight into their electronic structure and composition. In our experiments with highly dispersed Co/MgO nanocubes, a considerable color change is observed when adsorbing oxygen, connected to oxidation of Co^{2+} to Co^{3+} and formation of O_2^- on the surface.

To elucidate the observed photochemistry, we use both multi-reference and single-reference quantum chemical approaches. We model absorption spectra of Co^{2+}/MgO combining molecular dynamics and spin-orbit calculations on the CoO_6^{10-} cluster model embedded in point charges (in Co^{2+}, 96 electronic states are present within 3 eV). For adsorbed O_2^-, we follow the shift of the spectrum with various adsorption sites and discuss the influence of O_2^- on the observed spectrum.

We show that the absorption spectra are deeply affected by the molecular structure and less probable conformations (defects, surface structures) might contribute considerably to the total spectrum due to the higher oscillator strength of the respective transitions.

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Do “Salty Chlathrate Hydrates” Exist?- A Theoretical Approach

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Clathrate hydrates are crystalline inclusion compounds where guest molecules are accommodated by a hydrogen bonded framework formed by water molecules. They are known to be able to host a variety of guest molecules. However, these inclusion molecules are typically small inert molecules, such as H_2, CO_2, CH_4, or THF. [1]

It is the goal of the present study to explore to what extent ionic species might occupy guest-sites within the clathrate hydrate framework while still forming stable (co-)clathrates by using multi-phase molecular dynamics (MD) simulations.

We start by investigating the methane hydrate formation by using temperature dependent MD simulations of a triphasic water/methane/clathrate system with a stoichiometric composition as suggested earlier by Vega et al. [2]

By turning the methane phase gradually into pairs of methane-like molecules with fractional opposite charges, a destabilizing effect on the hydrate phase is observed, and the melting temperature is lowered in a diverging fashion. In fact, methane-like particles with fractional charges above +-0.4 e do not seem to form stable hydrates at all. A different scenario, however, is observed, if these “ionic” methane species are accompanied by neutral methane molecules to form a methane/salt co-hydrate. With increasing (neutral) methane content the stability of the hydrate phase is elevated. Our MD simulations seem to suggest that “salty clathrate hydrates” are an entire possibility.

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When Like-charged Ions Attract: The Influence of Hydroxyl Defects on the Size and Distribution of Cation Clusters in Ionic Liquids

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Attraction between opposite-charged and repulsion between like-charged particles is a commonly accepted concept in science. In contrast, like-charged attraction seems to be counterintuitive at first glance. However, in specifically designed ionic liquids (ILs) with hydroxyl functionalized cations, we found evidence for clustering of cations [1]. Structural and dynamical features, such as the formation of cation clusters, strongly affect the properties of ILs, and a deeper understanding of the relationship between both is worthwhile.

By utilising molecular dynamics simulation as well as neutron diffraction experiments, we are able to investigate the liquid nanostructure of mixtures of $[HOC_4Py][NTf_2]$ and $[C_5Py][NTf_2]$. Data from these studies provide us insight into the formation of cation clusters, and the effects of hydroxyl defects on the clusters' structure and distribution. These clusters are formed via hydrogen bonding between the hydroxyl groups terminating the alkyl chains of the cation. The cations of both ILs are very similar except that the alkyl chain of the former is terminated by a hydroxyl and the latter by a methyl group. The study is aimed towards better understanding the relationship between cluster structures and larger scale nanostructures, which has a strong impact on the properties of ILs.

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Efficient and Accurate Nonadiabatic Molecular Dynamics Simulations of S_1-S_0 Transitions within Time-Dependent Density Functional Theory

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Time-dependent density functional theory (TDDFT) has nowadays become the workhorse of computational photochemistry. However, its incapability of describing S_1-S_0 transitions and its relatively high computational cost (compared to, for example, semi-empirical methods) are still limiting its range of applicability in nonadiabatic molecular dynamics simulations.

Here, we present our recent advances in tackling these challenges. First, by using fractional occupation numbers within TDDFT, we significantly improve the behavior of simulations in the vicinity of conical intersections [1]. Second, recently developed methods for graphics processing units lead to a remarkable reduction of the computation time [2,3]. The benefits and applicability of these methods are demonstrated for several prototypical examples covering the fields of S_1-S_0 photoswitches, molecular machines, and photoactive proteins.

Literature and Footnotes:

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Importance of the random force for molecular dynamics simulations with electronic friction.

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Energy transfer from atomic particles to a metal surface involves both phonon and electron-hole pair excitations. Molecular dynamics with electronic friction (MDEF), governed by the Langevin equation, is a well-established method to describe low energy electronic excitations in those elementary gas-surface processes. [1] In many theoretical studies, however, the random force $\boldsymbol{F}_\mathrm{L}(\eta_\mathrm{el},T_\mathrm{el})$ is neglected based on the argument that the electron-hole pair distribution at few hundreds Kelvin hardly deviates from its 0 K ground state. [2] We demonstrate that the accounting for the random force in MDEF simulations is crucial for reproducing experimental energy loss distributions of H atoms scattered from metal surfaces. [3,4] A simple physical interpretation for this is the maintenance of detailed balance between a projectile and the surface, which means that the possibility of the energy transfer from thermally excited electrons back to the projectile has to be included in the MD propagator.

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DEVELOPMENT OF A FORCE FIELD FOR CELLULOSE IN AQUEOUS 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE

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Cellulose is one of the most important bio-polymers and has a broad range of applications. Because of its poor solubility in most solvents, only a small percentage of cellulose can be further processed. Ionic liquids such as 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc]) can dissolve cellulose [1], but the reason for the solubility is still not fully understood. With the help of molecular dynamics (MD) simulations, it is possible to observe the solvation process on a molecular level. This can be realized by force field MD simulations instead of time consuming *ab initio* MD simulations (AIMD). Therefore, we developed the novel force field *BILFF (**B**io-Polymers in **I**onic **L**iquids **F**orce **F**ield)* for [EMIm][OAc] with water [2] to reproduce radial *(exemplarily shown in Fig. 1)*, spatial, and combined distribution functions, hydrogen bond lifetimes, diffusion coefficients, and several other quantities from reference AIMD simulations. The force field is validated by comparison to experimental data such as density, bulk modulus and thermal expansion coefficients at different temperatures. The development of BILFF enables further considerations of interactions, concentration-related effects and the behavior of the system under external influences.

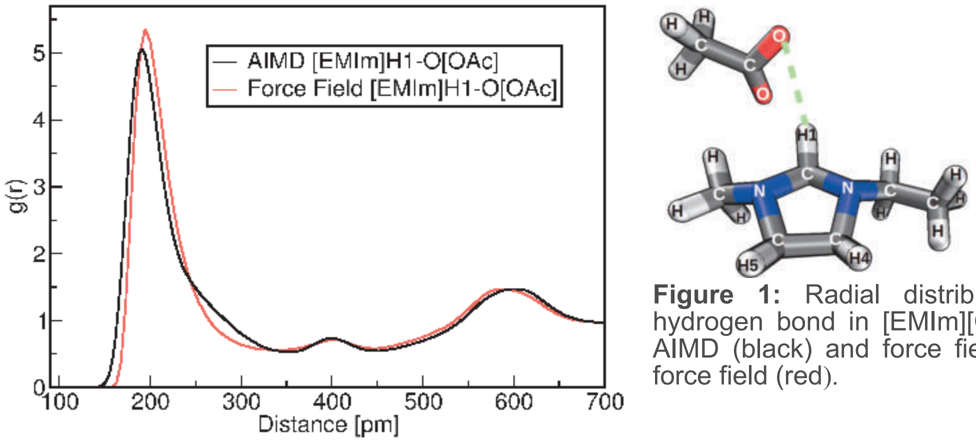

Figure 1: Radial distribution function of a hydrogen bond in [EMIm][OAc] calculated from AIMD (black) and force field MD with our new force field (red).

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Influence of PO_uN_{4-u}-structural units in LIPON on the formation and transport of Li-vacancies: A DFT study

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The application profile of mobile energy storage devices such as lithium-ion batteries is continuously increasing, which leads to an ongoing development. In this context all-solid-state lithium ion batteries (ASSB) are of particular interest, that mainly uses amorphous lithium phosphorus oxynitride (LIPON) as solid state electrolyte. LIPON describes a material class with the stoichiometry of $Li_xPO_yN_z$ (with $x = 2y+3z-y$). The main structural feature is the anionic PO_uN_{4-u}-structure lattice [1]. In order to obtain a deep understanding of ion transport in amorphous LIPON, the Li-vacancy formation and transport in three LIPON model systems [2-4], which differ in their PO_uN_{4-u}-cross-linking, have been investigated using the density functional theory (DFT). We focused on two aspects: I) In order to estimate the calculated values we determined a fluctuation range caused by the DFT approach, which we labelled as uncertainty $\tilde{U}$. In this context, we used several XC-functionals (LDA, GGA [with and without D3(BJ)] and vdW-DF) [5]. II) The dependence of the Li-vacancies formation and the transport properties on structural features of LIPON [6].

Literature:

[1] J. B. Bates, et al., Solid State Ion., 1992, 53-56, 647-654. [2] A. Al-Qawasmeh, N.A.W. Holzwarth, J. Power Sources 2017, 364, 410-419. [3] K. Senevirathne, et al., Solid State Ion. 2013, 233, 95-101. [4] S. Sicolo, K. Albe, J. Power Sources 2016, 331, 382-390. [5] P. Henkel, D. Mollenhauer, Manuscript to be submitted. [6] P. Henkel, D. Mollenhauer, Manuscript in preparation.

Liquid Thermodynamics from First Principles:
Accurate Gibbs Energies Through Integration of Scaled DFT Forces

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All thermodynamic systems strive to minimize their Gibbs energy - the perhaps single most important quantity to predict (physico-)chemical behavior. While modern quantum chemistry paved the way for accurate energies and enthalpies, the determination of Gibbs energies, or more specifically the entropy term, remains a challenge. This is of particular relevance for systems with highly anharmonic potential-energy surfaces, such as liquids and for intermolecular interactions.

To address this challenge, I have recently composed a semi-classical approach for the thermodynamic integration (TDI) of DFT forces on a Born-Oppenheimer surface. Incremental perturbative refinement and rescaling of the internal energy eventually provides Gibbs energies with meV accuracy, enabling reliable thermodynamic predictions of, e.g., phase transition temperatures.

In this contribution, I will demonstrate the application to the normal boiling points (BP) of a representative set of elemental liquids (Fig. 1, ref. 1), as well as the melting and boiling points of Group 12 (Zn, Cd, Hg, Cn) and super-heavy oganesson [2] at various levels of (relativistic) DFT. Analysis of these results provides some valuable insights into the the nature Cn and Og, but also the connection between melting points, the shape of the inter-atomic potential-energy curve, and London-dispersion in DFT. Lastly, I will show some surprisingly accurate results for the BP of molecular liquids and outline how the approach can be generalized to molecular systems and arbitrary interactions.

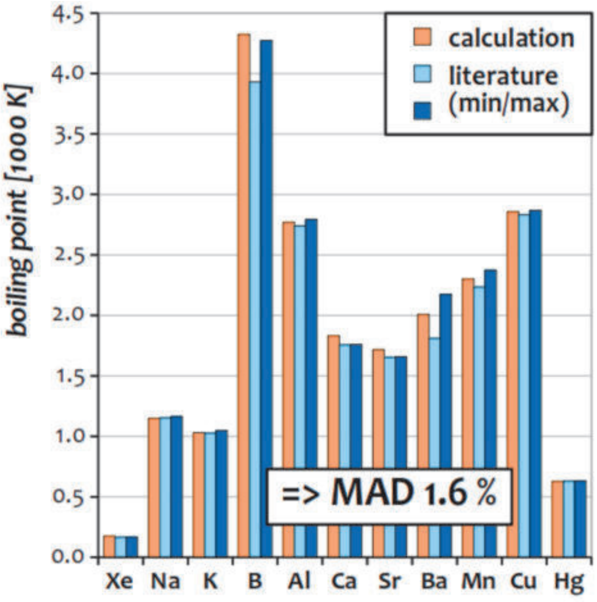

Figure 1: *Calculated and experimental BPs of a representative set of elemental liquids.*

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Role and activity of Fe^{3+} and In^{3+} impurities on coarsening and functional properties in MgO nanoparticle derived ceramics

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Nanoscale grain boundary design is an emerging field in materials science. It addresses the knowledge based transformation of well-defined nanocrystalline starting materials into consolidated networks of nanograins, with designed particle interfaces and grain boundaries. Moreover, controlled impurity segregation into solid-solid interfaces during sintering can be a strategy to induce functional properties that originate from interparticular, impurity-rich crystalline phases. [1,2]

In this study the flexibility of flame spray pyrolysis was used to synthesize MgO based mixed metal oxide nanopowders from the gas phase, with high control over composition up to 20 at% of Fe^{3+} and In^{3+} admixtures. Functional oxide ceramics were obtained by dry uniaxial pressing of as-synthesized nanoparticle powders followed by a pressureless sintering step up to 1373 K and/ or 1673 K, respectively.

Comprehensive structural characterization of the porous ceramics (X-ray diffraction and electron microscopy) revealed both phase separation and impurity segregation. Moreover, we tracked that impurity concentration sensitively influences the intergranular wetting behaviour, thus either favouring the formation of thin intergranular films or the formation of triple- and/or multiple grain junctions. Whereas, sintering at 1373 K of Fe-Mg-O was found to be sufficient to form the magnetic magnesioferrite phase (VSM PPMS) in case of In-Mg-O sintering at 1673 K triggered the formation of an intergranular $MgIn_2O_4$ percolation path, decreasing the ceramics' grain boundary resistivity by orders of magnitude (4 Point Probe Resistivity).

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Polyelectrolyte conformation and dynamics in solution measured by rheology and pulsed field gradient NMR

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Polyelectrolytes in solution display complex dynamics due to the long range electrostatic forces between dissociated groups. Scaling approaches offer a simple way of describing polyelectrolyte conformation and dynamics. Here, we report the single chain diffusion (D) and viscosity (η) properties of NaPSS in salt-free aqueous solution as a function of degree of polymerisation and concentration. These are measured by rotational rheometry and pulsed field gradient NMR. It is shown that while D and η depart from scaling predictions, their product does not, suggesting that the observed differences between theory and experiments are due to a concentration dependence of the monomeric friction coefficient. The concentration dependence of the monomeric friction coefficient exceeds that expected from free-volume models of diffusion, and while its origin remains unclear, it is presumably related to an electroviscous effect. Viscosity and diffusion data are combined using the Rouse model to calculate the single chain dimensions of NaPSS in salt-free solution. It is shown that this method yields results that agree with direct measurements by small angle neutron scattering to within 20%.

Molecular self-assembly and boronate ester synthesis at the liquid-solid interface, a STM study

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The “graphene rush” has triggered immense interest in two-dimensional materials (2DMs), which have promising applications in optics, energy storage and catalysis. 2D covalent organic frameworks (2D COFs) are a sub-class of these 2DMs. 2D COFs are typically synthesised using the solvothermal approach, in which the polymerisation reaction is carried out in solvent mixtures at high temperatures. The solvothermal approach suffers from long reaction time and, at times, poor crystallinity of the final product. Furthermore, 2D COFs are typically obtained as poorly soluble powders due to stacking of the 2D sheets, which hinders their characterisation at the nanometre scale. The on-surface synthesis of 2D COFs affords single layers of 2D COFs with high crystallinity and a low number of defects. By using the external electric field (EEF) of a scanning tunnelling microscope (STM), different boronic acid based 2D COFs were synthesised on surface. [1–3]

In this study, we report on the attempts to fabricate a boronate ester linked 2D COF based on porphyrin-5,10,15,20-tetrayltetrakis(phenyltetraboronic acid) (PB_4) at the solid-liquid interface. [4–7] PB_4 forms a well-ordered self-assembled network at the octanoic acid/graphite interface. STM data also shows formation of a partial second layer atop the monolayer physiosorbed on the graphite surface. The PB_4 monolayer is stabilised by strong molecule-substrate interactions and laterally by *H*-bonding interactions between the boronic acid groups.

In the next step, different aromatic di-diols were tested towards their ability to form a 2D COF when mixed with PB_4 at the solid-liquid interface. Matching HOPG binding strengths between the molecules (PB_4 and di-diol) seem to be important to facilitate the on-surface reaction. Especially too small di-diols are too mobile and too weakly interacting with the surface (covered with the stronger binding porphyrin), hindering the 2D COF formation. In further studies, metallised species will be examined, and the properties of the resulting COFs will be analysed by different on-surface techniques.

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Carbon Nanomembranes from Alkanethiol Monolayers

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Carbon nanomembranes (CNMs) are mechanically stable, chemically inert, and permeable 2D carbonaceous materials, which are highly promising for efficient separation processes, with a typical thickness of around 1 nm. [1-3] CNMs were produced by low energy electron irradiation (100 eV) of a self-assembled monolayer (SAM) covalently bonded to a metal surface. So far, the molecular building blocks for those SAMs range from aromatic to hybrid aliphatic-aromatic as well as cycloaliphatic precursor molecules. Up to now, it is commonly believed that the cyclic nature of the molecules balances the cross-linking and defragmentation during the irradiation process and that it is the key characteristic for producing a CNM. [4-6]

Here, we demonstrate the formation of stable carbon nanomembranes using linear aliphatic precursor molecules. We investigated the effect of the number of carbon atoms within the hydrocarbon chain (n = 12, 14, 16, 18, and 22) on the membrane's formation process. Performing a case study for 1-Octadecanethiol (ODT, $C_{18}H_{37}SH$), we examined mechanical properties, permeation behaviour and carried out a comparative topographical analysis between the SAM and CNM.

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Investigation of a redox mass for rechargeable oxide batteries: $(Fe_{1-x}Mn_x)_yO_z$ with a $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ scaffold

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The transition from fossil fuels towards renewable and thus carbon free power supply leads to the demand of convenient storage facilities for the amount of energy provided in times of excess power delivery. One possible solution to this problem could be the conversion of electrical into chemical energy by a rechargeable oxide battery (ROB). An ROB is a metal-air battery relying on an oxide-ion conduction mechanism, and operates at temperatures of around 700 °C. During discharging, the metal, for which iron has been used in several studies [1], is oxidized by oxygen provided by means of a gaseous H_2/H_2O redox shuttle (Fig. 1). An advantage of the ROB is its high energy density, however, the iron based storage masses have shown a strong capacity degradation due to severe morphological changes of the storage material even after only a few charging cycles.

In our study, we introduced a scaffold material ($Ce_{0.8}Gd_{0.2}O_{2-\delta}$) into the redox-active storage mass in order to maintain its morphological properties and prevent passivation. By using an oxide-ion-carrier for this function the accessibility of the whole redox mass for oxidation can be maintained. An iron-manganese compound that oxidizes to $(Fe_{1-x}Mn_x)_yO_z$ (with $0.2 < x < 0.8$) was used as redox mass. Adding manganese to the iron diminishes the oxygen partial pressure of oxidation in comparison to pure iron oxide, yielding a higher OCV. Therefore scaffolded redox masses of different composition were exposed to H_2/H_2O- and H_2/CO_2-atmospheres with variing pO_2 and, in this way, cycled between the charged and discharged state. The experiments were observed by DC-conductivity measurements and TGA. Afterwards the samples were analysed by different methods including XRD, SEM imaging and WDX to evaluate the reduction and reoxidation amount as well as degradation and redox kinetics.

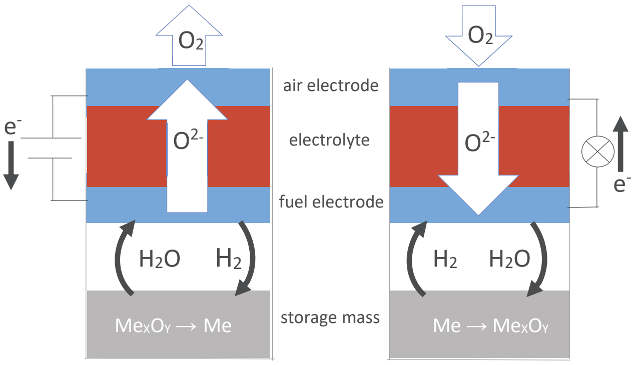

Fig. 1: Schematic structure and processes while charging (l.) and discharging (r.) the ROB.

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The Intrinsic Structural Resistance of a Grain Boundary to Transverse Ionic Conduction

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Ion transport across grain boundaries in diverse polycrystalline ionic conductors is often found to be hindered. Such behaviour is commonly attributed to the presence of a highly resistive second phase or to the presence of space-charge zones, in which mobile charge carriers are strongly depleted. One other possible cause – the severe perturbation of the crystal structure within the grain-boundary core – is widely ignored. Employing molecular dynamics (MD) simulations of the model Σ5(310)[001] grain boundary in fluorite-structured CeO_2, we demonstrate an approach to extract the intrinsic structural resistance of a grain boundary (to ionic transport across it), and we determine this excess resistance as a function of temperature. Compared with space-charge resistances predicted for a dilute solution of charge carriers the structural resistance of this interface is orders of magnitude smaller at temperatures below T≈1000 K but at T>1200 K it is no longer negligible.

Discrete Modeling of Space Charge Zones in Solids

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A discrete modeling of space charge zones in solids is presented, which reveals and remedies a variety of problems with the classic Gouy-Chapman solution, occurring for pronounced space charge potentials. When considering charge-carrier containing systems, electroneutrality is broken at interfaces and individual charge carrier redistribution will occur there, which leads to transport but also storage anomalies. The continuum picture in space charge zones is usually described by classic Gouy-Chapman model. It is well-known that the calculated space charge capacitance needs to be corrected by a rigid layer capacitance. Besides problems of internal consistency, it is essentially the extremely steep profile close to the interface which makes this continuum approach questionable. Here discrete modeling provides a much more realistic picture. Also considering only crystalline materials the geometry can be well defined. Even structural variations can be addressed by modifying the standard chemical potential of the first layers.

The effect of long-range order on charge transport in self-assembled nanocrystal and nanocluster superlattices

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The self-assembly of nanoparticulate building blocks into superlattices with long-range order bear immense potential for customized materials with novel structure-related properties by design. However, such structure-transport relationships have remained unenlucidated so far. We present correlative studies of the structure and transport properties of highly defined superlattices of two state-of-the-art model systems.

First, electric transport measurements and synchrotron-based X-ray nanodiffraction are performed on PbS nanocrystal superlattices.[1,2] This allows us to fully characterize the superlattice symmetry and nanocrystal orientation in direct correlation with the charge transport properties. We found strong evidence for a beneficial effect of the crystallinity on charge transport, and we reveal a charge transport anisotropy in long-range ordered monocrystalline superlattices based on the dominant effect of shortest interparticle hopping distances. We suggest that this is an inherent feature of weakly coupled superlattices.

Second, we report the first structure-transport correlation study of gold nanocluster exhibiting semiconducting behavior.[3] The conductivity of long-range ordered crystalline domains of self-assembled Au_{32} nanocluster exceeds that of glassy assemblies of the same nanoclusters by two orders of magnitude. Accompanied with emerging optical transitions, this points to an enhanced electronic coupling in highly ordered superlattices, attributed to a vanishing degree of structural and energetic disorder.

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Combined experimental and theoretical study of $Li_{(1-x)}FePO_4$ as a function of the state of lithiation

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In recent work, Schuld et al. demonstrated that a complete thermodynamic cycle for the description of a lithium ion battery, Li//$LiCoO_2$, can be set up, based on the measurement of electronic and ionic work functions [1]. While that work employed photoelectron spectroscopy for the electronic work function and thermionic emission for the ionic work function, recent progress demonstrated the ability to measure both electronic and ionic work functions by thermionic emission [2].

In this work we present a systematic investigation of ionic and electronic work functions for a typical cathode material $Li_{(1-x)}FePO_4$ by a combined experimental and theoretical effort [3]. We demonstrate that the ionic work function, w(Li^+), experimentally measured by thermionic emission is approximately 3.0 eV for $0 < x < 0.2$. The experimental electronic work function increases from 4.0 to 5.3 eV when going from $x=0$ to $x=0.2$. The finding that for small values of x the ionic work function is independent of the state of lithiation is also predicted by our molecular dynamics simulations of (010) $Li_{(1-x)}FePO_4$ surfaces in an electric field. Therein we observe a quick refilling of the boundary layers on the nanosecond scale keeping the effective Li concentration in the boundary layer transiently constant, while the bulk is gradually delithiated. The results are complemented by comparison to electronic work function information available in the literature [4].

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Cation Exchange Reactions on Semiconductor Nanoparticle Gel Networks

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Cation exchange reactions are a useful tool for modifications on semiconductor nanoparticles[1] and gel networks[2]. Semiconductor nanoparticle gel networks are highly voluminous and porous structures, which are formed by controlled destabilization of colloidal semiconductor nanoparticle solutions. In comparison to semiconductor nanoparticles cation exchange reactions[1], the reaction conditions for gel networks are mostly limited to room temperature synthesis. However, in the present work, we show that a number of cation exchange reactions can be transferred to nanoparticles gel networks. We successfully perform various cation exchange reactions at semiconductor gel networks from CdSe/CdS (core/shell) and CdS nanorods[3] via a copper chalcogenide based intermediated state to other metals and also back to cadmium. The obtained gel networks are investigated with regarding their optical properties by absorption and photoluminescence spectroscopy and regarding their structure and composition by XRD, TEM and SEM/EDXS. In addition, TEM and SEM measurements provide information on changes in the porosity of the gel structure due to cation exchange reactions. The success of the cation exchange reactions was clarified by recording SEM/EDXS.

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On the Optimum Binding Energy in Electrocatalysis

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Electrochemical transformations, particularly those involving hydrogen, oxygen, and water, are discussed as fossil-free pathways to produce fuels and chemicals of global importance, thereby reducing harmful carbon dioxide emissions.[1] For the corresponding electrocatalytic reactions, active, stable, and selective electrocatalysts need to be developed that preferably do not contain scarce noble metals to enable large-scale operation of these processes. To identify promising electrode materials, commonly, material-screening techniques in a heuristic fashion are applied that enable categorizing electrodes into active and inactive materials.[2] Most of these studies rely on the initial idea of Nørskov, Rossmeisl, and co-workers in that only the binding energies (thermodynamics) of potential reaction intermediates (RIs) within the electrocatalytic cycle are assessed, whereas the kinetics (transition states) or the applied overpotential are neglected in the analysis. The thermodynamic framework of Nørskov et al. purports that the optimum electrocatalyst corresponds to an electrode material that stabilizes all RIs thermoneutrally at zero overpotential.[3]

Recent studies, however, indicate that thermoneutral bonding at zero overpotential is not encountered with the ideal situation for a two-electron process when factoring the applied overpotential and kinetics into the analysis.[4] For the hydrogen and chlorine evolution reactions, it was demonstrated that the optimum binding energy shifts to weak bonding with increasing overpotential.[5] This can be explained by an extension of the Sabatier principle,[6] specifying that the optimum electrocatalyst stabilizes the RI thermoneutrally at the target overpotential rather than at zero overpotential.[7] Consequently, the energetics of multiple-electron processes was re-investigated, identifying a shift of the optimum binding energy with increasing overpotential.[8]

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Photo-responsive conduction in nanoporous crystalline thin films

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The dynamic control of physicochemical properties is one of the key challenges for functional, smart materials. An intriguing realization of materials with remote-controllable properties is based on photochromic molecules incorporated in porous crystals with modular design, like metal-organic frameworks (MOFs). Under the irradiation with light of different wavelengths, molecules like azobenzene and spiropyran can undergo reversible *trans-cis* or bond cleaving isomerizations. Thin films of MOFs incorporating such molecules grown on suitable substrates provide a fascinating model system for exploring and altering the physicochemical properties.

In the presentation, I will focus on the charge transfer between the molecules in the porous confinement of the MOF film and show its control *via* the host-guest interaction. The embedment of proton-donor and -acceptor molecules in the MOF pores makes the material proton conducting. The proton conductivity of the material is modulated by photo-switching the host material. In a different approach, the material becomes electrically conductive by loading the pores with molecules with delocalized frontier orbitals in close proximity, enabling intermolecular electron or hole hopping. The light-induced isomerization of such molecules, like spiropyran, enables to remote control the electrical material properties. Further aspects of photo-responsive MOF films and conduction in the pores will be presented.

The Deutsche Forschungsgemeinschaft (DFG): Funding Opportunities for Early Career Researchers

Wolfgang Wachter, Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), Bonn/Germany

DFG's funding programmes place particular emphasis on supporting early career researchers. Flexible funding instruments are tailored to meet the specific needs of young scientists and academics, thereby enabling them to pursue their research careers.

For example, the Walter Benjamin Programme enables researchers in the postdoctoral training phase to independently conduct their own research project at a location of their choice in Germany or abroad. The Emmy Noether Programme supports researchers in achieving independence at an early stage of their scientific careers. Postdocs gain the qualifications required for a university research career during a DFG-funded period, in which they lead their own independent junior research group. The Heisenberg Programme provides researchers who have qualified for professorship with the opportunity to prepare for a leading position in science. Other programmes are open to researchers at all career stages, but provide opportunities of special interest to young scientists.

In this contribution, the DFG funding opportunities for early career researchers will be highlighted. There will be also room to discuss some “dos and don’ts” when preparing a funding proposal.

yPC-Forum:

Chancengleichheit und Diversity in der Wissenschaft

Studien zeigen, dass eine vielfältig zusammengesetzte Arbeitsumgebung sich positiv auf die Kreativität und Produktivität auswirkt, insbesondere in der Wissenschaft. Dennoch trifft man immer wieder auf Hürden, wenn es darum geht, die Vielfalt zu erhöhen. Noch immer sind Wissenschaftlerinnen in Karrierestufen nach der Promotion unterrepräsentiert. Menschen mit Behinderungen finden nur schwer Zugang zu den experimentellen Wissenschaften, oft stehen scheinbar Sicherheitsbedenken im Wege.

Im diesjährigen yPC-Forum sprechen wir mit drei Gästen über dieses Thema, mit Fokus auf die persönlichen und institutionellen Faktoren, die den Lebensweg geprägt haben:

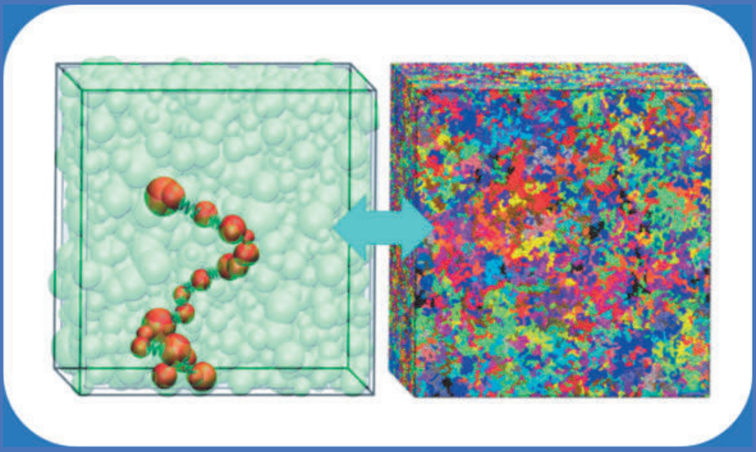
Prof. Dr. Stefanie Dehnen, Philipps Universität Marburg:
Vereinbarkeit von Karriere und Familie

Dr. Lukas Guggolz, Philipps Universität Marburg:
Karriere in der Chemie mit Behinderung

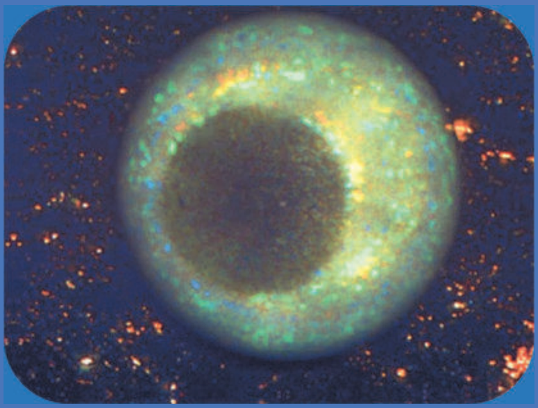
Dr. Lisa Pecher, Wiley-VCH, Weinheim:
Gender Equality in der Wissenschaft

Mit jedem der drei Gäste werden wir 20 Minuten interaktiv diskutieren, wobei es ausreichend Gelegenheit für Fragen aus dem Publikum gibt. Abschließend werden wir das Thema noch einmal gemeinsam in einer **Podiumsdiskussion** betrachten. Ziel dieser Veranstaltung ist es, allen Teilnehmer:innen konkrete Handreichungen zu geben, wie man sich selber für eine buntere und dadurch auch kreativere und erfolgreichere Wissenschaft einsetzen kann.

Organisator:innen: Klaus Boldt, Jannika Lauth, Katharina Meyer, Maria Wächtler



POSTER ABSTRACTS



Gas-phase charge distribution of nanoparticles generated by IR-MALDI

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IR-MALDI from the liquid phase inherently charges the dispersed droplets, and thus the molecules contained in these droplets, with only a few charges per primary droplet. This was found for a large range of molecules from small clusters up to large proteins [1, 2]. The charge distribution of particles between 50 and 600 nm in electromobility diameter hitherto lacks detailed experimental and theoretical characterization. This is the motivation for the present work.

As an experimental setup for the investigation of nanoparticles (NPs) in the gas-phase, a differential mobility analyzer with IR-MALDI as the charging source was used. Well-resolved electromobility spectra of up to octuply charged NPs were obtained over a dynamic concentration range of more than four orders of magnitude ($R^2 = 0.97$, $n = 12$). This holds true for a variety of classes of NPs and types of surface functionalization.

Based on this data, a Poisson-deduced charge distribution [2] and the Wiedensohler charge distribution [3] were tested. Here, the latter predicts a size-to-charge dependence for larger NPs. The results, however, show a size-independent charge distribution of the NPs. The, thus favored, Poisson-deduced model in fact closely fits the data and therefore could now be extended from the known salt cluster size regime of a few nanometers [2] to the sub-micron size range. This outcome presents the first theoretical and experimental approach to elucidate and build a model for the charge distribution generated by the IR-MALDI source in the sub-micron size range.

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Interpretable Embeddings from Molecular Simulations using Gaussian Mixture Variational Autoencoders

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Extracting insight from the enormous quantity of data generated from molecular simulations requires the identification of a small number of collective variables whose corresponding low-dimensional free-energy landscape retains the essential features of the underlying system. Data-driven techniques provide a systematic route to constructing this landscape, without the need for extensive a priori intuition into the relevant driving forces. In particular, autoencoders are powerful tools for dimensionality reduction, as they naturally force an information bottleneck and, thereby, a low-dimensional embedding of the essential features. While variational autoencoders ensure continuity of the embedding by assuming a unimodal Gaussian prior, this is at odds with the multi-basin free-energy landscapes that typically arise from the identification of meaningful collective variables. In this work, we incorporate this physical intuition into the prior by employing a Gaussian mixture variational autoencoder (GMVAE), which encourages the separation of metastable states within the embedding. The GMVAE performs dimensionality reduction and clustering within a single unified framework, and is capable of identifying the inherent dimensionality of the input data, in terms of the number of Gaussians required to categorize the data. We illustrate our approach on two toy models, alanine dipeptide, and a challenging disordered peptide ensemble, demonstrating the enhanced clustering effect of the GMVAE prior compared to standard VAEs.

Data driven characterisation of the free energy landscape of polymorphic system

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Syndiotatic polysterene (sPS) exhibits complex polymorphic behaviour, resulting in rugged free energy landscapes (FELs). In these FELs, the high energy barriers that separate different polymorph basins hinder their systematic exploration by traditional molecular dynamics simulations. Enhanced sampling methods have the potential remedy this problem with prior knowledge of collective variables (CVs) that can resolve the relevant transition pathways, typically identified through physical or chemical expertise. Recently, data driven methods have attracted considerable attention for learning the CVs without significant a priori insight. We aim to use different dimensionality reduction methods varying from linear methods like principal component analysis (PCA) to more complex non-linear methods like UMAP, EncoderMAP and Gaussian mixture variational autoencoder (GMVAE), in order to compare the low dimensional embedding. In order to efficiently describe the local environment of sPS monomers, we adapt an atomic representation used in machine learning. One of the advantages of using these descriptors is that they do not require incorporation of excessive system-specific intuition and demonstrate good transferability properties. With this data-driven approach, we aim to characterise the pathways between polymorphic transitions

Effect of Steric Hindrance on the Self-Assembly of Crystallized Polymer Bundles

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Understanding the self-assembly mechanism of polymer-grafted nanoparticles is of high interest, due to their promising applications in electronic and biomedical materials. Therefore, these systems have been simulated numerous times in the past, modeling the central particle as a sphere and the ligands as flexible chains of beads. Some polymers, however, crystallize in rigid bundles; thus, the flexible bead chain model is no more valid.

For this reason, we developed a versatile coarse-grained rod-sphere model capable not only of simulating the self-organization of nanospheres with partially crystallized stretched polymeric graft bundles, but also of other building blocks, such as rigid surfactants and end-tethered nanorods. Changes in the dimension of the completely repulsive spheres, compared to the mutually attractive rods attached to them, lead to the emergence of diverse self-assembled structures. We show that the distinct shapes of such particle clusters are determined by steric limitations caused by the spheres. With this knowledge, the self-organization of these particles in clusters of determined shapes can be predicted.

Near-infrared plasmon-exciton interactions in colloidal nanostructures

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Near-infrared emitting colloidal semiconductor nanocrystals draw a lot of attention due to various fields of their potential application, such as bio-imaging, photovoltaics, photodetectors, light emitting diodes and optical amplifiers for telecommunication systems. Due to the fact that brightly emitting colloidal quantum dots consist mainly of toxic materials, while low-toxic alternatives typically show lower photoluminescence quantum yields, strategies to increase their quantum yields are of outstanding importance for their further application. One of the means to improve fluorescence of quantum dots is their coupling with structures exhibiting localized surface plasmon resonance. As has been demonstrated for the visible active nanostructures, plasmon-exciton interactions can enhance photoluminescence of CdSe and CdTe quantum dots.

In this work, we study the influence of the electromagnetic field of plasmonic semiconductor nanocrystals based on copper chalcogenide or silver on the photoluminescence of quantum dots in the near-infrared region.

Quantifying soft degrees of freedom in volatile organic compounds: insight from quantum chemistry and focused single molecule experiments

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Predicting the structure of ethyl 2-methyl pentanoate (EMPE) remains a challenging task in computational chemistry. Despite their sample molecular strutcure, this class of esters is very sensitive to quantum methods. Therefore, using focused experiments, such as high-resolution molecular spectroscopy, to benchmark several selected theoretical techniques is considered a powerful approach to experimentally validate the conformational sampling of small volatile compounds.[1-2] Here, we report a benchmark study at quantum chemical level, on the most abundant gas-phase structure of EMPE, involving several exchange-correlation DFT functionals and ab initio methods validated according to microwave spectrum which was recorded in the frequency range from 8.5 to 12.0 GHz using a MJ-FTMW spectrometer operating in the frequency range from 3.0 to 26.5 GHz. The observed conformer of EMPE in the gas-phase is of C_1 symmetry and exhibits a large amplitude motion around the C-C bond in proximity to the carbonyl moiety which make it difficult to characterize this system with accuracy. The dihedral angle of the lowest energy conformer is optimized to absolute values of ±20°. This is far above the usual convergence error of the theoretical methods and has a tremendous impact on the rotational constants of this conformer. Our benchmark calculations further indicate the potential relevance of the wB97X-D functional for this ethyl pentanoate and other related ethyl esters.[3]

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Ionic Liquids As A Fluoride Ion Source

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Ionic liquids are a new paradigm in organic synthesis due to their very low vapor pressure, wide liquid range, and high density as compared with common organic reagents. Chen *et al.* recently designed a poor solvate ionic liquid (SIL) based fluorinating agent, 1-Ethyl-3-methylimidazolium fluoride ([EMIM]F) solvated in ethylene glycol (EG) i.e. [EMIM]F-xEG, at various EG concentrations[1]. As [EMIM]F.xEG is liquid at ambient conditions; experimental tools other than NMR and vibrational spectroscopy are limited in their scope to provide a comprehensive microscopic perspective. Moreover, Gerken *et al.* have shown that although the theoretically calculated NMR shifts are comparable with the experimentally reported values, the binding energy values do not correlate with the NMR chemical shifts[2]. That is where molecular dynamic (MD) simulations are powerful, realistic, and have often played critical roles in providing microscopic insights. We utilized multi-scale computational modeling to investigate the microscopic nature of the SIL and its compositional range of stability. The geometries of hydrogen bonds that a fluoride ion makes with the acidic protons on the EG molecule and on the [EMIM] cation.Fluoride ions are seen to form a stronger hydrogen bond(s) with the acidic proton of EG than with that of the [EMIM] cation. Fluoride ions in [EMIM]F.xEG have different local coordination environments. Moreover, the Probability of finding a fluoride ion in one kind of coordination environment varies with the change in ethylene glycol concentration. Consequently, the fraction of EG in the solution can influence the stability and fluorination efficiency of the SIL[3].

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Backbone modification via deamidation: An unconventional route to the thermostability of enzyme

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The formation of succinimide backbone post-translational modification (PTM) by intramolecular cyclization at Asn-Gly or Asp-Gly segments in proteins is an intermediate step in the process of deamidation, which, described as a “molecular clock” of cellular processes, generally decreases the thermostability of the protein. Surprisingly, the deamidation at Asn109-Asp110 segment of *Mj* glutamine amidotransferase (MjGATase) increases its thermostability through the formation of a stable succinimide (SNN109) PTM. The observations obtained from Hamiltonian replica exchange with solute scaling (REST2) and well-tempered metadynamics simulations of wild-type (WT) MjGATase and its SNN109S mutant explain this unexpected experimental finding. The negatively charged electrostatic shielding by the succeeding residue (Asp110) as well as the n to π* interactions from the preceding residue (Glu108) prevent the hydrolysis of succinimide, which induces the formation of a “conformational-lock”, thus reducing protein flexibility. Free energy profiles for the WT and SNN109S mutant using the radius of gyration of the succinimide containing loop as the reaction coordinate yielded a single, stable minimum at a lower value of the reaction coordinate for the former and an additional higher energy state at a higher value of the reaction coordinate for the mutant with the complete unfolding of the loop, consistent with the experimentally found reduced thermostability of the mutant lacking succinimide. Furthermore, sequence analysis on 84 archaeal GATases shows that succinimide and its neighbouring residues are highly conserved. Thus, the present study on MjGATase reveals how the introduction of a backbone modification in the protein sequence can lead to the adaptation of an apparently detrimental process to enhance thermal stability, under an evolutionary imperative.

Thermodynamic Driving Forces of Guest Confinement in a Photoswitchable Cage

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Photoswitchable cages that confine small guest molecules inside their cavities offer a way to control the binding/unbinding process through irradiation with light of different wavelengths. However, a detailed characterization of the structural and thermodynamic consequences of photoswitching is very challenging to obtain by experiment alone. Thus, to gain insight into the relationship between structure and binding affinity, an all-atom force field was parametrized with and validated against quantum chemical calculations, and subsequently used for molecular dynamics (MD) simulations in explicit solvent. Binding free energies of the $B_{12}F_{12}^{2-}$ guest were obtained for all photochemically accessible forms of a photoswitchable dithienylethene (DTE) based coordination cage synthesized by Clever and coworkers [1]. The MD simulations show that successive photo-induced closure of the four individual DTE ligands that form the cage gradually decreases the binding affinity. Closure of the first ligand already significantly lowers the unbinding barrier and increases the binding free energy, and therefore favours guest unbinding both kinetically and thermodynamically. The effect of bound guests on the ultrafast photodynamics of the DTE ligands is currently being investigated through transient absorption spectroscopy. Analysing our MD simulations in terms of the different enthalpy contributions to the free energy reveals that binding is enthalpically unfavourable and thus an entropy-driven process, in agreement with experimental data. Dissecting the enthalpy into the contributions from electrostatic, van der Waals, and bonded interactions in the force field shows that the unfavourable binding enthalpy is due to the bonded interactions being more favourable in the dissociated state, suggesting the presence of structural strain in the bound complex. Thus, the simulations provide microscopic explanations for the experimental findings and offer a possible way for a targeted design of switchable nanocontainers with modified binding properties.

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Theoretical structure modelling of molecular clustermaterials considering small model systems

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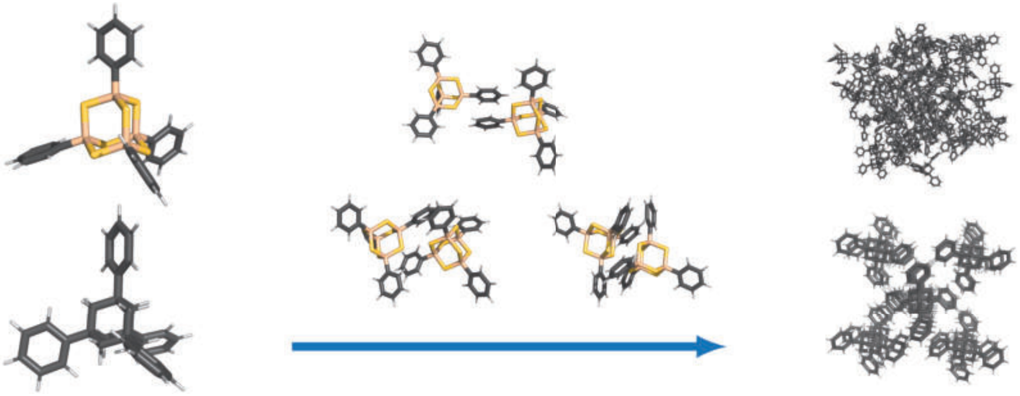
Recent investigations show that molecular cluster materials based on adamantane-like core structures with organic substituents with the general composition $[(RT)_4S_6]$ (R=organic substituent) exhibit non-linear properties that lead to white-light generation or second harmonic generation [1,2]. The characterization of the geometric structure of the amorphous cluster material is a critical step to understand the origin of the unique optical properties. For this purpose, we considered cluster-dimer structures as model system und investigated the decomposition of the binding energy the core-core distance and dissociation energy of a large number of different cluster compositions [3]. The gained information helps to describe amorphous and crystalline cluster materials and to classify the material regarding different interaction types.



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Ab initio study of migration in NASICON $NaZr_2(PO_4)_3$

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All-solid-state batteries are considered to be the next stage in the development of density energy storage systems. For such electrochemical devices, solid electrolytes with high ionic conductivity are mandatory. Derivatives of the original NASICON-structure $NaZr_2(PO_4)_3$ represent a promising class of sodium ion conductors. Si-doping on P-sites and Sc-doping on Zr-sites in $Na_{1+x+y}Zr_{2-x}Sc_xP_{3-y}Si_yO_{12}$ introduces additional sodium into the structure and results in high ionic conductivity in the range of some mS/cm at room temperature. [1]

On the atomic scale the conductivity is determined by the local site energies and migration energies of the mobile sodium ions. These energies vary in presence of dopant ions. The knowledge of the atomic scale energy landscape enables the understanding of migration processes and the influence on the macroscopic conductivity. In this study, we investigate NASICON structures with composition $Na_{1+x+y}Zr_{2-x}Sc_xP_{3-y}Si_yO_{12}$ ($0 \leq x \leq 2$; $0 \leq y \leq 3$) using density functional theory (DFT) calculations. We examine the site preference of sodium ions in vicinity of dopant ions as well as the migration mechanism of the sodium ions.

A pair interaction model was constructed to fit the energies obtained by DFT and describe the influence of the cation occupation on the site energy of sodium ions. The model shows that with increasing amount of silicon and scandium ions as well as decreasing amount of sodium ions in nearest neighbor positions the energy decreases.

The collective migration of mobile sodium ions on regular lattice sites proceeds by a chained pushing-out mechanism with low migration barriers. Three different migration pathways are considered defined by their angles. The migration energy decreases with increasing angles and increasing amount of sodium ions in the surrounding of the pathway because of the repulsive Coulomb interactions which facilitates the pushing-out migration.

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Mesoscopic Simulations of Crystallinity in Polymers: Partially Ordered Morphologies

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The behaviour of many industrially-relevant polymeric materials depends strongly on crystalline order in their morphologies. Unfortunately, it is notoriously difficult to study crystallisation of polymers at application-relevant lengthscales using computer simulations. Due to high molecular weights, it is necessary to use drastically coarse-grained approaches, but as crystallisation tends to depend on fine atomistic details, this methodology is generally insufficient to reproduce experimental observations.

Our approach to tackling this problem is to consider partially ordered morphologies. These mesophases [1] bridge the gap between amorphous and crystalline systems, creating a gradual approximation towards crystalline symmetry via a family of related models. Our mesoscopic Monte Carlo technique uses a coarse-grained approach, with bonded potentials taken from single chain atomistic simulations. ‘Soft’ anisotropic phenomenological non-bonded potentials are used to reproduce the generic symmetries of molecular order in each mesophase, making this methodology relatively forgiving to the inaccuracies of coarse-graining. [2]

Here, we focus on soluble semiconducting polymers, where crystallinity and/or partial order are known to crucially affect optoelectronic properties. We choose poly(alkylthiophenes) as a model system and investigate the orientation of their lamellar grains in thin films, which are relevant for photovoltaic devices.

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From Oxidation States to Phase Transitions: Predictions of High-Dimensional Neural Networks

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Advances in battery technology require a detailed understanding of the involved processes at the atomic scale. While quantum mechanical calculations in principle provide a reliable description of battery materials, the high computational costs prevent simulations of realistic model systems. In recent years it has been shown that machine learning algorithms trained to quantum mechanical information allow extending the time and length scales enabling such simulations without loss in accuracy. However, these simulations usually do not provide any information about the electronic structure, which would be crucial to understand important properties like electrical conductivity.

Here we present a high-dimensional neural network to predict the oxidation and spin states of Mn ions in the lithium manganese oxide spinel,[1] which is a frequently used positive electrode material in lithium ion batteries. Using this method we are able to unravel a series of interesting properties like the phase transition between an ordered low-temperature orthorhombic phase and a high-temperature cubic phase between 280 and 300 K, which is related to the order of Mn ions with different oxidation states. Further, we show that electron hopping between Mn ions is an activated process providing an explanation for changes in the electrical conductivity caused by the phase transition.

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Multi-Scale Modelling Approach for the Emulsion Polymerization Process of Styrene

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Describing a heterogeneous process like the emulsion polymerization includes simultaneously occurring physicochemical events over a wide range of time and length scales. The emulsion polymerization is described at the macroscale by the monomer balance, at the mesoscale by particle size distributions and at the microscale by molecular weight distributions. The reactions take place in two different reaction spaces, the aqueous phase and the particles. The main polymerization occurs in the particles. Not only the implementation of the detailed reaction mechanism with all elementary reaction steps must be considered, moreover, radical phase-transfer processes, like radical entry and radical exit or monomer transport, needs to be respected. Here, kinetic Monte Carlo (kMC) modeling is reported, which deals with a large ensemble of discrete molecules, and is applied to all processes occurring in emulsion polymerizations.[2] The entire simulation is parallelized effectively and processed with multiple tasks of the *mcPolymer* simulator[1].

The aqueous phase is simulated to generate the radicals, which will be transferred into the particles by using the Message Passing Interface. Each particle is treated as a nanoreactor and equipped with an independent kMC model. Within each simulation an ensemble of thousands of particles is modeled in parallel.

The consideration of monomer transport, first from the droplets into the particles and later between the particles leads to individual particle growth, which is also considered in the simulation and influences the distribution of the particles.

As an example, the multi-scale modeling approach is applied to the emulsion polymerization of styrene. Styrene is selected since critically evaluated kinetic data are published.

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Solubility predictor of Hepatitis B (HBV) virus core proteins as a function of C-terminal length

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VLPs are produced by self-assembly of viral structural proteins into spherical structures (capsids). VLPs were approved to be used as novel vaccines, and are being investigated for promissing future applications in the targeted administration of therapeutical molecules. eg. in gene therapy. Production of HBV based VLPs starts with recombinant expression of viral proteins in E.Coli, upon which particles are disassembled in vitro and re-assembled in presence of target RNAs. These processes are modulated by the solution conditions, especially by pH, salt type and concentration.

Here, we present multiscale approach to model the optimal assembly conditions of HBV dimers (HBcAg) by calculating second osmotic virial coefficients(B_{22}), which was shown to correlate with crystallization behavior.[1] For this, we combined shape-based coarse-graining of proteins and xDLVO theory, while including new potential term which can better describe ion-protein interactions.[2] Structures of HbcAg dimers are reconstructed and equilibrated by all-atom molecular dynamics simulations, following by shape-based coarse graining which serves as input to xDLVO model. The model is used to calculate B22 of HBcAg dimers of different lengths and C-terminus, which are known to undergo different assembly behavior. As a result, phase diagram can be constructed giving information about assembly behavior at wide range of salt types and concentrations.

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Computer simulations on the molecular origin of shear thinning in polymer melts

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We investigate the molecular origin of shear thinning in melts of flexible, semiflexible and rigid polymers with coarse-grained simulations of a sheared polymer melt and simulations of single chains in Couette flow. We identify molecular alignment along the shear direction as the major cause of shear thinning. In addition, stretching and tumbling modes or the suppression of the latter as well as collective modes also play a role in understanding how macroscopic flow properties arise from the molecular level.

Molecular dynamics simulation of surfactant-stabilized hexadecane-water interface upon cooling

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Recently, we have discovered that micrometer drops exhibit a spectacular series of shape transformations upon cooling.[1] The shapes encompass spheres, icosahedra, prisms, and even fibers or drops bursting into nanoparticles.[2] Theoretical analysis suggested that the shapes are caused by freezing layers of surfactants, adsorbed at the alkane-water interface, acting as a 2D template for ordering of alkane molecules.[3] The drop dynamics shows: (1) the alkane multilayers resemble “intermediate rotator phases”[4] and (2) all phenomena depend strongly on the interfacial curvature. The factors governing these events at the molecular level still need to be understood. In this study, molecular dynamics simulations are performed by gradually lowering the temperature of the system to monitor the freezing of the adsorption layers and the formation of a alkane rotator phase. We studied two types of models - flat and cylindrical, where bulk water and hexadecane phases were separated by adsorption layer/s. We checked the effect of cooling rate and starting temperature on the crystallization. We analyzed the thermodynamic parameters and changes in the intermolecular orientation to quantify the phase state of all studied systems.

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MODELLING ROTATOR PHASES OF ALKANE-CONTAINING SYSTEMS

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Medium- and long-chain alkanes form intermediate-structured (between crystal and isotropic liquid) phases. These are called “rotator phases” because they have long-range positional order while retaining some freedom for molecular rotation. Rotator phases have peculiar visco-plastic rheological behaviour, which is important for their numerous applications in chemical industry and pharmacy. In emulsions containing alkane droplets with rotator phase structure, the drops can spontaneously acquire diverse non-standard shapes [1]. One possible application of this property is synthesis of building blocks for construction of complex hierarchical structures [2]. At present, however, the structure of the rotator phases and how it is influenced by various factors of the medium is not fully understood at the molecular level.

In the current study, models representing bulk hexadecane and hexadecane/water interfaces are simulated with atomistic molecular dynamics using the CHARMM36/TIP4P force fields. The bulk hexadecane systems are frozen by gradually cooling down to different temperatures below the freezing point and monitoring the liquid-to-solid transition. The obtained results show that the force field is able to capture the main characteristics of the freezing process. The effect of curvature on the mechanism of this transition and on the type of rotator phase obtained is tracked for the alkane/water models. Structural and thermodynamic parameters are analyzed to quantify the intermolecular ordering and the phase state.

This study is funded by the Bulgarian Ministry of Education and Science, under the National Research Program "VIHREN", project ROTA-Active (no. KP-06-DV-4/16.12.2019).

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INTRODUCING MEMORY IN COARSE-GRAINED MOLECULAR SIMULATIONS

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Coarse-grained models which aim to reproduce dynamical properties are typically described in terms of variations of the (generalized) Langevin equation ((G)LE) [1-4]. While Markovian and Non-Markovian models based on pairwise friction (dissipative particle dynamics (DPD)) in the past were parameterized in a bottom-up approach [1-2] based on physical arguments, a similar approach for Langevin-thermostat models did not perform as well [4]. The origin for this mismatch remained somewhat obscure. While recently an iterative optimization scheme was successfully applied for the parameterization of GLE-thermostat models [3], we were interested in a better understanding of the physical origin of the inconsistencies in earlier models.

In this talk I will illuminate the origin of the shortcomings of earlier Langevin-thermostat models and propose an alternative bottom-up approach for the parameterization of (generalized) Langevin-thermostat models. I will demonstrate the relevance of the relation between interactions on the fine-grained and the coarse-grained scale, and show how memory effects lead to a change of diffusive dynamics due to the interplay with conservative interactions.

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Combined experimental-simulation study of the role of pH in the synthesis and growth of gold nanoparticles using L-Asparagine

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The use of large (bio)molecules as capping and reducing agents in the synthesis of metallic nanoparticles have the potential to achieve desired functional properties with minimal toxicity [1]. Due to the complexity of the problem, a detailed examination of a simplified version of the system provides a better understanding of effects due to different experimental conditions. Here, we discuss the synthesis of gold nanoparticles with L-asparagine, an archetypal amino acid building block of large bio-molecular systems, in aqueous solution at controlled pH [2]. Nanoparticles synthesized in a neutral environment (pH=6) exhibit a more spherical symmetry, while those synthesized at higher pH (pH=9) are moderately anisotropic. Raman spectroscopy and force field-based molecular dynamics simulations show prominent adsorption of amine groups at higher pH, which is uniform over all the surface planes. By contrast, in neutral conditions, the (111) surface is selectively more protected. Our results indicate that pH is a potentially valuable control variable in green-synthesis protocols.

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Effects of shear flow on metal-confined ionic liquid

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For about two decades ionic liquids have been proposed as good candidates for lubricants. Recently an apparent liquid-solid transitioning of metal-confined ionic liquids have been reported, making their proposed candidature for lubricants even more a viable claim. However, properties of a good lubricant goes beyond its ability to undergo a phase transition under certain confinement conditions. We investigate here, using atomistic molecular dynamics simulations, the microscopic response to shear of [BMIM][BF4] confined between gold electrodes, discussing in details its structural reorganisation at the interface and its tribological properties.

Magnetic deflection of neutral sodium-doped ammonia clusters

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The discovery of concentration-dependent colours of alkali metal-ammonia solutions in the early 19th century by Sir Humphry Davy and later reported by W. Weyl, sparked a slew of experimental and theoretical work on excess electrons in alkali metal ammonia solutions. Nevertheless, the underlying correlation effects of the solvated electrons are still not well understood. While such effects have been probed by magnetic measurements on alkali metal solutions, the involved diamagnetic and paramagnetic species have not yet been identified in bulk phase experiments. Our work is a first attempt to understand the magnetic properties of isolated, weakly-bound clusters with relevance to the variety of diamagnetic and paramagnetic species expected in solvated electron systems. We describe the setup and the performance of a new pulsed Stern-Gerlach deflector, and present results for small sodium-doped ammonia clusters $Na(NH_3)_n$ ($n = 1$-4) in a molecular beam. $NaNH_3$ shows the expected deflection of a spin ½ system, while all larger clusters exhibit much less deflection. Experimental deflection ratios are compared with values calculated from molecular dynamics simulations. The comparison reveals that intra-cluster spin relaxation in $NaNH_3$ takes place on a time scale significantly longer than 200 μs. For all larger clusters $Na(NH_3)_n$ ($n = 2$-4) intra-cluster relaxation times seem to be on the order of 200 μs, assuming that intra-cluster relaxation is the cause of the reduced deflection. We propose an acceleration of intra-cluster spin relaxation in clusters with $n > 1$ as a result of Zeeman-like spin rotation coupling. The emergence of low frequency internal rotational modes for $Na(NH_3)_n$ with $n > 1$ leads to a drastic increase in the thermally accessible density of rovibrational states to which the spin can couple. This could explain the abrupt decrease of the deflection for clusters with $n > 1$.

Influence of nanoparticle fillers on the molecular mobility in ionic-liquid-based gel polymer electrolytes

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Ion-conducting polymer composite materials based on poly(vinylidene-co-hexafluoropropylene) (PVdF-HFP) have recently been studied in terms of their rheological, thermal, and electrical properties [1,2]. The materials investigated here are composed of PVdF-HFP, multi-walled carbon nanotubes (forming an electron conducting network), an electrolyte solution made of a lithium salt dissolved in an ionic liquid (acting as plasticizer and providing ionic conductivity) and ferroelectric $BaTiO_3$ nanoparticles [2]. Nuclear magnetic resonance can give an insight into the mobility and interactions of the different ionic species. Using multinuclear NMR spectroscopy and relaxation measurements, the influence of the additives ($BaTiO_3$ and carbon nanotubes) on the different ionic species was investigated. Information on the lithium ions, the 1-ethyl-3-methylimidazolium (EMIM) cations of the ionic liquid, and the BF_4^- counterions of both lithium salt and ionic liquid was obtained from ^7Li, ^1H, and ^{11}B NMR, respectively. For each type of ion, the NMR spectra of samples containing $BaTiO_3$ reveal the presence of two different populations which differ in their mobility. The effect is most pronounced for ^7Li, where the line width of the broad component is about 20 times larger. The fraction of the broad spectral component, corresponding to the less mobile lithium ions, increases upon raising the concentration of $BaTiO_3$. The mobile lithium fraction disappears almost completely at $BaTiO_3$ mass fractions of 15 % and higher. There is a good correlation between the conductivity and the fraction of mobile ^7Li species for these samples.

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Separation of Small Diameter SWCNTs in 1 – 3 Steps with Aqueous Two Phase Extraction

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An aqueous two phase extraction (ATPE) technique capable of separating small diameter single walled carbon nanotubes in 1, 2 or at the most 3 steps will be presented. Separation is performed in the well studied two phase system containing polyethylene glycol (PEG) and dextran but it is achieved without changing the initial concentration or ratio of cosurfactants. Instead, the technique is reliant upon the unique surfactant shell around each nanotube diameter at a fixed surfactant concentration. The methodology to optimize the surfactant to a single set of conditions for the diameter range (0.69 0.91 nm) is provided and 11 different chiralities with a purity of 73 – 97% are isolated. These include semiconducting and both armchair and non armchair metallic nanotube species. Titration of cosurfactant suspensions reveal separation to be driven by the pH of the suspension with each (n,m) species partitioning over a unique pH range. This allows for an (n,m) separation approach to be presented that is as simple as pipetting known volumes of acid into the ATPE system.

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Analysis of the Sedimentation Behavior of Colloidal Semiconductor

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Magic size clusters (MSCs) are ultrasmall semiconductor nanocrystals and known reaction intermediates in the synthesis of nanoparticles.[1,2] Due to their small size and limited stability it is difficult to study MSCs by common nanoanalytical techniques like transmission electron microscopy (TEM), X-ray diffraction, or dynamic light scattering (DLS). Analytical ultracentrifugation provides the possibility to determine the molecular mass, hydrodynamic radius of the particle, and theoretical radius of the inorganic core, as well as the density of the clusters in solution and density of the ligand shell with relatively low effort.[3]

In the present work, different MSCs and mixtures thereof were analyzed by analytical ultracentrifugation with multi-wavelength UV/vis detection to determine the cluster sizes and the potential to separate several, overlapping MSC populations. Thus, the method offers the possibility to perform analysis of a crude reaction mixture of MSCs without disturbing their equilibrium with free ligand and monomer in solution.

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Influence of Mg-doping in ZnO Photoanodes on their Characteristics in Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) typically are based on a photoanode of TiO_2. ZnO with its higher electron mobility has long been seen as a possible alternative to the commonly used titanium dioxide, but cells based on ZnO show a lack of efficiency. To improve on this, Mg-doped ZnO (MZO) nanoparticles, thin-films and core-shell like structures with a pure ZnO core and an MZO shell have been prepared through wet-chemical synthesis. Incorporation of Mg ions into the ZnO wurtzite structure has been confirmed for a Mg-concentration of up to 20 % and a linear increase in the band gap could be found. The performance of DSSCs based on ZnO photoanodes doped with 0, 5, 10 and 20 % Mg was studied using photoelectrochemical and photoluminescence measurements. As a result of Mg-doping, a significantly increased V_{OC} was found. Further, DSSCs with low concentrations of 5 % Mg showed an increased short-circuit photocurrent J_{SC}, which, however, dropped for higher Mg-concentrations. Electrochemical impedance spectroscopy (EIS) revealed changes in the electron transport resistance as well as the recombination rate as underlying causes. Such loss in current could be reduced in the case of the core-shell structured MZO utilizing the higher mobility in pure ZnO.

Stimuli-Responsive Behavior of PNiPAm Microgels under Interfacial Confinement

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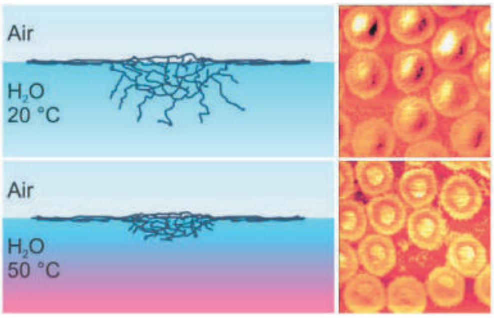
While the stimuli responsive volume phase transition of poly(N-isopropylacrylamide) microgels is very well understood for particles suspended in bulk,[1,2] it is still unclear how microgels react to changing temperatures while adsorbed to an interface. Here, we demonstrate that their behavior is drastically altered in interfacial confinement, as the volume phase transition is largely suppressed for the core of the particle and completely absent for the corona surrounding it. Additionally we observed a hysteresis in core morphology and interfacial tension between heating and cooling cycles, which we explain by the presence of a kinetically trapped state.[3] The fact that the volume phase transition does not occur as expected leads to the conclusion that the temperature-induced destabilization of microgel-based emulsions is more complex than expected and requires a careful reconsideration and extension of existing models.[4–5]



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Influence of Polymer Additives During Spin-Coating of WO_3 Thin Films on their Spectroelectrochemical Performance

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“Smart windows” offer a tunable shading, which can increase the indoor occupant comfort and reduce the energy consumption of a building [1]. WO_3 is widely used because of its high transparency but high coloration achievable with good switching behavior upon reduction and intercalation of charge-balancing counter-cations [1,2]. Most technical applications rely on preparation of WO_3 layers via sputter deposition. Alternative preparation techniques to obtain WO_3 thin films with improved switching characteristics are sought. The electrochromic switching characteristics of WO_3 are highly depending on the internal structure of the films [3].

In this work, thin films of WO_3 were prepared by spin-coating of precursor solutions with peroxotungstic acid or tungsten chloride. Either poly(ethylene glycol) or poly(isobutylene)-*block*-poly(ethylene oxide) as structure-directing agents allowed fine-tuning of the film structure, leading to small lamellar-like or highly ordered pores. The electrochromic behavior of the thin films was studied by electrochemical measurements. UV/Vis spectroscopy was performed in operando to monitor the color changes. WO_3 prepared with an optimum composition of the additives led to an improvement in switching characteristics. Intercalation of Li^+ ions into the films was directly studied by time-of-flight secondary ion mass spectrometry. Rather compact films prepared without additives showed an accumulation of lithium at the film surface as opposed to optimized porous films prepared in the presence of polymer additives that led to a homogenous distribution of lithium. The relevance of an increased accessibility of WO_3 and a porous film structure was thereby confirmed.

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Radiation damage and protection in microsolvated biomolecules

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Solvation effects have a strong influence on the structure and function of complex biological systems. The photophysical and photochemical properties of model UV absorbing chromophores, such as indole or pyrrole, are sensitive to their local hydration environment. The role of the hydration environment on the radiation-induced biological damage is not well understood so far. We investigated how the fragmentation dynamics of ionized biomolecule changes in the vicinity of a single water molecule. The microsolvated biomolecule serves as a model system for the interaction between biomolecules and water in general.

We produced pure samples of a bimolecular hydrogen-bonded cluster, pyrrole with water, using a combination of a cold molecular beam and electrostatic deflector. For the comparative fragmentation studies after valence ionization, a strong-field ionization scheme was employed in combination with photoion-photoion coincidence imaging. Overall, new relaxation pathways facilitated by the hydrogen-bonded water have been observed for the microsolvated biomolecules, thereby demonstrating the potential of water acting as a radiation protection agent for ionized biomolecules. Albeit the protective effects in the cluster, we also observed a secondary process of enhanced strong-field ionization that resulted in the formation of highly charged ions, but only for the microsolvated molecules.

Synthesis and structure formation of colloidal dumbbells

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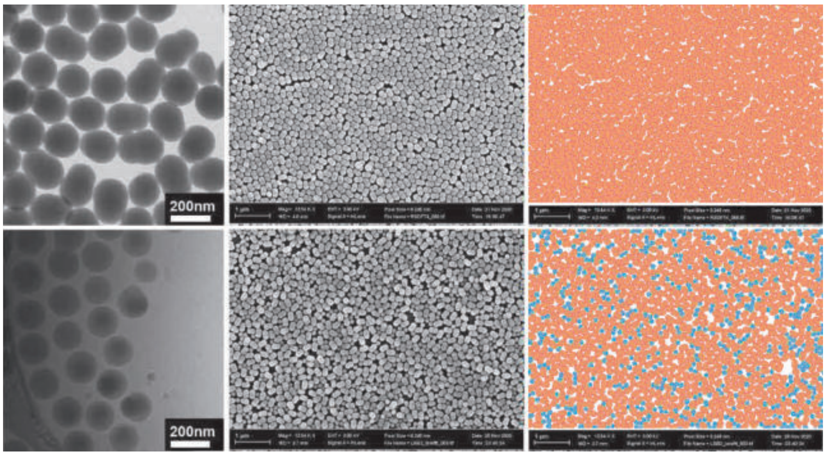

Building on previous work in our group, that explored assembly of colloidal clusters in spherical oil droplets and investigated the dynamics of said clusters [1], we present detailed elucidation of dumbbell particle formation and their self-assembly. The procedure for the gram-scale synthesis of colloidal dumbbells was described by Dufresne *et al.* [2] and their formation mechanism is probed by our work in significant detail, concerning the mechanism of swelling, post-functionalisation and hybrid material particles. To our knowledge our work contains the first direct imaging of the separated monomer droplet during dumbbell formation imaged by cryo electron microscopy. The resulting dumbbell particles were assembled in monolayers *via* the Langmuir-Blodgett technique and exhibit a rich phase behaviour, which is characterized by a variety of parameters, including packing density, orientation and pair correlation. Binary monolayers consisting of isotropic and anisotropic particles were assembled by the same method and give considerable insight into the structure formation in mixed particle systems.

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Synthesis and Characterisation of NIR photoluminescent Aerogels

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Semiconductor nanoparticles exhibit astonishing properties which are based on quantum confinement and high surface area, unreachable for bulk materials. Since nanoparticle solutions are often hard to implement into working devices the assembly of individual nanoscopic building blocks to macroscopic materials is a very viable strategy to utilize these properties in applications like catalysis, sensing, electrochemistry and photovoltaics. One of the most successful techniques to obtain these materials is the gelation of nanoparticles through controlled destabilisation and the assembly into three dimensional networks. Subsequent solvent exchange and supercritical drying gives excess to so called aerogels, which have been synthesized for different materials such as metal chalcogenides, metal oxides and perovskites with different potential applications and properties. [1, 2]

One of the most interesting properties to investigate when talking about nanoparticle gels and nanoparticles themselves are their optical properties. The most prominent materials used for gel synthesis exhibit optical properties in the UV and Vis, while the NIR and IR is vastly unexplored, especially when it comes to photoluminescence. In this work the catalogue of available semiconductor nanoparticle aerogels is extended into the IR in terms of their optical properties and especially their photoluminescence. Different gelation methods have been used and optimized for the investigated materials. The resulting Gels have been characterized with optical spectroscopy, transmission and scanning electron microscopy and X-Ray diffraction, as well as compared to the individual building blocks themselves.

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Foam-Analogue Nanostructure of a Water-Rich L_3-Phase

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Early studies [1-3] on water – *n*-alkane – ionic surfactant microemulsions provide first hints for the possible existence of a foam-analogue nanostructure, i.e. a dense packing of polyhedral nanometer-sized water droplets in a continuous oil phase. We chose the system water/NaCl - hexyl methacrylate (C_6MA) - dioctyl sulfosuccinate sodium salt (AOT) because our ultimate goal is to polymerize the continuous oil (monomer) phase, i.e. to synthesize genuine nanoporous polymerfoams. We studied the phase behaviour of this system inspired by the pioneering work of Skouri et al. [4]. We located an isotropic one-phase channel, the L_3 phase, on the water-rich side of the phase diagram at ambient temperature in addition to the isotropic oil-in-water microemulsion at high temperatures [5]. In this channel the conductivities are very low and the viscosities are rather high. In addition, we were able to picture by freeze fracture electron microscopy the foam-analogue nanostructure (see Fig.1). The structure is reminiscent of that of Wolf et al. [7] for a related system with a technical grade nonionic / anionic surfactant mixture. Currently, we are studying the kinetics of the polymerization of the oil (C_6MA) phase with the crosslinker propylene fumarate dimethacrylate. Moreover, the structural evolution within the one-phase L_3 channel will be investigated by small angle neutron scattering (SANS) and NMR self-diffusion (FTPGSE).

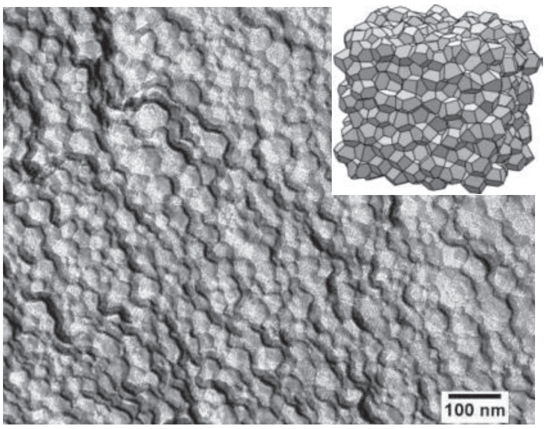

Fig. 1: *Freeze fracture electron microscopy (FFEM) image of an oil-continuous microemulsion H_2O/NaCl – C_6MA – AOT with AOT mass fraction $\gamma = 0.15$ and C_6MA mass fraction $\alpha = 0.04$. Scale bar = 100 nm. The inset illustrates the polyhedral foam-analogue taken from [6].*

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Composition Dependent Optical Properties of Cu-Zn-In-Se Nanocrystals Synthesized via Cation Exchange

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The speculation that the broad photoluminescence (PL) spectra of I-III-VI_2 semiconductor nanocrystals (NCs) is an intrinsic property like other unique properties of these nanomaterials, namely large Stokes shifts and long radiative lifetimes, has been challenged by recent single particle studies. These studies have shown that the PL line width of a single I-III-VI_2 NC can be narrowed down to 60 meV, as compared to the commonly observed broad PL spectra of the corresponding NC ensemble, which is approx. 300 meV.[1] However, the development of synthetic strategies to observe such narrow PL line widths remains a challenge. In this work, we present simultaneous cation exchange of Cu-to-In and -Zn in template binary $Cu_{2-x}Se$ NCs. The simultaneous incorporation of In and Zn cations results in the formation of alloyed Cu-Zn-In-Se (CZISe) NCs. These NCs exhibited extremely narrow PL bands ranging from approx. 110 meV to 170 meV, which is rarely observed in the case of copper chalcogenide-based nanomaterials. The PL quantum yield (QY) also showed a drastic increase to 15% from the previously reported CISe NCs (<1%)[2]. Along with achieving narrow PL bands and high PLQY without the shell growth, we studied the composition dependence of the optical properties of these CZISe NCs within a narrow size distribution. A variation in the feed ratios of the guest cations, i.e. In:Zn, resulted in the variation of the composition of the synthesized NCs and a corresponding tuning in the PL maxima ranging from approx. 1000 nm to 1180 nm depending on the final ratio of In:Zn in the synthesized particles.

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Mechanosynthesis of polymer-stabilized lead bromide perovskites: insight into the formation and phase conversion of nanoparticles

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The application of polymers to replace oleylamine (OLA) and oleic acid (OA) as ligands for perovskite nanocrystals is an effective strategy to improve their stability and durability especially for the solution-based processing.[1] Herein, we report a mechanosynthesis of lead bromide perovskite nanoparticles (NPs) stabilized by partially hydrolyzed poly(methyl methacrylate) (h-PMMA) and high-molecular-weight highly-branched poly(ethylenimine) (PEI-25K).[2] The as-synthesized NP solutions exhibited green emission centered at 516 nm, possessing a narrow full-width at half-maximum of 17 nm and as high photoluminescence quantum yield (PL QY) as 85%, while showing excellent durability and resistance to polar solvents, e.g., methanol. The colloids of polymer-stabilized NPs were directly processable to form stable and strongly-emitting thin films and solids, making them attractive as gain media. Furthermore, the roles of h-PMMA and PEI-25K in the grinding process were studied in depth. The h-PMMA can form micelles in the grinding solvent of dichloromethane to act as size-regulating templates for the growth of NPs. The PEI-25K with large amounts of amino groups induced significant enrichment of $PbBr_2$ in the reaction mixture, which in turn caused the formation of $CsPb_2Br_5$-$m$$PbBr_2$ and $CsPbBr_3$-Cs_4PbBr_6-nCsBr NPs. The presence of $CsPbBr_3$-Cs_4PbBr_6-nCsBr NPs was responsible for the high PL QY, as the Cs_4PbBr_6 phase with a wide energy bandgap can passivate the surface defects of the $CsPbBr_3$ phase. This work describes a direct and facile mechanosynthesis of polymer-coordinated perovskite NPs and promotes in-depth understanding of the formation and phase conversion for perovskite NPs in the grinding process.

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Spectroscopic Investigation of the Electron Transfer between Inorganic Semiconductor Nanoparticles and Redoxactive Organic Molecules

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Inorganic semiconductor nanocrystals, such as CdSe- and CdS-based quantum dots and nanorods, have been established as extremely potent and versatile materials for many photonic applications: their high extinction coefficients and tuneable (by means of size variation) absorption and photoluminescence characteristics render them ideal candidates as light-harvesters for photovoltaics and photocatalysis as well as active material in light-emitting diodes.

Upon photoexcitation of these nanomaterials, an exciton is generated. In photocatalysis, the electron can subsequently be transferred to or from a catalytically active center, where catalysis, e.g., the hydrogen evolution reaction, can occur. Detailed knowledge about the principal electron transfer steps is pivotal in the design of efficient photocatalytic systems. Here, we report on the interplay of photoexcited nanocrystals with different redoxactive organic molecules, which can act as electron acceptors or donors, i.e., electron or hole quenchers. By utilizing steady-state and time-resolved absorption and photoluminescence spectroscopies, different quenching behaviors are observed, which can be correlated with the adsorption of quenchers to the nanocrystal surface.

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Microscopic modeling of entropic effects in protein transport through membrane proteins and in colloid-polymer solutions

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Long, repetitive protein chains of the cap the cytoplasmatic side of the nucleopore complex, which connects the nucleus to the remainder of an eukaryotic cell. We study the properties of three fundamental polymer models that represent these filaments using Monte Carlo computer simulations [1]. Random walks and the worm like chain model cannot account for the unusual size selectivity of the pore, while a two-dimensional arrangement of intrinsically disordered block copolymers with a high content of α-helices is in agreement with the biochemical findings. We predict a linear increase of the free energy barrier of protein transport through the pore with increasing protein diameter, which can be probed experimentally using atomic force microscopy or optical tweezers.

In solutions of colloidal particles and polymer chains, entropic effects induce depletion forces, which lead to the aggregation of colloidal particles to clusters or even to condensed phases. We are able to reproduce this effect using a microscopic model of hard spheres that represent the colloidal particles and random walks that describe the polymer chains. Phase separation is attested by grand canonical Monte Carlo simulations.

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Structure and rheology of wormlike micelles

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The rheology of wormlike micelles (WLM) has been discussed intensely in the past decades by experimentalists [1] as well as theoreticians [2]. Thereby the nonlinear flow curve is a key feature and an indication that the underlying (viscoelastic) properties are unique. Within our studies we explore a catanionic micellar system consisting of a mixture of a short-chained C_8 cationic surfactant with three different sodium salts of omega-9 fatty acids serving as long-chained anionic surfactants [3]. The variation of the latter one yields an increase of the cross-sectional radius of the WLMs and therefore also influences the persistence length. To characterize the structure of these elongated micelles we performed extensive neutron and light scattering experiments. Further, we investigated the wormlike micellar system under shear. Hereby, the focus is set to dynamic processes such as relaxation and breaking of the micelles, which is reflected within oscillatory shear experiments. Additionally, we performed static shear experiments to characterize the flow properties of the system especially focusing on the nonlinear flow curve. All obtained results are to be taken to complete the structural picture of WLMs and to gain a more comprehensive picture in terms of their molecular composition. In addition, this experimental data it to serve as basis for further theoretical calculations and simulations regarding their nonlinear flow behaviour.

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DELAYED SETTLING AND SEDIMENTATION OF BIDISPERSE POLYMER SUSPENSIONS IN AQUEOUS POLYMER SOLUTIONS

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The paper is concerned with the relation between separation quantified at given centrifugal acceleration(s), to the behaviour at other accelerations or at earth gravity. Selected dispersions of monodisperse polymer particles (6 and 15 μm) and their bidisperse mixtures in aqueous solutions of carboxmethyl cellulose sodium salt (NaCMC) were investigated in the range of negligible hindrance.

At gravity, in particular in case of smaller particles and in the range of high polymer concentrations, delayed sedimentation was observed, which is related to the strength of depletion interaction. There is a critical viscosity of surrounding media necessary to counteract mass forces against interparticle forces to prevent separation. This balance decides whether agglomeration affects sedimentation velocity but also whether delayed sedimentation can be observed or not. At gravity the following steps of delayed sedimentation were observed: I – aging (coarsening) of flocculated particle network without visual separation, II – release of a thin clear layer of the continuous phase on top of samples, III – breakdown of network of coarse flocs and its compression.

In case of separation in centrifugal field, delay time was only experienced for the monodisperse smaller particles, at low RCA and high dissolved polymer concentration. The results of settling of bidisperse particle suspensions in polymer solution show that the reducing / enhancing effects of the second kind of particles is due to interaction with dissolved polymers either by increasing or decreasing, respectively, the local apparent (micro) viscosities experienced by the particles.

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Bundesministerium
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und Energie

Quantitative Determination of Polymer Grafting Density on Colloidal Particles by Energy-Filtered Transmission Electron Microscopy

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Polymer grafted nanoparticles (PGNPs) represent a widely used type of hybrid colloids with exciting properties and emerging applications in advanced technologies. The polymeric coating determines how these colloidal particles interact with their environment, and often times such interaction is dependent on the grafting density of the adsorbed polymers: For example, matrix compatibilization of PGNPs [1], their surface patterning via constrained de-wetting [2], and their performance in nanomedicine applications depend on this parameter. [3] Hence, quantitative determination of this parameter is of utmost importance. However, all currently available analytical methods result in ensemble averages; none of these are capable of obtaining quantitative absolute values from individual NPs (allowing to judge the fluctuation of polymer grafting densities among different PGNPs in a sample) or from distinct sites of anisotropic PGNPs. [4] In the current investigation, we achieved this goal by using energy-filtered transmission electron microscopy. By analyzing the variations of the ratio between inelastically and elastically scattered electrons for the organic and inorganic components of PGNPs, we calculated the grafting density and its distribution for the thiol-terminated polystyrene chains grafted onto the surface of (isotropic) gold nanospheres (AuNSs) and (anisotropic) gold nanorods (AuNRs). Fundamentally, our results provide a deeper quantitative understanding of polymer grafting on curved surfaces. We submit that the understanding of these physicochemical underpinnings will facilitate the rational design of PGNPs in many technological fields such as optoelectronics, catalysts, sensors and drug delivery systems.

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The aggregation behaviour of hydrophobically modified thermo-responsive block-polymers in solution

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Mediation between hydrophilic and hydrophobic phases is necessary for almost every application or process, e.g. cleaning, solubilization, drug delivery, and colloidal stabilization. Best known for this purpose are amphiphilic molecules like surfactants. Very important is usually the ability to control and adjust the rheologic properties of a solution, for which commonly polymers are used. In addition, having the option for a distinct temperature response of the rheological properties for many potential applications. To combine and understand these properties of self-assembly and temperature response, in this work, hydrophobically modified (HM) thermo-responsive (TR) block-polymers were studied with respect to their phase behavior and structure in solution. In order to have at the same time a relatively high loading with hydrophobic material they were combined with microemulsion droplets.

The HMTR block-polymers are built of a dodecyl (C_{12}) chain as hydrophobic end-cap, a permanently hydrophilic poly(*N*-dimethylacrylamide) block (PDMA) and a hydrophilic/hydrophobic temperature switchable block with a lower critical solution temperature (LCST) such as poly(*N*-isopropylacrylamide) (PNIPAM), poly(*N,N*-diethylacrylamide) (PDEA) and poly(*N*-acryloylpyrrolidin) (PNAP). The PDMA block was kept constant with ~200 units and the responsive block of 20 and 40 units. The aggregation behaviour in pure state and their mixtures with microemulsions was studied for different TR block length and variable LCST. The HMTR block-polymers were investigated in aqueous solution in the range of 20-60°C for concentrations between 0.5 and 5 $\%_{wt}$.

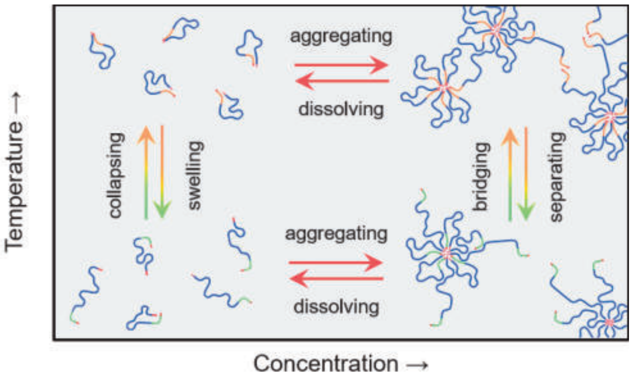

Figure 1: Scheme of interaction and aggregation behaviour of HMTR block-polymers in solution

Synthesis and Characterization of Gold Nanocubes: An Investigation on Organic Ligand Exchange

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Gold nanoparticles are interesting due to their unique optical properties, which result from the size- and shape-dependent localized surface plasmon resonance in the visible spectral range.[1,2] In particular for cubic nanoparticles, an extraordinary strong electromagnetic field can be generated on their edges and corners compared to spherical ones.[2] The properties and applications of nanoparticles are influenced not only by the shape but also by the stabilizing ligand. Therefore, a ligand exchange enables a wider range of applications. For example, ionic compounds can be replaced by sterical ligands.[3]

This motivated us to synthesize colloidal gold nanocubes in an aqueous solution.[4] We investigated the influence of the reaction temperature on the formed nanoparticles and show that different particle shapes are obtained depending on this parameter. Via a subsequent phase-transfer step, the ionic stabilizing ligand was exchanged by an organic amine and therefore the nanoparticles were transferred into an organic solvent. Depending on the reaction conditions it is possible to maintain or even change the particle shape. To investigate the optical properties as well as the particle size and shape, we used UV/Vis absorption spectroscopy and transmission electron microscopy. By additionally X-ray photoelectron spectroscopy, the stabilizing ligand shell was studied.[5]

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Investigation of the Influence of High-Energy Laser Pulses on Colloidally Dispersed Nanoparticles

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Due to their size-dependent optical properties (LSPR, *localized surface plasmon resonance*), metal nanoparticles are very well suited for heating by laser irradiation. The interaction of nanoparticles with light is an interesting subject that has been studied in many publications in recent decades.[1,2] Metal nanoparticles are characterized by a large number of free charge carriers that can interact with an electromagnetic field. The electron gas of the metal is able to quickly absorb large amounts of energy and pass it to the lattice by electron-phonon coupling. In this way, it is possible to strongly heat nanoparticles in colloidal solution to a degree, which cannot be realized in conventional ways due to the limitation by the boiling point of the solvent. Depending on the used laser system (nano-, pico-, femtosecond laser), temperatures well above the melting point can be reached in very short periods of time, while the surrounding medium remains cold.[3]

In this work, we investigate the melting behavior of platinum nanoparticles upon irradiation with the second harmonic (532 nm) of a nanosecond pulsed Nd:YAG laser. The used platinum nanoparticles initially have a rough, cloud-like surface, which can be smoothed by melting processes. In addition to the smoothing of the surface, the influence of laser irradiation on the crystallinity and optical properties of the particles were also investigated.

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Investigation of Colloidal Nanoparticles with Metal-Insulator Transitions

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The localized surface plasmon resonance (LSPR) is a phenomenon well known from noble metal nanoparticles (NPs). To show a LSPR, the material must have a large free charge carrier density. Materials that show a transition from a non-conductive to a conductive phase should also show a LSPR in their conducting phase. This leads to possible plasmonic systems with temperature switchable optical properties. To have an easy accessibility of the phase transition a material with a transition temperature near the room temperature was chosen. Vanadium(IV)oxide (VO_2) shows that phase transition at 68 °C and the charge carrier density of the metallic phase suggests a LSPR in the NIR range. These NPs could find their application in solar cells or smart windows.[1] To prove those expectations VO_2-NPs were synthesized and characterized via temperature dependent optical spectroscopy and thermal analysis. The structural analysis was done with X-ray powder diffraction and transmission electron microscopy. The results show first hints of a switchable LSPR in the near infrared range.

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Sensing with chirality pure near infrared fluorescent carbon nanotubes

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Semiconducting single wall carbon nanotubes (SWCNTs) fluoresce in the near infrared (NIR) and the emission wavelength depends on their chirality (*n*,*m*).[1] Interactions with the environment affect the fluorescence and can be tailored by functionalizing SWCNTs with biopolymers such as DNA, which is the basis for fluorescent biosensors. So far, such biosensors were mainly assembled from mixtures of SWCNT chiralities with large spectral overlap, which affects sensitivity as well as selectivity and prevents multiplexed sensing. The main challenge to gain chirality pure sensors has been to combine approaches to isolate specific SWCNTs and generic (bio)functionalization approaches. Here, we created chirality pure SWCNT-based NIR biosensors for important analytes such as neurotransmitters and investigated the impact of SWCNT chirality/handedness as well as long-term stability and sensitivity [2]. For this purpose, we used aqueous two-phase extraction (ATPE) to gain chirality pure (6,5)-, (7,5)-, (9,4)- and (7,6)-SWCNTs (emission at ~ 990, 1040, 1115 and 1130 nm). Exchange of the surfactant sodium deoxycholate (DOC) to specific single-stranded (ss)DNA sequences yielded monochiral sensors for small analytes (dopamine, riboflavin, ascorbic acid, pH). DOC residues impaired sensitivity and therefore substantial removal was necessary. The assembled monochiral sensors were up to 10 times brighter than their non-purified counterparts and the ssDNA sequence determined absolute fluorescence intensity as well as colloidal (long-term) stability and selectivity for the analytes. $(GT)_{40}$-(6,5)-SWCNTs displayed the maximum fluorescence response to the neurotransmitter dopamine (+140 %, $K_d = 1.9 \times 10^{-7}$ M) and a long-term stability > 14 days. The specific ssDNA sequences imparted selectivity to the analytes mostly independent of SWCNT chirality and handedness of (+/-) (6,5)-SWCNTs, which allows a predictable design. Finally, multiple monochiral/single-color SWCNTs were combined to achieve ratiometric/multiplexed sensing of the important analytes dopamine, riboflavin, H_2O_2 and pH. In summary, we demonstrated the assembly, characteristics and potential of monochiral (single-color) SWCNTs for multiple NIR fluorescent sensing applications [3].

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Phase transitions in interfacial assemblies of microgels

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Colloidal particles strongly adsorb to liquid interfaces. Such two-dimensional confinements provide ideal model systems to fundamentally study self-assembly phenomena and phase behavior. The most widespread colloidal model systems, silica or polymer latex particles generally assemble in hexagonal packing, as expected for spheres in two dimensions. Microgels, however, show a significantly more complex interfacial behavior. Compared to their rigid analogues, their soft and swollen nature leads to a significant deformation under the influence of surface tension, leading to a characteristic core-corona morphology. Under compression, the particles can further deform and alter their shape. The interfacial properties of such particles, are therefore predominantly governed by their internal molecular structure, such as their crosslinking density.

I will first introduce how microgels deform at the air/water interface as a function of their internal architecture and then present the phase behavior of these particles at the air/water interface under compression. Depending on the molecular architecture and the resulting interfacial morphology, we observe different phase behavior. Typically, microgels undergo an isostructural hexagonal-hexagonal phase transition between a hexagonal non-close-packed phase and a hexagonal close-packed phase. The former is characterized by particle arrays in corona-corona contact, with a separation of the cores. Upon compression, the coronae collapse, leading to microgel arrays with core-core contact. With decreasing crosslinking densities, the nature of the phase transition changes and percolated, chain-like structures are observed. Very loosely-crosslinked microgels, in contrast, exhibit a homogeneous decrease in interparticle distance upon compression, without undergoing a phase transition.

We rationalize the phase behavior via the shape of the interaction potential of microgels interacting at the air/water interface and discuss similarities and differences with traditional simulations of particles systems interaction via a soft repulsion shoulder, introduced by Jagla et al. decades ago.

Perfluorocarbons suppress efficiently coalescence in foams

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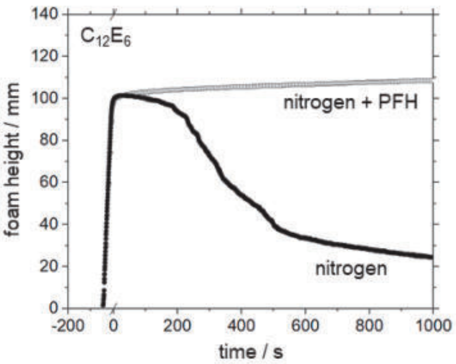
The stability of foams is determined by three main mechanisms: drainage, coalescence and Ostwald Ripening. In order to prevent these three mechanisms various approaches are used. Ostwald Ripening, for instance, can be prevented by the osmotic effect of gases with low solubility in water. Perfluorocarbons having the lowest solubility, they are heavily used in foam science for this purpose [1]. However, their influence on other foam properties, such as coalescence, is commonly neglected and has never been investigated. Using the nonionic surfactant hexaethylene glycol mono dodecylether ($C_{12}E_6$), which is known to form very unstable foams [2], we show here that perfluorocarbons have an unexpected and significant effect on foam coalescence! Tuning the concentration of perfluorohexane (PFH) in the nitrogen bubbles of foams characterised by the commercially available Foam Scan (TECLIS), we show that only low PFH concentrations are enough to reduce significantly coalescence [3]. Surface tension measurements at different PFH concentrations confirm that it adsorbs rapidly to the bubble surface [4]. We hypothesize that it impacts the interfacial rheological properties in a way which stabilizes the thin films between the gas bubbles against rupture. To elucidate the underlying mechanisms, we investigate isolated thin films using a thin film pressure balance [5].



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Drainage and Stability of Solidifying Hydrogel Films

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Polymer foams can be open-cell, closed-cell, or a combination thereof. Controlling the connectivity of polymer foams is of utmost importance for controlling foam properties, such as absorption, mechanical or acoustic properties. Here, we are particularly interested in hydrogel foams, which are widely used in the biomedical field. Several studies investigated hydrogel foams produced via foam templating, i.e. the gelation of a liquid foam containing a polymer in solution, in which some pores were open, and others were closed (see Figure 1) [1-4]. However, a clear understanding of the underlying mechanisms has yet to be elaborated. For this purpose, we use a model system consisting of an alginate hydrogel, cross-linked with calcium ions. We design simplified experiments to study isolated, free-standing vertical and horizontal foam films undergoing cross-linking. The horizontal films are investigated within a home-designed microfluidic thin film pressure balance which allows for a precise observation of the film thinning and apparition of holes in the gelling films. We tweak both, the pressures controlling the film thinning process as well as the kinetics of the hydrogel gelation to quantify the different regimes of film response. This investigation leads us to address the issue of cross-linking in the presence of interfaces and under soft confinement, since the characteristic film thickness before hole formation (10-100 nm) is smaller than the unconstrained mesh size.

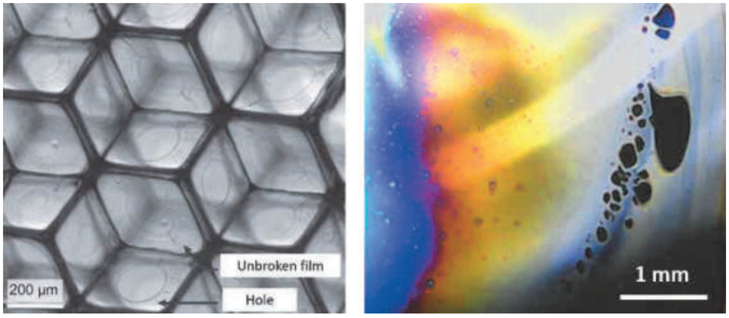

Figure 1: (left) Alginate hydrogel foam showing unbroken films and holes in the films. (right) Model experiment showing a gelified alginate hydrogel film with numerous small holes.

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2D assembly of CdSe nanoplatelets for application in electronic devices

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Quasi-two-dimensional semiconductor nanoplatelets (NPLs) are promising candidates for a lot of optoelectronic applications such as LEDs, photodetectors and field-effect transistors. They possess a strong quantum confinement in just one dimension, leading to exceptionally narrow photoluminescence spectra, short lifetimes, giant oscillator strength, low laser threshold, and high absorption cross section. Thus, they demonstrate many advantages over corresponding quantum dots. While their lateral size can be as large as synthesis parameters allow, confinement of excitons is achieved through keeping the thickness smaller than the exciton Bohr radius. Therefore, optical and electronic properties are thickness dependent and can be tuned by varying the number of monolayers constituting the NPLs.

Because of their large lateral dimensions, NPLs are promising candidates for electronic devices as the number of hopping events in a solid film made of such NPLs is reduced in comparison to spherical quantum dots. Therefore, it is reasonable that 2D objects will present larger neighbour-to-neighbour coupling than the point like contact between adjacent spheres. Coupling between nanocrystals can be influenced by a variety of parameters, such as their morphology, orientation, and surface ligands. Achieving ordered transition dipole moments in ordered 2D assemblies of NPLs plays a vital part in overall device performance.

We use two different techniques, spin-coating and a modification of the Langmuir-Blodgett assembly method, to obtain 2D layered structures of CdSe NPLs and investigate the effect of ligands, thickness and assembly type on the electronic properties of the obtained films.

NADES-based Surfactant-Free Microemulsions for Solubilization and Extraction of Curcumin from *Curcuma Longa*

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Natural Deep Eutectic Solvents (NADES) are a relatively new class of non-aqueous solvents. They are eutectic mixtures of naturally occurring, often hydrophilic hydrogen bond donors and acceptors, which exhibit a low melting point as compared to their single components. Through their desirable solvent characteristics, like low melting point and volatility, combined with high stability, solving capability, and biocompatibility, they can be considered as an attractive, green alternative to common solvents [1].

Choline chloride-based NADES were used as adjuvants to ethanol/triacetin mixtures to obtain ternary systems with a superior solubility of curcumin (2 to 5-fold increase), compared to previously studied water-based surfactant-free microemulsions (SFMEs) [2]. An easy and fast room temperature extraction procedure was applied, extracting up to ~ 80 % of the total curcuminoid content of ground rhizomes of *Curcuma Longa L*. The high solubility of curcumin in the solvent systems allowed multiple extractions of fresh rhizomes in the same solvent until saturation [3]. While using the same amount of solvent, even more concentrated curcuminoid tinctures could be achieved, when using the ternary NADES systems as compared to the aqueous SFMEs.

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An aqueous route for the synthesis of In_2O_3 aerogels

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Aerogels are increasingly sought after, in the field of catalysis, due to their porous nature and their extraordinarily high specific surface area. In a previous work, In_2O_3 aerogels have been shown to be well-suited for the catalysis of the methanol steam reforming process. Thus far, however, only an epoxide assisted route for the synthesis of In_2O_3 aerogels has been reported. In order to reduce the environmental footprint and the use of epoxide, aqueous routes need to be explored.[1] Herein, we report on the development of a facile two-step aqueous sol-gel route for the synthesis of In_2O_3 gels. The first step to aerogels consists of the creation of a stable Indium hydroxide colloidal solution. This is done by exploiting the pH behavior of aqueous indium salt solutions.[2] The colloidal sol is monitored mainly by light scattering methods and ex-situ transmission electron microscopy, the long term stability by zeta potential measurements. In a subsequent step, the aim is to destabilize the electrostatically stabilized sol particles to form a gel. In the final step, after drying of the gels, the resulting aerogels are compared to their counterparts produced by the epoxide assisted gelation using BET surface analysis. To optimize this process, the influence of reactant concentrations, temperature and the concentration and nature of destabilizing agents, were studied.

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Core-shell latexes for tailored wetting properties

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Facile surface functionalization of latex colloids makes them most promising materials for broad thin film applications. However, the effect of these colloids on chemical film and wetting properties is not easily evaluated. Core-shell particles can deform and coalesce on the nanoscale during thermal annealing yielding tailored physical properties. We investigated two different core-shell systems (soft and rigid) with identical shell but with chemically different core polymer and core size [1]. These core-shell colloids are probed during thermal annealing on surfaces in order to investigate their behavior as a function of nanostructure size and rigidity. X-ray scattering allows us to follow the re-arrangement of the colloids and the structural evolution in situ during annealing. Evaluation by real-space imaging techniques reveals a disappearance of the structural integrity and a loss of colloids’ boundaries. We present the possibility to tailor and fine-tune the wettability by tuning the core-shell colloid morphology in thin films, thus providing a facile template methodology for repellent surfaces.

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Annealing of polymer colloids on CNF

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Layer formation and annealing of colloidal inks applied to porous materials is very relevant for printing and functional coatings. The goal is to distinguish and quantify the differences in structure formation during annealing of deposited colloidal inks on a porous and a solid material. Therefore, we compare two different substrates: As porous template we use a layer of cellulose nano fibers (CNF) – so-called nanopaper [1] – and as non-porous reference medium silicon. We use novel colloidal inks consisting of poly-butylmethacrylate (PBMA) and poly-sobrerolmethacrylate (PSobMA) in aqueous solution. We studied the deposition and the subsequent structural and morphological changes during annealing of the colloidal layers in real-time using grazing incidence small-angle X-ray scattering (GISAXS). During deposition, we expect that part of the liquid enters the CNF layer while part of the solvent and the colloids remain on top of the nanopaper surface, leading to a complex drying process. Subsequently, the structural changes in the colloidal layer are induced by annealing. With GISAXS we monitor these different processes and their effect on the CNF template.

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Ionic Liquids $[M^{3+}][A^{-}]_3$ with three-valent cations and their possible use to easily separate rare earth metals

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Ionic Liquids (ILs) are generally defined as salts with a melting point below 100 °C, and have garnered large popularity due to their high customisability and beneficial properties. Most conventional ILs are composed of organic cations such as imidazolium, pyrrolidinium, pyridinium or phosphonium derivatives, and weakly coordinating anions [1,2]. However, these compounds are often toxic and poorly biodegradable, and their synthesis and the subsequent purification is laborious and costly.

Alkyl polyethylene oxide carboxylates provide a simple and clean way to liquefy rare earth metals (REM) by incorporating the corresponding cations, in particular Eu^{3+}, La^{3+} and Y^{3+} into polyvalent Ionic Liquids. In contrast to conventional methods, this is achieved not by transforming them into anionic complexes, but by keeping them as bare cations and combining them with convenient, cheap and commercially available anions [A] in the form $[REM^{3+}][A^{-}]_3$. To do so, we follow the COncept of Melting Point Lowering due to EThoxylation (COMPLET) [3]. Despite the similarities of their cations, the provided ILs possess remarkably different properties, and their water-octanol partition coefficients *P* show that the studied rare earths can be separated via liquid/liquid extraction without the use of toxic extractants.

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Influence of aromatic additives on the phase transition behaviour of thermoresponsive Poly(N-isopropylacrylamide) microgels with different cross-linker densities

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Thermoresponsive polymers bear a large potential for drug delivery applications, however, the influence of small molecules on the phase transition is a critical issue. Our work investigates the effects of different additives such as benzene derivatives, employed as model drugs, on the phase transition behaviour of differently crosslinked Poly(N-isopropylacrylamide)/*N*,*N'*-methylenebisacrylamide (PNiPAM/BIS) microgels.

While the homopolymer PNiPAM has already been studied earlier in the presence of various aromatic additives,[1] in the present work the influence of a selection of additives (dihydroxybenzenes, dihydroxybenzaldehydes) on the VPTT of PNiPAM microgels is determined. NMR Spectroscopy, Differential Scanning Calorimetry (DSC) and Dynamic Light Scattering (DLS) are employed to determine the characteristic Volume Phase Transition Temperature (VPTT), transition widths and incorporation/release behavior towards additives.

All additives investigated induce a shift of the VPTT to lower temperatures, consistently observed in all temperature-dependent characteristic parameters. This shift is sensitively dependent on the microgel architecture, as the VPTT shift depends on crosslinking density.

Furthermore, as a result from temperature dependent ^{1}H-NMR spectra, this work proofs the existence of an incorporated additive fraction at $T >$ VPTT. A quantification of the incorporated additive fraction is achieved. By investigation of the transverse spin relaxation rates R_2 of the aldehyde protons, additive molecular dynamics below and above the collapse temperature of the microgels are clarified.

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Photoelectrochemical investigation of CdSe/CdS core/shell nanoparticles and their three-dimensional assembly

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Semiconductor nanoparticles are known as promising materials for photovoltaic, catalytic or sensoric applications. For most of these fields a large reactive surface is needed. Therefore, the assembly of nanoparticles into three-dimensional structures is required. These nanoparticle-based 3D structures are obtained by various methods, e.g., self-assembly by destabilizing agents or cations, inkjet printing and additive manufacturing.

Here, the proven concept of simultaneously inkjet printing nano-inks and destabilizing agents should be used with different sized, highly fluorescent core/shell nanoparticles to obtain gel networks with controlled macroscopic shapes.

As a building blocks CdSe/CdS core/shell nanoparticles are used. Therefore, cadmium selenide cores are prepared by hot-injection, while the cadmium sulfide shells are grown by slow precursor injection and decomposition. The nanoparticle monolayers as well as their three-dimensional assemblies were deposited onto indium tin oxide-coated glass slides. These coated electrodes were used to perform different photoelectrochemical measurements like linear sweep voltammetry and intensity modulated photocurrent spectroscopy.

New Insights in Sunscreen UV-Absorber Solubility – Crystallization Kinetics and Synergistic Effects in Oil Mixtures

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UV filters are the key ingredients of sunscreens. A further prerequisite for good performance of these products is the vehicle, which is needed to distribute the UV filters as uniform as possible on the human skin. As vehicles cosmetic formulations such as creams, lotions, sprays, and gels may serve. Some of the most efficient UV-absorbers for sunscreens are solid at ambient temperature and have to be dissolved in the oil phase of the vehicle. The solubility of such oil-soluble UV-absorbers can be a limiting factor when aiming for high protection against UV-radiation. In order to measure reliable solubilities, we assess the equilibrium state between sediment and saturated solution by following a protocol at a temperature of 25°C. However, in the preparation of sunscreen formulations the oil phase is often heated to higher temperatures, which may lead to oversaturated UV absorber concentrations after cooling. We therefore investigated experimentally the crystallization behavior of four different oil-soluble UV-absorbers and found striking differences in the crystallization velocities. Those can be explained by quantum-chemical calculations based on density functional theory (DFT) and the conductor-like screening model (COSMO). In addition to this kinetic investigation, optimizations of equilibrium solubilities were studied in binary oil mixtures by varying the fractions of the two components, where bis-ethylhexyloxyphenol methoxyphenyl triazine served as a model UV-absorber system. The experimentally determined solubilities revealed synergistic effects for a number of binary oil mixtures, and these results were in good agreement with theoretical calculations based on DFT theory and the COSMO-RS model. Our results indicate that such calculations may serve in future to better understand and predict the solubility behaviour of UV-absorbers in sunscreens.

Insights into the Synthesis of Colloidal 2D PbSe Nanoplatelets with Tuneable Optoelectronic Properties

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Lead chalcogenides based nanocrystals show optical activity in the NIR region as well as a large exciton-Bohr-radius and charge carrier multiplication, making them an interesting material for optoelectronic applications in the NIR window.[1] Therefore the preparation of 2D nanostructures from lead chalcogenides has recently risen in interest, as these nanoplatelets combine the material's inherent properties with the advantages of 2D nanostructures, such as increased exciton binding energies.[2,3]

We report a facile and direct wet chemical synthesis towards colloidal 2D PbSe NPLs with high photoluminescence quantum yield. The NPLs exhibit exciton features in the range of 800 -1000 nm and photoluminescence properties in the range of 900 - 1500 nm. The respective positions can be a precisely tuned by the amount of octylamine used in the synthesis, with smaller amounts causing a hypsochromic shift and an increase in PLQY. Postsynthetic ligand treatment with $CdCl_2$ allows quantum yields up to 40 %, ascribed to a reduction of non-radiative recombination as well as a stabilization of the band-edge state.

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Investigating the surface charge of microplastic particles with Colloidal Probe-Atomic Force Microscopy

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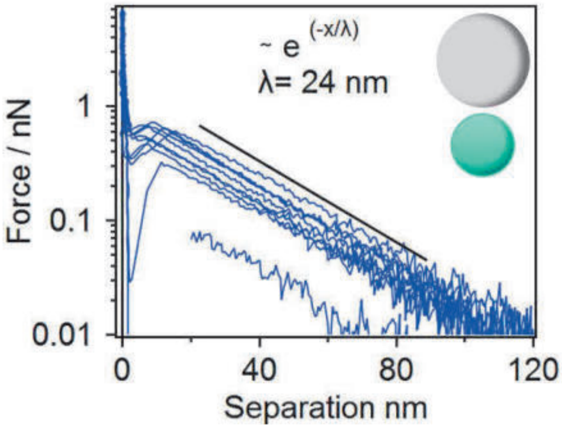
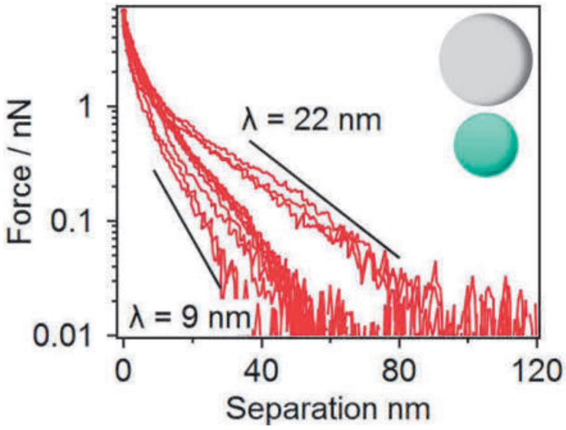
To date, plastic particles have mainly been categorized by polymer type, shape, and size [2]. But there is another important issue arising when investigating microplastic and its interaction with cells. With decreasing size, the surface-volume ratio increases which makes surface properties more important to take into account. It is generally believed that the surface properties of the particles influence the cell interaction. Therefore, we investigated un-functionalized polystyrene particles with the size of 3 µm with different surface properties of two different manufactures. We found out that the cellular interaction and uptake of microplastic particles (polystyrene) differs for the two particle types. Using Colloidal Probe-Atomic Force Microscopy (CP-AFM) we could show a significant difference in the electric surface properties: homogeneously charged particles vs. heterogeneously charged particles. The heterogeneous surface charge manifests itself in an electrostatic interaction of the particles that depends on the mutual orientation of the particles. CP-AFM is therefore a magnificent tool to obtain additional informations about surface charge and it's distribution on microplastic particles.





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Colloidal 2D PbSe Nanoplatelets with Tuneable Photoluminescence and High Quantum Yield

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Abstract

2D semiconductor nanocrystals are a unique class of nanomaterials providing promising optoelectronic properties. Lead chalcogenides are of particular interest for solution processable optoelectronics for applications in the NIR. While extensive work has been published on lead chalcogenide nanocrystals and thicker nanosheets, atomically thin nanoplatelets only recently moved into focus.[1-3] Lead chalcogenide nanoplatelets combine the inherent advantages of 2D materials, such as monodispersity in thickness or increased exciton binding energies, with a large exciton-Bohr radius or multiple exciton generation.[4]

We present PbSe nanoplatelets with tunable optoelectronic properties obtained by colloidal chemistry methods. The NPLs photoluminescence quantum yield can be increased by ligand treatment above 35 %, while the position of the emission can be finely tuned in a large wavelength region (900 nm – 1500 nm). This is explained by the influence of the lateral dimensions as it has been shown in literature, although the large exciton-Bohr radius in PbSe leads to a much stronger effect than in nanoplatelets of different materials.

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Structural and Thermodynamic Characterisation of Nonionic Surfactants Systematically Modified by CO_2 Incorporation in their Head Group

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In our investigations we studied nonionic surfactants of the C_iE_j type, which were modified by incorporating different amounts of CO_2 units into their hydrophilic head groups. This modifies their hydrophobicity and lowers their cmc. Most importantly the phase behavior of such CO_2 modified surfactants differs largely from their conventional analogues by the fact that for high concentrations no gel-like liquid crystalline phases are formed. Instead up to the highest concentrations simple Newtonian liquids are present. This unexpected phase behavior was studied by means of comprehensive light and neutron scattering experiments (SLS, DLS, SANS) and with respect to the bending elasticity of the amphiphilic monolayer by neutron spin-echo (NSE) spectroscopy. Furthermore, a thorough thermodynamic characterisation was done with respect to the enthalpic and entropic contributions to the micellisation process. These experiments showed that the incorporation of CO_2 units imparts a marked hydrophobic character to the surfactants. In addition, the repulsive interaction between the aggregates become reduced to such an extent that no longer liquid crystalline phases with their unfavorable flow properties are formed.

In addition, we studied the solubilisation properties of these surfactants with systematically varied CO_2 content for oils of different polarity. Interestingly, the solubilisation capacity increases largely with increasing CO_2 content. SANS experiments document the increasing droplet size for larger CO_2 content, which means that one can control the microemulsion properties via the molecular architecture of these modified surfactants. In general, these ecologically attractive surfactants allow for formulation at high concentrations and are attractive due to their substantially enhanced solubilisation properties. Accordingly, they could become attractive for various commercial applications, for instance in the fields of cosmetics, pharmacy, etc.

Colloidal synthesis methods for ultrathin metallic and semiconducting 2D MoS2 and WS2 nanosheets

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Two-dimensional (2D) transition metal dichalcogenides (TMDCs) exhibit highly interesting optoelectronic properties including strong spin-orbit coupling[1], successive widening of the indirect band-gap with decreasing layer thickness down to the monolayer having a direct band-gap[2], and a near-unity photoluminescence quantum yield[3]. Tungsten disulfide (WS_2) and molybdenum disulfide (MoS_2) are promising candidates to investigate and use these properties for application in sensors, nano electronics, catalysis, superconductors, and energy harvesting. Up to now ultrathin TMDC nanosheets are mainly produced by exfoliation methods or chemical vapor deposition[4]. Liquid exfoliation methods yield TMDC nanosheets only with rather high layer thickness.

We present a colloidal synthesis pathway for ultrathin TMDC nanosheets that is tunable with respect to important product properties such as size distribution and morphology. A particular focus is set on the control over the crystalline structure of the nanosheets since WS_2, MoS_2, and other TMDCs exhibit metallic or semiconducting properties depending on their modification. Samples are characterized by absorbance and fluorescence spectroscopy, X-ray diffraction, and transmission electron microscopy. Ultrafast charge carrier dynamics are studied by transient absorption spectroscopy.

We found that the formation of the metallic and semiconducting phase can be controlled by manipulating the activity of the precursors, for example by changing the solvent, the sulfur compound, or the reaction temperature.

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Adsorption of Proteins from Human Saliva to Self-Assembled Monolayers Varying in Charge and Wettability

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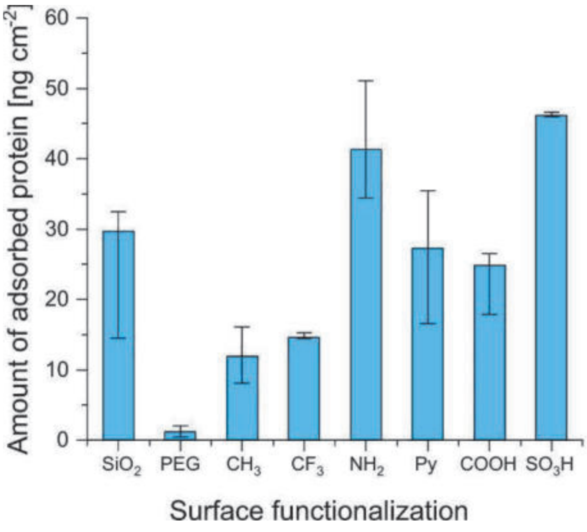
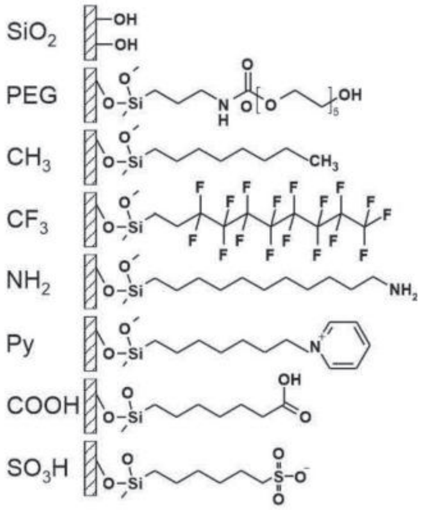
Protein adsorption from surrounding body fluids occurs as one of the first steps when a foreign material becomes inserted in living tissue. Because surface-adsorbed proteins modulate further biological processes like attachment of cells or colonization by bacteria, they may be decisive factors for the successful integration of medical or dental biomaterials and implants. To that purpose quantitative and qualitative adsorption of salivary proteins was studied on self-assembled monolayer model surfaces differing in surface charge and wettability. These coatings were prepared on silica-based surfaces via silane chemistry which was confirmed via infrared and X-ray photoelectron spectroscopy, and further characterized by contact angle and zeta potential measurements. The total amount of adsorbed salivary proteins was clearly influenced by the surface properties in that highest amounts of adsorbed proteins were found on moderate hydrophilic and charged surfaces, medium amounts on hydrophobic surfaces and lowest amounts on a hydrophilic and water-swellable surface. Qualitative protein adsorption, characterized by gel electrophoresis and Western blot, was also influenced by the surface properties in that, for example, the positively charged lysozyme was mainly found on negatively charged surfaces.





Cellulose model surfaces as an approach to study the interaction between fibers and additives in paper

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As a functional material, paper has a high importance in a variety of sectors, such as packaging, print media and speciality papers. This is especially crucial with regard to reducing plastic use and waste and replacing it with renewable and biodegradable resources.[1] The interactions of cellulose fibers with functional additives, such as wet-strength increasing polymers, have been investigated in the past with respect to the mechanical properties of the resulting paper.[2-4] Yet, a systematic understanding of the effects of the chemistry and structure of the polymer on the properties of the fibers is still missing and would lead to an exhaustive knowledge of the functionalization of paper.

In the present study model surfaces are prepared from carboxymethyl cellulose. Using the polyelectrolytes chitosan and PDADMAC, polyelectrolyte multilayers were build up under the variation of extrinsic conditions such as polymer concentration and pH value of the preparation solutions. Ellipsometry, QCM, and AFM measurements allow for a comprehensive investigation of the influence of these conditions on features like thickness and roughness of the synthesized films. The study shows that the surface properties can be controlled and tailored with subnanometer precision.

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Designing Pickering Emulsions for Hydroformylation: From nanoscale particles over microscale droplets to macroscale processes

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Pickering Emulsions (PEs) are particle-stabilized Emulsions [1]. PEs exhibit an outstanding stability and many suitable particle types are cheap, yet environmentally friendly. This makes them ideal candidates for innovative, robust and green environments for interfacial catalysis. The presented work shows new insights in the design of an PE environment for the hydroformylation of 1-dodecene via the catalyst Rh-Sulfoxantphos (Rh-SX) [2]. Rh-SX is water-soluble but insoluble in the oil phase. The PEs inherent high stability enables the retention of this high valuable catalyst in the water droplets while separating the continuous oil phase by membrane filtration [3]. The properties of the nano-sized particles *i. e.* their size, shape, charge and hydrophobicity stabilizing the PEs determine the PEs properties and therefore influence the reaction process heavily. While commercially, in large amounts available particles such as fumed silica are cheap and their use for PE preparation is simple, their behavior is hard to model due to their irregular size and shape. Therefore, a model system consisting of nano-sized silica spheres with controllable properties is used to understand the interplay between particles and catalyst at the interface on the PE properties and ultimately its effect on the reaction and filtration process.

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Experimental and theoretical investigations of $CuInS_2$ - carbon nanotube composites

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Quantum dot - carbon nanotube (QD/CNT) nanocomposites have attracted significant interest particularly due to their potential applications demonstrated in the areas of nanoengineering and nanotechnology such as optoelectronic devices [1]. The master idea behind using such nanocomposites lies in taking advantage of the combination of the interesting properties of both CNTs and QDs. Thus, the application of CuInS2 (CIS) QDs onto CNTs may produce novel hybrid materials that combine the properties of two functional nanoscale materials to achieve advanced optical and electronic properties and therefore broaden their fields of application.

In this work, beginning with the synthesis of CIS - CNT, nanocomposites were produced by chemical surface functionalization or modification of the single components and subsequent electrostatic linking. We investigated in detail influences on the optical properties upon connecting the two building blocks. Furthermore, since there are only few reports on theoretical investigations in terms of Density Functional Theory (DFT) calculations on CIS in a zero-dimensional geometry (as QDs), we show that properly calibrated and adjusted DFT calculations are able to reproduce and predict the optical and electronic structures of these nanomaterials.

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Composite Formation of Gold Nanoparticles and Polymer Brushes

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Composite materials of polymer matrix with embedded inorganic nanoparticles have been applied in many different fields. The combination of both material types on the nanometer scale enables the exploitation of novel properties while simultaneously covering the drawbacks of the individual components. Possible applications include nanoactuation, sensor design and many more. [1,2]

In the field of inorganic nanoparticles, gold nanoparticles (AuNPs) are extensively studied due to their versatile features. They are straight forward to synthesize with varying sizes and easy to stabilize due to thiol-based capping molecules. Furthermore, AuNPs exhibit a surface plasmon resonance in the visible range, which is sensitive to parameters of the particle itself as well as the environment.

One widely employed example of an organic matrix are polymer brushes, in which polymer chains are densely grafted from a surface by one end. This results in a stretched conformation perpendicular to the surface, which offers a lot of surface for nanoparticle adsorption.

In the presented work, citric acid capped AuNPs are adsorbed to polymer brushes in varying conditions investigating the fundamentals of the composite formation process. Firstly, the response of both individual components to varying salt concentrations is examined by UV-vis spectroscopy and ellipsometry before the composite material is considered. For the latter, AuNPs of different sizes are adsorbed to polymer brushes, whereby the salt concentration of the AuNPs suspension is changed at different points of time during the adsorption process. Since the aggregation behaviour of AuNPs is changed by the salt concentration even after adsorption has happened, the AuNP distribution is influenced, which can be measured with UV-vis spectroscopy.

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Quantum dot layers for high-order harmonic generation

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Colloidal semiconductor nanocrystals like quantum dots (QD), nanorods, nanoplatelets etc. are of interest to a broad range of optical and electronic applications having electronic properties which are tuneable by variations in size and shape and showing discrete energy levels due to spatial quantization of electron and hole motion instead of a band structure as in the bulk. Fabrication of optoelectronic devices; photovoltaic cells, photodetectors, LEDs using colloidal nanocrystal has been addressed in the last few years. Further, these structures are of highest interest in non-linear optical (NLO) applications.

The process of high-order harmonic generation (HHG) in solids is sensitive to electronic structure. It was predicted theoretically that the efficiency of HHG in quantum confined structures is significantly enhanced in comparison to bulk solids due to a reduction of quantum diffusion as a result of the reduced density of the available states. In this work we investigate the impact of quantum confinement on the HHG process in layers of QDs addressing the influence of QD size and inter QD coupling. We report on methods to generate thin films from colloidal QDs with various sizes entering different regimes from strong confinement ($r <$ bohr's radius) to weak confinement ($r >$ bohr's radius) with tuneable inter QD coupling via organic surface ligands with different lengths. Conventional steady-state spectroscopy (absorption, PL spectroscopy) along with time-resolved spectroscopy (e.g. transient absorption) delivers information on the degree of coupling between the quantum dots in the generated layers. Additionally, by applying Raman spectroscopy changes in the phonon confinement with QD size and modification of the surface ligands in QDs are monitored. First experimental results on HHG in these quantum dot layers demonstrate the dependence of harmonic spectra on size of the quantum dots reflecting the impact of size dependent electronic structure on the HHG process.

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Examination of the growth mechanism of Sb_2S_3 nanoparticles via hot-injection method

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As a semiconductor with a low bandgap and a high absorption coefficient, Sb_2S_3 has become a promising material for research in the field of photovoltaics. The quality of the solar cells made of Sb_2S_3 nanomaterial regarding application and efficiency strongly depends on the bandgap, morphology, and size of the nanomaterial used. Up to now, the syntheses of Sb_2S_3 nanomaterials lack sufficient control of the growth conditions resulting in nanoparticles with limited control of their size, shape, and crystallinity and hence, sub-optimal optical properties. The current work focuses on examining the growth mechanism to understand how the materials' properties can be controlled. The Sb_2S_3 nanoparticles were synthesized at moderate temperatures (150°C) via the hot-injection method. The relatively low temperature, compared to the frequently used hot-injection methods in literature (180-220°C)[1][2], was chosen to slow down the reaction. This gave a better insight into the different reaction stages. Shortly after the injection, small-sized, amorphous particles (~ 5-10 nm) nucleate which then form aggregates of around 30 nm diameter. These aggregates form even larger aggregates which merge, form superordinated structures, and finally, start crystallizing when the reaction time is increased. The bandgap of the particles depends on their size and crystallization state.

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Quantum Chemical Analysis of Nitrate Doped Sodium Chloride Clusters and Comparison with Experimental Absorption Cross Sections

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Atmospheric aerosols that act as ice nucleating particles (INP) contribute to cloud formation [1]. Reflection, transmission and absorption properties of atmospheric layers are therefore tied to the occurrence of INPs. Sea spray aerosols pose an important source of INPs. Photochemical processes in the atmosphere contribute to the ageing of sea-salt particles.

In this work, we focused on clusters that are composed of the two main ions in sea water, i.e. sodium and chloride, in combination with nitrate, one of the most important dopants of marine aerosols in the atmosphere [2,3]. We measured photodissociation spectra of the clusters using a Bruker APEX Qe 9.4 Tesla Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer. Quantum chemical calculations were performed using both multi-reference (multi-reference configuration interaction, MRCI) and single-reference (equation of motion coupled cluster, EOM-CCSD, and time-dependent density functional theory, TDDFT) approaches. Absorption spectra of those species were obtained in the framework of the reflection principle [4]. The ground state wave functions were sampled within a Wigner distribution and harmonic approximation.

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Morphology of Regular and Irregular Hydrogel using X-ray Scattering Method

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FG nucleoporins are intrinsically disordered proteins located in the nuclear pore complexes (NPCs) consist of FG repeating motifs. It has been proposed that repeating motifs play an important role in the formation of hydrogel due to their cohesive interactions and hydrophobic nature. These protein hydrogels show unique features of non-covalent interactions such as hydrogen bonding, Vander Waals interaction or π-π stacking. These interactions drive the protein self-assembly, leading to an anisotropic structural growth, thus forming hydrogels with unusual materials properties [1]. Our computational simulations, suggest different conformations and interactions between these FG repeating motifs and that these conformational variety may be the driving forces for the co-existing domains. To understand this molecular rationale of the protein kinetics during their gelation process, we have studied the first steps of self-assembling and structural organization of the protein hydrogels during the formation [2]. The studies showed that these hydrogels are composite materials consisting of protein-rich and protein poor domains and the gel formation is led by a hydrophobic collapse. These domains form continuous system of channels within the hydrogels. It suggests that the π-π stacking may create a connection between the secondary structural elements during the hydrogel formation but it is not the driving force as initially hypothesized by the selective phase model. We found a dependence of the assembly kinetics dependent on the chemical composition creating a hydrophobic environment which strongly determines the gelation in the system [3].

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How Hofmeister series influence the thermodiffusion of potassium salts in water?

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Thermal gradients induce a motion of solute molecules towards hot or cold regions. The motion of solutes in a solvent induced by a thermal gradient is termed thermodiffusion. Soret coefficient S_T is used to quantify the ratio of the established concentration gradient to the thermal gradient [1]. This has become an important tool to monitor protein-ligand binding [2,3], as it is very sensitive to the nature of solute-water interactions [1,4]. Buffers, which are used to stabilize the proteins, are multicomponent mixtures with different kinds of salts. Hence to obtain a better understanding of protein-ligand systems, the first step is the investigation of salt solutions. We investigated aqueous solutions of five potassium salts: potassium chloride, potassium bromide, potassium thiocyanate, potassium acetate and potassium carbonate where the corresponding anions cover the full Hofmeister range. We study the thermophoresis of all salt solutions between 15 to 45^oC in a molality range between 1 – 5 mol/kg using thermal diffusion forced Rayleigh scattering. We examine, in particular, whether the correlations found for non-ionic solutes [5] are carried over to ionic solutes. Our results are discussed in the context with the ionic and hydrogen bonding contributions to thermophoresis. This study shows how sensitive the thermophoretic phenomenon is to the ion species and its position in the Hofmeister series and how a change of the ion influences thermophoretic properties [6].

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Creating and controlling cryogenically-cooled beams of shock-frozen, isolated, biological and artificial nanoparticles

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Single-particle diffractive imaging (SPI) is emerging as a new technique for the three-dimensional (3D) imaging of aerosolized nanoparticles at x-ray free-electron lasers (XFELs). However, one of the primary bottlenecks in realizing SPI is the efficient delivery of isolated, reproducible target particles into the x-ray focus [1]. Here, we present novel approaches for the production of cold and high-density beams [2] of a broad variety of biological nanoparticles, ranging from single-domain proteins, including membrane proteins, to multi-subunit protein complexes and molecular machines, designed for use in XFEL experiments. This will also enable us to gain a better understanding of the ultrafast dynamics across extended biological systems. Fast freezing from ambient temperature to 10 K in less than 10 μs will help freezing room-temperature equilibrium state distributions and even the trapping of reaction intermediates.

Furthermore, we have developed a numerical simulation infrastructure that allows quantitative simulation of particle trajectories through the setup [3]. This allowed us to improve injection geometries and build aerosol injection systems optimized for specific particle sizes in order to produce the highest-density particle beams [2, 4]. We propose an optimized setup with cooling rates for few-nanometers particles on nanoseconds timescales. The produced beams of shockfrozen isolated nanoparticles provide a breakthrough in sample delivery, e.g., for diffractive imaging and microscopy or low-temperature nanoscience. The produced cryogenically-cooled particle beams can subsequently be further manipulated and controlled using electric [5] or optical fields, such as hollow-core vortex laser beams [6].

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Selection and control of (bio)nanoparticles with electric fields

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Single-particle imaging (SPI) experiments at free-electron lasers (FELs) promise high-resolution-imaging of the structure and dynamics of nanoparticles and macromolecules. Guiding sample particles into the focus of an FEL, diffraction patterns of individual particles can be collected. Sufficient amounts of patterns of identical nanoparticles are needed to overcome the inherently small signal-to-noise ratio and reconstruct the underlying 3D structure [1,2]. Optimized delivery of identical nanoparticles is key to efficient and successful SPI experiments.

Here, we present approaches for the production of purified high-density beams of a broad variety of biological nanoparticles. We establish control through electric fields, aiming at charge state or conformational state selectivity [3]. This is especially relevant for soft biological samples, such as proteins or protein complexes, which in uncontrolled environment are prone to structural instability [4]. We also discuss the possibilities to align nanoparticles in space to avoid the particles' arbitrary orientation in the diffraction experiment. Here, we build upon our expertise in the laser alignment of small molecules [5,6]. Furthermore, we characterize and improve sample aerosolization and injection methods, i.e., injection geometries [7] and setups optimized for specific particle sizes in order to produce high-density particle beams [8,9].

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Albumin Displacement at the Air/Water Interface by Polysorbate

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Polysorbate 20 (PS20) and 80 (PS80) are surfactants used for the development of parenteral protein drugs, due to their benefit safety profile and stabilisation properties [1]. To elucidate the mechanism, by which PS20 and PS80 stabilise proteins in aqueous solutions, either by a "direct" protein to surfactant interaction and/or by an interaction with the protein film at the air/water interface, we used spectroscopic (Infrared Reflection Absorption Spectroscopy, IRRAS) and microscopic techniques (Brewster Angle Microscopy, BAM) in combination with surface pressure measurements [2,3]. To this end, the impact of both Tweens with regards to the displacement of the protein from the air/water interface was studied. As model protein, human serum albumin (HSA) was used.

The results for the displacement of the adsorbed HSA films by PS20 and PS80 can partially be understood on the basis of an orogenic displacement mechanism, which depends on the critical surface pressure of the adsorbed protein film. With increasing concentration of Tween in the sub-phase, BAM images showed the formation of different domain morphologies. IRRA-spectra supported the finding that at high protein concentration in the sub-phase, the protein film could not be completely displaced by the surfactants. Comparing the impact of both surfactants, we found that PS20 adsorbed faster to the protein film than PS80. The adsorption kinetics of both Tweens and the speed of protein displacement increased with rising surfactant concentration. Tween 80 reached significant lower surface pressures than Tween 20, which lead to an incomplete displacement of the observed HSA film.

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Switchable Nanostructures of piezoelectric Polyamide 11

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Different plants, algae[1] and animals like silverfish[2] and butterflies[3] obtain their brilliant colouration due to structural colours. Those structural colours appear as a result of the interaction between light and a periodic nanostructure, so called photonic crystals.[4]

The upper layer of the skin of a panther chameleon consists of such photonic band gap materials based on guanine crystals embedded into cytoplasm and different pigments. Emotions of the chameleon evoke a variation in colour by changing the crystal distances, and thus, the interference pattern.[5]

The processes of the chameleon skin will be mimicked with the help of polymers (biomimetic equivalent to cytoplasm) and plasmonic gold nanoparticles (biomimetic equivalent to guanine crystals).[5]

Switchable polymer nanomaterials can be obtained via a template controlled synthesis[6] and later on combined with spherical gold nanoparticles. As a basic compound the monomer 11-Aminoundecanoic acid is used to synthesize piezoelectric Polyamide 11 (also known as Nylon 11).

The aim is to fabricate innovative biomimetic hybrid materials with the help of the above-mentioned systems to combine plasmonics with piezoelectricity.

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Colors in nature: a Science Project Day in High Schools

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Nature is full of colors which originate from natural and synthetic pigments,[1] nanostructures, interference effects[2] and also bioluminescence.[3] In particular, regular structures from nanomaterials to be found in animals (e. g. blue morpho butterfly[2]) and plants (e. g. peacock fern [4]) lead to so called structural colors.[2]

The panther chameleon *furcifer pardalis* has two layers of skin consisting of pigments and structural colors.[5] Due to variations of the nanostructure spacings inside the upper layer the chameleon is able to change its coloration as the conditions for interference effects are modified.

In contrast, the principle behind bioluminescent colors are very different. The comb jellyfish *mnemiopsis leidyi* is able to produce its own light by an enzymatic intermolecular reaction. Here, the protein coelenterazine reacts with molecular oxygen and calcium and disintegrates into CO_2 and coelenteramide.[6] The result is a cold blue light, known as bioluminescence.[6]

These everyday phenomena occur nearly everywhere. To give students an understanding of these different physical, chemical and biological processes in their environment, a school's project day for natural sciences focussing on colors of chameleons and jellyfish will be presented.

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Polysorbate photooxidation and the impact on protein stability

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Protein drugs can be degraded through light exposure (1) e.g. during production, storage and clinical application. In these situations, formulation components such as the active pharmaceutical ingredient and co-solutes are exposed to various light conditions which might lead to a broad variety of degradation processes (1). Since none of the pharmaceutical ingredients significantly absorb light in the UV-A (315-400 nm) and visible range (400-800 nm) of the electromagnetic spectrum, the initiating mechanism of photodegradation in these wavelength ranges remains unclear, as well as the underlining photo-degradation mechanism(s) (2). In literature, some impurities from the manufacturing process are described as photoactive compounds, which may act as photosensitizers (2, 3). For example, photosensitizers such as remaining riboflavin impurities from cell culture process are known to absorb light in the visible range (3). These species may start the photodegradation processes via formation of reactive oxygen species (ROS). However, there are limited studies on pharmaceutical co-solutes such as polysorbate, which can cause photodegradation of biopharmaceutical formulations (3). Hence within the UV-A and visible spectral range, we investigated studies how photodegradation processes mediated by polysorbate are influenced by light wavelengths. Degradation products can be determined by a broad variety of analytical techniques, whereas the formation of ROS was investigated via electron spin resonance spectroscopy."

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Conformation and orientation of LKα14 in water/ethanol mixtures

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Solvation is an important factor in the determination of the structure and functionality of proteins. Since it is difficult to investigate for proteins or even large peptides, small model peptides are used instead when studying solvation effects in general. We have used MD simulations to study a model peptide, LKα14, both in the bulk and at the solution/air interface in different mixtures of ethanol and water.

LKα14 has been shown to adsorb to the air/water interface, to assume an α-helical conformation, and an orientation parallel to the interface there [1-3]. Our simulations show that in ethanol the peptide does not adsorb to the surface and that in ethanol/water mixtures the adsorption is stronger the more water there is in the solution. The simulations also show that the more ethanol there is in the solution, the less the orientation parallel to the surface is preferred.

In contrast to its behaviour at the air/water interface LKα14 has no well-defined secondary structure in water bulk [1,4]. Our simulations show that in ethanol bulk the peptide assumes an α-helical conformation and that in ethanol/water mixtures α-helical structure is also the dominant secondary structure.

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ATP-peptide interactions studied by MD

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Recently, it was experimentally shown that the solubility of proteins in water can be enhanced by the addition of adenosine triphosphate (ATP) [1]. To investigate the underlying molecular interactions, we performed molecular dynamics (MD) simulations of ATP and homopeptide chains composed of glycine, tryptophan, lysinium and glutamate [2]. The potential of mean force (PMF) as a function of the ATP-peptide distance was calculated using umbrella sampling. Splitting of the interaction energy into a van der Waals and a Coulomb contribution gives further insight into the mechanism of the solubility enhancement. The analysis reveals that ATP is attracted to all studied proteins. This suggests that the enhancement of the protein solubility might stem from the affinity of ATP to the protein surface. Further analysis show that the adsorption of highly charged ATP leads to a build-up of electrostatic barriers in the effective protein-protein interaction which can prevent the aggregation of proteins in certain cases.

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Remote near infrared identification of pathogens with multiplexed nanosensors

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Infectious diseases are worldwide a major cause of morbidity and mortality. Fast and specific detection of pathogens such as bacteria is needed to combat these diseases. Optimal methods would be non-invasive and without extensive sample-taking/processing. Here, we developed a set of near infrared (NIR) fluorescent nanosensors and used them for remote fingerprinting of clinically important bacteria. The nanosensors are based on single-walled carbon nanotubes (SWCNTs) that fluoresce in the NIR optical tissue transparency window, which offers ultra-low background and high tissue penetration. They are chemically tailored to detect released metabolites as well as specific virulence factors (lipopolysaccharides, siderophores, DNases, proteases) and integrated into functional hydrogel arrays with 9 different sensors. These hydrogels are exposed to clinical isolates of 6 important bacteria (*Staphylococcus aureus*, *Escherichia coli*, …) and remote (≥25 cm) NIR imaging allows to identify and distinguish bacteria. Sensors are also spectrally encoded (900 nm, 1000 nm, 1250 nm) to differentiate the two major pathogens *P. aeruginosa* as well as *S. aureus* and penetrate tissue (>5 mm). This type of multiplexing with NIR fluorescent nanosensors enables remote detection and differentiation of important pathogens and the potential for smart surfaces. [1]

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Crystalline materials based on novel *T. maritima* encapsulin variants

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Using an innovative design approach with two oppositely charged protein containers as building blocks, a new type of protein-based material will be realized. Surface charged protein containers can be combined with inorganic compounds to unite biological features with the chemical and physical properties of abiotic materials. In particular, protein containers, with their inherent ability to encapsulate cargo molecules, are perfect platforms for the generation of multifunctional assemblies.[1, 2] Inorganic nanoparticles can be combined with biomolecules to unite properties of both materials. For the assembly of biohybrid materials based on protein containers, their inorganic cargo must be encapsulated into the protein container. Gold nanoparticles can be decorated with a small number of encapsulin cargo-loading peptides to fill protein containers. By lock-and-key interaction between the peptides and the peptide-binding pockets on the inner container surface, the nanoparticles will be encapsulated with high efficiency.[3] With the recent advances in computational redesign of protein containers, it is now possible to combine these results with nanoparticle synthesis and protein crystallography. Recently initial synchrotron data was collected and analyzed. Depending on crystallization condition we can tune the crystal structure. Because the protein scaffold is independent of the nanoparticle cargo, this modular approach will enable tuning of the optical properties by choice of nanoparticle content, assembly type and protein container type. For future applications, surface charged protein containers will be used as sustainable building blocks for bioinorganic nanomaterials.[4]

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Development of thermophoretic µ-device for measuring Soret coefficient

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Thermophoresis is the mass transport induced by a temperature gradient where the Soret coefficient S_T is a measure for the established concentration gradient in a temperature gradient. It has gained a lot of interest in the biotechnology to monitor the binding between proteins and ligands [1]. To obtain quantitative thermophoretic parameters in those complex systems, the existing methods are not suitable as they are limited to binary mixtures or consume large sample amounts in the order of 30-50 mL. Recently, a thermophoretic lab-on-a-chip device with a small sample volume of 10 µL was developed to measure S_T using a confocal microscope. With a microwire for heating, large temperature gradients up to ~10^6 K/m could be achieved [2]. However, a 3D temperature profile around the wire complicated the analysis for determining S_T. To overcome the drawback of this chip, we propose a thermophoretic µ-device with a 1D temperature profile. In this instrument a measurement channel with a sample volume of 20 µL lies between a heating and cooling channel. Temperature gradients up to ~10^4 K/m can be achieved. Using a confocal microscope, the temperature profile is measured by fluorescence lifetime imaging microscopy (FLIM) with Rhodamine B (RhB) and the concentration is determined from the fluorescence intensity. Fluorescent polystyrene particles with a diameter of 25 nm are used for comparing S_T to a validated optical method (Thermal Diffusion Forced Rayleigh Scattering (TDFRS)) [3] and the recently developed thermophoretic chip [2]. S_T probed by the developed device agrees within the uncertainty with TDFRS and thermophoretic lab-on-a-chip measurements.

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CNF thin films as sustainable carrier material and their role in layered systems

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Sustainable carrier materials will play an important role in the design of future functional items. One matching candidate for that purpose are cellulose nanofibrils (CNF). CNF are a wood-based, flexibel and lightweight material which can also be transparent when deposited as thin films.

Spray deposition is a suitable technique to fabricated such thin films. With this method it is possible to fabricate large scale, homogeneous films with a ultra-low roughness. At the same time this technique can be used to functionalize the fabricated CNF layers and to establish layered multi-component systems.

The fabrication and structural properties of such thin, layered structures are be studied with grazing incidence small angle X-ray scattering (GISAXS). In detail, the deposition of conductive silver nanowires as flexible electrodes, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as blocking layer and of the photoactive layer poly(3-hexylthiophene) and [6,6]-phenyl C61-butyric acid methylester (P3HT:PCBM) on nanostructured CNF thin films was studied in situ using GISAXS. Possible guiding, supportive or favouring effects of CNF as carrier material could be observed and insights into the interactions between the layers of CNF and the functional materials could be gained.

Silver nanospheres and nanostars for surface-enhanced Raman spectroscopy in the biosciences

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We describe the synthesis of silver nanoparticles, depending on the synthesis route nanospheres or nanostars, and their characterisation. We show that huge enhancement factors for Raman scattering of species interacting with the nanoparticles' surface are achieved, in excess of three orders of magnitude in a home-built Raman spectrometer. First applications of this surface-enhanced Raman spectroscopy (SERS) are demonstrated in the biosciences, with Raman spectra obtained for different bacteria and different strains. Due to its high sensitivity, SERS opens up opportunities for analytical detection of harmful bacteria. Since SERS essentially measures Raman active species attached to or in close vicinity of the nanoparticle surface, the assignment of Raman spectra allows the identification of species and components of the cell wall. This enables mechanistic studies of the interaction of bacteria with antibiotics, to mention just one highly relevant application.

In this contribution, we report our progress in applying SERS with silver nanoparticles to characterise bacterial suspensions and to gain insight into the mechanisms of the action of various antibiotics against bacteria, using *E. coli* as a model system.

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Long-path FTIR and CERS Raman Analysis of Volatiles Produced in the Respiration and Fermentation of Bananas

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Many different volatiles are produced in fruit ripening processes under aerobic (respiration) and anaerobic (fermentation) conditions. Monitoring of trace gas levels is thus very important for applications in biosciences and biotechnology. For instance, oxygen and carbon dioxide are frequently monitored online in bioreactors. Oxygen availability is a key parameter for aerobic bioprocesses as well as anaerobic systems that are sensitive to disruption by oxygen. Real-time, *in situ* gas detection can also give metabolic and mechanistic insights into the metabolism of fruit ripening. Gases can be detected in the headspace above fruit samples by techniques such as gas chromatography or mass spectrometry. Alternatively, laser spectroscopy offers distinct advantages as allowing laser light to pass through the headspace is both non-intrusive and requires no sampling.

We have recently introduced a new, highly sensitive technique for detecting Raman active species in the gas phase, cavity-enhanced Raman spectroscopy (CERS) [1]. Coupled with long path FTIR spectroscopy in a White cell, this allows the monitoring of key species during metabolic activities in biophysics, molecular biology and biotechnology [2]. In this poster contribution, we will introduce an application of our approach to study the ripening of banana and the transition from aerobic respiration to anaerobic fermentation.

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An Atomistic View of Solvent-Free Protein Liquids: The Case of Lipase A

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Solvent-free enzymes hold the promise of being able to deliver higher activity at elevated temperatures by virtue of them being not limited by the boiling point of the solvent. They have been realized in the liquid phase through a polymer surfactant coating on the protein surface.[1,2] However, a clear understanding of intermolecular interactions, structure, dynamics, and the behavior of the minuscule amount of water present in the solvent-free protein liquid is essential to enhance the activity of these biofluids. Using extensive atomistic molecular dynamics simulations of the hybrid liquid of Lipase A enzyme, we demonstrate that the inter-protein structure is comparable to inter-particle correlations in a noble gas fluid, after appropriate scaling of distances; the hydrophilic parts of the surfactants form a coronal layer around each enzyme which percolates through the liquid, while their hydrophobic parts form disjointed clusters embedded in this layer. Inter-surfactant interactions, determined to be attractive and in the range of -200 to -300 kcal/mol, stabilizes the liquid state. While the protein retains its native state conformational dynamics in the solvent-free form, the fluxionality of its side chains is much reduced; at 333K, the latter is found to be equivalent to that of the enzyme in aqueous solution at 249K. Despite the sluggishness of the solvent-free enzyme, some water molecules exhibit high mobility and transit between enzymes primarily via the interspersed hydrophilic regions. These microscopic insights offer ideas to improve substrate diffusion in the liquid to enable the enhancement of catalytic activity.

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Low-energy electron interactions with 5-aminoimidazole-4-carboxamide

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Low energy electrons (LEEs) play an important role in molecular chemistry. Moreover, reactions triggered by electrons can determine fragmentation routes and represent a tool in drug design. In fact, DNA damage in living systems caused by ionizing radiation may be attributed to secondary electrons interactions with DNA components or with surrounding water molecules leading to bond dissociation and consequent loss of DNA integrity [1,2]. Temozolomide (TMZ) is an alkylating agent indicated for the treatment of adults with newly diagnosed glioblastoma multiforme concomitantly with radiotherapy and then as maintenance treatment [7]. In the molecular acting mechanism, 5-aminoimidazole-4-carboxamide (AIC) is formed as a sub-product of TMZ, which is hypothesized to be a potential radiosensitizer.

It is suggested that AIC is fundamental for the effectiveness of the electron-induced DNA strand breaks. Therefore, we determined the DNA strand break cross sections of oligonucleotides incubated with AIC upon electron irradiation at 7eV using the DNA origami technique. After irradiation the remaining intact target strands are labelled with streptavidin in order to visualize them in atomic force microscopy (AFM). In addition, complementary DEA gas phase studies are going to be performed using a crossed electron-molecule beam apparatus equipped with a trochoidal electron monochromator and a reflectron time of flight mass spectrometer. Preliminary results demonstrated that there is a significant increase of the absolute cross-sections for irradiation-induced DNA strand breaks at 7eV that is comparable to halogenated nucleobases [4,5].

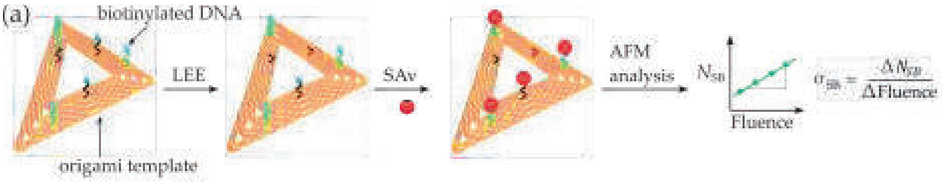

Figure 1: Scheme of the DNA origami technique to determine absolute cross-sections

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Testing the Limitations of MD Force Fields For the Quantification of Local Electric Fields Using the Vibrational Stark Effect in Solution: Pencillin G as a Test Case

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Electrostatics are one of the major physical forces that govern the strength of non-covalent interactions in processes ranging from solvation to molecular events in enzymatic catalysis. As such, traditional experimental observables, such as solvation energies, binding constants, and enzymatic rates, among many others, are often described as having a significant electrostatic origin. Unfortunately, it is rarely possible to deconvolute experimental observables precisely into a set of relevant local atomic interactions. As a consequence, molecular dynamics (MD) simulations have been routinely used to quantify contributions of local atomic interactions, asserting an accurate extrapolation of carefully parameterized MD force fields. Here, we demonstrate the limitations in fixed-charge and polarizable (AMOEBA) MD-based determination of local electric fields in solution via a comparison with the experimental vibrational Stark effect (VSE) of the β-lactam C=O stretch of penicillin G (PenG) and its derivatives. We identify these discrepancies as being due to a) conformation-dependent intramolecular electrostatic effects and b) considerably overestimated MD-derived local electric fields with routine water models in proximity to charged functional groups; the latter did not improve consistently using advanced water models. These observations point to insufficiently accurate MD parameters for structurally flexible and charged solute molecules as well as routinely used water models. At the same time, this work highlights the usefulness of the VSE for direct, experiment-guided refinements of MD force fields providing quantitative insight into the local electrostatics of non-covalent interactions in various environments.

InPd/Indiumoxide Aerogels for Methanol Steam Reforming

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The material class of aerogels exhibits many suitable properties for catalysis, for example a large specific surface area, large pore volume and a fine structure that consists of nanoparticulate components. This allows for the synthesis of homogeneous hybrid materials for the use in heterogeneous catalysis, which cannot be produced as consistently in the bulk material. In materials such as the presented, the interaction between the oxidic matrix and the intermetallic component is enhanced by the high contact surface area, which is accomplished by the nanoparticulate nature of the aerogel.[1] On this poster we present the synthesis of Palladium loaded Indium oxide aerogels beginning with an epoxide-assisted sol gel process, the following steps of activating the material, the preparation for catalysis and finally the results of the catalytic testing in methanol steam reforming. The gels are characterized by powder x-ray diffraction, nitrogen adsorption experiments, electron microscopy and dynamic scanning calorimetry coupled with thermogravimetric analysis and mass spectrometry.

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Nanoparticle substrate interactions: thermal treatment of gold nanoparticle arrays on different silicon-based substrates.

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The fabrication of nanoscale materials has been intensively studied for decades due to their special optical and electronic properties. Nowadays, a wide variety of different fabrication strategies is available. However, the full potential of subsequent modification of the fabricated nanomaterials by energy exposure has not been exploited yet - even though promising results have already been published.[1,2]

In this work, wet-chemically synthesized gold nanoparticle (Au NP) arrays were deposited on various silicon-based substrates and then thermally annealed. Temperatures at and above the glass transition temperature (T_g) of the selected silicon-based substrates were chosen for these studies. Annealing of the AuNP arrays at T_g caused the particles to sink into the substrate. This process was observed spectroscopically by monitoring changes in the spectral position of the localized surface plasmon resonance of the Au NPs. According to AFM measurements, the particles sank ~20 nm into the substrate.

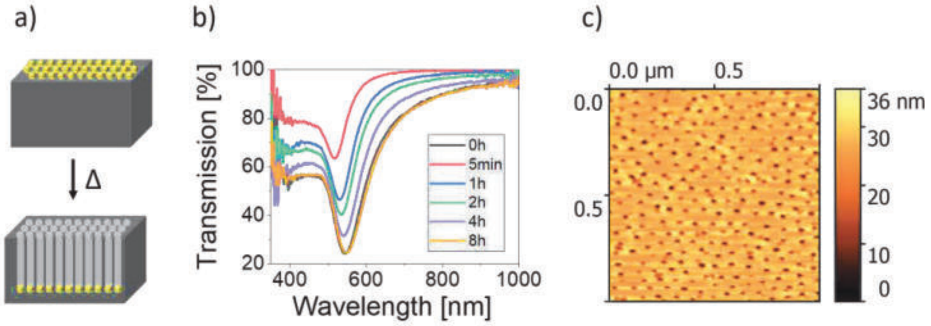

Figure 1: a) Schematic representation of AuNP arrays on silicon-based substrates before and after thermal treatment; b) transmission spectra of AuNP arrays on silicon-based substrates thermally annealed at 525 °C; c) AFM image of AuNP arrays on silicon-based substrates after thermal annealing at 525 °C for 8h and acqua regia treatment.

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The effect of atomic steps and oxygen coverage on the desorption rates of NH_3 and NO from Pd(111) surface

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Knowing rate of catalytic reactions is crucial for any technologically relevant process and it is therefore essential to understand how the reaction rate can be manipulated and quantified for potential catalytic systems. The catalyst's abilities to accelerate a chemical reaction is influenced by surface properties like atomic steps or co-adsorbed atoms and promoting molecules. The influence of both effects can be studied by determining the binding energies of potential reactants and products.

In this work we investigate NH_3 and NO desorption between 380 and 800 K from Pd(111) using molecular beam surface scattering and velocity resolved kinetics[1]. Besides the determination of binding energies on atomically flat and stepped surface, we investigate the effect of co-adsorbed oxygen on the desorption of NH_3 and NO. Since both molecules are unreactive at Pd(111) or O/Pd(111), we exclude parallel reactions and measure only the effect of the desorption rate. Investigation of the effect of atomic steps using desorption rates from Pd(332) reveals that NH_3 energetically prefers binding to steps rather than to terraces. NO does not show energetic preference for steps. In case of oxygen exposed surface, we observe an increase of NH_3 binding energy and a decrease of NO binding energy. The stabilization of surface bound NH_3 can be explained with hydrogen bonding to neighboring oxygen atoms. The labialization of NO is probably due to oxygen atoms blocking the most stable binding sites (fcc, hcp) of NO. In such a way, NO is forced to switch to a less stable binding site (top). The observed cooperative effect of reactant stabilization and product labialization indicates that oxygen atoms on Pd act as a potential reactant and a promoter at the same time.

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Catalytic performance studies of Amine-stabilized and Ligand-free Platinum Nanoparticles supported on Titania

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The selective hydrogenation of α,β-unsaturated aldehydes and ketones is a challenging task in heterogeneous catalysis. In this context, the hydrogenation of furfural and its derivates on supported Pt catalysts is of technical interest, due to its sustainable availability and its potential as platform compound.[1]

Spectators can play a key role in controlling the selectivity in the hydrogenation of α,β-unsaturated aldehydes, which has already been shown for the hydrogenation of acrolein on Pd(111) and Pd nanoparticles supported on Fe_3O_4.[2]

Before studying the influence of spectators on the selective hydrogenation of 5-methylfurfural, the hydrogenation of cyclohexene was used as model reaction for testing the catalytic activity of the platinum catalysts. Here, 1.6 nm and 2.8 nm amine-stabilized platinum nanoparticles on Titania showed a higher activity compared to the ligand-free platinum catalyst.

However, no conversion of 5-methylfurfural could be observed for all catalysts, even after variation of support, stirring rate, solvent and temperature.

In order to elucidate poisoning effects by 5-methylfurfural, the catalyst was checked for possible electronical and structural changes before and after reaction by Fourier-transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

When competing with the hydrogenation of cyclohexene, it can be shown that 5-methylfurfural poisons the catalyst in the temperature range investigated below the decomposition of the amine ligands.

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Generating defects in titania under ambient pressure and UHV for (photo-)catalysis

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Due to its high (photo-)catalytic activity in the purification of air and water[1] as well as the activation of small organic molecules such as methanol[2] and benzaldehyde[3] titanium dioxide (TiO_2) has a wide range of use in the chemical industry. This widespread use also stems from its non-toxicity and earth abundance.

Improving the (photo-)catalytic properties of TiO_2 is therefore a very important topic, not only in view of its unfavourable band gap, but also because defects enhance the catalytic activity.[2],[3] Band gap doping by introducing different defects like oxygen vacancies or Ti^{3+} and Ti^{2+} states is a common approach to enable the use of visible light including solar irradiation for photocatalytic reactions.[4] Under ultra-high vacuum conditions, TiO_2 Rutile (110) single crystals can be reduced via argon ion bombardment.[5] In ambient pressure or higher pressure regimes, calcination of powders in presence or absence of hydrogen can be used to achieve a sufficient reduction.[6] A photocatalytic way to reduce TiO_2 by producing Ti^{3+} states is to utilize UV-radiation in a methanol stream.[7] To further improve this system, oxide cocatalysts that interact with defects can be introduced.[8]

In this work we present studies on the reduction of different titanium dioxide substrates under ambient pressure as well as ultra-high vacuum conditions. For this purpose, the results of different reduction methods were compared. The process was monitored and further characterized via x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and electron microscopy (TEM and SEM). As a model for mixed catalytic systems, the combination with copper oxide shall be investigated.

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Desorption of alcohols from rutile TiO_2 – Comparative Testing of Analysis Methods for Thermal Desorption Spectroscopy

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To gain information about processes on the surface of heterogeneous model catalysts, thermal desorption spectroscopy (TDS) is a widely used method. [1] Quantitative analysis of coverage-dependent TDS spectra can yield more information about the adsorbates, such as the activation energy, the pre-exponential factor or the desorption order. Several papers summarize and evaluate analysis methods for TDS, mostly for desorption from metal surfaces. [2-3]

A more comprehensive view onto the analysis of TDS spectra for oxide surfaces will be presented. [4-5] For this purpose, we investigate the desorption of alcohols from the rutile TiO_2 (110) surface under ultrahigh vacuum (UHV) conditions, specifically, the desorption of methanol and isopropyl alcohol. Especially, the impact of a different signal to noise ratio and coverage calculation errors are addressed. We shall present a comparative overview about the most important TDS analysis methods either based on Arrhenius-like approaches, peak shape analysis or peak temperature measurements and elucidate their performance for desorption from the TiO_2 surface.

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Selective Oxygen Functionalization of the *h*-BN/Rh(111) Nanomesh

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2D materials such as hexagonal boron nitride (*h*-BN) and graphene are interesting due to their unique structural, chemical and electronic properties or as inert template structures. As a structural graphene analogue *h*-BN features a honeycomb structure. The morphology of a supported *h*-BN layer strongly depends on the underlying crystal surface, i.e. on the interaction strength and lattice mismatch between 2D material and support. In the case of Rh(111) as substrate, a Moiré pattern with pore and wire regions evolves, also known as nanomesh.[1] Chemical modification, e.g. covalent functionalization with hydrogen and oxygen, of Ni(111) supported *h*-BN has already been reported [2,3]. In the case of the *h*-BN nanomesh on Rh(111), such functionalization is especially interesting since the pores and wires may show different reactivity towards functionalization enabling spatially defined modification of *h*-BN.

Herein, we present detailed studies on the adsorption of molecular oxygen on the *h*-BN nanomesh on Rh(111). Using synchrotron radiation-based in situ high-resolution X-ray photoelectron spectroscopy we are able to provide a deep insight in this system regarding the adsorption behavior and the thermal stability of the covalent functionalization. Oxygen functionalization is performed via a supersonic molecular beam and is found to be an activated process occurring selectively in the pores of *h*-BN. The adsorbed oxygen is proposed to bind molecularly to two boron atoms in the pores of the Moiré. It is stable up to about 600 K.

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Reactivity and Passivation of Fe Nanoclusters on h-BN/Rh(111)

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Iron is a nontoxic and affordable element, which shows high catalytic activity. Iron containing catalysts are used in important industrial reactions, such as the Fischer-Tropsch synthesis and the Haber-Bosch process. Especially, iron nanoclusters are of interest because of their potential utilization in electrochemical devices or high-density data storage applications due to their magnetic properties.

To obtain monodisperse, ordered Fe nanocluster arrays, h-BN was used as a template on the Rh(111) surface. Due to the lattice mismatch, differences in the strength of interaction between the h-BN sheet and the Rh(111) surface occur, leading to corrugation of the nanosheet and the formation of pores and wires.

We studied Fe nanocluster arrays formed in the pores of h-BN/Rh(111) using in situ high-resolution X-ray photoelectron spectroscopy. CO was used as a probe molecule to investigate the morphology, such as the available adsorption sites and the reactivity of the nanoclusters. On the as prepared Fe clusters, CO was adsorbed at on-top and hollow/edge sites and dissociated at 300 K. For the C and O pre-covered Fe nanoclusters, we found a passivation of the catalytic activity as a result of adsorption site blocking, allowing for the determination of the most active sites of the Fe clusters.

Keto-enol tautomerization as a first step in hydrogenation of carbonyl compounds.

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Heterogeneously catalyzed hydrogenation of carbonyl compounds is a challenging chemical transformation for a variety of industrially relevant processes. Recent theoretical calculations predicted a significant lowering of the activation barrier in this process for the reaction pathway occurring in two consecutive steps: keto-enol tautomerization to enol followed by a low-barrier insertion of hydrogen into the C=C bond. However, the enol form of carbonyl compounds is normally thermodynamically less stable and quickly undergoes tautomerization back to ketone.

In this report, we explore the possibility of the enol-driven hydrogenation pathway and present a detailed mechanistic study on hydrogenation of acetophenone over well-defined Pt (111). We provide for the first time a clear experimental evidence that keto-enol tautomerization is a first crucial step in hydrogenation of the C=O bond in acetophenone, which agrees with the theoretical predictions.

We employ a rigorous surface science approach involving a unique combination of multi-molecular beam techniques, in-operando IRAS and STM to investigate the chemical nature and obtain a real space information on the reaction intermediates.

Specifically, we show that the absolute majority of acetophenone forms ketone-enol dimers under the reaction-relevant conditions, in which the normally unstable enol form is stabilized on the surface by strong hydrogen bonding between the OH-group of enol and the C=O group of ketone.[1,2] We demonstrate that the target process – hydrogenation of the carbonyl group – occurs not in acetophenone monomers but in the ketone-enol dimers and results in the formation of a partly hydrogenated acetophenone species attached via the hydrogen bonding to the second acetophenone molecule. The spectroscopically derived reaction intermediates suggest that the most likely reaction mechanism is based on the two-step process: formation of stabilized ketone-enol dimers followed by hydrogenation of the C=C bond in the enol part of the dimer.

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Influence of Lewis acidity of promoting metal oxides on the gas-phase hydrogenation of nitrobenzene

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Recently, state-of-the-art characterization techniques allowed the correlation of the reducibility and Lewis acidity of transition metal oxides with their promoting properties in methanol synthesis.[1] The addition of transition metal oxides to noble metal catalysts or support doping with nitrogen has a significant influence on the catalytic activity in nitrobenzene hydrogenation as well.[2,3] In the present study, we found evidence that the promoting effect of metal oxide layers may involve the direct participation of the reduced promoter in the surface mechanism of nitrobenzene hydrogenation by facilitating the abstraction of oxygen atoms from the nitro group.

The catalysts were synthesized by depositing Pd as the active metal via wet impregnation on the TiO_2 support, followed by the addition of the promoting metal oxides via grafting (i.e., V, Mn, Mo, Nb). The $V/Pd/TiO_2$ catalyst exhibited the highest steady-state conversion of NB at 240 °C, whereas the other catalysts were significantly less active. The $V/Pd/TiO_2$ catalyst showed the strongest gain in conversion with increasing temperatures, revealing a strong Arrhenius dependence of the NB hydrogenation rate. The Pd/TiO_2 and $Mn/Pd/TiO_2$ catalyst exhibited a similar temperature dependence. However, the Nb- and Mo-promoted catalysts performed significantly worse compared with the other catalysts. On the promoted pre-reduced Pd/TiO_2 catalysts, temperature-programmed pyridine desorption was investigated by applying DRIFTS in a heated Harrick cell. Pyridine was most strongly bound on the highest active $V/Pd/TiO_2$ catalyst, whereas a lower acidity was observed for the $Mn/Pd/TiO_2$ and the Pd/TiO_2 catalysts. From a mechanistic standpoint, a high Lewis acidity is assumed to increase the rate of abstraction/ transfer of the oxygen atoms from the nitro group of nitrobenzene to the metal oxide layer.

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Model catalysis with SCILLs: How does the ionic liquid layer change adsorption, desorption and surface reaction?

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Solid catalysts with ionic liquid layers (SCILLs) have recently attracted lots of attention since their ionic liquid (IL) coating can give rise to drastic changes of the catalytic activity and selectivity. In this work, we studied the influence of supported IL films on the adsorption behavior and reactivity of Pt(111) single crystal surfaces. Films of the room-temperature ILs [EMIM][NTf$_2$], [C$_4$C$_1$Pyr][NTf$_2$],[1] [C$_4$C$_1$Pyr][OTf], and [C$_4$C$_1$Pyr][PF$_6$] were deposited by physical vapor deposition (PVD) under ultrahigh vacuum (UHV) conditions. For all films, we studied the adsorption of CO by time-resolved and temperature-dependent infrared reflection absorption spectroscopy (TR-IRAS, TP-IRAS). In addition, we probed their permeability for CO by pressure modulation experiments under UHV conditions, and by polarization-modulated IRAS at high pressure (1 bar). All experiments were performed in-situ, i.e. during CO exposure or during thermal treatment.

The [NTf$_2$]$^-$ and [OTf]$^-$ based ILs adsorb specifically to clean Pt(111). If co-deposited onto a CO saturated surface, CO is forced into the more weakly bound bridging configuration to accommodate the strongly binding IL and forms a dense, compressed adsorbate layer. In consequence, the growth of the IL films is locally disturbed and allows for the dynamic adsorption/desorption of CO. A strong Stark shift due to the interfacial electric fields indicates the integrity of the films below to 500 K. For [C$_4$C$_1$Pyr][PF$_6$], we observe the growth of 3D particles on top of a weakly bound monolayer, which upon heating (>380K) dewets to allow for dynamic adsorption of CO. However, defragmentation products prevent the dynamic adsorption of CO shortly after.

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Operando Fischer-Tropsch synthesis on $Fe_3O_4(111)$ using HAXPES

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Magnetite is an ideal material with promising applications in hydrogen production, heterogeneous catalysis, drug delivery and novel nanocomposites [1-2]. The interface between the gas molecules and the distinct facets of magnetite nanoparticles is found to play an important role in the catalytic activity, so it is essential to obtain a comprehensive picture of the interaction of Fe_3O_4 with syngas. Using a combination of operando hard X-ray photoemission spectroscopy (HAXPES) and density functional theory calculations (DFT) we show the reaction intermediates and products under industrially realistic *operando* conditions, bridging the pressure gap between surface science and heterogeneous catalysis. At 500 mbar and 400 °C, the dominant product from Fischer-Tropsch synthesis is methoxy species and short chain alkanes. There is no evidence for aldehyde and ketone formation. Additionally we observe the formation of formate, indicating a competitive water gas shift reaction. The presence of CO_2 in the syngas mixture negatively influences the performance of the catalyst for Fischer-Tropsch synthesis. Morphology and structure of the magnetite surface after *operando Fischer-Tropsch synthesis* were further investigated using scanning probe microscopy, scanning electron microscopy and Low-energy electron diffraction.

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Water at the interface with the photocatalyst Strontium Titanate

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The direct conversion of solar energy to hydrogen is considered as a promising method to produce carbon neutral hydrogen fuel. In 1972 Fujishima and Honda described a first photo electrochemical system capable of generating H_2 and O_2 using a thin-film of TiO_2 [1]. The mechanism of water splitting involves the chemical breakdown of water into hydrogen and oxygen by light [2]. Our research focuses on the mechanistic understanding of the water splitting at the interface between the catalyst and water. Using the surface specific vibrational spectroscopy sum frequency generation (SFG) [3], our final goal is to describe the water splitting process by observing the oxygen-hydrogen bonds conformation along the reaction.

As a first step in the process, we studied the static structure of water at the interface with the photocatalyst Strontium titanate ($SrTiO_3$). From the SFG spectrum of the water-$SrTiO_3$ interface in the OH stretch region, we have been able to describe the water orientation at the interface, the point of zero charge of the catalyst and to observe changes of the hydrogen bonding strength as a function of pH. This study shows a first chemical characterization of the Strontium-water interface by SFG spectroscopy and it is a first step to unravel the dynamics of the photocatalytic water splitting process.

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Reactivity of Molybdenum Sulfide Clusters

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Molybdenum sulfides are very potent hydrogen evolution reaction (HER) catalysts and even have the potential to replace platinum in electrochemical water splitting.[1] Of particular interest are molybdenum sulfide clusters like $[Mo_2S_{12}]^{2-}$ and $[Mo_3S_{13}]^{2-}$, which can be used as homogeneous catalysts in order to enhance the electrocatalytic performance.[2] These clusters can be synthesized from molybdenum oxide using straightforward wet chemistry. In order to find better synthesis routes, the corresponding reaction steps have to be studied.

In our group we utilize electrospray-ionization mass spectrometry (ESI-MS) experiments to monitor the sequential substitution of oxygen with sulfur. Quantum chemical calculations are used to suggest possible reaction steps. Collision induced dissociation (CID) experiments with $[Mo_2S_{12}O_2]^{2-}$ show that the elimination of S_2O is dominant. Possible reaction steps leading to this elimination are determined via quantum chemical calculations. To make the calculations feasible, the calculations are restricted to smaller clusters.

Ion-molecule reactions with weak acids provide insight into charge reduction induced by proton transfer. Proton transfer reactions are studied for the $[Mo_3S_{13}]^{2-}$ cluster with various acids. Quantum chemical calculations are used to model the experimental results.

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Atomically defined model electrocatalysts: Morphological and chemical analysis of Pt/Co_3O_4

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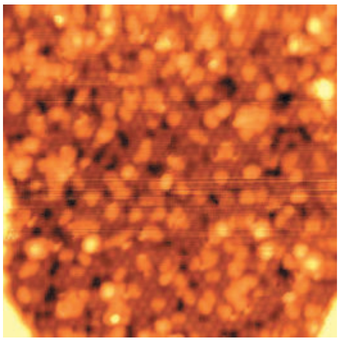
Pt nanoparticles (NPs) stabilized by Co_3O_4 supports are promising electrocatalysts for alcohol oxidation.[1] For a detailed understanding of their functionality, we prepare and study atomically defined model systems.[2-4] Pt NPs of different sizes – from ultrasmall sub-nanometer clusters to conventional NPs of several nm in diameter – were prepared by physical vapor deposition (PVD) on an ordered thin layer of $Co_3O_4(111)$. The systems were investigated by scanning tunneling microscopy (STM) and synchrotron radiation photoelectron spectroscopy (SRPES) under ultra high vacuum (UHV) conditions.



Atomically resolved STM images revealed nucleation of Pt dimers and trimers accompanied by the formation of defects in the $Co_3O_4(111)$ support. In the limit of low Pt coverage, we identified two different oxidation states of Pt species associated with sub-nanometer Pt clusters (partially oxidized $Pt^{\delta+}$ state) and with Pt^{4+} species, which are most likely related to defects. At high Pt coverage, mainly metallic Pt NPs are formed which remain partially oxidized at the interface. Generally, the growth of Pt on $Co_3O_4(111)$ yields a high density of Pt NPs and does not not require specific nucleation sites.

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Tuneable Distance of Nanoplatelets in Semiconductor Nanoplatelet/Polymer Hybrid Structures

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The assembly of nanomaterials to superstructures has been demonstrated to have a strong impact on the properties of those nanomaterials. Due to their highly anisotropic shape, CdSe nanoplatelets (NPLs) are able to self-assemble to stacks resulting in changed optical properties and the existence of charge carrier transport through the stacks.[1,2,3] Here, NPLs are assembled and surrounded by a polymer shell with special emphasis on the variation of the inter-particle distance and its impact on the properties of the resulting assemblies. The NPLs employed are CdSe as well as core/crown and core/shell heterostructures.

The arrangement and especially the distance of the NPLs inside the stacks can be varied by exchanging the native ligands of the NPLs prior to the assembly process. Hereby, the distance of the NPLs could be decreased to under 1 nm and thus, by half in comparison to pristine NPLs.[4] To investigate the influence of the resulting NPL distance on the charge carrier transport properties of the stacks, fluorescence spectroscopy, electrical and photo-electrochemical measurements were performed. The performed ligand exchanges were furthermore investigated through SEM-EDX, XPS and fluorescence spectroscopy.

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Role of Li Adsorption and Intercalation in the MoS_2 Catalyzed Hydrogen Evolution Reaction

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The 1T (octahedral O_h) phase of layered transition metal dichalcogenides (TMDs) has been demonstrated theoretically and experimentally to show excellent catalytic activity for the hydrogen evolution reaction (HER). The conversion of the common 2H (trigonal prismatic D_{3h}) to the 1T phase can be realized via intercalation of cations such as Li^+ or K^+.[1, 2] Although the significant enhancement of the HER activity after ion intercalation was ascribed to the surface reactivity of the metallic 1T-MoS_2 towards tuning the bonding of H_{ads} as well as improved charge transfer kinetics, the role of the alkali cations for HER remains largely unknown.

Here, we prepared 1T-MoS_2 via thermal sulfurization and intercalation of Li cations and correlated the extent of 2H-1T phase conversion as well as the adsorption of Li with HER performance. The influence of Li cations on phase conversion of MoS_2 was investigated by X-ray absorption (XAS) as well as photoelectron spectroscopies (XPS). An obvious shift of 0.9 eV of both Mo 3d and S 2p XPS binding energies to lower values after Li intercalation indicates the transformation of the 2H to the 1T phase. The catalytic properties towards HER were determined in 0.1 M H_2SO_4 and showed an increase of current density after Li intercalation whereby the enhancement depends on the Li content. Further FTIR study of NO adsorption on MoS_2 after Li intercalation was performed to identify the state of MoS_2 edge sites showing that Li cations were strongly adsorbed on the edge sites. Therefore, aside from the phase conversion, the adsorption of alkali cations especially on the edge sites, which are presumed to be the active sites for HER, is considered to enhance HER activity of 2H-MoS_2.[3]

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Modeling Aqueous Zinc-Ion Batteries: The Influence of Electrolyte Speciation on Cell Performance

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Zinc-based batteries are among the longest-used cell systems, yet they show increasing research interest in the last years[1]. The high specific capacity of zinc metal anodes combined with their stability in aqueous electrolytes and abundance highlights their potential in a growing market for energy storage systems. The long-commercialized alkaline cell chemistry, a zinc metal anode and a manganese dioxide cathode, showed increased rechargeability when switching to mildly acidic electrolytes[2]. While the charge transport of Zn^{2+} is widely acknowledged and distinguishes them from alkaline electrolytes, in-detail charge storage mechanisms are under debate[3]. The electrolyte's role in this process and its influence on cell performance and stability is often overlooked.

We employ a thermodynamically consistent dynamic cell model to describe aqueous zinc-ion batteries' behavior in our work. The model includes a thermodynamical equilibrium description of complex formations. Species composition significantly alters the transport properties and stability of both the electrolyte and the cathode. We predict cell behavior and cycling performance for different electrolytes and electrode materials. Putting this into the context of cell parametrization and rate limitations, we describe possible pitfalls and identify goals for the ongoing optimization of zinc-ion batteries.

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ToF-SIMS and XPS Characterization of Lithium Metal Surfaces

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The energy density of conventional lithium ion batteries (LIBs) will soon reach their physical limit, while the demand for batteries with even higher energy and power density will grow. This motivates the development of future lithium battery systems, such as all solid-state batteries with a lithium metal anode (LMA). [1] In this context, some publications highlight that the chemical nature, morphology and thickness of the LMA passivation layer influence the battery cell performance. [2, 3] However, these effects are often neglected in studies targeting battery cell performance.

In order to advance the knowledge in this field, we present fundamental studies on the characterization of Li metal surfaces and its passivation layer. The analysis of various LMA surfaces with X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) shows that all lithium samples are covered with a nanometer-thick inorganic passivation bilayer consisting of an outer lithium hydroxide and carbonate layer and an inner oxide-rich layer. The thickness and composition of the passivation film depends on the storage and transport conditions, as well as the treatment before use. The relevance of the analyzed passivation bilayer is linked to cell tests with lithium samples after different storage times and conditions. Also, we offer analysis guidelines for experimental design and data interpretation to ensure reliable results. Within, lithium plating during analysis and reactions under ultra-high vacuum conditions are discussed.

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MOCASSIN: A Monte Carlo Interface for Solid State Ionics

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The combination of density functional theory (DFT) and Monte Carlo (MC) is a powerful method to model ionic defects in crystals. It proved especially helpful in understanding the link between macroscopic properties and underlying microscopic processes, e.g. for analyzing the influence of defect interactions on the conductivity in doped ceria [1,2]. With the focus on strongly interacting systems, usability, high flexibility, and direct modelling with DFT data, we present MOCASSIN as a Kinetic (KMC) and Metropolis (MMC) Monte Carlo software to make this combined simulation approach accessible for all crystal geometries.

MOCASSIN [3] is based on the space groups and provides a user-friendly interface for translating high-level model descriptions to low-level MC simulations, thus, reducing the need for redundant MC code development by making arbitrary crystal geometries accessible with KMC and MMC. The model building system handles the symmetry expansion of reference data, simultaneous definition of multiple mobile species and complex mechanisms, pair- and cluster interaction definitions and provides model validation, geometry visualization, and fast generation of simulation sets for doping or temperature studies. The native simulator binaries enable optimized processing of built simulation sets, e.g. KMC simulation of defect diffusion or ionic conductivity, or simulation of the influence of defect interactions on the free energy of a system by multistage MMC sampling.

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Numerical simulations of the Hebb-Wagner polarization method of perovskite-type oxides

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Ternary oxides ABO_3 are known for their ionic and electronic conduction properties, which are well investigated depending on temperature, oxygen partial pressure, and composition. These make them a promising material for numerous devices, like atomic switches [1] or oxygen sensors [2]. This study aims to determine the electronic conductivity of the model system $SrTiO_3$ by simulating the Hebb-Wagner polarization method [3], [4] numerically. The advantages of the theoretical approach are the prediction of the expected relaxation time for experiments and the exact reproduction of the fluxes of all involved mobile species simultaneously.

A method that enables the determination of the partial conductivities is the Hebb-Wagner polarization technique. The electronic conductivity is measured by using an ion-blocking electrode, which is non-permeable for oxygen ions, on one side and a non-blocking, reversible electrode on the other side of the sample. The application of an external electric field results in the removal of oxygen from the sample until the net flux of oxygen within the sample converge to a steady state. The electronic conductivity can then be calculated from the steady state condition, which is thus a crucial requirement for a successful polarization process. Therefore, the mobility of the oxygen ions has a mayor influence on the duration of the relaxation process and consequently the time required for conductivity measurements with the Hebb-Wagner method.

The simulation results show an unexpected dependence of the relaxation time on the applied voltage; the relaxation time increases exponentially with higher voltage values. We propose that this effect originates from two different processes according to the fluxes of the involved species: (i) a limited oxygen exchange at the surface due to the surface exchange coefficient, extending the time to remove the oxygen; and (ii) an electrical induced *p*–*n* junction within the sample, which impedes the oxygen flux in the material.

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Model Studies in Electro-Synthesis: Structure Dependence of the Electrochemical Reduction of Acetone on Pt(hkl) Single Crystals

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The production of fine chemicals often involves catalytic processes with external energy input from fossil fuels. Electro-synthesis provides an alternative, which enables the use of electricity from renewable sources instead. To design selective electro-synthetic processes, however, it is necessary to gain a mechanistic understanding of the reactions occurring at electrode-electrolyte interface.

In this work, we investigated the reduction of ketones on low-index Pt single crystals using acetone as a model system. We used differential electrochemical mass spectrometry (DEMS) and electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) in combination with cyclic voltammetry (CV).

On Pt(110) electrodes, we identified propane as the main product, which is formed with high selectivity. We did not observe any formation of isopropanol under the applied conditions. Furthermore, we observe the onset potential for the reduction of acetone at 0.08 $V_{RHE.}$ At potentials of 0.00 V_{RHE} and below, the reaction competes with the hydrogen evolution reaction. The reduction of acetone is highly sensitive to the surface structure and the activity follows the trend Pt(110) > Pt(111). Noteworthy, the Pt(100) surface was found to be fully inactive towards acetone reduction.

On the electronic properties of LiO_2 and its importance during the electrochemical formation of $^1O_2$

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Due to their unparalleled theoretical specific energy capacity lithium-oxygen-systems present themselves as an ideal candidate for the future of energy storage in the form of the Li/air-battery. The main cell-reaction is, however challenged by a plentitude of side reactions that sabotage its functionality. Recently the importance of singlet-oxygen $^1O_2$ was emphasized in experimental studies, degrading electrolytes as well as redox mediators.[1] Comparable evolution of $^1O_2$ was observed during operation of other metal/oxygen-battery prototypes.

The undesirable presence of this parasitic oxygen-species appears closely connected to the formation of metal-oxide intermediates - LiO_2 in the case of the Li/air-system. Mechanisms postulated as a rationalisation of this phenomenon are based on a disproportion reaction of LiO_2, forming the final discharge product Li_2O_2 while releasing gaseous oxygen. This study presents the dissociation reaction of molecular LiO_2 as an unimolecular reaction pathway through which $^1O_2$ can evolve during operation.[2] The dissociation was investigated employing highly accurate Post-Hartree-Fock methods in the form of multireferent CASSCF/CASPT2-computation, illuminating the intricate electronic character as well as fundamental electronic transitions in the form of minimum energy crossing points. In addition, small-scale Li_4/O_2 models were explored to validate the descriptive capability of density functional theory for these systems relative to a CCSD(T) benchmark.[3]

The authors want to contribute to the improvement of the functionality and the overcoming of fundamental difficulties of future energy storage systems.

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Strain effect on ionic conductivity in doped ceria: Experimental and computational insights

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Stain engineering is a promising approach to modify properties of solid compounds, in particular ionic conductivity in oxides, and it is crucial to understand how the ionic transport is affected by the strain.

Here we investigate the change in ionic conductivity of biaxially strained thin films of doped ceria applying experimental and computational methods. The strain state as well as the dopant radius is varied, with the dopants La, Gd and Yb (experiment) and Lu (simulation).

Epitaxial thin films were grown by pulsed laser deposition and the strain was varied by applying different annealing conditions. The ionic conductivity in-plane and out-of-plane, with respect to the strained axes, was measured by impedance spectroscopy.

The conductivity was simulated with the Kinetic Monte Carlo algorithm based on energies from density functional theory and the effects of strain on the migration barriers and defect interactions were deconvoluted. It was revealed that both the barriers and interactions contribute to the strain-modified transport, but it is important to take into account the long-range motion rather than individual barriers and interactions.

Experiment and simulation reveal that transport in the out-of-plane direction is more sensitive to the strain state than in the in-plane direction. Furthermore, the size of the rare-earth dopants significantly impacts the extent of the strain effect on the ionic conductivity.

First-principles study of thiophenyl benzenethiol as sulfur host material for Lithium-Sulfur batteries

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Lithium-Sulfur (Li-S) battery is considered as one of the most viable candidates for next-generation rechargeable batteries. However, several main challenges hinder its practical application so far: the insulation of elemental sulfur, the shuttle effect of dissolvable lithium polysulfides, and the volumetric change of sulfur during the charge/discharge processes. One battery class that promises to overcome these drawbacks are polymer-based batteries which utilize organic materials as the active parts within the electrodes [1].

The here proposed cathode is a conductive, flexible, and free-standing polymer poly(4-thiophen-3-yl)benzenethiol) (PTBT) as a sulfur host material [2]. By a vulcanization process, sulfur is embedded into this polymer. We present a characterization of the molecular structure and electronic stability of different sulfurized PTBT monomers as the basic polymer unit within density-functional theory (DFT). Our calculations show that the main reaction of the vulcanization process leads to a short sulfur chain connecting adjacent TBT units of the same polymer backbone whereas the crosslinking of TBT units belonging to different polymer backbones is the side reaction. These products are further analyzed by calculating the formation energy of lithium insertion and the dissolution of lithium polysulfides in order to understand the reaction mechanism during the discharge process.

In the future, this first-principles study will be embedded into a multi-scale approach where the DFT results will be bridged to classical and ab-initio molecular dynamic simulations focusing on larger solvated polymer structures and spectroscopy calculations, respectively.

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Pd particles supported on ordered $Co_3O_4(111)$: Particle size effects in electrochemical environment

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Pd Nanoparticles (NPs) are efficient electrocatalysts for the oxidation of ethanol in alkaline direct ethanol fuel cells.[1] We investigated particle size effects and the stability of Pd NPs supported on well-ordered $Co_3O_4(111)$ films. The model catalysts were prepared on an Ir(100) single crystal by physical vapor deposition of Co in oxygen atmosphere to form a $Co_3O_4(111)$ film of ~6nm thickness. Afterwards, Pd was deposited by physical vapor deposition in ultrahigh vacuum to create Pd NPs of different sizes. By varying the Pd coverage we prepared either ultra-small particles (nominal Pd coverage 0.3Å) or conventional particles of several nm diameter (nominal Pd coverage 4.0 Å). The model catalysts were exposed to the electrolyte (pH=10, phosphate buffer) at different potentials within and out of the stability window of Co_3O_4 [2]. The oxidation states of both Pd nanoparticles and cobalt cations were analyzed by means of synchrotron radiation photoelectron spectroscopy (RPES) and synchrotron radiation photoemission spectroscopy (SRPES) as a function of Pd NPs size.

After preparation of the conventional Pd NPs, we observe metallic Pd^0 with traces of Pd^{2+} dispersed in $Co_3O_4(111)$. At potentials of 1.1 V_{RHE} and above we observe the oxidation from Pd^0 to PdO at the Pd NPs surface. At 1.5 V_{RHE}, PdO is the dominant species. Upon reversing the potential to 0.5 V_{RHE} we observed the reduction of PdO back to Pd^0 indicating partial reversibility. In sharp contrast, ultra-small Pd particles consist of PdO already after preparation, accompanied by a small fraction of Pd^{2+} species dispersed in the $Co_3O_4(111)$ film. With increasing potential, the PdO dissolves into the electrolyte and the Pd^{2+} migrates most likely deeper into the $Co_3O_4(111)$ film. The oxidation states of Pd in PdO as well as Pd^{2+} species dispersed in $Co_3O_4(111)$ do not change as a function of the potential.

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Harvesting vibrational energy to promote orientational isomerization in CO/NaCl(100)

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Solar light harvesting systems efficiently collect photons using chromophores and transport the resulting electronic excitation to a reaction center.[1] Although vibrational excitation can also greatly enhance reactivity,[2] similar systems based on vibrational energy have not yet been reported. Here, we demonstrate such a model system that uses controlled vibrational energy transport to promote a simple condensed phase reaction. The system consists of a $^{13}C^{18}O$ monolayer on NaCl(100) at 7 K, which is additionally covered by ~100 $^{12}C^{16}O$ overlayers. Following selective infrared laser excitation of the overlayer, we monitor the vibrational energy transfer dynamics with mid-infrared laser-induced fluorescence.[3] We find that a large fraction of the vibrational quanta produced in the $^{12}C^{16}O$ overlayer is transferred to the $^{13}C^{18}O$ monolayer, due to its lower vibrational frequency. Using this excitation scheme, the number of vibrational quanta transferred to the monolayer is 30× higher than what is achieved with direct monolayer excitation (on average ~1.5 eV/molecule). The high vibrational energy can efficiently promote the recently reported orientational isomerization of CO on NaCl(100) from its normal “C-down” orientation ($Na^+\cdots CO$) to its “O-down” orientation ($Na^+\cdots OC$).[4] We anticipate that this concept can be extended to other acceptor molecules and vibrationally promoted condensed phase reactions.

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Experimental and theoretical studies on the kinetics of the $CH_3OCH_2OCH_3$ + OH reaction

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In the discussion on the influence of combustion processes on climate change, the use of so-called e-fuels produced from sustainable electric energy sources plays an increasing role. In particular, oxymethylene ethers, $CH_3O(CH_2O)_nCH_3$ (OME-n) with $n \geq 1$, have recently come into focus as drop-in fuels or substitutes for conventional diesel fuels. Accordingly, the combustion chemistry of OMEs as well as their chemical fate in the atmosphere attracts increasing scientific attention. In both environments, the reactions of OMEs with hydroxyl radicals play a prominent role. Moreover, the reactions of OH radicals with oxygenated hydrocarbons are of fundamental kinetic-mechanistic interest because they may proceed via prereactive complexes.

In our contribution, we present measurements of the rate coefficient for the reaction dimethoxy methane (DMM, OME-1) + OH under pseudo-first order conditions. The hydroxyl radicals were produced by pulsed laser photolysis of HNO_3 and detected time-resolved by saturated laser-induced fluorescence. The experiments were carried out at pressures between 200 and 900 mbar and temperatures between 251 and 503 K with He as bath gas.

For further investigation of the reaction pathways of the DMM + OH reaction, critical points of the potential energy surface were characterized with density functional theory at B2PLYP-d3/def2-TZVPP level. Rate coefficients were obtained from statistical rate theory. The experimental and theoretical results are presented and compared. The observed temperature and pressure dependence of the rate coefficients will be discussed in terms of the underlying reaction mechanism, and conclusions regarding the corresponding reactions of higher OMEs will be drawn.

Lifetime of the Metastable Isomer of CO on NaCl(100)

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Infrared excitation of CO adsorbed on a NaCl(100) surface at cryogenic temperatures has been shown to result in a reversal of the adsorbate orientation, representing a condensed phase quantum isomerization.[1] This isomerization occurs following vibrational energy pooling, which produces CO molecules in the monolayer with sufficient internal energy to go from the stable ground-state orientation, where the C atom is closer to Na^+ (C-down), to a metastable orientation, where the O atom is closer to Na^+ (O-down). Previous work from our group using infrared laser induced fluorescence has established that this isomerization proceeds in both bare and buried monolayer samples.[2]

In this poster, we present recent results of experiments using time-resolved Fourier transform infrared (FTIR) spectroscopy to determine the temperature-dependent lifetime of the metastable O-down isomer in a $^{13}C^{18}O$ monolayer sample buried under approximately 100 layers of $^{12}C^{16}O$ overlayers. From this, we have calculated the activation barrier of the backward flipping reaction. Isotopic substitution to $^{13}C^{16}O$ in the monolayer is found to cause some significant increase in the reaction rate, representing an unusually high kinetic isotope effect for this heavy-atom system.

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Rotational and collision energy dependence of reactions in the HBr^+ + HCl/DCl system

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In previous work the ion molecule self-reactions, HCl^+ + HCl (DCl) and HBr^+ + HBr (DBr) have been investigated as a function of the center of mass collision energy and the ion external rotation [1,2,3]. In this contribution we extend that previous work by studying the cross reaction system HBr^+ + HCl (DCl) [4]. Resonance-enhanced multiphoton ionization (REMPI) was used to prepare rotationally state-selected ions in the vibrational ground state of the electronic $^2\Pi_{1/2}$ state. Cross sections were measured inside a guided ion beam apparatus as a function of the rotational energy, E_{rot}, varied between 3.4 meV and 46.8 meV, and as a function of the collision energy, E_{cm}, varied in the range from 0.12 eV to 5.85 eV.

Data will be presented for the proton transfer (PT_{HCl}) and charge transfer (CT) in the reaction system HBr^+ + HCl, whereas in case of the deuterated system, proton transfer (PT_{DCl}) and deuterium abstraction (DA) are accessible. For both exothermic PT-channels, (PT_{HCl}) and (PT_{DCl}) the cross section σ decreases with increasing E_{cm} and E_{rot}. For the endothermic CT reaction, σ increases with increasing E_{cm}. Near the thermochemical threshold, a rotational activation is observed. The cross section of the DA reaction decreases with increasing collision energy, despite the fact that the reaction is weakly endothermic.

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Experimental and theoretical studies on the kinetics of the methyl formate + OH reaction

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In the discussion about the anthropogenic climate change, alternative fuels are of increasing interest. Especially so-called e-fuels produced from sustainable electric energy sources and bio-fuels produced from renewable biological sources are possible solutions [1,2]. In this context, methyl formate (MeFo) is a promising drop-in component or substitute for conventional fuels. Furthermore, methyl formate acts as an archetype molecule because it has an isolated ester group, which is an important structural feature of many alternative fuels [3]. To draw conclusions about the combustion chemistry and the impact of methyl formate in the atmosphere, the reaction of methyl formate with OH radicals is investigated in this work.

Experiments were carried out by using pulsed laser photolysis of HNO_3 for the production and laser-induced fluorescence for time-resolved detection of OH radicals in an excess of MeFo. Comprehensive theoretical investigations were performed, employing the CCSD(F12*)(T*)/cc-pVQZF12//B2PLYP-D3/def2-TZVPP method to calculate molecular properties and energies for statistical rate theory calculations. To model the observed temperature dependence, master equations were solved by using both an inhouse code and the MESMER program package [4]. The molecular mechanism of the reaction is examined and kinetic consequences are discussed.

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Pyrolytic reactions of methyl formate: Shock-tube studies and kinetic modeling

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Due to the limited availability of fossil fuels and their impact on climate change, so-called e-fuels produced from sustainable electric energy sources attract more and more attention in current research. In this context, the combustion chemistry of the ester group, which is a structural feature of various biodiesel components, is gaining importance [1]. Since methyl formate is the smallest organic species bearing an ester group, it can serve as a prototypical compound to study the general role of ester groups in combustion processes. It is obvious that from the high-temperature kinetics of methyl formate, information about the kinetics of higher esters can be inferred, and insofar the combustion mechanism of methyl formate can be considered as a link between those of hydrocarbons and higher organic esters.

In our contribution, we present and discuss shock-tube experiments on pyrolytic reactions of methyl formate. Two different shock tubes with two different detection techniques were used namely hydrogen atom resonance absorption spectrometry and time-of-flight mass spectrometry. This combination allows observing a variety of species in a time-resolved manner. The obtained experimental concentration-time profiles are modeled on the basis of a reaction mechanism from the literature [2]. Rate coefficients of selected elementary chemical steps in this mechanism are adjusted by also taking into account results from quantum chemical and statistical rate theory calculations. The major aspects of these mechanistic modifications as well as the kinetic characterization of the elementary steps will be discussed.

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Photogeneration and Dynamics of Selenyl Radicals in Solution

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Organoselenium compounds have emerged as effective catalysts in organic synthesis [1]. Due to the low bond energy of selenium bonds, selenium-centered radicals can be formed photochemically with visible or near-UV light [2], thereby opening up new synthetic strategies based on the versatile reactivity of these radical species. A prominent precursor of the widely-used phenylselenyl radical ($PhSe^{\bullet}$) is diphenyl diselenide (Ph_2Se_2) which upon irradiation with UV light homolytically dissociates [3,4].

Here, we investigate the photochemical generation of $PhSe^{\bullet}$ in various solvent environments and follow the dynamics on a timescale from nano- to milliseconds with transient absorption from the UV to the NIR, recorded with a streak camera setup [5]. In non-degassed solvents, $PhSe^{\bullet}$ has a lifetime of about 5 µs before it can further react with oxygen [5] and eventually recuperate Ph_2Se_2 on a ms timescale. The photoreaction can be altered by variation of the solvent composition and the pH value. Employing the solvent hexafluoro-2-propanol that exhibits a high hydrogen-bond donating ability and a low nucleophilicity [6], we can show that also the radical $PhSeH^{+\bullet}$ can be photogenerated and has a lifetime well into the ms regime, thus making it accessible for participating in diffusion-controlled reactions.

Beyond Ph_2Se_2, we present investigations on further organoselenium compounds as light-triggered sources of $PhSe^{\bullet}$ and $PhSeH^{+\bullet}$ radicals, and the photocatalytic reactions that subsequently set in are followed and deciphered by time-resolved spectroscopy.

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Degradation Kinetics of Anionic and Cationic Dye Molecules under Nanosecond Laserpulse Induced Plasmonic Heating of Gold Nanoparticles

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We are investigating the kinetic behavior of the degradation process of several organic dye molecules with positive and negative charged moieties which are tending to have different adsorption affinities to the surface of colloidal MPA capped gold nanoparticles with a negative zeta potential which are being heated by their plasmonic resonance under nanosecond laserpulses. To get information about the space confinement of the temperature profile and the difference of reaction rate caused by the different properties of the dyes, kinetic experiments using UV-Vis spectroscopy as monitoring method for the determination of the maximum reaction rate were performed at different substrate (dye) concentrations. Also the laser intensity and the nanoparticle concentration were varied. The experiments show a quite clear dependence of the reaction rate on the available nanoparticle surface and the laser intensity of the cationic dye molecules. The anionic dye molecules show almost no degradation behavior and the laser irradation of the gold nanoparticles. Furthermore, we also performed several experiments to determine the reaction rate at different laser intensities to get an Arrhenius like curve depending on the inverse of the laser intensity. This should act as a starting point for the kinetic determination of the induced temperatures governing the degradation reaction at the gold nanoparticles.

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Hydrogen Atom Transfer (HAT) between phenol and phenoxy-radical.

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Hydrogen Atom Transfer (HAT) reactions involving phenoxy radicals occur in various biological processes, like the breaking of free-radical chain reactions by tocopherol (Vitamin E). The self-exchange of a hydrogen atom between phenol and its corresponding phenoxy radical is the simplest-case scenario for such reactions. As such, it lends itself as calibration point for theoretical models. Despite its seemingly simple nature, almost no experimental data exists for this reaction. We present a method for determining the rate constant of this exchange and its thermal behavior by looking at the pseudo-self-exchange between phenol and phenol-d_5. The radicals are produced by photolysis and the transient absorption of the samples in the µs range is recorded with a streak camera. Measurements at temperatures ranging from -5° C to 35° C yield rate constants for the exchange of $\approx 4 \times 10^5$ s^{-1} M^{-1}. Reversing the direction of the exchange, from phenol to phenoxy-d_5, we find the same rate constants. Hence we believe that our system is a good approximation to the phenoxy/phenol self-exchange reaction.

Conformationally selected polar cycloaddition reactions in the gas phase

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Multiple structural isomers of complex molecules can exhibit distinct reactivities. Spatial separation of conformers can be performed using inhomogeneous electric fields [1], which provides opportunities for unraveling their specific reactivities in the gas-phase. We studied gas-phase reactive collisions of conformer-selected neutral molecules [2, 3] or different nuclear-spin isomers [4] with cold ions in Coulomb crystals [5]. To explore this dependence further in bimolecular reactions, we applied this experimental approach to the investigation of Diels–Alder cycloadditions, in which a diene reacts with a dienophile to form a cyclic compound. The successful spatial separation of the conformers of 2,3-dibromobutadiene (DBB) [6] and methyl vinyl ketone (MVK) [7] paved the way toward studies of conformer-selected polar cycloaddition reactions in a cold and controlled environment. Here, we present our first experimental results on the kinetics and mechanisms of polar cycloaddition reactions.

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Formic Acid Oxidation on Pd(111)

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In order to understand large scale heterogeneous catalysis it is of fundamental importance to study elementary reactions and to determine their thermal rate constants. The investigation of the mechanism involved in formic acid (FA) decomposition on transition metal surfaces is important in order to get insights into vapor phase catalysis and to design direct FA fuel cells.[1]

In this work, we present a mechanistic study of FA decomposition on a clean and oxygen covered Pd(111) single crystal surface. We make use of a pump-probe experiment combined with detection based on universal fs-laser ionization and velocity resolved kinetics (VRK).[2] We observe that the reaction probability of FA is increased by the presence of oxygen adatoms and decreased by increasing the surface temperature. Under all conditions, CO_2 is the major carbon containing product, while the hydrogen containing product changes from H_2 for the clean to H_2O for the oxygen covered surface.

For CO_2 we observe a bimodality in the kinetic energy distribution where one component is thermal and the other hyperthermal. Both components show the same transient kinetics. While hyperthermal CO_2 has already been observed in the literature for CO oxidation[3], our study supports a formate mechanism rather than CO oxidation.

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Hydrogen recombination on Pd(111): Effect of Subsurface Penetration

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The hydrogen/palladium system is of special interest as hydrogen atoms easily penetrate into subsurface layers of Pd. Many permeation experiments were carried out to characterize bulk diffusion, but detailed experimental studies on the rate constants of hopping processes in the near surface layers are rare.[1]

In the present experiment HD molecules are formed on the Pd(111) surface after a short pulse of H_2/D_2-mixture dosed the surface. Molecules are detected with mass-resolved ion-imaging after non-resonant multiphoton ionization. A long and tailing HD formation is observed subsequent to the transient dosing pulse. The tailing is substantially longer than expected second order recombination of H and D.

A model was developed to describe both the hydrogen recombination on the surface and the subsurface penetration. Non-uniform grid-hopping was used to be able to account for the near surface layers explicitly but also for bulk diffusion to a depth of 1mm.

Using hopping rate constants from density functional theory,[2] the model can reproduce the observed traces for HD production, which shows that subsurface layers contribute to the transient HD kinetics. Simulation of temperature programmed desorption data from literature verifies the present results.

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Cryo kinetics and IR spectroscopy of N_2 and H_2 interactions with size selected Iron and Ruthenium clusters

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N_2 activation by transition metal surfaces is often rate limiting in catalytic valorization processes. We investigate suitable model systems with a modified Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS). By means of cryo kinetic studies and cryo InfraRed Photo Dissociation (IR-PD) spectroscopy supported by DFT modelling, we are able to investigate the vibrational and kinetic behavior of various transition metal cluster N_2/H_2 complexes (Co, Ni, Rh, Ru, Ta) and obtain information on reaction precursors and intermediates [1-5].

We present gas phase IR spectra and kinetics of N_2 adsorption on isolated cationic Fe_n^+ clusters at cryo temperatures. We find size dependent and pressure dependent effects. The recorded single and multiple IR bands are significantly red shifted with respect to the IR inactive stretching mode of free N_2 (2359 cm^{-1}).

Currently, we investigate the N_2 and H_2 adsorption on Ru_n^+ clusters also by means of IR spectroscopy and adsorption kinetics. We compare these results of cubic Ru_n^+ clusters with those of the icosahedral Fe_n^+ clusters, and we conduct exploratory DFT modelling as far as possible.

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Reaction Kinetics of CdSe Nanocrystal Intermediates

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During the formation of semiconductor nanocrystals, a class of intermediates has been reported that are called magic-sized clusters (MSC) due to the assumption that they are ultrasmall nanocrystals with defined stoichiometry and shape. These either appear in families that progress from small to large MSCs in a quantised growth before continuous growth of regular nanocrystals takes over. Under different conditions MSCs occur as transient side products that bind nucleation monomer but occur in parallel to regular nanocrystals [1-2]. We have identified a species of MSCs for CdSe and CdS that are characterised by sharp absorption lines at 350 and 309 nm, respectively. Under dry conditions these form 1D fibrils that are connected by phosphonic anhydride bridges and precipitate as a gel [3-4].

So far, the relationship between different species of MSC is not clear. Both growth of smaller MSCs into larger ones and conversion between similarly sized polymorphs have been proposed to explain the observed spectral shifts [1,5]. We elucidate the formation and decomposition kinetics as well as the structure of the MSCs using a combination of optical spectroscopy, analytical ultracentrifugation, and NMR spectroscopy. These methods allow us to correlate the MSC size with optical and structural properties in order to shed light onto the role of MSCs in the nucleation and growth of semiconductor nanocrystals.

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Plasmon induced hot-electron transfer on DNA-metal nanoparticle superlattices

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The ability of DNA to transfer charge through its double helix is well-known since the 90s with the studies carried out using optical and electrochemical techniques.[1] Herein we test the possibility of transferring hot-electrons produced at the interface of a plasmonic nanoparticle to DNA double helices within the superlattice structures. Using DNA self-assembly properties it is possible to control precisely the crystal structure of the superlattices, the distance between nanoparticles, and also provide hot spots for Raman signals, obtaining excellent SERS substrates. In here, we selectively introduced modifications into the DNA chains to track the occurrence of hot-charges carriers reactions transfer. DNA oligomers modified with the molecule 8-bromoadenosine (8BrdA) at different positions, in a manner that the distance between the surface and the molecule is known, Fig. 1A. 8BrA was chosen because it can be decomposed by plasmonically generated hot-electrons.[2] Our results showed that the generated hot-electron on the nanoparticle surface can decomposed the 8BrdA molecule at different separation distances from the surface. The control experiment (sequence without 8BrdA), Fig. 1B, does not show decomposition of DNA molecules during the experiment. However with the presence of one 8BrA in the DNA sequence, it is observed the characteristic vibration of the molecule, and that the peak intensity exponentially decays over the course of the hot-electron reaction (Fig. 1C). Our results shows that DNA is able to transfer hot-electrons from the nanoparticle surface, and that the hot-electron is energetic enough to decompose 8BrdA present in the DNA sequence, this result can open up opportunities to develop plasmonic devices composed of DNA self-assembled nanostructures.

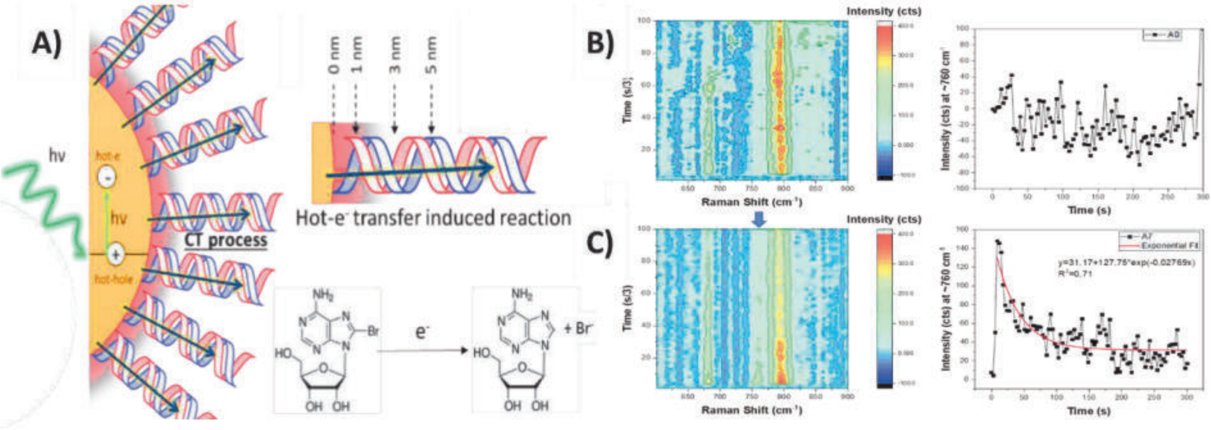

Fig. 1. A) Scheme showing the hot-carriers generation in the gold nanoparticle, and the hot-electron transfer by DNA, leading to the decomposition of 8BrdA into adenine. B) SERS experiment showing no decomposition of DNA over 5 minutes of irradiation. C) SERS time series showing the decomposition of 8BrdA at 3 nm from the nanoparticle surface

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Reductive Alkylation of s-SWNTs

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The covalent functionalization of semiconducting single-wall carbon nanotubes (s-SWNTs) leads to the formation of new low-lying energy levels which lend themselves to applications in bioimaging and quantum technologies [1]. Reductive alkylation with iodoalkanes and sodium dithionite provides a simple route for the covalent functionalization of s-SWNTs to generate bright photoluminescence (PL) in the NIR [2]. However, the mechanism of reductive alkylation as well as the nature of the defects generated and their effects on the photophysics of the s-SWNTs is not yet well understood. Here, we have investigated the kinetics of this reaction using PL spectroscopy. Experiments with constitutional isomers of iodobutane suggest that the reductive alkylation does not follow a radical, single-electron transfer reaction mechanism. The number of impurities introduced by the reaction and its rate constant indicate that functionalization of the nanotubes depends on both the s-SWNT- and the iodoalkane concentration as well as on the temperature. Moreover, we studied the temperature dependence of the PL in functionalized s-SWNTs down to 10 K.

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Hydration stop of cementitious suspensions by three techniques

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To characterize the properties of fresh concrete by the means of physically defined parameters rheology remains crucial in modern concrete technology. Rheological properties can be influenced by many factors. The most important factor is the water to cement ratio, which effects the properties of the paste level predominantly. Therefore, parameter studies are preferably done on the microscopic level of paste. Also for reasons of practicability, with set focus on limiting test duration and handling in general, more extensive concrete variations are performed on the paste level and not on the concrete level. Nevertheless, concrete remains the real object of reflection of concrete technology.

To obtain an understanding of influencing factors such as the underlying kinetics and mechanisms at the initial colloidal scale, as well as later on to transfer these influences to the paste and concrete level, a time dependent (kinetic) analysis of cementitious suspensions is necessary. This inquiry can be achieved by hydration stop at defined times using various methods, namely lyophilization [1], water-isopropanol exchange [2] or combination of both aforementioned methods [3]. The three different hydration stop methods are further investigated by evaluating the specific surface area by means of nitrogen physisorption. Additionally, scanning electron microscopy (SEM) as an imaging method is used.

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Investigation of photolabile protection groups as tools for time-resolved structural dynamics

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Photolabile protection groups (PPGs) are molecular compounds, which release a part of their structure upon a light trigger. PPGs are receiving increased interest as a tool in time-resolved biophysical experiments, in particular time-resolved serial crystallography experiments [1,2]. The use of a light trigger to release a substrate enables the time resolved investigation of non-light-sensitive enzymatic reactions [1]. Here, the light trigger sets the time-zero of the whole experiment and a spatial and temporal control of the substrate release is feasible.

There are many types of PPGs differing in excitation wavelengths, substrate release, -times and quantum yields [3]. Due to different solvents and pH conditions the excitation wavelengths can be shifted and potentially the reaction mechanism can change. To allow optimal control of the substrate release and no undesirable involvement of photoreaction intermediates with the enzymatic reaction, it is crucial to know the mechanism of the PPG of interest in detail. I approached the investigation of the PPG photoreactions on the respective fast (ms) to ultrafast (ps) timescales employing transient absorption spectroscopy (TAS), laser flash photolysis (LFP), advanced infrared spectroscopies and femtosecond Raman spectroscopy (fsRS). Especially, the complementary IR and Raman ultrafast methods are useful to resolve time-resolved structural changes allowing for the identification of individual reaction steps. As such, I successfully used the mentioned methods for detailed investigations of α-carboxynitrobenzyl-ʟ-aspartate [4] and especially *para*-hydroxyphenacyl fluoroacetate (pHP-FAc) in various pH conditions. In particular, at basic pH a redshift of the absorption is shown and further investigation into the reaction mechanisms of photouncaging in case of the deprotonated PPG is currently ongoing.

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Controlling Microgel Deformation via Deposition Method and Surface Functionalization of Solid Supports

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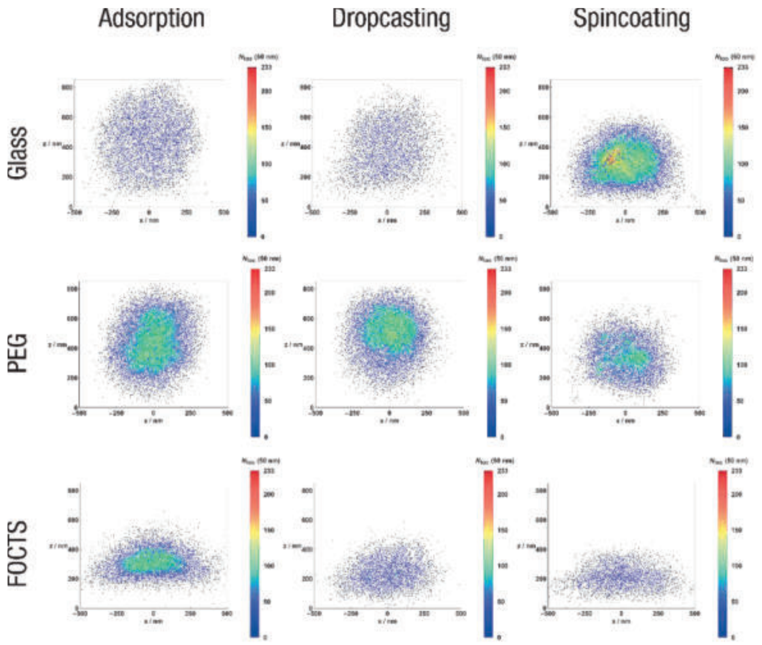
The behaviour of soft matter objects at solid-liquid interfaces plays a key role for a variety of investigations and applications. We present a study on the impact of sample preparation on the shape of micogels, i.e. soft colloidal particles, deposited on different types of surfaces.[1,2] More specifically, we studied the deposition of poly(*N*-isopropylmethacrylamide) (pNiPMAM) microgels to (i) a hydrophilic PEG surface, (ii) a slightly hydrophilic glass surface and (iii) a non-phobic fluorinated surface (FOCTS) by the methods of (a) drop-casting, (b) spin-coating, and (c) adsorption from dispersion. The deformation of the deposited microgels was visualized *in-situ* by 3D super-resolved direct stochastic optical reconstruction microscopy (dSTORM) imaging. The experimental results were compared with molecular dynamics simulations in order to understand the underlying molecular processes during adsorption of microgels on solid supports. We could demonstrate and rationalize the strong influence of the preparation method to the final microgel conformation.



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Investigation of the Optical Properties of Nickelsulfide Nanoparticles

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Nickelsulfide can crystallize in various crystal-phases, each with their own chemical and physical properties. One of the phases is the hexagonal α-Nickelsulfide. This, at standard ambient conditions, metastable crystal phase of the NiAs structure type shows very interesting and novel optical properties like other Nickelsulfide phases.[1] In bulk materials it is known that doping with cations and anions can influence these optical properties.[2] Through the investigation of the composition and optical properties of the prepared α-Nickelsulfide nanoparticles, the novel phenomenon can be investigated further under the addition of nanoscopic particle diameters. The presented work shows α-NiS and α-$Ni_{1-x}Fe_xS$ nanoparticles synthesized by hot-injection and cation exchange reactions and show different optical properties depending on the synthesis route and the used amount of iron precursors. The materials were characterized through UV/VIS, TEM, AAS and XRD.

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Ultrafast Dynamics of Ru^{II} Polypyridyl Complexes by Mass Spectrometry and Fragmentation Spectroscopy in an Ion Trap

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Ru^{II} polypyridyl complexes find application in various areas of photovoltaics and photomedicine. In the latter field the complexes are, e.g., used as photoactivatable prodrugs [1,2], for which it is essential to understand their photoactivity and how it could be controlled by ligand design. The efficiency of the key processes of photodissociation and -substitution depends critically on the energetics of the corresponding ^{3}MLCT and ^{3}MC excited states.

A series of Ru^{II} polypyridyl complexes: $[Ru(bpy)_2(CN\text{-}py)_2]^{2+}$, $[Ru(bpy)_2(NA)_2]^{2+}$, $[Ru(bpy)_2(pyr\text{-}NA)_2]^{2+}$ and $[Ru(ec_2bpy)_2(NA)_2]^{2+}$ possessing bidentate bipyridine ligands (bpy= 2,2'-bipyridine, ec_2bpy= 4,4′-di-ethoxycarbonyl-2,2′-bipyridine) and mono-dentate pyridine ligands (CN-py= 4-cyanopyridine, NA= nicotinamide, pyr-NA= N-nicotinoyl-pyrrolidine) have been examined by a combination of mass spectrometry and laser spectroscopy in the frequency and time domain in an ion trap.

The gas phase investigations gave evidence for the electron withdrawing substituents on the pyridine ligands to destabilize the Ru^{II}-pyridine bond in the ground state, while the electronically excited ^{3}MC state is stabilized. Electron donating substituents on the pyridine are observed to stabilize the coordinative bond, but in parallel stabilize also the ^{3}MLCT state showing in excited state lifetime elongation. The general conclusions were drawn from the study of UV photofragmentation spectra and pump-probe excited state lifetime measurements, and are further supported by quantum chemical (TD-)DFT calculations.

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The Optical Spectrum of Au_2^+

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We recently published the first optical spectrum of the gold dimer cation.[1] The electronic configuration of Au_2^+ seemingly resembles that of H_2^+, both having a single unpaired electron in the highest bonding σ orbital. The electronic structure of Au_2^+ is interesting especially in the context of catalysis because Au_2^+ serves as a model system to understand fundamental catalytic processes like the activation of the C-H bond. It is important to have appropriate theoretical tools available that can describe such processes.

Our measurements, which allow resolving the vibronic transitions, show that the optical spectrum of Au_2^+ is very complex and does not resemble that of H_2^+. Also, standard high level TD-DFT methods fail completely in describing the observed spectrum. Only after applying multireference methods and considering spin-orbit coupling and relativistic corrections we are able to qualitatively describe the observed spectrum.

This poster will present the experimental setup and discusses the sensitive measurement method required to obtain the vibrationally resolved spectra in detail. We also compare different computational methods in detail (TD-DFT vs MRCI - CASSCF with and without Spin-Orbit coupling) and have a look at the respective influences of the different levels of theory on the calculated transitions.

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Investigation of alcohol-formic acid dimers and trimers

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For the benchmarking of quantum chemical methods it is advantageous to have a comprehensive set of experimental spectroscopic data for a small base of molecules, which covers different strengths of hydrogen bonds [1]. Alcohols and carboxylic acids are natural candidates for such a data base. Here, we present an FTIR spectral analysis of clusters formed by alcohols with formic acid in supersonic expansions. They coexist with the chemical reaction product methyl formate [2] for the simplest case of methanol.

The most stable structures of those barely investigated mixed dimers consist of two cooperative hydrogen bonds, which result in a cyclic form similar to the formic acid-water complex [3]. The influence of harmonic and anharmonic couplings in such mixed dimers and trimers is dependent on the alcohol used. Here, we illustrate the differences between methanol and trifluoroethanol. Our preliminary spectroscopic data indicate that it will be a long way until these systems will be understood well enough to be included into a benchmark data set [1].

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Lable-free detection of rapamycin in human skin

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Human skin acts as a barrier for topically applied substances and may inhibit their penetration if their molecular weight exceeds 500 Dalton. This work reports on the penetration of the anti-inflammatory drug rapamycin ($C_{51}H_{79}NO_{13}$), molecular weight MW = 914.172 g/mol through the stratum corneum, a drug that barely penetrates intact human skin. This situation may change due to inflammatory skin diseases or skin treatment affecting the skin barrier. In this work, we present detailed studies on the transport of rapamycin across the impaired skin barrier due to treatment with the serine protease trypsin prior to topical application of rapamycin formulations. The penetration of rapamycin of human skin *ex vivo* is studied by X-ray microscopy (UVSOR III Synchrotron Facility, IMS, Japan), a label-free and quantitative approach. Selective detection of rapamycin is accomplished by excitation at the O 1s absorption edge. X-ray absorption spectra were taken at each pixel of images recorded in the top skin layers with a spatial resolution of 100 nm. This allows us to apply a singular value decompostion approach in order to distinguish the O 1s absorption of fixed human skin from that of the drug. This approach requires a comparison with untreated reference skin samples and measuring their thickness by atomic force microscopy. It is found that the treatment of skin samples with serine protease leads to an enhanced uptake of the drug into the stratum corneum, specifically into the corneocytes and the viable epidermis. In contrast, rapamycin barely penetrates the intact skin barrier. Advantages of the singular value decomposition data evaluation method is highlighted in comparison with an analysis that is based on two photon energies, according to the Beer-Lambert-law. We also present results on the penetration of redox-sensitive core-multishell nanocarriers (CMS) that are intended to facilitate drug penetration through the stratum corneum and selective drug release at epidermal inflammation sites.

Label free drug detection in 3D cancer models by atomic force microscope infrared-spectroscopy

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The treatment options of head and neck cancer are limited due to poor efficacy, frequent tumor recurrence as well as systemic side effects. The epithelial localization offers the general option for topical treatment, which would offer high drug concentrations at the tumor side. Yet this drug administration route is not exploited for clinical use. Improved knowledge on topically and systemically applied drugs, their transport, and distribution within the tumor tissue is essential for the efficient and directed treatment of tumors by potent actives.

Here, we report on the detection of the monoclonal antibody cetuximab in a 3D tumor oral mucosa model. The multi-layered *in vitro* model consists of multiple layers of SCC-25 tumor cells, which were grown onto a lamina propria compartment, composed of human oral fibroblasts in a collagen scaffold. We aim to determine the particularities of topical treatment, if topical drug delivery achieves increased drug concentrations at the target site and if topical drug delivery affects intracellular drug distribution compared to systemic treatment.

Atomic force microscope infrared-spectroscopy (AFM-IR) is a label-free approach for spatiallly resolved and selective detection of drugs. It tracks the drug with its unique vibrational properties. We present recent results operating in the mid-infrared regime, which are based on photothermal expansion of the sample following resonant excitation by a tunable quantum cascade laser. This approach gathers the full spectral information in each pixel. The hyperspectral imaging in the fingerprint region is combined with a singular value decomposition approach, yielding from the spectroscopic signatures the local drug concentration within single tumor cells, at a high spatial resolution reaching below 50 nm. Additionally, we investigated the influence of the sample treatment by phosphate-buffered saline with respect to changes in drug penetration in the tumor cell model. The differences between drug distributions following topical or systemic application are discussed in detail.

UV-VIS-Spectroscopy of $CO_3^-(H_2O)_{1,2}$ and $CO_4^-(H_2O)_{0,1,2}$

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Molecular clusters $CO_3^-(H_2O)_{1,2}$ and $CO_4^-(H_2O)_{0,1,2}$ are found in the lower region of the ionosphere [1]. Investigation of their properties can be helpful to understand atmospheric chemistry. In this work, we focus on the spectroscopic properties of $CO_3^-(H_2O)_{1,2}$ and $CO_4^-(H_2O)_{0,1,2}$ in the UV and visible range.

The spectra of the clusters are measured by a Fourier Transformation Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS) and a tunable laser system. The experimental data is compared with quantum chemical calculations using the Reflection Principle and the Franck Condon Principle to provide information about the contributing excited states and structures. Furthermore, multireference calculations are used to analyze dissociation pathways.

For the clusters $CO_3^-(H_2O)_{1,2}$ we observe water loss in the range between 1.5 eV and 3.0 eV. The measured cross sections are in accordance with literature [2] and supported by the quantum chemical calculations.
Additionally, we measure the first spectrum of $CO_4^-(H_2O)_{0,1,2}$ between 3.2 eV and 5.5 eV. Above 4.0 eV, photochemical formation of CO_3^- takes place. The experimental photodissociation cross sections are on the order of 10^{-19} cm^2 to 10^{-18} cm^2. First results of spectra simulations suggest that the cross sections for CO_4^- reach their maximum at energies above 5.5 eV, reaching values up to the 10^{-17} cm^2 range.

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Photolytic Decarboxylation of Ferric EDTA by Time Resolved Infrared Spectroscopy

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The photolytic decarboxylation of iron carboxylates is a widespread phenomenon mostly based on a ligand-to-metal charge transfer excitation[1]; a notable example of which is the primary step of ferrioxalate actinometry[2]. The same decomposition pathway is also accessible for the ligand, ethylene diamine tetraacetic acid (EDTA), with a multitude of different metal centres[3], M; however, a conclusive reaction mechanism for complexes of the type $[M(EDTA)]^Q$ has yet to be confirmed.

Here, we investigate the decarboxylation of the EDTA ligand bound to the iron(III) centre after photoexcitation at 266 nm in liquid (heavy) water at ambient conditions. To this end, we utilised femtosecond UV-pump-MIR-probe spectroscopy as well as UV-pumped step-scan FTIR spectroscopy to resolve the time evolution of the characteristic CO-stretching vibrations of the EDTA's acetate groups in the regions from 1280 cm^{-1} to 1460 cm^{-1} and 1520 cm^{-1} to 1680 cm^{-1}. In addition, the asymmetric stretching vibration of the CO_2 in the region from 2260 cm^{-1} to 2440 cm^{-1} was also probed. On the ultrafast timescale, the data reveals a near instantaneous cleavage of a vibrationally excited CO_2 fragment with a quantum yield of about 30 %. The remaining 70 % of parent complex return non-radiatively to the electronic ground state of the parent, where they undergo vibrational energy relaxation on a timescale of several picoseconds. Furthermore, the experimental step-scan FTIR data indicate that the Fe-containing primary photoproduct fragment engages in a bimolecular reaction with the ground state parent complex on a microsecond time scale to form a secondary photoproduct, whose structure remains to be clarified.

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Dynamic Tuning of Giant Circular Dichroism in Templated Colloidal Assemblies

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Thin-films of precisely arranged metal nanoparticles, also known as metasurfaces, enable control of amplitude, phase and polarization state of light. That way, bulky optical setups can be condensed into functional thin-films, contributing to device miniaturization and integrated photonic circuits. However, traditional, lithography-based fabrication routes are cost and time intensive. Especially, layered fabrication of chiral arrangements to control circular polarizations is tedious and lacks full freedom of post-fabrication tuning.

Building on our experience in the production of plasmonic 1D[1-4] and 2D arrays[5] via scalable colloidal assembly, we explore the third dimension to create chiral metal nanostructures. Simple cross-stacking of two particle chain arrays on elastic substrates generates a chiral nanoarrangement. Strong plasmonic coupling of the closely spaced nanoparticles yields circular dichroism (CD) of 11 degrees, which surpasses other colloidal strategies by two orders of magnitude. Reversible re-stacking of the two substrates at different angles and compression normal to the interface allow dynamic modulation of CD magnitude/sign and spectral position, respectively. As a unique advantage over lithographic structures, our re-stackable design makes the enhanced superchiral plasmonic near-fields in the inter-layer gap region accessible to analytes to allow ultrasensitive, enantio-selective detection of chiral analytes.

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Rotational and translational dynamics of hydroxyl-functionalized ionic liquids investigated by means of fast-field cycling NMR relaxometry

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For hydroxyl-functionalized ionic liquids (ILs) it has been shown that two types of hydrogen bonds are possible: between cations and anions (ca) and between two cations (cc). [1] The latter counter-intuitive attraction between like-charged ions influences macroscopic properties such as phase behaviour and viscosity. [2] In this work we have studied a set of ILs having either the 1-(2-hydroxyethyl)-3-methyl-imidazolium (functionalized) or the 1-methyl-3-propyl-imidazolium (not functionalized) cation in common. Both cations were combined with either BF_4^-, NTf_2^-, or OTf^- anions, indicating an increasing anion-cation interaction strength in that particular order.

Using a STELAR FFC 2000 fast-field cycling NMR relaxometer we have studied the spin-lattice relaxation time, T_1, as a function of resonance frequency, ν_0, for a frequency range between 10 kHz and 42,6 MHz. Since we deal with ^1H and ^{19}F relaxation, the dominating relaxation mechanism is due to magnetic dipole-dipole interactions. As relaxation pathway both, intramolecular as well as intermolecular contributions have to be considered. While the intramolecular coupling is solely modulated by rotational motion, the intermolecular interactions are mediated by both, rotational as well as translational motions. This enables us to determine rotational correlation times, τ_{rot}, as well as translational diffusion coeffcients, D_{trans}, in one single experiment. In this study both quantities have been determined depending on the temperature and on the interaction strength of the anion. Finally, the question whether cationic cluster formation influences the rotational and/or translational dynamics of the ILs can be answered.

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Combined IR/UV spectroscopic and quantum chemical studies on chromone/methanol aggregates – investigation of dispersion interactions

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Dispersion forces have often been underestimated in the description of intra- and intermolecular interactions. Within aggregates, the balance between different sites of dispersion interactions and electrostatic forces can be the deciding factor for the preference of a certain binding motif and is difficult to model with current theoretical methods. Systematic probing of dispersion interactions in aggregates with two or more possible binding motifs enables better understanding and description of these phenomena.

In this work, complexes of chromone with methanol were investigated experimentally by performing mass- (and isomer-) selective combined IR/UV investigations in a molecular beam experiment. The experimental results are compared to theoretical predictions obtained from (TD)DFT-, DLPNO-CCSD(T)- and SAPT-calculations, including transition state calculation with respect to different isomers. In the chromone-methanol cluster always a hydrogen-bond is formed between the OH group of methanol and the carbonyl group of chromone but there are different possible orientations for the methanol moiety due to different dispersion interactions of the methyl group with the chromone moiety. Both the electronic ground state (S_0) as well as the electronically excited triplet state (T_1) were studied in detail. Two different isomers in both electronic states are observed and assigned. To the best of our knowledge, we present the first transient IR investigations of isolated aggregates (gas phase) between an alcohol and another organic molecule in a triplet state.

Inhomogeneity of the intermolecular hydrogen-bond modes in aqueous salt solutions

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In aqueous solution, many chemical and biological substances, from simple salts to proteins and DNA, are charged. The solvation of ions in water is accompanied by the formation of a hydration shell – a layer of water molecules, which interacts strongly with the ions. Intermolecular thermal fluctuations of a hydration shell are essential in substitution and elimination reactions, where they provide the energy needed to surmount the reaction barrier. Due to the altered intermolecular forces, the spectrum of thermal fluctuations of a hydration shell is significantly different from that of the bulk water, as revealed by the far-infrared absorption spectroscopy. However, little is known about the inhomogeneity of these intermolecular vibrations. Here, we report the use of the novel two-dimensional Terahertz-InfraRed-Visible (2D TIRV) spectroscopy [1] to measure the coupling between the intermolecular hydrogen-bond vibrations and the intramolecular OH-stretching mode in the hydration shells of simple inorganic ions. We found that ions increase this coupling in liquid water and induce inhomogeneity of the intermolecular hydrogen-bond modes.

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Alkynyl- and phenyl-extended phenanthroline based Cu(I) photosensitizers and their photophysical properties

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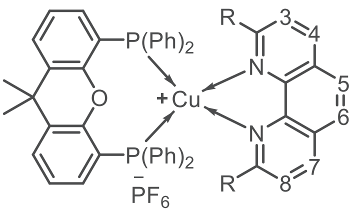
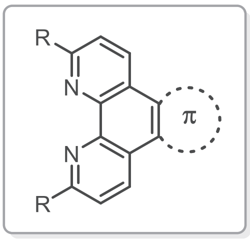
Heteroleptic diimine–diphosphine Cu(I) complexes of the type $[(P^\wedge P)Cu(N^\wedge N)]^+$ (see below) are a viable alternative to noble-metal containing photosensitizers like $[Ru(bpy)_3]^{2+}$. A major drawback of such Cu(I) systems, however, is their limited ability to efficiently absorb visible (sun)light.[1]

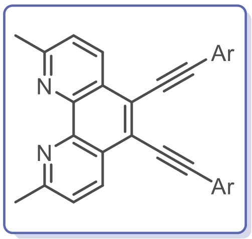
To tackle this issue, several studies already dealt with the introduction of fused aromatic rings in 5,6-position at the phenanthroline moiety (see below).[2,3,4]



general structure



previous studies
fused aromatic rings



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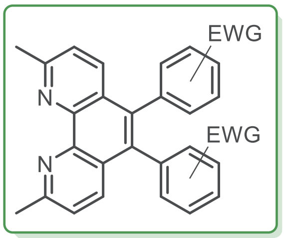

this work
phenyl-based

As a promising alternative we recently tested the introduction of different alkynyl-based (blue) and phenyl-based (green) substituents in 5,6-position. Consequently, a systematic series of 11 novel Cu(I) complexes was prepared and systematically investigated by photo- and electrochemical methods.

In consequence, distinct differences between both ligand classes were revealed. Also a correlation between luminescence quantum yield and the steric demand of the substituents could be deduced. Furthermore, emission lifetimes are strongly dependent on the substituents electronic characteristics and more than doubled for some examples, demonstrating the tunability of these diimine based photosensitizers.

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Studies on the photochemistry of $Co^{III}(EDTA)^-$

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$Co^{III}(EDTA)^-$ is a highly stable complex, which can be decomposed by photocatalytic oxidation to extract the metal ion for further use. Previous investigations analyzed the photoproducts after UV irradiation of the complex and proposed a reaction mechanism involving the release of CO_2, but it was contested.[1],[2],[3]

Here, the primary processes of the complex were studied in water following photoexcitation at 266 nm. To this end, femtosecond UV-pump/mIR-probe spectroscopy was carried out and the evolution of the inner and outer C=O stretching vibrational resonances of the EDTA ligand between 1270 cm^{-1} and 1700 $cm^{-1}$was recorded for time delays between 250 fs and 100 ps. Furthermore, the spectral region of the asymmetric stretching vibration of CO_2 was tracked in the same manner. The data revealed a prompt CO_2 cleavage from the parent complex with a primary quantum yield of 17 %. The triatomic fragment was dressed with excess vibrational energy, which dissipated into the solvent within 60 ps. CO_2-loss competes with internal conversion of the excited parent complex followed by a vibrational energy redistribution within 20 ps. The bond ruptures give rise to a photoproduct having EDTA–C=O stretching absorptions, which are clearly distinct compared to the parent complex.

The spectro-temporal evolution on the nano–to–millisecond time scales was investigated with Step–Scan spectroscopy. The vibrational bands of the CO_2–fragment and the Co-containing photoproduct observed in the pump–probe experiments remained unchanged over these long time scales thereby contradicting bimolecular reactions proposed in the literature.[1],[2] The assignment of the primary photoproduct was aided by ab initio calculations within the framework of density functional theory.

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Vibrational Spectroscopy to study Proton Mobility in Ionic Liquids

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Ionic Liquids (ILs) are very promising materials for future applications due to their properties. Recently, a class of proton-conducting ionic liquids has been demonstrated[1], which are potential candidates for applications as fuel cell material. However, the detailed mechanism of proton conduction in this class of ionic liquids remains to be determined. Our experimental study intends to identify the proton transfer pathway and the mechanism of proton transport between anion and cation and the solvent as a medium.

The FTIR measurements on 1-Methyl-3-(4-sulfobutyl)-imidazolium para-Toluene-sulfonate (IL1) and 1-Methyl-3-(4-sulfobutyl)-imidazolium methyl-sulfonate have been performed in different concentrations and different solvents, including H_2O as polar and protic solvent and MeOH. FTIR spectra show several spectral shifts in the IR region corresponding to the sulfonate groups, specifically 1250-1030 cm^{-1}. Based on the FTIR analysis it becomes apparent, that the equilibrium between protonated cation and deprotonated anion is influenced by the solvent, in particular H_2O and the solvent's concentration. There appears to be a stable solvent concentration shielding the positive charge (anion, imidazole), more pronounced in MeOH, indicating the formation of a solvent cage.

The current, steady-state, FTIR results demonstrate already that proton conduction could be facilitated via a proton shuttle between the two sulfonate groups (anion and cation head groups).

In order to follow this proton shuttle on relevant ultrafast time scales, we plan to perform ultrafast spectroscopy, in particular, 2D IR[2] in the region from 1250-1000 cm1, and are currently building a dedicated setup for this.

To support the current study DFT calculation and conductivity measurements to observe the influence of the temperature, concentrations and solvent´s type on proton mobility are underway.

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Colloidal photonic crystal slabs for sensing and energy harvesting

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For many photonic applications, it is important to confine light of a specific wavelength at a certain volume of interest at low losses. So far, it is only possible to use the polarized light perpendicularly to the solid grid lines to excite waveguide plasmon polaritons in metallic photonic crystal slabs. In this contribution, we demonstrate colloidal photonic crystal slabs (cPhCs), fabricated by self-assembly of metallic nanoparticles [1] and an ultrathin semiconductor injection layer, to guide the resonant modes selectively [2]. Colloidally grown gold nanoparticles, directly self-assembled over a linear template on a titanium dioxide (TiO_2) layer is characterized with conventional UV-vis-NIR spectroscopic methods to explore the dispersion relation. Compared to metallic grids, the experimentally observed (supported by simulation) range of hybridized guided-modes inside the semiconductor can now be extended to modes along the nanoparticle chain lines, resulting in hybrid plasmonic line shapes with sharp features. Such characteristics can be used to enhance the resolution and figure of merit of plasmon-resonance based refractive index sensors. Moreover, the sharp line features, arising in these cPhCs due to suppression of the radiative damping, can be advantageous in the extraction of plasmonic charge carriers. Such energy harvesting schemes are thus explored and discussed, highlighting the advantages of colloidal fabrication approaches.

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Distribution of Core-Shell-Nanoparticles with Radial Gradient

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Colloidal semiconductor nanoparticles have gained wide interest over the past decades due to their possible applications in biological or photoelectronical areas.[1,2] Using Core-Shell nanoparticles with tunable composition and interfaces allows precise control over optical and electronical properties.[2] Features like charge carrier lifetime or extraction are depending strongly on the interfacial architecture, but the exact quantification of the structure still remains unter debate.[3]

In the presented work we investigated the interface of Typ II-VI-Core-Shell nanoparticles with a radial gradient. Detailed examination of the interface was carried out by different Raman techniques such as surface-enhanced Raman Spectroscopy (SERS) and Resonant Raman Spectroscopy.

Having a deep understanding of the exact interface greatly supports the knowledge about the underlying optoelectronic properties and therefore enables more precisly tunable semiconductor nanoparticles for further applications.

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Dispersion-Bound Isolated Dimers in the Gas Phase: Observation of the Shortest Intermolecular C–H•••H–C Distance via Stimulated Raman Spectroscopy

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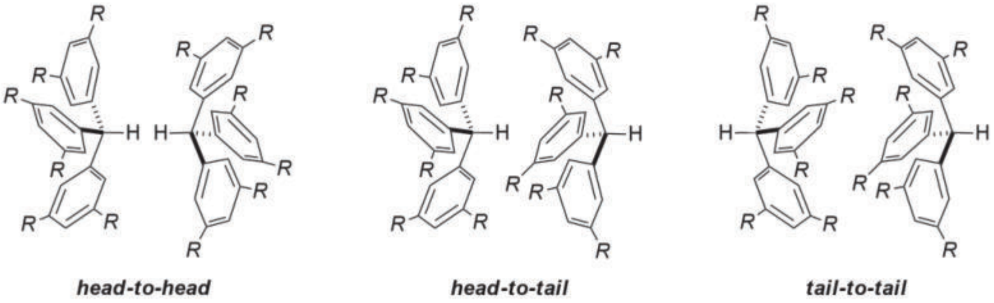
Although they have a “weak nature” London dispersion interactions are omnipresent and of fundamental importance for many aspects of chemistry and biology leading to important structural preferences. We investigate isolated dimers of triphenylmethane $(TPM)_2$ and a derivative, the singly deuterated all-*meta tert*-butyl triphenylmethane dimer $(T^tBuPM\text{-}d_1)_2$. We show that $(T^tBuPM\text{-}d_1)_2$ forms a head-to-head dimer with an unusually short C-H(D)•••(D)H-C distance in the gas phase. Our investigations clearly show pure dispersion interactions, outbalancing Pauli repulsion, are the driving force to form unusual arrangements without the support of any environment and are realised by application of combined IR/UV and very demanding combined stimulated Raman/UV spectroscopy. In case of $(TPM)_2$ the contrary tail-to-tail structure is formed due to the absence of the *tert*-butyl groups, acting as dispersion energy donors.

These analyses demonstrate that the structure of isolated, symmetric and nonpolar molecular aggregates can be determined by application of very sophisticated spectroscopic methods within molecular beam experiments. This opens a unique opportunity to analyse dispersion interactions. The presented textbook example is an important further step in understanding intermolecular balances between dispersion interactions and steric repulsion.



The photophysics and photochemistry of phenol-ammonia and pyrrole-ammonia complexes.

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Excited-state hydrogen transfer (ESHT) reactions provide photostability of biomolecules and are applied for the photoprotection of compounds (e.g. plastics) exposed to sunlight. Mechanistic proposals include hydrogen transfer and electron coupled proton transfer (ECPT). Clusters of phenol or pyrrole with ammonia have been used as model systems. Previous studies on the dissociation of such clusters into a neutral phenoxy or pyrrolyl radical and a neutral ammonia cluster carrying the extra hydrogen were limited to clusters containing at least five ammonia molecules with phenol [1,2], and two ammonia molecules with pyrrole [3].

Here we report experiments on clusters containing a single ammonia molecule. We use time-of-flight mass-spectroscopy, REMPI-spectroscopy and the velocity map ion imaging technique in combination with quantum chemical calculations. In order to detect the Rydberg molecule NH_4 we use deuteration [4] to lengthen its very short (ps) lifetime [5]. We conclude that, unlike pyrrole-ammonia, the phenol-ammonia cluster does not dissociate into phenoxy radicals and NH_4 upon excitation to the S_1 state.

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Multi-spectroscopic investigations of dinuclear copper(I) and silver(I) complexes

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This contribution presents the investigation of dinuclear copper and silver complexes with a butterfly-shaped halide containing M_2X_2 core (M = Cu, Ag; X = I, Br, Cl), which are related to previously investigated OLED (organic light emitting diodes) relevant highly luminescent copper complexes. The influence of the metals and halides on the photophysical properties is analyzed by systematically exchanging the metal and halide centers.

The electronic properties and the relative energies of electronically excited states are investigated by UV/VIS absorbance and luminescence spectroscopy, including time-correlated single photon counting to determine the lifetimes of the emissive states. Furthermore, structural information on the excited states are obtained by time-resolved step-scan FTIR spectroscopy, in combination with (TD)DFT calculations. The presented spectroscopic experiments are performed at different temperatures (from 290 K to 5 K) to analyze thermally activated photophysical processes (e.g. thermally activated delayed fluorescence, TADF).

The cooperative effects between the copper, silver and halide centers are probed, at first, *via* their luminescence properties, where the metal centers turned out to have a huge impact on the radiative deactivation channels. A red-shift of the emission band arising from TADF is observed at low temperature for the copper complexes, in contrast to the rather constant emission wavelength of the silver systems. However, the quantum yield of the silver complexes strongly depends on temperature. Secondly, step-scan FTIR spectroscopy revealed a large influence of the metal exchange on the excited state infrared absorption, whereas the halides have a much smaller influence.

Investigating dispersion-controlled ketone-solvent balances as experimental benchmarks

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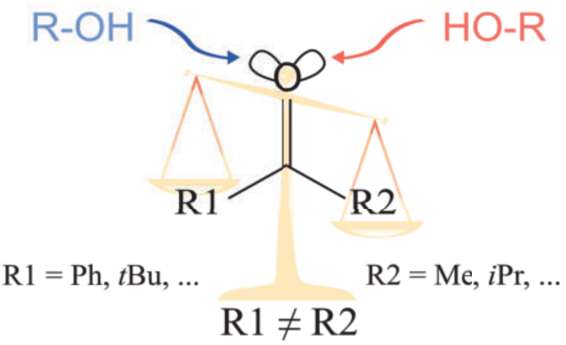
Side preferences of hydrogen bond donors docking onto an asymmetrically substituted ketone-oxygen are probed with FTIR spectroscopy in a supersonic jet. Thus, the abundance ratio of the ideally two isomers formed at low temperatures is determined, allowing for experimental benchmarking of theoretically predicted relative conformational derivatives on a kJ mol^{-1} or even finer scale.[1,2] Previously, this approach has been applied to acetophenone derivatives with methanol and *tert*-butyl-alcohol, showing a good agreement between experiment and theoretical predictions.[3] Further, zero-point vibrational energy cancellation improves upon balances with furan[4] and anisole[5,6] complexes, where the π-system provides the second hydrogen docking site. A study of pinacolone balances with different alcohols confirmed the observed effects and allowed to investigate the influence of London dispersion and steric hindrances on the favored docking site by varying the solvent alkylation.[7] Current extensions involve further variations of ketone alkylation and amines as hydrogen bond donors.



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An efficient approach for hydrophobic-to-hydrophilic transition of oleate-capped upconversion nanoparticles

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Lanthanide-doped upconversion nanoparticles (UCNPs) have become known as efficient luminescent materials owing to their long luminescence lifetimes, sharp-band emission, low toxicity, as well as their excellent physical and chemical stability. [1]

High-quality lanthanide-doped upconversion nanoparticles are generally synthesized by employing long-chain oleic acid as the ligand in the synthetic process, rendering them hydrophobic, and preferentially dispersed in nonpolar solvents. Thus, post-synthetic surface modifications are required prior to practical applications. Herein, we developed a facile approach to remove the surface ligand from oleate-stabilized UCNPs (OA-UCNPs) using short-chain acids as stripping agents by a simple vortexing method on a time scale of 10 seconds, [2] which was confirmed by FT-IR, ^{1}H NMR, TGA, and TEM.

This method allows for the fast and efficient hydrophobic-to-hydrophilic transition in either biphasic solvent systems or single hydrophobic media without any noticeable detrimental effects on size, shape, and phase of crystals during the ligand removal process. Furthermore, the obtained ligand-free UCNPs can be readily transferred to the aqueous solution and further modified with water-soluble capping molecules by sequential surface functionalization.

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Dehydrogenation Reactions of O-Heterocyclic LOHC Molecules

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With the dwindling of fossil fuels and the alarming progression of global warming, the ecological and social demand for cleaner and more sustainable energy sources has never been as high. As renewable sources, such as wind and solar power, give no continuous and constant power output, hydrogen is a promising candidate for the chemical storage of energy. The concept of Liquid Organic Hydrogen Carriers (LOHCs) avoids unfavorable handling of elemental hydrogen. [1]

Heterocyclic LOHC molecules display advantageous thermodynamic properties regarding their heat of dehydrogenation. [2] Consequently, several N-heterocycles have been successfully investigated, e.g. the indole-based systems and their derivatives. [3, 4]

In order to investigate the feasibility of O-heterocyclic compounds as possible LOHCs, synchrotron radiation-based high resolution X-ray photoelectron spectroscopy and temperature-programmed desorption measurements of furan and benzofuran were performed on Pt(111) under UHV conditions. By applying heating ramps after the adsorption experiment, the respective dehydrogenation and decomposition reactions are monitored via evaluation of the characteristic spectra. This allows for fundamental insights into the reactivity and stability and helps assessing the viability of the compound class as LOHC.

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"Intra-ionic" or "Inter-ionic" hydrogen bonding in hydroxy-functionalized omnium halides: A combined X-ray, ATR-IR and quantum chemistry approach

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Hydroxy-functionalized pyridinium cations $[OHC_nPy]^+$ with n = 2,3,4 interact with chloride, bromide and iodide anions via hydrogen bonding. In these omnium halides we observed two types of hydrogen bonding: "intra-ionic" H-bonds, wherein the anion interacts with both, the hydroxy group and the positively charged ring of one cation, and "inter-ionic" H-bonds, wherein the anions are solely interacting with the hydroxy group of one cation but with the positively charged ring of another cation. We show that the formation of hydrogen bonding is controlled by the length of the hydroxyalkyl chain as well as the interaction strength of the anion. The H-bond geometries from the X-ray structures correlate with the OH vibrational frequencies measured by Attenuated Total Reflection infrared (ATR-IR) spectroscopy, supporting the Badger-Bauer rule. The formation of either "intra-ionic" or "inter-ionic" H-bonds is analyzed by the Natural Bond Orbital (NBO) analysis. [1]

The calculated NBO descriptors, the second-order stabilisation energy ΔE and the charge transfer qCT, reflect the structural and spectroscopic properties of the omnium salts and indicate the preference for one or the other type of hydrogen bonding. This situation changes with the water uptake of the salts. The water molecules compete for the interaction with the anion in favor of "inter-ionic" hydrogen bonding. [2]

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Intramolecular charge transfer in metal-photoacid-complexes

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Photoacids show an increase of acidity upon excitation by light and subsequent proton transfer to nearby acceptors (excited-state proton transfer, ESPT).[1] Often being aromatic alcohols, in literature, intramolecular charge transfer (ICT) from the OH-moiety to the aromatic backbone is discussed as fundamental to the weakening of the OH-bond followed by ESPT.[2, 3] In contrast, influence of ICT on metal ions, replacing the acidic proton in aromatic alcohols giving metal-photoacid-complexes, has not been investigated explicitly. Potentially, charge transfer, triggered by light, could render manipulation of electron density and thereby altering Lewis acidity of the metal ions possible. As Lewis acidity is a key parameter of metal catalysts, in that case, metal-photoacid-complexes might open up new synthetic pathways.

Regarding these prospects, change in dipole moment ($\Delta\mu$) of Zn- and Sc-complexes of a pyranine-derived photoacid[4] upon excitation was determined by means of Lippert-Mataga-Analysis,[5,6] as $\Delta\mu$ can be considered correlating to electron distribution on the metal ions. Plotting excitation against emission wavelength revealed a connection between Lewis acid strength and emission wavelength shift. Moreover, substantial $\Delta\mu$ was found to hint at charge transfer in studied Zn- and Sc-complexes. Accordingly, calculations suggest rising electron density reallocation being linked to decreasing strength of bonded Lewis acid.

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Quantification of Material Gradients in Core/Shell Nanocrystals

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Core/shell nanocrystals with a graded interface between core and shell exhibit improved opto-electronic properties compared to particles with an abrupt, sharp interface, as material gradients mitigate interfacial defects and define the shape of the confinement potential [1,2]. So far few works exist that allow to quantify the width of the gradient.

In this study ZnSe/CdS nanocrystals with graded shells made at different temperatures were characterised using extended X-ray absorption fine structure (EXAFS) and Raman spectroscopies [3]. The gradient was quantified by fitting the average coordination number of the probed element with respect to the two possible counterions to a simple, geometric model. It can be shown that at the lower temperature limit for shell growth (260°C) substantial interfacial alloying can be attributed mainly to cation migration. At higher temperature (290°C) an anomalous trend towards a lower degree of phase mixing was found, which cannot be accommodated with the picture of a continuous, radial gradient. It is explained by formation of an ordered alloy under thermodynamic control to minimise strain.

This is a general method that can be employed for all radially graded core/shell nanocrystals with ternary or quaternary composition.

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Infrared Spectrum of the Adamantane$^+$-Water Cation: Hydration-Induced C-H Bond Activation and Free Internal Water Rotation

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Adamantane is the parent molecule of diamondoids, which are nanometer-sized H-passivated nanodiamonds [1]. These and their derivatives are of interest in a variety of disciplines with applications in materials and polymer sciences, molecular electronics, medical sciences, chemical synthesis and astrochemistry [2]. Diamondoid cations are reactive intermediates in their functionalization reactions in polar solution [3]. Hydration is predicted to strongly activate their C-H bonds in initial proton abstraction reactions. To study the effects of microhydration on the properties of diamondoid cations, we characterize herein the prototypical monohydrated adamantane cation ($C_{10}H_{16}^+$-H_2O, Ad$^+$-W) in its ground electronic state by infrared photodissociation (IRPD) spectroscopy in the CH and OH stretch ranges and dispersion-corrected density functional theory (DFT) calculations (D3-B3LYP/cc-pVTZ) [4]. These spectra provide the first spectroscopic information of any microhydrated diamondoid cation cluster. The W ligand binds to the acidic CH group of Jahn-Teller distorted Ad$^+$ via a strong CH…O ionic H-bond supported by charge-dipole forces. Although W further enhances the acidity of this CH group along with a proton shift toward the solvent, the proton remains with Ad$^+$ in the monohydrate. We infer essentially free internal W rotation from rotational fine structure of the ν_3 band of W, resulting from weak angular anisotropy of the Ad$^+$-W potential.

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Optical spectra of small gold cluster cations

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Gold is a versatile material with unique properties that underpin its many applications; from medicine, catalysis, (opto)electronics to basic research. The theoretical description even of very small Au clusters however is still very challenging due to relativistic effects, d electrons participating in the bonding, spin-orbit coupling and charge-transfer effects.

Here we present our latest results on the optical spectra of $Au_{n=2–4}^+$ clusters that were measured in a hitherto unavailable quality and thus allow for a detailed analysis of the ground and excited state surfaces of these important model systems.[1-3]

The presentation will focus on the findings on Au_4^+, that show that an unexpected isomer contributes to the optical spectrum [2] and on the findings on Au_2^+, where we demonstrate that an understanding of the complex optical spectrum is not possible without multireference and relativistic theoretical treatment including spin-orbit effects, despite its seemingly simple H_2^+ like electronic configuration.[1] We will furthermore discuss the experimental improvements necessary to allow for such sensitive measurements [3] and present our latest results on Au_3^+.

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Optical Spectra of Si_nO^+ Cluster of Astrophysical Interest

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The understanding of interstellar dust is essential to disentangle the formation mechanisms of star systems in dust clouds and thus also the history of our own solar system and Earth [1]. Furthermore, dust grains dominate the extinction and emission of electromagnetic radiation in the interstellar medium (ISM) and a detailed knowledge about their interaction with radiation is crucial to understand stellar outflows and winds [2]. Large µm-sized silicates are a major constituent of interstellar dust. The origin and arising processes of these large particles is still poorly understood. So far, only few possible precursors like SiO have been identified in the ISM [3]. Experimental data as well as theoretical calculations related to the dissociation and absorption behaviour of small, possible intermediate silicates, namely Si_nO^+ (n = 10 - 12) are presented.

The acquired spectra measured by photodissociation with our improved quadrupole/ time-of-flight tandem mass spectra setup are the first available optical absorption spectra of silicate cations [4]. We compare our obtained mass spectra, dissociation spectra, and optical spectra with TD-DFT calculations at the CAM-B3LYP level of theory. These results will be discussed in an astrophysical context as well as in terms of molecular structure.

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Low-energy electron irradiation induced synthesis of molecular nanosheets: influence of the electron beam energy

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Aromatic self-assembled monolayers (SAMs) can be cross-linked into molecular nanosheets – carbon nanomembranes (CNMs) – *via* low-energy electron irradiation. Due to their favorable mechanical stability and tunable functional properties, they possess a high potential for various applications including nanosensors and separation membranes for osmosis or energy conversion devices. Despite this potential, the mechanistic details of the electron irradiation induced cross-linking process still need to be understood in more detail. Here, we studied the cross-linking of 4'-nitro-1,1'-biphenyl-4-thiol SAM on gold. The SAM samples were irradiated with different electron energies ranging from 2.5 to 100 eV in ultra-high vacuum and subsequently analysed by complementary techniques including X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction with micrometre sized electron beams (µLEED) and low-energy electron microscopy (LEEM). To demonstrate the formation of CNMs, the formed two-dimensional molecular materials were transferred onto grids and oxidized wafer and analyzed by optical, scanning electron (SEM) and atomic force microscopy (AFM). We found a strong energy dependence for the cross section for the cross-linking process, the rate of which decreases exponentially towards lower electron energies by about four orders of magnitude. We conduct a comparative analysis of the cross sections for the C–H bond scission *via* electron impact ionization and dissociative electron attachment and find that these different ionization mechanisms are responsible for the variation of the cross-linking cross section with electron energy. C. Neumann, R. A. Wilhelm, M. Küllmer, A. Turchanin, Faraday Discuss. **2020** DOI: 10.1039/C9FD00119K

A BUNSEN project: Benchmarks Using a New Setup for FTIR-Jet Spectroscopy of Intermolecular Energy Balances

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Ketones R-(C=O)-R' offer two similar docking sites for hydrogen bond donors such as water – the two lone pairs at the oxygen atom [1]. The energy difference between docking to the two sites can be influenced by varying the substituents R and R'. This gives rise to a subtle intermolecular energy balance that can be probed with FTIR-jet spectroscopy. By recycling the gas mixture after the expansion, the new and sustainable *gratin* (gas-recycling atom-economic infrared) jet spectroscopy setup reduces substance consumption by more than one order of magnitude compared to previous experiments, allowing to measure more expensive chemicals such as water isotopologues.

In contrast to O/π balances [2,3], carbonyl balances minimize zero point energy corrections, allowing for a more direct detection of electronic energy contributions such as dispersion [4]. In addition to hydrogen bond isomerism, the water complexes exhibit a characteristic vibrational resonance which can be exploited for quantum dynamics benchmarking.

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Photolytic Formation of Nitrile Imine in Solution by Femtosecond Spectroscopy

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Nitrile imines are reactive intermediates in organic synthesis and polymer chemistry. Such species are typically prepared *in situ* by thermolysis or photolysis of tetrazoles under release of dinitrogen. Moreover, their quantum chemical treatment is challenging as their description requires multi-reference approaches, which yield partially contradictory results regarding the importance of the various valence isomeric forms of the electronic structure. Most nitrile imines are inherently unstable and could therefore only be investigated under cryogenic conditions so far.[1,2]

Herein, we investigate the primary processes of 2,5-diphenyltetrazole in liquid THF under ambient conditions following its 266 nm photoexcitation. To this end, we employed femtosecond UV-pump-MIR-probe spectroscopy and tracked the evolution of the characteristic vibrational resonances of the reactant and the products in the spectral regions ranging from 1480 to 1620 cm^{-1} and from 2000 to 2280 cm^{-1} and for time delays up to 1 ns. The data reveal a primary quantum yield of the dinitrogen release of 100 %. The N_2-loss occurs within less than 1 ps after the absorption of the pump photon. In addition, significant spectral shifts of the product absorption bands indicate that the fragments are born with excess vibrational energy; the dissipation of which occurs on a time scale of roughly 10 ps. The characteristic absorption band of the asymmetric stretching vibration of the nitrile imine product is detected at 2205 cm^{-1}. In contrast to earlier findings from matrix isolation spectroscopy,[2] the band is much broader, less intense and shifted to slightly lower frequencies. Furthermore, we observed an extended low-frequency tail expanding to ca. 2000 cm^{-1}, which has not been seen in the cryogenic matrix and may hint at an inhomogeneous distribution of the valence isomers and their dynamic exchange in liquid solution. At a phenomenological level, the overall lineshape can be described well by three overlapping bands; yet, their assignment is still a topic of our ongoing research.

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High resolution ro–vibrational analysis of molecules in doublet electronic states: The ν_1 fundamental of chlorine dioxide ($^{16}O^{35}Cl^{16}O$) in the X^2B_1 electronic ground state

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Chlorine dioxide is of interest for fundamental aspects of chemical bonding and electronic structure and in relation to atmospheric chemistry. Chlorine dioxide is one of the most effective, fast–acting disinfectants, capable of eliminating bacteria, viruses, biofilms, molds, and spores. Highly topical is the controversial discussion of the role of ClO_2 as a powerful disinfectant addressing the COVID–19 pandemics.

We report the spectrum of the ν_1 fundamental of chlorine dioxide centered in the infrared atmospheric window at 945.592 cm^{-1} measured with essentially Doppler limited resolution at an instrumental line width of 0.001 cm^{-1} using the Zürich prototype ZP2001 Bruker IFS 125 HR Fourier transform infrared spectrometer. The ro–vibrational line analysis is carried out with an improved effective Hamiltonian and a newly developed computer code ROVDES for ro–vibrational spectra of open–shell free radical molecules including spin–rotation interactions. Accurate values of rotational, centrifugal and spin–rotation parameters were determined for $^{16}O^{35}Cl^{16}O$ in the vibronic ground state X^2B_1 from more than 3500 ground state combination differences. The number of 7239 assigned transitions for the ν_1 fundamental with $N^{max} = 76$ and $K_a^{max} = 26$ provide a set of 32 accurate effective Hamiltonian parameters for the ν_1 fundamental (ν_1 ν_2 ν_3) = (100) (21 rotational and centrifugal distortion parameters and 11 spin–rotational interaction parameters). This effective Hamiltonian (A-reduction and I^r-representation) reproduces 1703 upper state energies from the experiment with a root–mean–square deviation $d_{rms} = 1.67 \times 10^{-4}$ cm^{-1} and the 7239 transition wavenumbers with $d_{rms} = 3.45 \times 10^{-4}$ cm^{-1}. Our results provide a considerable improvement over previous results with which we compare and should provide a benchmark for theoretical studies with applications to atmospheric spectroscopy and laser chemistry, which are discussed in relation to our spectra.

Chirality Recognition and Synchronisation: Complexes of 1-Phenylethanol and Phenylmethanol

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Subtle molecular recognition can take place between chiral molecules when one of them is replaced by its mirror image. Depending on whether the interaction partners are locked in a permanently chiral constitution or can interconvert between conformations of opposite transient chirality, these phenomena can be classified as chirality recognition respectively chirality synchronisation.[1] In the first case spectral signatures of homo- and heterochiral complexes can be distinguished by varying the enantiomeric composition, but information about the relative stability is not readily accessible due to largely statistical formation. Provided that interconversion barriers are shallow, chirality synchronisation on the other hand leads to an excess of the more stable complexes, but their identification can be ambiguous. By comparing the aggregation of closely related permanently and transiently chiral molecules this complementary information can be combined.[2,3]

This concept is demonstrated for 1-phenylethanol and phenylmethanol (benzyl alcohol), which form very similar dimers tightly bound by two hydrogen bonds and dispersion interaction.[3] We employ supersonic jet expansions, probed by FTIR and Raman spectroscopy, and DFT calculations. After the investigation of the dimers we are currently exploring larger complexes.

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Imaging Flexible Molecules in Supersonic Jet Expansions

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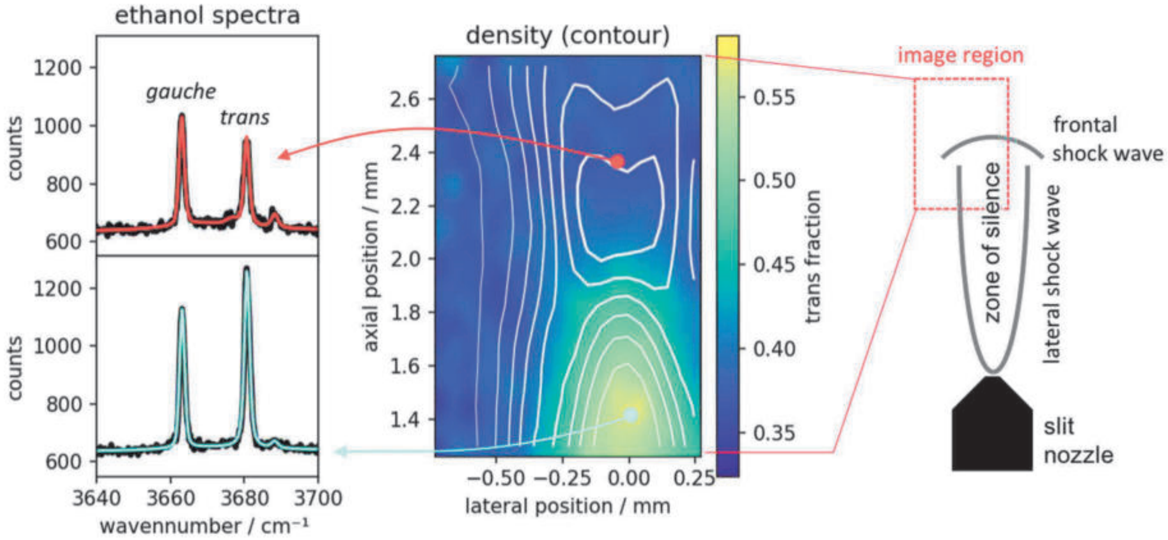
Supersonic jet expansions are a popular method to prepare cold molecules in the gas phase, for example in spectroscopic investigations. In supersonic expansions, complex flow patterns can form and properties such as the density, velocity or effective temperature of the seeded particles may change rapidly. The energy re-distribution can be made visible by imaging spectroscopy [1], for example by mapping rotational and vibrational temperatures of small molecules in the different zones of the expansion [2].

For the purpose of mapping supersonic expansions and investigating local conformational distributions, a Raman jet-spectrometer [3] was upgraded: a second actuator was added to scan a slit nozzle in two dimensions with micrometer resolution. With the upgraded setup, we studied the evolution of the trans/gauche conformer abundance of ethanol in helium expansions while varying the expansion conditions with small amounts of nitrogen serving as a probe for the rotational temperature. The low interconversion barrier of ethanol allows for conformational cooling in the rotationally cold regions of the jet, while the high-energy gauche conformer of pentane is frozen out.



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Dinuclear Design of Iridium(III) Complexes to Afford Strong Enhancement of Phosphorescence Rate

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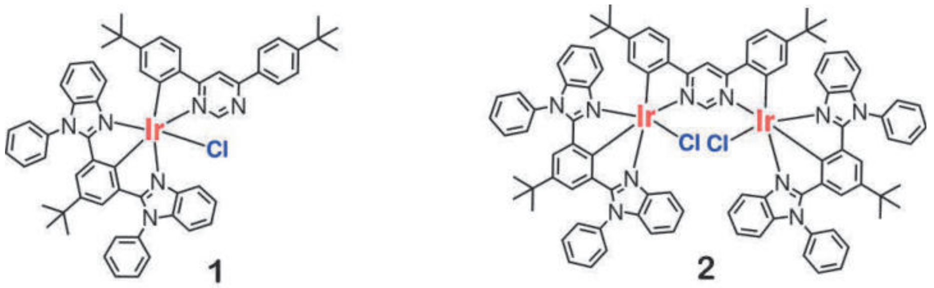
In recent years the emerging class of multinuclear transition metal complexes were reported to show enhanced phosphorescene rate compared to the mono-nuclear analogues. Researchers explained the advantage of multinuclear systems assuming that additional metal center(s) induce extra spin-orbit coupling (SOC) of state T_1 with singlet states, but the exact mechanism of the effect remained unclear.



1

$k_{Ph.} = 0.8 \cdot 10^6\ s^{-1}$

2

$k_{Ph.} = 2.3 \cdot 10^6\ s^{-1}$

Figure 1. Mono-nuclear Ir(III) complex **1** and the dinuclear analogue **2.** The corresponding phosphorescence rates are measured for degassed CH_2Cl_2 solutions at room temperature.

To unravel the details, we synthesized two analogous complexes **1** and **2** (Figure 1) of mono- and dinuclear design, respectively. Complex **2** shows about threefold faster phosphorescence than complex **1**. Theoretical analysis of the molecular orbitals revealed electronic coupling of the two coordination sides in complex **2.** This resulted in the twice the number of excited singlet states available for SOC with state T_1, compared to **1**, thus strongly enhancing the rate of $T_1 \rightarrow S_0$ phosphorescence.

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Fragmentation of Isocyanic acid, HNCO, following core excitation and ionization

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Hydrogen, oxygen, nitrogen, and carbon are the basic building blocks of all organic life. Isocyanic acid, HNCO, is the smallest molecule that consists of those elements. Isocyanic acid is also ubiquitous in interstellar systems[1] and has been linked to the formation of formamide, a potentially prebiotic molecule.[2]

Our group previously investigated the normal and resonant auger electron spectra of isocyanic acid.[3] In order to further elucidate the interaction of HNCO with cosmic x-ray radiation we investigated the fragmentation after these auger processes. These experiments were carried out at the PLÉIADES Beamline at the SOLEIL Synchrotron in St. Aubin, France. The fragmentation was examined with the EPICEA detector. With this setup we simultaneously recorded the auger electrons and the time of flight of the created ions. Additionally, we recorded coincidence information for those electrons and ions that were formed from the same mother molecule. This information reveals detailed insights into the various fragmentation pathways.

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Tuning the excited state landscape of zinc (II) compounds in solution – a comprehensive study

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Bis(dipyrrinato) zinc complexes have received more attention due to their applications as luminophores and light-harvesting systems. These complexes are known to have high fluorescence quantum yields up to 0.66, comparable to BODIPYs, but their excited state dynamics have not been investigated in a systematic way. [1] Thus, it remains an open question about the nature of competitive relaxation channels besides fluorescence.

Recently, we reported on one possible side channel involving excited-state charge transfer, which is usually unfavored in homoleptic complexes in a nonpolar solvent such as cyclohexane. [1] In contrast, polar solvents are known to favor those states. [2] Interestingly, new experiments demonstrated that this charge transfer state is unaltered in polar solvents, like ethanol. This behavior suggests the existence of additional relaxation pathways, e.g. via triplet states [3], to play an important role in the relaxation behavior of these photoexcited complexes. Further comprehensive solvent-polarity dependent broadband transient absorption studies from the UV to the NIR region indicate subtle differences of homoleptic and heteroleptic complexes.

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Temperature-dependent decomposition reactions of O-containing LOHC contaminants on Pt(111)

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Liquid organic hydrogen carriers (LOHCs) represent an attractive way for energy storage and transportation utilizing the reversible hydrogenation of an organic compound. The system of dibenzyltoluene (H0-DBT) and perhydro dibenzyltoluene (H18-DBT) has been reported as promising candidate featuring suitable physicochemical properties and a favourable toxicology. Technical H0-DBT, however, contains up to 1% of oxygenate impurities, which might negatively affect the quality of the released H_2 gas from the hydrogenated molecule. [1, 2, 3, 4]

To gain insight in the surface reaction of these oxygenates, we investigated several model compounds on Pt(111) using high-resolution temperature-programmed X-ray photoelectron spectroscopy (HR-TPXPS). Diphenylmethanol, benzophenone and dicyclohexylmethanol are found to undergo C–O bond cleavage at the methylene bridge around 350 K, leading to an oxygen-free carbon fragment and adsorbed atomic oxygen. By contrast, dicyclohexylketone shows C–C bond cleavage and the formation of carbon monoxide above 220 K.

CO represents a catalyst poison and is problematic for further applications of the released H_2 gas. A possible solution might be pre-purification of industrially produced H0-DBT.

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Line shape investigations of the electronic origin of phthalocyanines, porphin and their water-clusters in the gas phase

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The spectral shape of the zero-phonon-line in the electronic (Stark-) spectra of organic molecules such as phthalocyanines [1] and porphin [2] and their clusters with small molecules (e.g. H_2O) recorded in superfluid helium nanodroplets is determined by molecular contributions and the influence of the helium environment. The analysis of such line shapes is not straightforward due to the interplay of these characteristics. Therefore, corresponding gas phase studies are crucial for dissecting helium induced spectral features from molecular rotor fingerprints.

The observed partially resolved rotational fine structure of jet cooled molecules and associated simulations give insight into the structure of the molecular systems for both the ground and the electronically excited state. Moreover by taking advantage of the Stark-effect, information about the polarity of the clusters and polar molecules can be deduced from the experiment and corresponding simulations. Utilizing a rule of thumb for transition from gas phase to helium droplet conditions we compare these simulations with spectra measured in helium droplets. Mismatches reveal helium induced contributions to the line shape and provide valuable insights to the physics of molecular rotors inside helium droplets.

Ultimately, this project heads for a better understanding of solvation processes on nanoscale (microsolvation) and the dynamics of electronic excitation of molecules embedded in superfluid helium nanodroplets.

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Photoelectron Circular Dichroism of anionic metal complexes

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Determination of absolute chirality, enantiomer differentiation and determination of enantiomeric excess for gas-phase species are topics within a currently very active research field [1]. A general problem in such studies is the low particle density in the gas phase and that the absorption circular dichroism usually is a very small effect. More recently, new methods have been developed to investigate the circular dichroism in the photoionization of chiral molecules and in the spatial distribution of the photoelectrons. In this case the dichroism can be orders of magnitude larger than the one observed in photoabsorption spectra.

We are extending this approach to anionic gas-phase systems. This not only allows for obtaining mass-specific information but usually also the electron affinities of neutral molecules are much lower than their ionization energies, such that they are in the range of the photon energies of common UV/vis table-top lasers.

Here, complexes between metal anions and chiral molecules or deprotonated chiral molecules are prepared in a molecular beam, mass selected and subsequently Velocity Map Imaging (VMI) is used to obtain the Photoelectron Angular Distributions. First results are presented for the electron detachment from chiral complexes of the atomic gold anion and deprotonated alaninol.

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Exploring the Optical Properties of Small Cationic Silicon Carbides

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Bulk silicon carbide shows a promising set of properties: a wide bandgap, high thermal stability, chemical inertness, and high thermal conductivity, making it a versatile semiconductor material for the use in electronics operating in harsh environments [1]. Beside these technical applications of bulk silicon carbide, small Si_nC_m molecules may also play an important role in the circumstellar chemistry of carbon-rich stars. Small molecules like SiC [2], Si_2C [3], as well as SiC dust grains [4] have been observed in the circumstellar environment of carbon stars like IRC +10216, but medium-sized intermediate species remain undetected.

In this contribution, we characterize the energetic, geometric, and optical properties of small cationic silicon carbide clusters obtained via photodissociation spectroscopy, mass spectrometry, and quantum chemical calculations to obtain a better understanding of silicon carbide as a material and new insight into the possible formation routes of interstellar silicon carbide dust particles. We present the first optical spectrum of $Si_4C_2^+$ and former unknown photofragmentation channels of a selection of small $Si_nC_m^+$ clusters.

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The Frozen Density Embedding method in combination with Pair Natural Orbitals

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We present a new Frozen Density Embedding implementation within the TURBOMOLE program package. The new implementation works with an arbitrary amount of subsystems and is able to use density functional theory and wave function theory for the subsystem description. That also includes higher order methods like MP2 and CC2. With the help of Pair Natural Orbitals this implementation offfers an solution to the problem of subsytems, which are still large but cant be devided into smaller subsystems any further. We will show the theory behind the implementation and its efficency for the computation of excitation energies of chromophores in solution.

Spatial Extent of Fluorescence Quenching in Mixed Semiconductor-Metal Nanoparticle Gel Networks

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In the recent decade, colloidal synthesis provides reliable nanocrystals with controllable size, shape, and surface chemistry.[1] Consequently, building up self-assembled structures, such as hydrogels and aerogels, from well-designed nanoparticles created a new class of materials, that are of great research interest due to their high volume to mass ratio.[2] The properties of the building blocks can be combined and even extended upon combination of different materials at the nanoscale. Therefore, multicompound gels consisting of interconnected semiconductor and metal nanoparticles (network structures) have been introduced recently.[3] The question arises how such two compounds are interacting in a gel. Upon illumination, excitons can be generated in the semiconductor parts of the assembled structures with a significant mobility of the electrons.[4] The contact to a metal compound allows the accumulation of the electron in the metal region, while the hole can be trapped in the semiconductor. In the present work, the above-mentioned system is composed of CdSe/CdS nanorods and noble metal nanoparticles as two different compounds building up the hybrid, multifunctional gel network. By means of optical spectroscopy, insight in the mobility of the charge carriers of such multicompound system is gained. Therefore, absorption and emission spectra are recorded and discussed. Time correlated single photon counting and quantum yields are determined for both the hydrogels and aerogels. A model explaining the observations is discussed.

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Dynamics of Photo-induced Guest Uptake and Release by a Photochromic Coordination Cage

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Recently, Clever and coworkers developed a supra-molecular cage that is composed of four photo-switchable dithienylethene (DTE) ligands [1]. They showed that it is possible to reversibly change the conformation of the cage upon irradiation with different wavelengths. UV excitation may start a ring closure of the DTE ligand while visible radiation initiates the ring opening reaction. Furthermore, NMR measurements revealed that the affinity of a guest molecule to fill the cavity of the cage changes drastically if the cage changes its conformation. In molecular dynamics calculations, we showed that affinity for guest binding decreases the more ligands are in a closed configuration. In this work, we investigate whether this trend is also reflected in differing photodynamics of the cages' DTE ligands in the presence of different guest molecules.

Using transient absorption spectroscopy, we compare the ultrafast dynamics of the cage systems with all DTE ligands either closed or open, and the cages being either empty or filled with three different guest molecules of varying shape. We show that the ring-opening reaction of the cage with four closed DTE ligands happens on a timescale of less than 10 ps and is very similar to the dynamics that are observed for the free ligand. Furthermore, the time constants that are found using global analysis are in good accordance with experimental results already described in the literature on similar DTE monomers [2]. However, while the influence of two guest molecules used in this work on the ring-opening of a DTE cage ligand is modest, adding a ferrocene into the cage cavity significantly increased the efficiency of the ring-opening reaction. For the experiment starting with a cage with four ring-open DTE ligands, for all guest molecules a small decrease of the ring-closure efficiency is observed. We both discuss a global analysis of the time-resolved data, indicating an altered motion on the potential energy surface in the excited state, and thermodynamical as well as sterical aspects possibly causing these findings.

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Through Bonds or Contacts? Mapping Protein Vibrational Energy Transfer Using Non-canonical Amino Acids.

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J. G., Löffler, Frankfurt/DEU, K. B., Eberl, Frankfurt/DEU, A., Gulzar, Freiburg/DEU,
S., Wolf, Freiburg/DEU, P. M., Durkin, Berlin/DEU, R. Kaml, Berlin/DEU,
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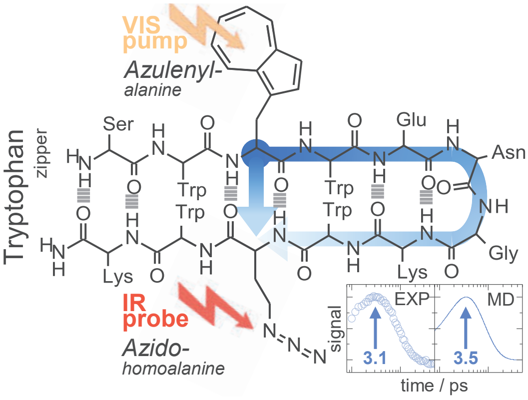
Vibrational energy transfer (VET) in proteins is responsible for efficient energy dissipation[1] and has also been linked to allosteric communication.[2] VET occurs via backbone as well as non-covalent contacts. Only little is known about the competition of these two transport channels, which determines the pathways of VET.

Here, we tackle this question by utilizing the stable hairpin structure of tryptophan zippers (TrpZip). We synthesized TrpZip variants with a pair of the non-canonical amino acids azulenylalanine and azidohomoalanine, serving as ultrafast heater and VET sensor in femtosecond VIS-pump IR-probe experiments.[3]

Accompanying extensive non-equilibrium MD simulations agree with experimentally determined VET timings for different heater-sensor distances. The quantum-corrected master equation approach[4] allows for disentangling the contributions of different VET pathways.



This joint computational/experimental study reveals contact transport pathways as the dominant channels of vibrational energy for crossing β-sheets, even if cutting short backbone stretches of only 3 to 4 amino acids.

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Proton Transfer of excited aminopyrene-based superphotoacids in sulfuric acid investigated by ultrafast time-resolved spectroscopy

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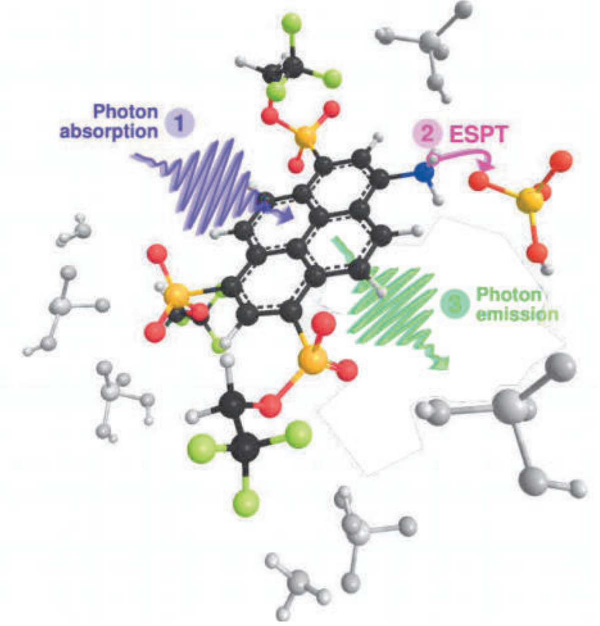
Delivering protons on demand is most conveniently achieved by photoacids, which typically allow the study of excited-state proton transfer (ESPT) to protic or strongly basic solvent molecules. Recently, aminopyrene-based superphotoacids have been developed with an excited-state lifetime of its conjugate base of several nanoseconds[1]. It was shown by fluorescence titration and Förster-cycle analysis that the excited-state acidity is as high as concentrated sulfuric acid and, thus, exceeding any previous photoacidity by several orders of magnitude.

Here, we extend the study by ultrafast time-resolved absorption spectroscopy monitoring the actual proton transfer following photo-excitation of fluorescent and non-fluorescent aminopyrene-based superphotoacids. A distinct kinetic isotope effect is observed, when investigating the system in deuterated sulfuric acid, and characteristics of the ESPT are determined with special emphasis on the influence of deuteration.



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A systematic study on ^{14}N nuclear quadrupole coupling and its relation with atomic and molecular properties.

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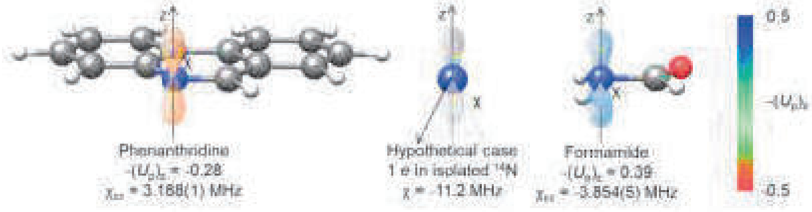
In high resolution spectroscopy, nuclear quadrupole coupling is observed when a nucleus of spin I>1/2 interacts with the local electric field gradient. The Townes-Dailey (TD) model correlates the orientation of molecular orbitals with the interacting field gradient. As such, the nuclear quadrupole coupling is related to the electronic structure of the molecule and can give information about chemical bonds, polarization, and resonance in the molecule or the hybridization state of the coupling atom. To obtain reliable information of these properties, a detailed understanding of how orbital occupancy scales with nuclear quadrupole coupling is needed. This scaling factor is expressed by a parameter, eQq_{n10}, that represents the hypothetical interaction caused by a single unpaired electron in a *p* orbital in the isolated atom. However, the values for most of the atoms seem not to be reliable, being an open question for physical chemistry. We present a simple method based on the representation between the out-of-plane nuclear quadrupole coupling constant and the electron occupancy in the valence shell *p* orbital perpendicular to the molecular plane, from which it is possible to derive a value for eQq_{n10}. We performed a literature search and used experimental data from more than 40 years of rotational spectroscopy, including 98 molecular systems. The electron occupancy was obtained from straightforward quantum-chemical calculations. Three levels of theory were tested to compare their performance and refine the results. We used this extensive dataset together with the calculations to analyze the polarization and resonance processes. Finally, the eQq_{210} value for ^{14}N was obtained with high accuracy.



$$\underbrace{\chi_{cc}}_{\text{Experimental coupling}} \approx \chi_{zz} = \underbrace{-(U_p)_z}_{\text{Unbalanced } 2p_z \text{ electrons}} \cdot \underbrace{eQq_{n10}}_{\text{Coupling from a single electron}} \longrightarrow \chi_{cc}/_{eQq_{n10}} = -(U_p)_z$$

Time-resolved photoelectron spectroscopy of Bengal Rose Dianions in the Gas Phase

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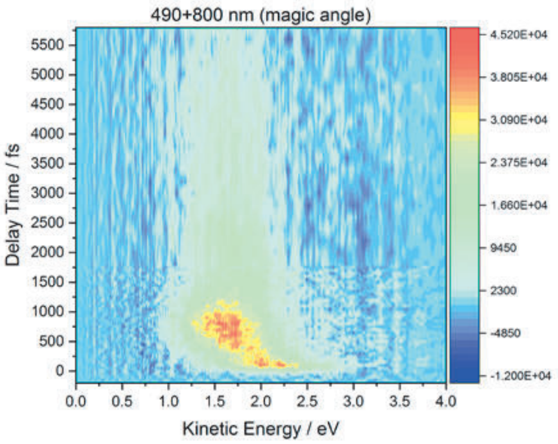
We present time-resolved photoelectron spectroscopy measurements of Rose Bengal dianions in the gas phase. The ions were isolated by electrospray ionisation from MeOH/H$_2$O (4:1) solution - followed by charge state separation via time of flight mass spectrometry. According to literature, Rose Bengal dianion has an adiabatic detachment energy (ADE) of 1.1 ± 0.1 eV and a repulsive Coulomb barrier of 0.6-0.9 eV (Stockett et al, *The Journal of Physical Chemistry A* **2020** *124* (41), 8429-8438). The absorption maximum in the gas phase is at 538±5 nm which corresponds to a S$_1$(ππ*) excitation. Therefore, the excited state is approximately 0.3 eV above the ionization threshold.

Upon pump excitation to the S$_1$-state concurrent with probe detachment (1.55 eV photon energy), we observe electrons with a kinetic energy of 2.2 eV. After a pump-probe delay of a few hundred fsec, this changes to a strong signal at 1.6 eV. This signal itself has a lifetime of less than 1 ps. We suggest that it results from an ultrafast change of electronic states followed by electron autodetachment. Polarisation-dependent measurements as well as the observation of an oscillatory transient underpin this conclusion. Interestingly, Rose Bengal is known for its high triplet quantum yield in solution.



Structural characterization of large gas-phase molecular ions by Trapped Ion Mobility Spectrometry (TIMS) and DFT calculations

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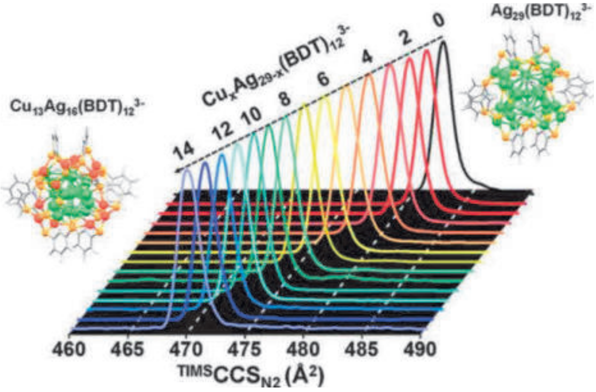
Trapped Ion mobility spectrometry (TIMS) is a new high-resolution method to determine the Collision Cross Section (CCS) of gaseous ions – typically in N_2 or He. By comparing experimental CCS with predictions from theory it is possible to identify different isomers present in gas phase as well as their relative intensities. We have studied several types of large molecular ions in order to determine their structures and to gauge the quality of different theoretical methods to simulate the CCS. In general, we have used a combination of DFT and trajectory method (TM) calculations for this. We find that the quality of CCS prediction depends significantly on the level of theory applied (basis set, functional and charge algorithm).

Here we report on three systems. Firstly, we have probed the structural changes of a ligand protected cluster $[Ag_{29}(BDT)_{12}]^{3-}$ upon doping with Cu.[1] Secondly, in yet unpublished data, we have studied the gas-phase structure and thermally activated structural changes of sulfonated, covalently linked porphyrin dimers. And thirdly, we have probed the structure of the above mentioned silver clusters after adsorption of different numbers of porphyrin monomers.



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The Interplay of Ionic Liquid Phase Boundaries: Liquid-Liquid and Vapor-Liquid Equilibria of Imidazolium Triflate Ionic Liquids with *n*-Alkyl Alcohols

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We have performed a systematic study of isobaric liquid-liquid (LLE) and vapor-liquid equilibria (VLE) of binary mixtures of different 1-alkyl-3-methlimidazolium trifluoromethanesulfonate ($C_{n=2,4,6,8}$mimTfO) ionic liquids (ILs) and different *n*-alkyl alcohols (C_nOH; methanol - *n*-dodecanol $C_{1\text{-}12}OH$). By a gradual variation of the chain lengths of one component of the systems small changes of the molecular interactions are achieved resulting in characteristic shifts of the phase behavior. Therefore, mixtures with shorter chained alcohols allow for a combined view on the VLE and the LLE which is shown for the IL 1-ethlyl-3-methylimidazolium trifluoromethanesulfonate (C_2mimTfO) and $C_{3\text{-}5}OH$. For mixtures of the ILs with higher homologues alcohols ($C_{n>5}OH$) the solubilities / the LLE have been determined. Partially, the limits of both chemical and temperature stability have been reached. The VLE have been obtained at pressures of p = 500, 700 and 1000 mbar while the LLE have been determined at ambient pressure. At arbitrary temperatures the two components IL + C_nOH show partial miscibility with an upper critical (liquid-liquid) solution temperature (UCST, T = 251 K– 380 K). Complementing previous studies, the LLE have been analyzed in accordance to Ising criticality yielding critical temperatures, critical compositions and coefficients describing the shape of the phase diagram. The results are discussed and compared with other alcoholic IL mixtures formed by imidazolium based salts. The VLE of mixtures of $C_{1\text{-}4}OH$ have been determined and evaluated in terms of the PC-SAFT EoS and the NRTL model. A corresponding state approach for the congruent description of both, the LLE and the VLE, is proposed.

Liquid-Liquid Phase Behavior of Ternary Mixtures of *n*-Alkanes with Ethanol

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Complementary to the systematic determination of the liquid-liquid phase behavior of binary mixtures of *n*-alkanes with *n*-alkyl alcohols, we have extended the scope to somehow more complex ternary systems. Therefore, we have examined particular mixtures of two different alkanes with ethanol. The selected mixtures of different amounts of the different alkanes, mimic either lubricants as technical mixtures of alkanes (e.g., *n*-dodecane and *n*-hexadecane) or diesel fuel surrogates for the purpose of fundamental research (*n*-hexadecane and 2,2,4,4,6,6,8-heptamethylnonane). This contribution describes a systematic investigation on the liquid-liquid phase behavior of such mixtures with ethanol. By applying the cloud point method in the temperature range of T = (240 - 330) K at ambient pressure the phase diagrams were obtained. The binary sub systems of both isomeric alkanes show partial miscibility with upper critical solution points. The behavior of the ternary mixtures is examined by a stepwise determination of quasi-binary subsystems where the ratio of the two alkanes / isomers was varied. By changing the ratio of the different components / isomers the region of the liquid-liquid coexistence is gradually shifted towards lower temperatures when adding the lighter alkane or the branched isomer, respectively. The general shape of the phase bodies of the pseudo-binaries, mainly pre-defined by the quite similar properties of the components, show only a slight change. A master curve obtained when applying the corresponding state principle on the single pseudo-binary mixtures proves the validity of the assumption of evaluating the different mixtures by the well known concepts applied for binary solutions. Therefore, Ising criticality is presumed for the analysis of the mixtures. A superposition of the different results allows for a comprehensive description of the liquid-liquid phase behavior, the loci of critical points, and tie lines. The limits of the range of validity of the descriptions are determined by the appearance of solid phases, which are also reported here.

Determining the mean cluster size of a pulsed supersonic jet at high densities using Rayleigh scattering

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We present a systematic study of elastic light scattering of a pulsed supersonic jet to investigate the dependence of the mean cluster size on the source pressure and temperature, covering the gaseous, liquid, and supercritical state of the expanded fluid. An adiabatic jet expansion of pure Ar and CO_2 through a parabolic nozzle at a source pressure between 20 bar and 96 bar and a source temperature between 230 K and 410 K is interrogated at a distance sufficiently large to have collisions virtually ceased.

The observed change of the Rayleigh signal with source pressure and temperature is discussed in terms of the empirical scaling law of Hagena (J. Chem. Phys. 56, 1793, 1972). Specifically, a pronounced dependence of the scaling parameters on the aggregation state of the expanded fluid is reported, corresponding to different cluster formation mechanisms.

Proline isomerization regulates the phase behavior of elastin-like polypeptides in water

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Responsiveness of polypeptides and polymers in aqueous solutions plays an important role in biomedical applications and in designing advanced functional materials. Elastin-like polypeptides (ELPs) are a well-known class of synthetic intrinsically disordered proteins (IDPs), which exhibit a lower critical solution temperature (LCST) behavior in pure water. The LCST transition can be further tuned by proline isomerization. Here, we study and compare the influence of *cis/trans* proline isomerization on the phase behavior of ELPs in dilute aqueous solution. Our results reveal that *cis* isomers play an important role in tuning the phase behavior of ELPs by hindering peptide-water hydrogen bonding while promoting intramolecular interactions. In particular, an ELP does not display any noticeable LCST-like behavior if all proline residues are in the *cis* state, while showing a signature of first-order-like LCST transition if all proline residues are in the *trans* state.

On how the Morphology Affects Water Release of Porous Polystyrene

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A typical blowing agent for the production of expanded polystyrene (EPS) foams is pentane. We wanted to replace pentane by a blowing agent that is both safe to use and environmentally friendly, namely water! In previous studies, the use of w/o-emulsion templates for the preparation of water expandable polystyrene (WEPS) was reported [1,2]. However, in all these studies w/o-emulsions with low water volume fractions were used. Our aim was to incorporate as much water as possible. Thus, we used water-in-styrene high internal phase emulsions (HIPEs) with water volume fractions of 74 vol% and more as templates for the synthesis of highly water-loaded polystyrene [3]. To find the best system for the preparation of WEPS beads, we varied the water volume fraction, the crosslinker concentration etc. systematically and determined the properties – especially the morphology and the water release – of the resulting water-loaded porous polystyrene matrix. Our results show that there is a direct link between the release of the incorporated water and the morphology of the polystyrene matrix (Figure 1). Monoliths with a closed-cell morphology retained the incorporated water well, while open-cell monoliths lost the incorporated water rapidly.

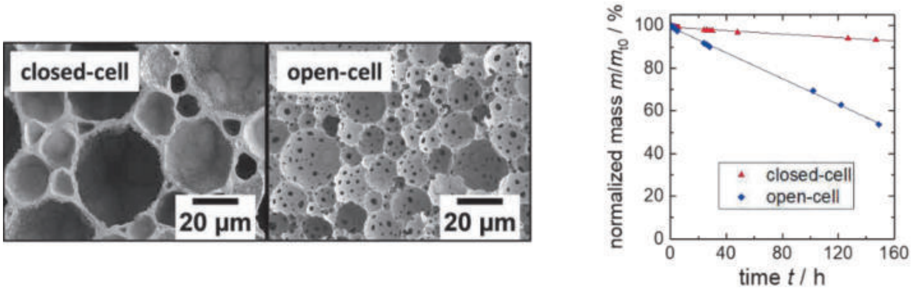

Figure 1: SEM images of open-cell and closed-cell porous PS monoliths (left). Normalized mass over time as a measure for the loss of incorporated water (right).

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Dissemination of the SI units mole and kilogram: Impact of isotope enrichment on measurement uncertainty

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The revised SI units mole and kilogram are realized and disseminated applying the XRCD-method (X-ray-crystal-density), based on “counting” silicon atoms in a silicon sphere. The latter highly enriched in the ^{28}Si isotope (amount-of-substance fraction $x(^{28}\text{Si}) > 0.999\,98$ mol/mol) with an extremely homogeneous crystal lattice and high chemical purity.[1,2] The mass spectrometric determination of the molar mass M of this enriched silicon material with lowest possible uncertainty is performed via high-resolution multicollector-ICP-MS.[2,3] A study on the enrichment-related uncertainty associated with M is presented, initiated by the idea to use also silicon spheres with natural isotopic composition – easier to produce and much more cost efficient.

For enriched Si, relative uncertainties $u_{\text{rel}}(M)$ in the 10^{-9} range are routinely obtained; but it was not possible to fall below a value of $u_{\text{rel}}(M) < 4 \times 10^{-6}$ when using natural silicon, meaning a difference of three orders of magnitude! Several analytical models to determine M were developed and compared with regard to their uncertainties associated with M. The use of state-of-the art high-resolution isotope ratio mass spectrometry accompanied with thoroughly investigated models suggests an intrinsic cause for the larger uncertainty associated with M of natural silicon compared to the enriched material.

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KMC Simulations of the Onsager Transport Coefficients of reduced Ceria

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Reduced ceria ($CeO_{2-\delta}$) has been the subject of many studies due to its promising applications within environmental and energy technologies. [1] This can be explained by high ionic (i) and electronic (e) conductivities at medium temperatures. By removing oxygen from the structure, oxygen vacancies as well as polarons are created, which leads to the aforementioned conductive behavior. One important result from a previous experimental study is that the migrations of oxygen ions and polarons are not independent. Thus, the effective charge of the oxygen vacancy is not equal to its ideal value but expressed by $2-\alpha_i$. [2] To further analyze this observation, we conduct Kinetic Monte Carlo (KMC) simulations with interaction and migration energies from density functional theory calculations. [3] We are then able to determine the Onsager transport coefficients L_{kk} (k = i, e) and $L_{ie} = L_{ei}$ which describe the defect fluxes due to their own electrochemical potential gradient and that of their corresponding counter defect, respectively. The coefficients are subsequently used to determine the deviation of the vacancy charge from its ideal value, $\alpha_i = L_{ie}/L_{ii}$.

The simulations are carried out with an external driving force which only affects oxygen vacancies. Polarons are dragged by the vacancies due to their attractive interaction. The flux of polarons and vacancies in field direction subsequently enables the calculation of the transport coefficients. [4]

Acknowledgments
Simulations were performed with computing resources granted by RWTH Aachen University under project rwth0329, rwth0526 and jara0141.

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Nanodiamond-Adsorbate Interactions studied by DFT

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Nanodiamonds (NDs) are a very recent class of materials with favourable properties such as hardness, inertness, biocompatibility, as well as unique electronic properties. These properties have been exploited in many fields of application, including boimedicine and photocatalysis.[1] For the theoretical investigations, the set of smallest possible NDs, called diamondoids, is used most often. Here, experimental data on the electronic properties (i.e., the optical gap) is available,[2–4] allowing calibration and verification of the theoretical methods. However, different optical gaps have been obtained from optical absorption experiments in the gas phase[2,3] and from X-ray emission/absorption studies on diamondoid powders.[4] We clarify the experimental difference by providing density functional theory (DFT) calculations for single diamondoids in vacuum and small diamondoid clusters.

Furthermore, it is known that small NDs have unique frontier orbital shapes.[5] Especially, the lowest unoccupied molecular orbitals (LUMOs) of NDs resemble atom-type orbitals. We show that these orbital shapes are not only obtained for single, spherical NDs, but also for their three-dimensional clusters.

For the application in nanomedicine and photocatalysis the NDs are dispersed in aqueous media. For bulk diamond in contact with water it is known that electrons can leave the diamond surface and move into the aqueous adlayer.[6] This process is known as surface transfer doping and strongly depends on surface configuration and the presence of oxidative adsorbates.[7] We characterize this effect for different small nanodiamonds and four aqueous adsorbates.

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Studying clusters of hydroxyl-functionalised cations stabilised by cooperative hydrogen bonds

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"Unlike charges attract, while opposite repel each other." This conventional wisdom has recently been challenged for ionic liquids. To investigate like-charge interactions in detail, quantum chemical calculations were deployed to analyse clusters of hydroxyl-functionalised cations exhibiting cooperative hydrogen bonding despite Coulomb repulsion. We discuss the importance of hydrogen bonds and dispersion forces for the stability of differently sized clusters. The role of polarizability and alkyl chain length of the cations for the kinetic stability of the clusters is demonstrated. Therefore, short-chained cations are studied for different types of cations ranging from hard to polarisable. Increasing the alkyl chain length, the Coulomb effect diminishes and the kinetic stability is predominantly governed by the alkyl chain tether increasing the distance between the positively charged rings of the cations. By adding the counter ion tetrafluoroborate (BF_4^-) to the cationic clusters, the binding energies switch from strongly positive to strongly negative. In the neutral clusters, the hexamer cluster with the cyclic H-bond motive and "released" anions is almost as stable as the hexamer built by H-bonded ion pairs exclusively.

For cationic and neutral clusters, geometric and spectroscopic properties are discussed as sensitive probes of opposite-charge and like-charge interaction. In conclusion this study is showing that like-charge clusters of ionic liquids can be kinetically stabilized by hydrogen bonding despite strongly repulsive electrostatic forces [1].

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First Principles Studies of Electrical Conductance and Thermopower Properties of π-Conjugated Organometallic Complexes in Single Molecule Junctions

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Thermoelectric generators are an auspicious substitute for batteries in small electronic devices, proceeding the fulfillment of the internet of things. In this context, molecular junctions between bulk material electrodes and a self-assembled monolayer of organometallic complexes represent a promising thermoelectric material. Their high Seebeck coefficients and low thermal conductance can lead to a high figure of merit [1]. For a better understanding of their electrical behavior, first principles calculations of single molecule junctions can be employed. Thereby, the coherent electron transport through a junction can be calculated using the Non-Equilibrium Green's Function (NEGF) method [2].

In this study single molecule junctions consisting of gold electrodes and highly π-conjugated transition metal (Ru and Pt) complexes [3] were investigated by density functional theory calculations [4]. Our aim was to estimate the influence of surface bonds by the thioether anchor groups and the influence of large side chains of the ligands to the electron transmission. Therefore, multiple junctions with different surface contacts and alkyl side chains have been studied. The transmission functions showed a decrease of electric conductance for large organic complexes due to intramolecular dispersion interactions. Furthermore, weak bonds between complex anchor and electrode surface lead to a shift of the conductive (HOMO) orbitals towards the Fermi energy, resulting in an increased Seebeck coefficient.

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Automated Guidance for (Non-)Expert Users of Quantum Chemistry Software

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With an abundance of possible quantum chemical methods implemented in commonly available software packages, choosing an appropriate method for a given problem usually is an ambiguous task, especially for non-expert users. For each method there is a trade-off between computational resources that it requires and the accuracy that it delivers. For instance, tuned (system-specifically parametrized) range-separated hybrid functionals [1] lead to generally improved predictions of observables compared to fixed-parameter hybrid functionals. The iterative tuning procedure is computationally expensive, however. A possible solution to this issue is one-shot tuning via machine learning [2]. To ensure accessibility in terms of both computational resources and expertise, an automated guidance tool based on data-driven methods [3,4] is proposed. The current version of “the Guide” renders functional tuning accessible to a wider audience, especially to those that do not have access to extensive computational resources, provides an uncertainty associated with a given prediction, and ideally crowdsources already-collected data points to combat redundancy. We present the detailed workflow of our computationally efficient and data-economic tool and offer a live demo for the interested user.

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Self-assembled monolayers of para-aminobenzoic acid on V_2O_5 – a theoretical and experimental study

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Lithium ion batteries (LIB) can contribute to environment-friendly energy supply due to the storage for renewable energies. As important part of their characteristics, the number of charge/discharge cycles and the capacity after several cycling processes strongly depend on the electro-chemical reactions taking place on the surface of the electrodes. The reduction of the electrolyte (*e.g.* ethyl carbonate) leads to the formation of a solid layer of lithium salts (*e.g.* Li_2CO_3) on the electrode, building the so called solid-electrolyte interface (SEI), which is usually disorganized. To control the formation of the SEI, the surface can be functionalized with organic molecules, building a self-assembled monolayer (SAM).

We investigated the assembling of *para*-aminobenzoic acid (pABA) on V_2O_5, a potential cathode material for LIB, in a collaborative experimental (XPS) and theoretical study. The simulations using Density Functional Theory with dispersion corrections include several configurations letting different sides of the pABA interact with the V_2O_5 surface. Due to the size of our slab model, we were able to investigate the aggregation of one, two and three molecules, analyzing the adsorption energy as well as the contribution of the dispersion energy.

We found out that for low concentrations, the molecules prefer a lying down configuration, while for higher concentrations they are in an upright configuration building a more organized SAM. The interaction via the carboxylic moiety is preferred for the upright configuration and intermolecular dispersion forces are decisive for the erection process. From the comparison with the experimental data, a high coverage of the surface with pABA can be concluded. Hence, we infer the existence of the upright configuration and also the building of a well-ordered SAM.

Hopping in High Concentration Electrolytes - Long Time Bulk and Single-Particle Signatures, Free Energy Barriers, and Structural Insights

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Although ion-hopping is believed to be a significant mode of transport for small ions in liquid high concentration electrolytes (HCE), its bulk signatures over sufficiently long time intervals are yet to be shown. We computationally establish the long and short time imprints of hopping in HCEs using LiBF4-in-sulfolane mixtures as models. The high viscosity of this electrolyte leads to significant dynamic heterogeneity in Li-ion transport. Li-ions exhibit a preference to transit to previously occupied Li-ion-sites, bridged through anion or solvent molecules. Hopping in the liquid matrix was found to be an activated process, whose free energy barrier and transition state structure have been determined. Evidence for nanoscale compositional heterogeneity at high salt concentrations is also presented. The simulations shed light on the composition, stiffness, and lifetime of the solvation shell of Li ions. The understanding of HCEs gleaned from this study will spearhead the choice, engineering and applicability of this class of electrolytes.

New Insights into the Transport of Electrolytes in Supercapacitors

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Diffusion of ions in energy storage devices, such as, e.g., supercapacitors, is the process enabling their charging and discharging ability. This process is primarily determined by the pore size and connectivity of the used porous electrodes. Only very recently, the direct experimental assessment of the ion transport characteristics within the pores of carbon materials became accessible using the pulsed field gradient (PFG) NMR [1]. Inspired by this breakthrough methodological achievement, we succeeded to probe the diffusion characteristics of each individual electrolyte component – anion, cation and solvent confined to model carbons [2]. Unexpectedly, it was observed that the presence of a network of mesopores in addition to smaller micropores—the concept widely used in heterogeneous catalysis to promote diffusion of sorbates—does not necessarily enhance ionic transport in carbon materials (Fig. 1).

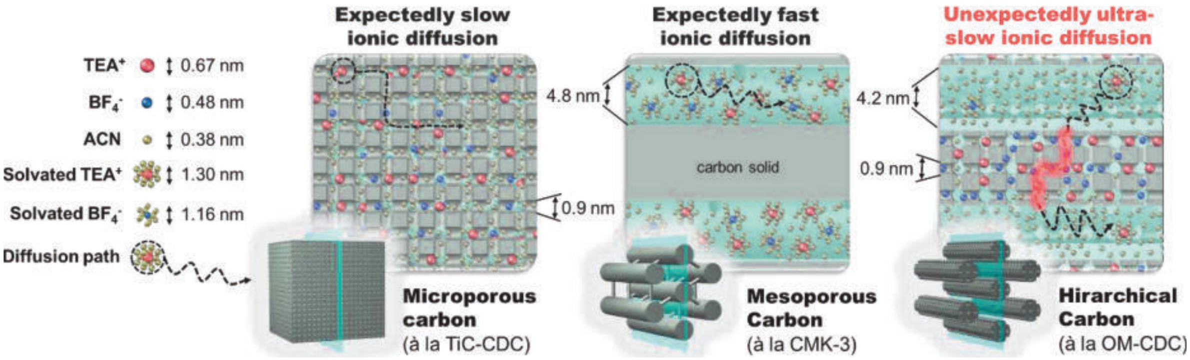

Fig. 1: A sketch representing anticipated arrangement and diffusion mechanisms of the ions and solvent molecules adsorbed into different model carbon materials.

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The Li$^+$ ion site energy distribution in Lithium aluminum germanium phosphate

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Abstract

Lithium aluminum germanium phosphate (LAGP) has been studied by means of the femtosecond laser plasma charge attachment induced transport (fs-plasma CAIT) [1]. The technique is based on attaching polarity selected charge carriers from a plasma to the front side of a sample, which induces transport of mobile charge carriers in the bulk of this sample [2],[3]. First, in a conductivity study an activation energy of 0.73 eV for lithium ion transport has been measured by means of proton attachment. Second, a constant-voltage attachment (CVA) experiment in deuterium atmosphere has been performed and subsequently analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS). The resulting concentration depth profile revealed a replacement of native lithium ions by deuterons in the first 350 nm of the sample. A theoretical analysis of the profile by means of the Nernst-Planck-Poisson (NPP) equations provides access to the concentration dependent diffusion coefficient and the unique site energy distribution (SED) of the natively contained lithium ions. A full width half maximum of 113 meV for the SED of the Li$^+$ ions is determined, which is significantly lower than in previously studied Na$^+$ conducting glasses [4],[5]. As a consequence, this study is the first experimental indication that site energy distributions in solid materials are chemically specific and most likely vary from material to material. In the future, the approach discussed can be applied to many more materials, where the potential energy landscape affects the function.

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Liquid and Vapor Permeation through Carbon Nanomembranes made from Terphenylthiol SAMs on Ag(111)

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Carbon nanomembranes (CNMs) are few-nanometer thick sheets produced by electron-induced crosslinking of self-assembled monolayers (SAMs). Due to their high mechanical, thermal and chemical stability, as well as facile surface functionalization, CNMs are used as molecular sieves, dielectric layers, supports for transmission microscopy. Recently, a remarkably high water permeance with high selectivity has been achieved by a 1.2 nm thick free-standing CNM made from SAMs of p-terphenyl thiol (TPT) on Au(111) substrates. [1] These TPT-CNMs allow water to pass through, while organic solvents, gases and ions are blocked by the porous network with pore sizes of ~0.7 nm, opening up possibilities to use them as efficient semipermeable membranes for osmosis [2]. Pursuing this approach, we studied the influence of the formation of SAMs on different metallic substrates on the pore network of the resulting CNMs. We investigated TPT-CNMs on Ag(111) by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and helium ion microscopy (HIM). As SAMs grow differently on different noble metals [3-4], the substrate also affects the structure of the pores in cross-linked SAMs and, consequently, the permeability and selectivity of CNMs. Results of single liquid and vapor permeation through TPT-CNMs formed on Ag(111) will be compared with CNMs formed on Au(111).

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Mass storage: from bulk to interfacial storage

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In typical insertion electrodes for batteries, most of the capacity is contributed by bulk storage within electroactive particles. In contrast, supercapacitor electrodes are dominated by interfacial storage. Here we present a generalized picture that unifies both concepts. The transition from bulk storage to interfacial storage is investigated experimentally using TiO_2 films as a model system and Nb:STO as well as carbon as substrates. There is clear excess storage after subtracting the bulk contribution. Ultra-thin films show a higher storage capacity than the theoretically expected value. On Ti, Ni substrates, a much larger interfacial storage contribution is observed for the native passivation layer. These effects are quantified, and the associated storage mechanisms are discussed.

Alkali-Aluminum-Germanium-Phosphates –
From ionic DC conductivity to thermal electropoling –

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Lithium-Aluminum-Germanium-Phosphate (LAGP) is one of the materials considered as electrolytes in solid state Lithium ion batteries. The base version belongs to the class of NASICON type structures. Besides from all the mono-alkali-AGPs a corresponding number of mixed Alkali-AGP exist. Here, we present a systematic study of the transport properties of the mono-alkali-AGPs, Li-AGP, Na-AGP, and K-AGP, and the corresponding four mixed-alkali-AGPs.

We demonstrate that in the limit of little charge transported the total ionic conductivity can be measured directly in a classical DC setup employing two metal electrodes. The overall conductivity decreases with increasing ion radius for the mono-alkali-AGPs. The activation energies increases from 0.66 eV for the Li-AGP, to 0.68 eV for the Na-AGP and 0.87 eV for the K-AGP.

For significantly longer times of DC experiments, the total current transported through the electrochemical cell decreases – as expected. This marks the beginning of charge carrier blocking. The evolution of charge carrier blocking is accompanied by the evolution of a blocking zone as evidenced from the quantification of concentration depth profiles obtained in secondary ion mass spectra (SIMS). The evolution of blocking zones involves transient dielectric breakdown [1,2]. The analysis of these concentration profiles discloses clear differences in the partial diffusivity of different alkali ions.

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Direct assessment of ultralow Li^+ jump rates in single crystalline Li_3N by evolution-time resolved ^7Li spin-alignment echo NMR

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Diffusion processes of small cations and anions play important roles in many applications such as batteries and sensors. Despite the enormous progress we witnessed over the past years in characterizing the irregular movement of ions such as Li^+, new methods able to sharpen our view and understanding of fast and slow diffusion phenomena are steadily developed. Still, very few techniques are, however, available to directly sense extremely slow Li^+ diffusion processes.

Here, we took advantage of 1D evolution-time resolved ^7Li spin-alignment echo NMR that is able to probe the extremely slow interlayer Li^+ hopping process in layer-structured Li_3N, which served as a model substance for our purposes. The use of single crystals enabled us to study this translational process without being interfered by the fast intralayer Li^+ motions. At 318 K the corresponding jump rate of interlayer dynamics turned out to be in the order of 2500(200) s^{-1} resulting in a diffusion coefficient as low as 1×10^{-17} m^2 s^{-1}, which is in excellent agreement with results from literature. The method, comparable to 1D and 2D NMR exchange spectroscopy, relies on temporal fluctuations of electric interactions the jumping ions are subjected to. ^7Li single crystal 1D SAE NMR offers new opportunities to precisely quantify slow Li^+ diffusion processes needed to validate theoretical models and to develop design principles for new solid electrolytes.

Li-ion dynamics in the micro and nano-crystalline form of the solid electrolyte Li_3YBr_6

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The Y-halides Li_3YBr_6 and Li_3YCl_6 were recently considered as potential electrolytes for all-solid-state batteries [1] as they exhibit sufficiently high ionic conductivities at room temperature. The aim of this study [2] is to elucidate the relationship between several parameters such as the morphology, defects and size effects on the Li ion hopping processes in Li_3YBr_6. Here, the ternary halide was prepared by both conventional solid-state synthesis and directly via mechanosynthesis under ambient conditions. Morphology and structure of nanocrystalline and annealed Li_3YBr_6 were studied by x-ray powder diffraction and ^{6}Li, ^{79}Br MAS NMR. Broadband impedance spectroscopy was employed to determine total conductivities over a wide temperature range. As an example, for annealed Li_3YBr_6 we obtained 1.52 mS/cm, the activation energy E_a was 0.28 eV. Time-domain ^{7}Li NMR spin-lattice relaxation measurements were used to investigate ion transport also from the atomic-scale point of view. The elementary jump process is characterized by an activation energy as low as $E_a = 0.15$ eV; at 313 K the Li^+ self-diffusion coefficient is in the order of 6×10^{-12} m^2 s^{-1}. Changes or kinks seen in both broadband conductivity and ^{7}Li NMR could be attributed to changes of the cation sublattices recently determined by neutron diffraction [3]. Most interestingly, the ion transport in nanocrystalline Li_3YBr_6, which we obtained after only 1 h of milling, is only slightly slower than that in the annealed analogue. Hence, such a non-annealed sample (0.44 mS/cm) might indeed serve as an alternative and sustainable electrolyte for all-solid-state batteries.

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Influence of defects on ionic transport in $LiTaO_3$ – a study using EXAFS and positron annihilation lifetime spectroscopy

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Virtually all properties of crystalline and nanocrystalline materials are influenced by defects. This is especially the case for diffusion in most solid electrolytes. Introducing structural disorder in highly crystalline $LiTaO_3$ leads to a tremendous increase in ionic conductivity σ_{DC}. Here, nanocrystalline $LiTaO_3$ served as a model substance to shed light on the question to what extent the degree of structural disorder decreases by annealing an originally defect-rich oxide. Defects were formed via high-energy ball milling of $LiTaO_3$ crystallites with diameters in the µm-range. We employed broadband conductivity spectroscopy, EXAFS, and positron annihilation lifetime spectroscopy to better understand the correlation between ionic conductivity, interatomic distances, and bond disorder, respectively. Interestingly, a short milling time of only 30 min is sufficient to generate a highly defective oxide which retains its enhanced conductivity even if annealed at T = 200 °C. Only if annealed above 250 °C, significant defect-healing decreases the ionic conductivity. This change is accompanied by a decrease of the entropy-controlled Arrhenius prefactor and an increase of the activation energy governing ionic transport. However, even if annealed at 750 °C for several hours, the activation energy remains lowered in the milled sample (0.81 eV) compared to its microcrystalline counterpart (0.97 eV). Such heat treatments especially affect interatomic distances and bond disorder while leaving the vacancy concentration almost unchanged and thereby reveal that it is the distortion of the framework that affects ionic conductivity the most. Altogether, milling and annealing allows adjusting σ_{DC} in $LiTaO_3$ over 4 to 5 orders of magnitude.

Ionic transport in the Ge-substituted argyrodite-type materials $Li_{6+x}Ge_xP_{1-x}S_5I$ (x = 0–0.6) as investigated by ^7Li and ^{31}P solid-state NMR spectroscopy and neutron powder diffraction

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Argyrodite-type materials show very promising properties as solid electrolytes. Li_6PS_5X (X = Cl, Br, I) has attracted considerable interest and many groups tried to improve the already high ionic conductivity. Recent attempts explored the substitution of P by Ge, which allowed a higher Li-content in Li_6PS_5I.[1-2] Substitution resulted in increased ionic conductivity, however, the origin of the faster ionic transport is not yet fully elucidated. Here, we investigated ion dynamics in the substitution series $Li_{6+x}Ge_xP_{1-x}S_5I$ (x = 0–0.6) by means of neutron powder diffraction and solid-state NMR. Rietveld analysis of the diffraction data revealed the occupation of new Li-sites. Additional to the sites forming cage-like Li-structures in Li_6PS_5I, samples with a Ge-content of 30at% and 60at% accommodate also type 2 Li sites close to the Li cages and type 4 sites, placed in between the Li cages. The introduced site disorder is also directly sensed by high resolution ^{31}P MAS NMR; already for 10at% Ge five different chemical environments are revealed with increasing disorder for higher levels of substitution. ^7Li NMR spin-lattice relaxation measurements point to correlated motion and allow the distinction of two different Li-jump processes. The low-temperature flank of the $1/T_1(1/T)$ rate peak is characterized by an activation energy of approximately 0.1 eV and indicates short-ranged motion. It likely represents the intercage jumps of the Li^+ ions. Complementary, spin-lock NMR experiments, being sensitive to slower dynamic processes, reveal a second jump process characterized by a higher barrier, which we assign to exchange processes connecting the Li-rich cages. The corresponding rate peak is also observed for the unsubstituted Li_6PS_5I, however, shifted toward significantly higher temperatures. As revealed by NMR, Ge substitution clearly facilitates intercage ion dynamics that finally enable the ions to move over long distances in argyrodite-type $Li_{6+x}Ge_xP_{1-x}S_5I$.

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The role of association colloids on the oxidation of lipids: Polar paradox and stabilisation of vegetable oils and biofuels

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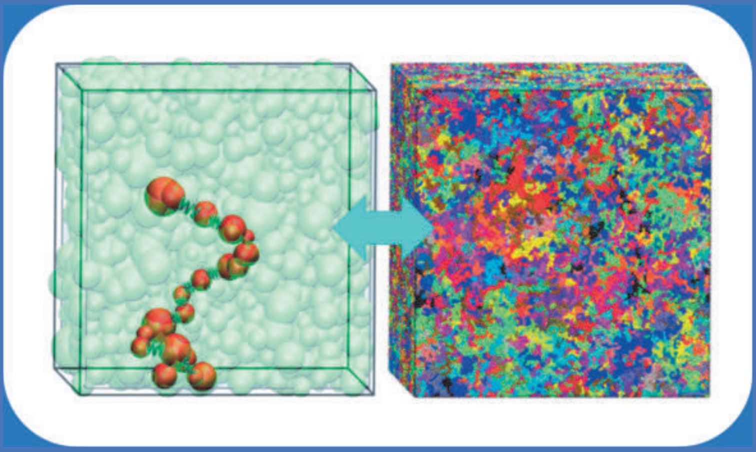
Vegetable oils and their products are often prone to oxidation processes leading to a deterioration of the quality of oil during processing, transport, and storage. To prevent this deterioration, antioxidants are added in industry. In the last two decades, considerable scientific and political interest has arisen about what antioxidants should be used based on both their effectiveness and their toxicity towards humans and the environment.

In this work, we show that natural, hydrophilic (i.e. oil-insoluble) antioxidants can be solubilised in oils by using amphiphilic hydrotropes. Several natural antioxidants were found to be distinctly more effective than oil-soluble, synthetic antioxidants commonly used in industry to stabilise edible oils and biofuels. In this context, the so-called *polar paradox theory* is discussed, which assumes association colloids to form in the presence of amphiphilic substances that then represent the site of oxidation. This theory is then further extended by showing that there are additional parameters to consider than solely the polarity of an antioxidant.

Based on the results of oxidative stability measurements, we conclude which antioxidants represent promising alternatives to the currently used ones in industry and how to identify effective antioxidants for the stabilisation of hydrophobic oils.



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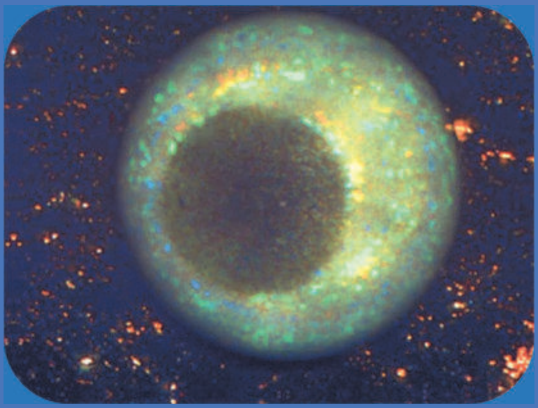

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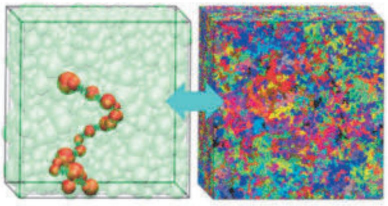
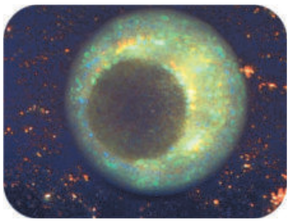


Illustration of the mapping scheme between a soft blob representation of a polymer melt and the corresponding particle based explicit monomer polymers as employed for the equilibration of high molecular weight chain systems

Picture: AK Kremer, MPI for Polymer Research, Mainz



Supraparticle made of colloidal silica subunits

Picture: AK Gradzielski, TU Berlin