BUNSEN-TAGUNG 2024

High-Resolution Structural Methods in Material and Life Sciences

RWTH Aachen University
March 25-27, 2024

BOOK OF ABSTRACTS

POSTERS

D B G
Deutsche Bunsen-Gesellschaft
für physikalische Chemie

TABLE OF CONTENTS

As of March 24th, 2024

POSTER LIST

KEY TOPIC 01: High-Resolution Structural Methods in Material and Life Sciences

P01_01	**Advanced combined rheometer setups to in-situ correlate molecular dynamics and molecular structure formation with mechanical properties** M. Wilhelm, Karlsruhe/DE,
P01_02	**Structural and electronic properties of MoS2 and MoSe2 monolayers grown by ambient pressure chemical vapor deposition on Au(111)** C. Neumann, Jena/DE, J. Picker, Jena/DE, M. Schaal, Jena/DE, Z. Gan, Jena/DE, M. Gruenewald, Jena/DE, A. George, Jena/DE, F. Otto, Jena/DE, R. Forker, Jena/DE, T. Fritz, Jena/DE, A. Turchanin, Jena/DE
P01_03	**Nanocellulose Hydrogels Incorporating Melanin and Polypyrrole for Energy Storage and Environmental Sensing Applications** N. Al-Shamery, Singapore/SG, T. Benselfelt, Singapore/SG, P. S. Lee, Singapore/SG
P01_04	**Implementation of an in situ atomic force microscope (AFM) setup to study the dynamics of (electro)catalytic interfaces** S. Reindl, Erlangen/DE, F. Hilpert, Erlangen/DE, O. Brummel, Erlangen/DE, T. Retzer, Erlangen/DE, J. Libuda, Erlangen/DE
P01_05	**How the ioniq liquid [C2C1][OTf] affects the stability of Pt(111) during potential cycling** F. Hilpert, Erlangen/DE, Q. Yunsheng, Erlangen/DE, L. Lahn, Erlangen/DE, V. Briega-Martos, Erlangen/DE, S. Cherevko, Erlangen/DE, O. Kasian, Erlangen/DE, K. Mayrhofer, Erlangen/DE, O. Brummel, Erlangen/DE, J. Libuda, Erlangen/DE
P01_06	**Drift Correction and Calibration of High-Resolution SPM Image Data with unDrift** T. Dickbreder, Bielefeld/DE, F. Sabath, Bielefeld/DE, L. Höltkemeier, Bielefeld/DE, R. Bechstein, Bielefeld/DE, A. Kühnle, Bielefeld/DE
P01_07	**On-surface Synthesis of Nitrogen-Doped Carbon Nanostructures** T. Naumann, Marburg/DE, Z. Ruan, Marburg/DE, O. Kleykamp, Marburg/DE, A. Kaczmarek, Gießen/DE, E. Sharikow, Marburg/DE, J. Sundermeyer, Marburg/DE, D. Mollenhauer, Gießen/DE, J. M. Gottfried, Marburg/DE
P01_08	**High Resolution GHz and THz Spectroscopy for Tunneling Structure and Dynamics of Chiral Molecules Including Parity Violation** G. Wichmann, Zürich/CH, K. Keppler, Zürich/CH, E. Miloglyadov, Zürich/CH, G. Seyfang, Zürich/CH, M. Quack, Zürich/CH
P01_09	**Structural and compositional investigation of a marine worm 'tooth'** N. Oehlsen, Freiberg/DE, L. Stegbauer, Freiberg/DE, S. Weiner, Rehovot/IL, J. von Döhren, Bonn/DE
P01_10	**On-Surface Synthesis of Non-Alternant Nanographenes** L. Heuplick, Marburg/DE, Q. Fan, Marburg/DE, A. Ihle, Gießen/DE, P. Liu, Tianjin/CN, X. - Y. Chen, Tianjin/CN, J. Cao, Tianjin/CN, J. Herritsch, Marburg/DE, D. Ebeling, Gießen/DE, X.-Y. Wang, Tianjin/CN, A. Schirmeisen, Gießen/DE, J. M. Gottfried, Marburg/DE
P01_11	**High Resolution THz (FTIR) Spectroscopy for Tunneling Structure and Dynamics of the Hydrogen Fluoride Dimer (HF-HF)**

	M. Quack, Zürich/CH, H. Hollenstein, Zürich/CH, M. Hippler, Sheffield/GB, G. Seyfang, Zürich/CH
P01_12	**Electrospray Ionization Ion Beam Deposition of Organic Molecules** F. Münster, Marburg/DE, L. Heuplick, Marburg/DE, G. Pasko, Marburg/DE, J. Herritsch, Marburg/DE, J. M. Gottfried, Marburg/DE
P01_13	**High resolution infrared spectroscopy and ro–vibrational analysis of the v6 fundamental of 13CHF3: Line positions, energy structure, absolute line strengths** S. Bauerecker, Braunschweig/DE, S. Bauerecker, Braunschweig/DE, O.N. Ulenikov, Tomsk/RU, O.V. Gromova, Tomsk/RU, E.S. Bekhtereva, Tomsk/RU, A.L. Fomchenko, Tomsk/RU, M. Quack, Zürich/CH, H. Hollenstein, Zürich/CH, D. Zindel, Zürich/CH, C. Sydow, Braunschweig/DE, C. Maul, Braunschweig
P01_14	**Water Influence on Cathodic Corrosion of Au(111) in Ionic Liquids: an in situ STM study** M.-K. Heubach, Ulm/DE, F. M. Schuett, Ulm/DE, A. Abdelrahman, Ulm/DE, L. A. Kibler, Ulm/DE, T. Jacob, Ulm/DE
P01_15	**Solid State Electrolyte Li7P2S8I – Structural investigations for the amorphous and heat-treated phase** H. M. Wenzel, Marburg/DE, B. Paulus, Marburg/DE, J. R. Stellhorn, Kyoto/JP, V. Miss, Marburg/DE, B. Roling, Marburg/DE, W.-C. Pilgrim, Marburg/DE
P01_16	**Estimation of water content in microgels using super-resolution fluorescence microscopy** H. Höche, Aachen/DE, S. Jana, Aachen/DE, O. Nevskyi, Göttingen/DE, J. Enderlein, Göttingen/DE, E. Siemes, Aachen/DE, A. Fürstenberg, Geneva/CH, D. Wöll, Aachen/DE
P01_17	**An in Depth Study of the Bonding Situation for the Many-Electron Bonds in N2 and C2H2 with Probability Density Analysis** M. Heinz, Aachen/DE,
P01_18	**Mechanism Investigation of the Cation-Exchange Reaction on CdSe/CdS-Dot-in-Rods with Lead Halides in Oleylamine** V. Mittag, Hamburg/DE,
P01_19	**Free Energy Based Quantum Chemical Microsolvation in Arbitrary Solvents** L. B. Magenheim, Wien/AT,
## TOPIC 02: Biophysical Chemistry and Biophotonics	
P02_01	**A trick of the tail: computing the entropic contribution to the energetics of quinone-protein unbindung** J. Haxhija, Freiburg/DE, F. Guishard, Freiburg/DE, T. Koslowski, Freiburg/DE
P02_02	**Label-free surface plasmon resonance detection of SARS-CoV-2 proteins with biofunctionalized 1 nm thick carbon nanomembranes** G. Eshaghi, Jena/DE, D. Kaiser, Jena/DE, H. R. Rasouli, Jena/DE, R. Ennaciri, Jena/DE, M. Frey, Jena/DE, C. Neumann, Jena/DE, D. Gary, Bad Langensalza/DE, T. Fischer, Bad Langensalza/DE, K. Frankenfeld, Bad Langensalza/DE, A. Turchanin, Jena/DE
P02_03	**Snapshot hyperspectral imaging in the NIR** J. Stegemann, Duisburg/DE, F. Gröniger, Duisburg/DE, S. Kruss, Bochum/DE
P02_04	**Fluorescence lifetime imaging of membrane tension during immune cell function**

	J. Mohr, Bochum/DE, L. Sistemich, Bochum/DE, J. Gretz, Bochum/DE, S. Jung, Bochum/DE, L. Erpenbeck, Münster/DE, S. Kruss, Bochum/DE
P02_05	**NrfH in external electric field:Protonation and dielectrics** Z. Rahimi, Freiburg/DE, J. Haxhija, Freiburg/DE, M. Castellano, Freiburg/DE, T. Koslowski, Freiburg/DE
P02_06	**Protein Adsorption on Smart Switchable Germanium Interfaces** A. Das, Düsseldorf/DE, M. Rabe, Düsseldorf/DE
P02_07	**in cellulo investigation of the excited state dynamics of Ruthenium based photosensitisers** A. Valavalkar, Jena/DE, T. Yang, Jena/DE, A. Chettri, Jena/DE, H. Cole, Arlington/US, G. Shi, Arlington/US, C. Cameron, Arlington/US, U. Pischel, Huela/ES, S. McFarland, Arlington/US, B. Dietzek-Ivanšić, Jena/DE
P02_08	**Magnetic bio-nanohybrid materials based on T. maritima encapsulin** N. Mucke, Hamburg/DE, M. Rütten, Hamburg/DE, T. Beck, Hamburg /DE
P02_09	**Investigation of synthesis parameters and characterization of protein-templated semiconductor quantum dots** T. Katenkamp, Hamburg/DE, H. Böhler, Hamburg/DE, T. Beck, Hamburg/DE
P02_10	**Hofmeister Effects Cause Hydrophobic Interaction Driven Biomolecular Condensate Formation** A. Czajkowski, Dresden/DE, E. M. Adams, Dresden/DE
P02_11	**Characterization of FUS Condensate Dissolution by Isothermal Titration Calorimetry** P. Priya, Dresden/DE, E. M. Adams, Dresden/DE, J. Oertel, Dresden/DE, K. Fahmy, Dresden/DE
P02_12	**Establish protein containers as building blocks for the assembly of anisotropic nanorods into optical hybrid nanomaterials** V Yadav, Hamburg/DE,
P02_13	**Convergence of SERS with CRISPR/Cas: towards real-time, multiplexed and amplification-free detection of nucleic acids** H. Giesler, Essen/DE, N. Choi, Essen/DE, L. Supovec, Essen/DE, S. Schlücker, Essen/DE
P02_14	**Surface-enhanced Raman scattering identifies a systematic error in conventional one-step lateral flow assays** N. Choi, Essen/DE, R. Grzeschik, Essen/DE, A. Hoffmann, Essen/DE, S. Schlücker, Essen/DE
P02_15	**Vibrational spectroscopy (IR, Raman, UV Resonance Raman) of isotopically labelled (13C,15N, 18O) N-methylacetamide: a model system for site-specific probing of peptides** L. Supovec, Essen/DE, S. Schlücker, Essen/DE
P02_16	**Thermodiffusion of Aqueous Solutions of Guanidinium Salts** B. Rudani, Jülich/DE, A. Jakubowski, Jülich /DE
P02_17	**Structural dynamics of the intrinsically disordered SNARE protein SNAP25a in its pre-fusion conformation** T. Stief, Jülich/DE, K. Vormann, Jülich/DE, L. Gremer, Jülich/DE, N.-A. Lakomek, Jülich/DE, R. Biehl, Jülich/DE, Á. Pérez-Lara, Granada/ES, S. Pribicevic, Göttingen/DE, D. F. Espinueva, Göttingen/DE, R. Jahn, Göttingen/DE

P02_18	**Protein-based Adsorbents for Uremic Toxin Clearance in Chronic Kidney Disease Patients** H. Wagler, Hamburg/DE, H. Böhler, Hamburg/DE, S. Alampour, Aachen/DE, M. Riedner, Hamburg/DE, J. Jankowski, Aachen/DE, T. Beck, Hamburg/DE
P02_19	**NV- qubit in nanodiamond for precise sensing of rotational and translational mobilities of active proteins.** I Perez, Jena/DE, L. Spantzel, Jena/DE, F. Rashidi, Jena/DE, T. Heitkamp, Jena/DE, M. Börsch, Jena/DE

TOPIC 03: Catalysis

P03_01	**(Photo)electrochemical Characterization of Cocatalyst-decorated CdS Nanorods for Oxygen Evolution Catalysis** J. Voss, Hamburg/DE, A. Mews, Hamburg/DE
P03_02	**Tailor-made ordered mesoporous silicates and metallosilicates prepared by directly templating lyotropic liquid crystals** J. R. Bruckner, Stuttgart/DE, S. Itzigehl, Stuttgart/DE, T. Ott, Stuttgart/DE, Ch. Vogler, Stuttgart/DE, S. Naumann, Stuttgart/DE
P03_03	**Synthesis of metal-alloy tipped CdSe/CdS dot-in-a-rod nanostructures** C. Frost, Hamburg/DE,
P03_04	**Effect of subsurface hydrogen on formation and stabilization of enol form of 2-acetylpyridine** P. Hubert, Kiel/DE, P. Haugg, Kiel/DE, J. Smyczek, Kiel/DE, C. Schröder, Kiel/DE, S. Schauermann, Kiel/DE
P03_05	**HR-XPS Study on the Adsorption of CO on Graphene-Supported Co Clusters** N. J. Waleska-Wellnhofer, Erlangen/DE, F. Düll, Erlangen/DE, U. Bauer, Erlangen/DE, P. Bachmann, Erlangen/DE, J. Steinhauer, Erlangen/DE, C. Papp, Erlangen/DE
P03_06	**Catalytic activity of ligand-stabilised platinum nanoparticles towards the hydrogenation reaction of citral** O. Schmidt, Oldenburg/DE, N. Brinkmann, Oldenburg/DE, M. Osmic, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE
P03_07	**Interaction between CdSe@CdS nanorods and Ru-based water-oxidation catalysts** S. Lander, Kaiserslautern/DE, A. Mengele, Ulm/DE, K. Siewerth, Ulm/DE, S. Rau, Ulm/DE, M. Wächtler, Kaiserslautern/DE
P03_08	**UHV-studes of adsorbed CO2 on Cu und Cu2O at Rutile (110)** J. Klimek, Oldenburg/DE, M. Grebien, Oldenburg/DE, K. Al-Shamery, Oldenburg/DE
P03_09	**SERS-based Kinetic Monitoring of the Pt-catalyzed Reduction of the three Nitrothiophenol Isomers on Gold Nanorods** D. Schäfer, Essen/DE, J. Jose, Essen/DE, R. Grzeschik, Essen/DE, S. Schlücker, Essen/DE
P03_10	**Creating Artificial Photosystems in Lipid Bilayers** A. Pannwitz, Ulm and Jena/DE,
P03_11	**Dealing with high pressure infrared gas phase contributions: A new and novel method to subtract unwanted gas phase interactions for more accurate IR band assignments on metal decorated catalysts.**

	L Caulfield, Karlsruhe/GROSSBRITANNIEN, E Sauter, Karlsruhe/DE, C Wöll, Karlsruhe/DE
P03_12	**Electronic structure analysis for understanding spectroscopic features of hexadecafluoro iron phthalocyanine** R Kornievskii, Darmstadt/DE, J Krampe, Darmstadt/DE, T Zankel, Darmstadt/DE, K Heckenberger, Darmstadt/DE, V Krewald, Darmstadt/DE, C Thiele, Darmstadt/DE

TOPIC 04: Electrochemistry

P04_01	**Investigation of OER Activity Enhancement of Fe-Effect on Nickel-based Electrodes through Solution Immersion** S. Zhang, Düsseldorf/DE, M. Rabe, Düsseldorf/DE, I. Efthimiopoulos, Düsseldorf/DE
P04_02	**Operando-XRD of electrochemical reactors for selective Li+ extraction from brines and seawater** A. Kuhlmann, Paderborn/DE, M. Huck, Paderborn/DE, E. Skrentny, Paderborn/DE, V. Vinci, Grenoble/FR, J. Drnec, Grenoble/FR, H.-G. Steinrück, Paderborn/DE
P04_03	**A solid proton conductor realized by the encapsulation of ionic liquids in the metal-organic framework ZIF-8** W. Yang, Jülich/DE, C. Korte, Juelich/DE, C. Rodenbücher, Juelich/DE, J. Luo, Chengdu/CN
P04_04	**Electrochemically triggered back-conversion of (Z)-4,4'-(diazene-1,2-diyl)bis(N,N-diethylaniline)** Z. Hussain, Erlangen/DE, D. Schatz, Gießen/DE, N. Oberhof, Heidelberg/DE, A. Dreuw, Heidelberg/DE, E. Franz, Erlangen/DE, A. W. Hermann, Gießen/DE, O. Brummel, Erlangen/DE, J. Libuda, Erlangen/DE
P04_05	**Electrochemically controlled hydrogen bonding 1,4-dinitrobenzene as redox dependent receptors for diphenyl urea containing co-polymer** J. Bisht, Jena/DE, B. Dietzek-Ivansic, Jena/DE
P04_06	**Photoelectrochemical Investigation of Different Semiconductor Nanoparticles in Cross-linked Gel Structures** P.J. Thomsen, Hamburg/DE, J. Schlenkrich, Hannover/DE, F. Lübkemann-Warwas, Hannover/DE, R.T. Graf, Hannover/DE, J.G. Eckert, Hannover/DE, C. Wesemann, Hannover/DE, M. Rosebrock, Hannover/DE, N.C. Bigall, Hamburg/DE
P04_07	**Influence of oxidation state and vacancies on low transition metal migration barriers during in situ exsolution** A. Bonkowski, Aachen/DE, A. Klein, Darmstadt/DE, R. A. De Souza, Aachen/DE
P04_08	**Electrochemical redox behavior of Pt(II)-N-heterocyclic carbene complexes: An in-situ IR spectroscopy study** J. Yang, Erlangen/DE, A. Bergen, Erlangen/DE, C. Wick, Erlangen/DE, A. Smith, Erlangen/DE, K. Meyer, Erlangen/DE, B. Brummel, Erlangen/DE, J. Libuda, Erlangen/DE
P04_09	**X-Ray Absorption Microscopy to Measure Concentration Profiles in Battery Electrolytes** E. Skrentny, Paderborn/Aachen/DE, M. Huck, Paderborn/Aachen/DE, A. Kuhlmann, Paderborn/Aachen/DE, H.-G. Steinrück, Paderborn/Aachen/DE

P04_10	**Proton migration in doped barium zirconate from a computational point of view** S. Neitzel-Grieshammer, Steinfurt/DE, G. Winterhoff, Aachen/DE
P04_11	**A direct observation of the influence of the nitrogen-doping on ion dynamics for electric double layer capacitor performance** H.R.N.B. Enninful, Leipzig/DE,

TOPIC 05: Reaction Kinetics and Dynamics

P05_01	**Exploring the Influence of Environmental Factors on the Photoinduced Activation of RuIItpphzRhIIICp*Cl** L. Blechschmidt, Jena/DE, L. Zedler, Jena/DE, B. Dietzek-Ivanšić, Jena/DE
P05_02	**On the so-called Hydrophobic Cavity Around Anions in Bulk Aqueous Solution** A. Jindal, Bochum/DE, P. Schienbein, London/GB, D. Marx, Bochum/DE
P05_03	**Unusual shell morphologies of responsive amino core-shell microgels induced by pH during shell synthesis** M. Annegarn, Bielefeld/DE, T. Hellweg, Bielefeld/DE
P05_04	**Elucidating the Dissociation Behaviour of Cationic Caesium Iodide Clusters Through Multiple-Isomer RRKM Theory** G. Schöpfer, Innsbruck/AT, M. Salzburger, Innsbruck/AT, M. Juanes, Innsbruck/AT, M. K. Beyer, Innsbruck/AT, M. Ončák, Innsbruck/AT
P05_05	**OH Radical Kinetics of Lactic Acid, Glyceric Acid and Methylmalonic Acid in the Aqueous Phase as a Function of Temperature and pH value** T. Schaefer, Leipzig/DE, Y. Hu, Leipzig/DE, Y. Zhang, Leipzig/DE, H. Herrmann, Leipzig/DE
P05_06	**Colloidal synthesis of 2D copper chalcogenides and their optical properties** U. Parekh, Rostock/DE,
P05_07	**Ignition Characteristics and Species Analysis of Furan Alcohol Blends for Sustainable Aviation** G. Wang, Braunschweig/DE, S. Nadiri, Braunschweig/DE, B. Shu, Braunschweig/DE, R. X. Fernandes, Braunschweig/DE
P05_08	**Radical yields and temperature dependence of Fenton-like reactions in the presence of oxalic acid** D. Scheres Firak, Leipzig/DE, T. Schaefer, Leipzig/DE, P. Senff, Leipzig/DE, H. Herrmann, Leipzig/DE
P05_09	**Direct observation of ring-puckering in monosaccharides with 2D-IR spectroscopy** T. Stensitzki, Potsdam/DE, P. Gasse, Potsdam/DE, Y. Mai-Linde, Potsdam/DE, T. Linker, Potsdam/DE, T. Jansen, Groningen/NL, H. Müller-Werkmeister, Potsdam/DE
P05_10	**GC-MS studies of Reactive Oxygen Species (ROS) and the pH impact on the Iron Catalytic Cycles** Poschart H., Leipzig/DE, H. Herrmann, Leipzig/DE
P05_11	**Introducing Hyperreactor Dynamics for Efficient Reaction Space Exploration** A. Stan-Bernhardt, Munich/DE, L. Glinkina, Munich/DE, A. Hulm, Munich/DE, C. Ochsenfeld, Munich/DE

P05_12	**The role of phenylnitrene in the formation of polycyclic aromatic nitrogen containing hydrocarbons** R. Arns, Paderborn/DE, R. McClish, Boulder/US, P. Hemberger, Villigen/CH, A. Bödi, Villigen/CH, J. Bouwman, Boulder/US, T. Kasper, Paderborn/DE, D. Schleier, Paderborn/DE
P05_13	**Dissociative Photoionization of Quinoxaline, Quinazoline and Cinnoline** G. Sariyar, Paderborn/DE, D. Schleier, Paderborn/DE, H. Hrodmarsson, Paris/FR, A. Boedi, Villigen/CH, P. Hemberger, Villigen/CH, J. Bouwman, Boulder/US
P05_14	**Dissociative Photoionization of Quinoxaline, Quinazoline and Cinnoline** G. Sariyar, Paderborn/DE, D. Schleier, Paderborn/DE, H. Hrodmarsson, Paris/FR, A. Boedi, Villigen/CH, P. Hemberger, Villigen/CH, J. Bouwman, Boulder/US
P05_15	**Identification of critical process parameters in the synthesis of gold nanoparticles using a home-built synthesis robot** R. Grzeschik, Essen/DE, A. Dankov, Essen/DE, L. Hensen, Essen/DE, S. Schlücker, Essen/DE
P05_16	**Cation exchange on 2D CdSe nanoplatelets: where, why and what for?** V. Shamraienko, Dresden/DE,
P05_17	**Understanding light-induced reaction dynamics of molecular systems in polar and non polar solvents using pump-probe methods.** M Sekkal, Hamburg/DE,

TOPIC 06: Spectroscopy

P06_01	**Excited state dynamics of molecular dyads for light driven catalysis** M. Semwal, Jena/DE,
P06_02	**Spectroelectrochemical methods for the elucidation of photoredox processes** N. Hagmeyer, Jena/DE, F. Weick, Karlsruhe/DE, H.-A. Wagenknecht, Karlsruhe/DE, B. Dietzek-Ivanšić, Jena/DE, N. Mroweh, Grenoble/FR, M. Chavarot-Kerlidou, Grenoble/FR
P06_03	**Formation of Nanoplasma by Spatially Inhomogeneous Light Fields inside NaCl Particles** H. Tang, Zurich/CH, L. Ban, Zurich/CH, J. Heitland, Zurich/CH, C. West, Zurich/CH, B. Yoder, Zurich/CH, I. Thanopulos, Patras/GR, R. Signorell, Zurich/CH
P06_04	**Investigating the microsolvation of TEMPO by large halogenated alcohols** E. Sennert, Göttingen/DE, M. A. Suhm, Göttingen/DE
P06_05	**Microhydration of tertiary amines: Robust resonances in red-shifted water** E. Lwin, Göttingen/DE, T. L. Fischer, Göttingen/DE, M. A. Suhm, Göttingen/DE
P06_06	**Particle Size-Dependent Onset of the Tunneling Regime in Ideal Dimers of Gold Nanospheres** S. Schlücker, Essen/DE, J. Jose, Essen/DE, L. Schumacher, Essen/DE, M. Jalali, Duisburg/DE, G. Haberfehlner, Graz/AT, J. Svejda, Duisburg/DE, D. Erni, Duisburg/DE
P06_07	**h-BN in the Making – The Surface Chemistry of Borazine on Rh(111)** E. M. Freiberger, Erlangen/DE, F. Düll, Erlangen/DE, P. Bachmann,

	Erlangen/DE, J. Steinhauer, Erlangen/DE, H.-P. Steinrück, Erlangen/DE, C. Papp, Berlin/DE
P06_08	**Surface Science Investigations of Oxanorbornadiene/Oxaquadricyclane Ester Derivatives as MOST Systems on Pt(111)** F. Hemauer, Erlangen/DE, V. Schwaab, Erlangen/DE, E. M. Freiberger, Erlangen/DE, N. J. Waleska-Wellnhofer, Erlangen/DE, D. Krappmann, Erlangen/DE, H.-P. Steinrück, Erlangen/DE, C. Papp, Berlin/DE
P06_09	**Aerogel lined capillaries as liquid core waveguides for real time spectroscopy in aqueous systems.** M. Lippold, Freiberg/DE, L. Jakob, Freiberg/DE
P06_10	**Two-Dimensional IR Spectroscopy of Bifunctional Vibrational Probes** C. Gräve, Bonn/DE, S. Flesch, Bonn/DE, L. I. Domenianni, Bonn/DE, J. Lindner, Bonn/DE, P. Vöhringer, Bonn/DE
P06_11	**Tailoring the composition of ultrathin colloidal 2D MoS2/WS2 alloyed nanoplatelets** M. Fröhlich, Tübingen/DE, M. Kögel, Tübingen, Reutlingen/DE, L. Kahlmeyer, Tübingen/DE, J. Meyer, Tübingen, Reutlingen/DE, J. Lauth, Tübingen, Hannover/DE
P06_12	**High Resolution Spectroscopy of trans-c-2,3-di-deutero-oxirane and additional isotopomers** K. Keppler, Zürich/CH, S. Albert, Zürich/CH, Z. Chen, Lanzhou/CN, C. Manca Tanner, Zürich/CH, G. Wichmann, Zürich/CH, J. Stohner, Wädenswil/CH, V. Schurig, Tübingen/DE, O. Trapp, München/DE, M. Quack, Zürich/CH
P06_13	**Environmental Shifts of Hydrogen Bond Vibrations in Ne Cryomatrices and He Nanodroplets - Filling Gaps in the Vacuum Reference Data Base** M. Bödecker, Göttingen/DE, M. A. Suhm, Göttingen/DE
P06_14	**Chiral Recognition from NMR and Computational Studies** T. L. Gomes Cabral, Magdeburg/DE, C. F. Tormena, Sao Paolo/BR, M. Stein, Magdeburg/DE
P06_15	**Filling the gaps: Raman jet spectroscopy of halogen bonds** J. N. Hasselhorn, Göttingen/DE, S. Lambert-Klemme, Göttingen/DE, B. Hartwig, Göttingen/DE, M. A. Suhm, Göttingen/DE
P06_16	**Designing an electro-optical modulator with quantum dot supercrystals** R. Thalwitzer, Tübingen/DE, J. Hiller, Tübingen/DE, M. Scheele, Tübingen/DE
P06_17	**Spectroscopic investigations of reactive selenium intermediates** C. Allacher, Regensburg/DE, D. J. Grenda, Regensburg/DE, E. Harrer, Regensburg/DE, F. Bergmeier, München/DE, R. J. Kutta, Regensburg/DE, A. Breder, Regensburg/DE, J. Rehbein, Regensburg/DE, E. Riedle, München/DE, P. Nuernberger, Regensburg/DE
P06_19	**Model Catalytic Studies on the Thermal Dehydrogenation of Alcohol-Based Liquid Organic Hydrogen Carrier Systems** V. Schwaab, Erlangen/DE,
P06_20	**Expanding the toolbox of in cellulo transient absorption spectroscopy** A. Valavalkar, Jena/DE, M. Mueller, Munich/DE, O. Thorn Seshold, Munich/DE, B. Dietzek-Ivanšić, Jena/DE
P06_21	**Traceable hydrogen measurement using laser absorption spectroscopy** Z. Qu, Braunschweig/DE, S. Agarwal, Braunschweig/DE, D. Zhu, Braunschweig/DE, B. Shu, Braunschweig/DE, R. Fernandes, Braunschweig/DE

P06_22	**In-situ measurements of Prussian Blue as cathode material for sodium ion batteries** Ying Hu, Jülich/DE, Christian Rodenbücher, Jülich/DE, Carsten Korte, Jülich/DE
P06_23	**Accurate Small Molecule Property Data from Theory** D. Andrae, Berlin/DE,
P06_24	**Towards plasmon-enhanced Raman spectroscopy of single molecular adsorbates with defined surface orientation** S. Mennicken, Essen/DE, D. Schäfer, Essen/DE, D. Ohm, Mainz/DE, S. Mehrpavar, Essen/DE, J. Neumann, Essen/DE, G. Haberhauer, Essen/DE, K. Domke, Essen/DE, S. Schlücker, Essen/DE
P06_25	**Structure and dynamics of the Sars-CoV-2 NSP3 Ubiquitin-like domain 1 characterized by NMR spectroscopy and further biophysical methods** K. Vormann, Düsseldorf, Jülich/DE, T. Stief, Düsseldorf, Jülich/DE, R. Bartenschlager, Heidelberg/DE, N.L. Lakomek, Düsseldorf, Jülich/DE
P06_26	**Room-temperature luminescence from a dinuclear CrIII complex** D. Fritzler, Osnabrück/DE, C. Wang, Osnabrück/DE
P06_27	**Rull-triad enables one-component photon upconversion and initiates photopolymerization with red light** H. Hammecke, Osnabrück/DE, C. Wang, Osnabrück/DE
P06_28	**Polyaromatic Hydrocarbon substituted phenanthroline ligands for Cu(I) Photosensitizer: Migration of the Excited State** J. P. Zurwellen, Braunschweig/DE, O. Lange, Braunschweig/DE, F. Doettinger, Braunschweig/DE, M. Karnahl, Braunschweig/DE, S. Tschierlei, Braunschweig/DE
P06_29	**Photorearrangement reaction of theophylline derivatives** T. Rittner, Regensburg/DE, R. E. Rodríguez-Lugo, Regensburg/DE, K. Heilmeier, Regensburg/DE, F. Arp, Regensburg/DE, S. Dietzmann, Regensburg/DE, S. Wortmann, Regensburg/DE, R. Kutta, Regensburg/DE, E. Riedle, Munich/DE, R. Wolf, Regensburg/DE, P. Nuernberger, Regensburg/DE
P06_30	**Quantum Cascade Laser in IR Difference Spectroscopy: Exploring Protein Photoreactions** M. Diedrich, Bielefeld/DE, T. Kottke, Bielefeld/DE
P06_31	**Markov Chain Monte Carlo methods to model multiexciton dynamics in CdSe quantum dots** R. Baruah, kaiserslautern/DE, K. Kumar, Jena/DE, M. Wächtler, Kaiserslautern/DE
P06_32	**Investigation of energy flow in COFs by 2D-IR spectroscopy** Y. Pfeifer, Potsdam/DE, A. Thomas, Berlin/DE, H. Müller-Werkmeister, Potsdam/DE
P06_33	**Temperature dependent NMR data reveal a "dark state" in the interaction of a-synuclein with the aggregation inhibitor AS69** S. Werner, Düsseldorf/DE,
P06_34	**Ultrafast photoisomerization dynamics of protonated azobenzene and azobenzene containing complexes in an ion trap** M. J. P. Schmitt, Kaiserslautern/DE, P. Weber, Kaiserslautern/DE, R. I. Petrikat, Kaiserslautern/DE, J. Hornbogen, Kaiserslautern/DE, R. Diller, Kaiserslautern/DE, S. Becker, Kaiserslautern/DE, C. Riehn, Kaiserslautern/DE

P06_35	**Nanodisc reconstitution and NMR analysis of the vesicular SNARE protein Synaptobrevin-2** M. Kraus, Düsseldorf/DE, K. Vormann, Düsseldorf/DE, M. Lemke, Düsseldorf/DE, N. Lakomek, Düsseldorf/DE, H. Heise, Düsseldorf/DE
P06_36	**Investigations on light-driven processes in novel biomimetic [FeFe]-hydrogenase complexes** K. Rediger, Kaiserslautern/DE, C. Kasahara, Jena/DE, I. Basma, Jena/DE, S. Kupfer, Jena/DE, H. Abul-Futouh, Zarqa/JO, M. Micheel, Kaiserslautern/DE, W. Weigand, Jena/DE, M. Wächtler, Kaiserslautern/DE
P06_37	**Zero-field splittings in photo-generated high-spin main group compounds studied by THz-EPR** T. Al Said, Berlin/DE, M. Neben, Göttingen/DE, K. Holldack, Berlin/DE, S. Schneider, Göttingen/DE, A. Schnegg, Mülheim an der Ruhr/DE
P06_38	**Probing mechanochemical racemic-crystal formation by solid-state NMR spectroscopy** S Moos, Aachen & Mülheim/DE, C Quaranta, Aachen/DE, I d'Anciães Almeida, Mülheim/DE, E Bartalucci, Aachen & Mülheim/DE, C Bolm, Aachen/DE, T Wiegand, Aachen & Mülheim/DE
P06_39	**Amplified Spontaneous Emission in Colloidal Nanoplatelets: Towards Lasing in Hollow Core Glass and Polymer Fibers** D. A. Rudolph, Hannover/DE, H. Menzel, Braunschweig/DE, J. Lauth, Tübingen/DE, L. F. Klepzig, Hannover/DE, S. Spelthann, Hannover/DE, V. Adolfs, Hannover/DE, D. H. Chau, Hannover/DE, S. L. Hachmeister, Braunschweig/DE, F. Li, Braunschweig/DE, H. H. Johannes, Braunschweig/DE, M. Stei

TOPIC 07: Surfaces and Interfaces

P07_01	**Formation of {111} oriented defects in heteroepitaxial Ir/YSZ/Si(001) layers** J. Weippert, Freiburg im Breisgau/DE, L. Kirste, Freiburg im Breisgau/DE, P. Straňák, Freiburg im Breisgau/DE, B. Sundarapandian, Freiburg im Breisgau/DE, J. Engels, Freiburg im Breisgau/DE, S. Oeser, Freiburg im Breisgau/DE, A. Graff, Halle an der Saale/DE, V. Lebedev, Freiburg im Breisgau/D
P07_02	**Layer-by-Layer Deposition of Thin Films based on Polyoxometalate-Composites** R. Frigge, Freiberg/DE, Y. Joseph, Freiberg/DE
P07_03	**Silver-Based Semiconductor Nanoparticles for Novel Transistor Structures** N. Metzkow, Dresden/DE,
P07_04	**Nanostructure of Metal Nanoparticle Covered Supported Ionic Liquids Studied by Nano-IR Spectroscopy** C. Mehrmann, Düsseldorf/DE, J. Johny, Mülheim an der Ruhr/DE, P. Ebbinghaus, Düsseldorf/DE, A. Das, Düsseldorf/DE, M. F. Tesch, Mülheim an der Ruhr/DE, M. Rabe, Düsseldorf/DE
P07_05	**Controlled Growth of Two-Dimensional SnSe/SnS Core/Crown Heterostructures by Reactivity of the Precursors** J. Schulz, Hamburg/DE, A. Mews, Hamburg/DE
P07_06	**Investigating the phase behavior of polymer blends at the air-water interface at the molecular level**

	B. Kővágó, Vienna/AT, Z. Peng, Cergy/FR, A. el Haitami, Cergy/FR, S. Cantin, Cergy/FR, E. H. G. Backus, Vienna/AT
P07_07	**Metalworking influence on the corrosion behaviour of sterling silver and silver-coated copper** W. Kautek, Vienna/AT, V. Ljubić Tobisch, Vienna/AT, A. Selimović, Vienna/AT
P07_08	**Graphene coating generation by femtosecond Laser-assisted reduction of Graphene Oxide** W. Kautek, Vienna/AT, M. Pfaffeneder-Kmen, Vienna/AT, A. Naghilou, Vienna/AT, I. Falcón Casas, Vienna/AT
P07_09	**Surface Chemistry of a (Sub-)monolayer [C2C1Im][OTf] Film on Pt(111): A Combined XPS, IRAS, and STM Study** H. Bühlmeyer, Erlangen/DE, T. Talwar, Erlangen/DE, R. Eschenbacher, Erlangen/DE, J. Baretto, Erlangen/DE, J. Hauner, Erlangen/DE, F. Maier, Erlangen/DE, H.-P. Steinrück, Erlangen/DE, J. Libuda, Erlangen/DE
P07_10	**Spectroscopic and microscopic study of (car)borane-based 2D materials** M. Frey, Jena/DE, J. Picker, Jena/DE, J. Višňáḱ, Prague/CZ, C. Neumann, Jena/DE, T. Baše, Prague/CZ, A. Turchanin, Jena/DE
P07_11	**Antimicrobial 2D materials for bone implants** R. Ennaciri, Jena/DE, C. Neumann, Jena/DE, S.H. Han, Jena/DE, Z. Gan, Jena/DE, A. George, Jena/DE, G. Gupta, Jena/DE, L. Tuchscherr de Hauschopp, Jena/DE, A. Turchanin, Jena/DE
P07_12	**Dissipative supramolecular equilibrium-balanced actuation and motion of messenger droplets** L. Zeininger, Potsdam/DE,
P07_13	**Novel fast X-ray Reflectivity setup for studying electrochemical interfaces** W. Corts, Jülich/DE, T. Matar, Jülich/DE, S. Frücht, Jülich/DE, X. Ge, Jülich/DE, H. - G. Steinrück, Jülich/DE, F. Bertram, Hamburg/DE, M. Lippmann, Hamburg/DE
P07_14	**Magnetic Aerogels from FePt and CoPt3 directly from Organic Solution** L. Schoske, Hannover/DE, F. Lübkemann-Warwas, Hannover/DE, I. Morales, Hannover/DE, C. Wesemann, Hannover/DE, J. G. Eckert, Hannover/DE, R. T. Graf, Hannover/DE, N. C. Bigall, Hannover/DE
P07_15	**Laser Direct Ink Writing of TMDC-based Photodetectors from Atomically Precise Gold Nanoclusters** W. Roberts, Tübingen/DE, M. Strienz, Tübingen/DE, A. Schnepf, Tübingen/DE, K. Braun , Tübingen/DE, M. Scheele, Tübingen/DE
P07_16	**In-situ AFM Imaging of photocatalytically active semiconducting microcrystals** M. Voigtmann, Dresden/DE, I. Siretanu, Enschede/NL, M. Wittmann, Dresden/DE, J. Simmchen, Dresden/DE, F. Mugele, Enschede/NL
P07_17	**Defect engineering at MoS2 interfaces by ion sputtering and heterostructuring** E. Juriatti, Tübingen/DE, P. Haizmann, Tübingen/DE, H. Peisert, Tübingen/DE, M. Scheele, Tübingen/DE
P07_18	**Structure and chemical reactivity of clean and Pt-decorated oxide surfaces** S. Chen, Karlsruhe/DE, Z. Yu, Karlsruhe/DE, E. Sauter, Karlsruhe/DE, A. Nefedov, Karlsruhe/DE, C. Wöll , Karlsruhe/DE, Y. Wang, Karlsruhe/DE

P07_19	**Surface Space-Charge Potential and Oxygen Surface Exchange Coefficient of SrTiO3: The Effect of Surface Orientation** J. Kler, Aachen/DE, J. M. Börgers, Aachen/DE, R. A. De Souza, Aachen/DE
P07_20	**Exploring Reactivity of Oxygen Radicals, O2- and O3-, on MgO Nanocubes in the Presence of Water** F. Kloiber-Tollinger, Innsbruck/AT, M. Belina, Prague/CZ, E. Muchová, Prague/CZ, M. Ončák, Innsbruck/AT
P07_21	**Toward High-throughput Surface-sensitive X-ray Scattering Studies of Electrochemical Interfaces** T. Matar, Jülich/DE, W. Corts, Jülich/DE, H.-G. Steinrück, Jülich/DE
P07_22	**Porous Thin Films with Large Specific Surface Area on the Basis of Spray-Coated Metal Aerogels** P Khavlyuk, Dresden/DE, V Shamraienko, Dresden/DE, F Tenhagen, Dresden/DE, J Kresse, Dresden/DE, N Weiß, Dresden/DE, N Gaponik, Dresden/DE, A Eychmüller, Dresden/DE
P07_23	**Microphase separation of copolymeric architectures for gas separation membranes** D. Kösters, Göttingen/DE, S. C. Wendler, Göttingen/DE, P. Vana, Göttingen/DE
P07_24	**The Effect of Doping in Inelastic H Atom Scattering from Silicon** M. Opfermann, Göttingen/DE, S. Tödter, Göttingen/DE, K. Krüger, Göttingen/DE, O. Bünermann, Göttingen/DE
P07_25	**Operando Diffuse Reflectance Infrared Spectroscopy for Real-Time Monitoring of Metal-Organic Framework Degradation in the Presence of Volatile Organic Compounds** E Sauter, Eggenstein-Leopoldshafen/DE, L Caufield, Eggenstein-Leopoldshafen/DE, S Okur, Eggenstein-Leopoldshafen/DE, E Bogdanova, Eggenstein-Leopoldshafen/DE, T Hashem, Eggenstein-Leopoldshafen/DE
P07_26	**Operando Diffuse Reflectance Infrared Spectroscopy for Real-Time Monitoring of Metal-Organic Framework Degradation in the Presence of Volatile Organic Compounds** Eric Sauter, Eggenstein-Leopoldshafen/DE,
P07_27	**Colloidal Synthesis of Two-Dimensional MoTe2 and WTe2** O. Strolka, Tübingen/DE, A. Niebur, Hannover/DE, D. Rudolph, Hannover/DE, J. Lauth, Tübingen/DE

TOPIC 08: Theory and Data Science

P08_01	**Where the Schrödinger equation works and where it does not** I. Frank, Hannover/DE,
P08_02	**MolBar: A Molecular Identifier for Inorganic and Organic Molecules with Full Support of Stereoisomerism** N. van Staalduinen, Aachen/DE, C Bannwarth, Aachen/DE
P08_03	**Utilizing Machine Learning for the Approximation of Hessian Matrices based on GFN2-xTB derived Features** G. Feldmann, Aachen/DE, C. Bannwarth, Aachen/DE
P08_04	**Next Generation Quantum Chemistry of Water Adsorption in Acidic Zeolites** H. Windeck, Berlin/DE, F. Berger, Cambridge/GB, J. Sauer, Berlin/DE

P08_05	**Application of a tensor train based global optimization algorithm to conformer sampling of large molecules** C. Zurek, Aachen/DE, C. Bannwarth, Aachen/DE
P08_06	**Volume phase transition of copolymer microgels with non-thermoresponsive comonomers. A Hill-like adaptation of the Flory-Rehner theory** J. Krüger, Bielefeld/DE, T. Hellweg, Bielefeld/DE
P08_07	**Temperature Dependence of the Methyl-Group Dynamics in 2-13C-Ethyl-1-13C-Acetate in a Glycerol-Water Environment** M. Brandt, Rostock/DE, E. R. Bensons, Rostock/DE, B. Corzilius, Rostock/DE, D. Paschek, Rostock/DE
P08_08	**OrthoBoXY: A Simpler Way to Compute True Self-Diffusion Coefficients and Viscosities from Molecular Dynamics Simulations** D. Paschek, Rostock/DE, J. Busch, Rostock/DE
P08_09	**A First Principles Based Approach to Determine the Frequency-Dependent Dipolar 19 F-NMR Relaxation in an Ionic Liquid from Molecular Simulations** A. M. Chiramel Tony, Rostock/DE, L. Kruse , Rostock/DE, A. Strate, Rostock/DE, R. Ludwig , Rostock/DE, D. Paschek, Rostock/DE
P08_10	**"50 Ways" of Computing the Viscosity of Poly(Ethylene Glycol) Ethers from Molecular Dynamics Simulations** F. Freytag, Rostock/DE, J. Busch, Rostock/DE, D. Paschek, Rostock/DE, R. Ludwig, Rostock/DE
P08_11	**Combining low-cost electronic structure theory and low-cost parallel computing architecture** P. Steinbach, Aachen/DE, C. Bannwarth, Aachen/DE
P08_12	**Structure and Reactivity of First Row Transition Metal Substituted Aluminum Oxide ClusterA Gas-Phase Study Combining Experiment and Theory** W. Schwedland, Berlin/DE, F. Müller, Berlin/DE, H. Windeck, Berlin/DE, S. Leach, Berlin/DE, Y. Li, Leipzig/DE, A. Chakraborty, Leipzig/DE, F. Berger, Berlin/DE, K Asmis, Leipzig/DE, J. Sauer, Berlin/DE
P08_13	**Ab Initio Studies on the Location and Stability of Bronsted Acid Sites in H–MOR** P. Neuendorf, Berlin/DE, H. Windeck, Berlin/DE, F. Berger, Berlin/DE, J. Sauer, Berlin/DE
P08_14	**First-principles study on the electrical conductivity of transition metal oxides** A. Öztürk, Berlin/DE, P. Kraus, Berlin/DE
P08_15	**Software Development Tools For Reproducible Research** N. O. B. Lüttschwager, Göttingen/DE,
P08_16	**A Case Study on the Photochemistry of Monosubstituted N-Donor Triarlymethyl Radicals** Lars Roß, Aachen/DE, Christoph Bannwarth, Aachen/DE, Mona E. Arnold, Ulm/DE, Alexander J. C. Kuehne, Ulm/DE, Ludwig A. Kibler, Ulm/DE
P08_17	**An Automated Reaction Discovery Approach via New Atomic Frontier Orbital Features** Y Chen, Aachen/DE,

P08_18	**Magnetic coupling analyses of µ-oxo-bridged dinuclear first row transition metal complexes** J Krampe, Darmstadt/DE, V Krewald, Darmstadt/DE
P08_19	**Computational Design of New Anthracene-based Imine Ligands and Cu(I) Complexes** L. Zitta, Braunschweig/DE, O. Lange, Braunschweig/DE, S. Tschierlei, Braunschweig/DE
P08_20	**Exploring Efficient Density Matrix Methods for Potentially Linear Scaling in Extended Tight-Binding Density Functional Theory Calculations** T. K. Schramm, Aachen/DE, C.-M. Röper, Aachen/DE, C. Bannwarth, Aachen/DE

TOPIC 09: Transport and Storage

P09_01	**Alkali deuteron substitution in a S53P4 bioglass** K. Rein, Marburg/DE, K.-M. Weitzel, Marburg/DE
P09_02	**Lithium Diffusion in Doped Crystalline Silicon** T. Kassubek, Marburg/DE, K.-M. Weitzel, Marburg/DE
P09_03	**A molecular dynamics study of oxygen diffusion in brownmillerite $Sr_2Fe_2O_5$** S. Ambaum, Aachen/DE, N. L. Allan, Bristol/GB, R. Dittmann, Juelich/DE, R. A. De Souza, Aachen/DE
P09_04	**Reading between the grain of oxide-ion conductors: the thermal history of space-charge layers** A. L. Usler, Aachen/DE, F. Ketter, Aachen/DE, R. A. De Souza, Aachen/DE

High-Resolution Structural Methods in Material and Life Sciences

Advanced combined rheometer setups to in-situ correlate molecular dynamics and molecular structure formation with mechanical properties

C. Fengler, K.F. Ratzsch, S. Nie, R. Nonkululeko, Ch. Klein. R. Figuli, C. Iacob, M. Heck, M. Wilhelm*;

Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

*Manfred.wilhelm@kit.edu

Molecular understanding of mechanical properties over a broad length and time scale is crucial to develop advanced materials. Our research aims to design and built unique combined rheometer setups that can monitor in-situ molecular observables, such as molecular dynamics or chemical functional groups that are directly correlated to the macroscopic mechanical responses. These combined experimental setups overcome the experimental challenges associated with offline measurements and facilitate the understanding of structure-property relationships.

Over 20 years, we developed a unique combination of rheology and low-field time domain ^{1}H NMR by implementing a compact 25 MHz NMR magnet into a high end rheometer. This Rheo-NMR device can quantify segmental motion of polymer chains via transverse relaxation times (T_2) while simultaneously performing advanced rheological protocols. Examples in polymer crystallisation, rubber crosslinking and polymer synthesis will be displayed for this unique Rheo-NMR set-up.

To correlated molecular dynamics and mechanical properties broadband dielectrics spectroscopy was combined with a rheometer, Rheo-BDS. By using anionic polymerization of isoprene derivatives more than 30 decades in dynamic range could be covered.

Covalent bond formation during polymerization was directly related to mechanical properties. To do so IR spectroscopy was in-situ correlated to mechanical characterization (Rheo-IR) to investigate e.g. hydrogel formation of polyacrylic acid. In the later stage of the chemical reaction a scaling exponent of 10 was determined for G' as a function of chemical bond (c_B) formation, $G' \sim c_B^{10}$.

Structural and electronic properties of MoS_2 and $MoSe_2$ monolayers grown by ambient pressure chemical vapor deposition on Au(111)

Julian Picker[1], Maximilian Schaal[2], Ziyang Gan[1], Dr. Marco Gruenewald[2], Dr. Christof Neumann[1], Dr. Antony George[1], Dr. Felix Otto[2], PD Dr. Roman Forker[2], Prof. Dr. Torsten Fritz[2], Prof. Dr. Andrey Turchanin[1]

[1] *Institute of Physical Chemistry, Friedrich Schiller University Jena, Lessingstraße 10, 07743 Jena.*

[2] *Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena.*

The exceptional electronic and photonic properties of the monolayers of transition metal dichalcogenides including the spin–orbit splitting of the valence and conduction bands at the *K* points of the Brillouin zone make them promising for novel applications in electronics, photonics and optoelectronics. Scalable growth of these materials and understanding of their interaction with the substrate is crucial for these applications. Here we report the growth of MoS_2 and $MoSe_2$ monolayers on Au(111) by chemical vapor deposition at ambient pressure as well as the analysis of their structural and electronic properties down to the atomic scale. To this aim, we apply ultrahigh vacuum surface sensitive techniques including scanning tunneling microscopy and spectroscopy, low-energy electron diffraction, X-ray and angle-resolved ultraviolet photoelectron spectroscopy in combination with Raman spectroscopy at ambient conditions. We demonstrate the growth of high-quality epitaxial single crystalline MoS_2 and $MoSe_2$ monolayers on Au(111) and show the impact of annealing on the monolayer/substrate interaction. Thus, as-grown and moderately annealed (<100 °C) $MoSe_2$ monolayers are decoupled from the substrate by excess Se atoms, whereas annealing at higher temperatures (>250 °C) results in their strong coupling with the substrate caused by desorption of the excess Se. The MoS_2 monolayers are strongly coupled to the substrate and the interaction remains almost unchanged even after annealing up to 450 °C. [1]

References:

[1] J. Picker, M. Schaal, Z. Gan, M. Gruenewald, C. Neumann, A. George, F. Otto, R. Forker, T. Fritz, A. Turchanin, *Nanoscale Advances*, **2023**, DOI: 10.1039/D3NA00475A

Nanocellulose Hydrogels Incorporating Melanin and Polypyrrole for Energy Storage and Environmental Sensing Applications

N. Al-Shamery, Singapore/SG T. Benselfelt, Singapore/SG, P. S. Lee, Singapore/SG
Noah Al-Shamery, School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore

The well-known pigment eumelanin has gained recent attention for its use in electrochemical applications. [1] The main challenge associated with the usage of the material in industrial applications is the poor solubility in polar solvents like water. To address this fundamental issue, one approach found to be successful has been to use cellulose nanofibrils (CNFs) for stabilizing and better dispersing melanin nanoparticles. [2] This work showcases a multifunctional composite consisting of eumelanin dispersed within hydrogels made from CNFs that are combined with vapor-phase polymerized conductive polypyrrole (PPy) to make the composite "MelaGel". [3] Through spectroscopic and microscopic analysis, the material was found to possibly contain conductive pathways formed by the PPy inside the hydrogel, making bulk eumelanin redox centers accessible. This improved the sensitivity of the material when applied as a pH-sensor (detecting pH values from 4 to 10) and metal ion-sensor (detecting iron(III), copper(II), and zinc(II)), showcasing how MelaGel could possibly be used in environmental sensor or biomedical applications. Furthermore, the material was tested as working electrode in aqueous Zn coin cell devices with a maximum specific discharge capacity of 5.4 mAh/g, validating that the composite of eumelanin, PPy and CNFs is a promising combination to explore in the future together with other melanin derivatives for applications in organic energy storage and sensing.

Literature:
[1] M. D'Ischia, K. Wakamatsu, A. Napolitano, S. Briganti, J. C. Garcia-Borron, D. Kovacs, P. Meredith, A. Pezzella, M. Picardo, T. Sarna, J. D. Simon and S. Ito, Pigment Cell & Melanoma Res. 2013, 26, 616-633.
[2] F. Ramn, P. Yadav and K. Shanmuganathan, J. Mater. Sci. 2022, 57, 14188-14216.
[3] N. Al-Shamery, T. Benselfelt and P. S. Lee, ACS Appl. Mater. Interfaces. 2023, 15, 25966-25979.

Implementation of an in situ atomic force microscope (AFM) setup to study the dynamics of (electro)catalytic interfaces

Simone Reindl, Erlangen/DE, Felix Hilpert, Erlangen/DE, Olaf Brummel, Erlangen/DE, Tanja Retzer, Erlangen/DE, Jörg Libuda, Erlangen/DE

Simone Reindl, FAU Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Solid/liquid interfaces play a fundamental role in heterogeneous and electrocatalysis and are highly dynamic under operation conditions. One example is the so-called "Solid Catalyst with Ionic Liquid Layer" (SCILL), where a thin layer of ionic liquid (IL) improves the selectivity of supported, catalytically active metal nanoparticles.[1-3] Some SCILL systems outperform conventional catalysts, e.g., in selective hydrogenation reactions, and are even applied in large-scale industrial processes.[4] To further improve the performance of SCILL systems in a knowledge-driven way, we need to understand the dynamic interaction of the IL with the (electro)catalytic surface and the morphological changes of the (electro)catalyst at the molecular/atomistic level.

High-resolution atomic force microscopy (AFM) can provide the required information. We implemented a new in situ AFM setup (Cypher AFM, Oxford Instruments), which permits studies under reaction conditions at gas/solid, liquid/solid, and electrochemical interfaces. In particular, the in-situ cells allow us to precisely control the experimental parameters such as temperature, pressure, the and flow rates of gases and liquids, and the applied potential. Thus, we can study (electro)catalytically active interfaces under (or close to) reaction conditions by in situ AFM. In a first step, we investigated the influence of ILs on the stability of electrode materials, such as Au(111).

Literature:
[1] T. Bauer et al, J. Phys. Chem. C, 120, 4453–4465 (2016)
[2] T. Yang et al, Angew. Chem. Int. Ed., 61, e20220297 (2022)
[3] R. Eschenbacher et al, Top Catal (2023)
[4] N. Szesni et al, EP 2583751 A1, (2013)

How the ionic liquid [C$_2$C$_1$Im][OTf] affects the stability of Pt(111) during potential cycling

F. Hilpert, Erlangen/DE, Q. Yunsheng, Erlangen/DE, L. Lahn, Erlangen/DE,
V. Briega-Martos, Erlangen/DE, S. Cherevko, Erlangen/DE, O. Kasian, Erlangen/DE
K. Mayrhofer, O. Brummel, Erlangen/DE, J. Libuda Erlangen/DE.

Felix Hilpert, FAU Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

The modification of electrocatalysts with ionic liquids (ILs) makes it possible to control the selectivity[1,2] and can also have a direct effect on the stability of the electrocatalyst[3,4].

In this work, we study how the IL 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [C$_2$C$_1$Im][OTf] affects the electrochemical stability of Pt surface in acidic electrolyte (0.1 M HClO$_4$) during oxidative and reductive cycling (0.05 – 1.6 V$_{RHE}$). We used complementary electrochemical in-situ methods, namely electrochemical scanning tunneling microscopy (EC-STM), online inductively coupled plasma mass spectroscopy (ICP-MS), and cyclic voltammetry (CV).

In the absence of the IL, Pt(111) dissolves during oxidative cycling via cathodic transient dissolution. In consecutive cycles, small Pt clusters are redeposited, which grow with increasing cycle number. In the presence of the ionic liquid, the dissolution rate increases by a factor of 3 and an additional anodic dissolution pathway occurs, typically known for polycrystalline Pt. The changes in the dissolution behavior, however, have only minor effect on the morphological changes of the Pt(111) surface during oxidative and reductive cycles.

[1]   T. Yang, J. Yang, X. Deng, E. Franz, L. Fromm, N. Taccardi, Z. Liu, A. Görling, P. Wasserscheid, O. Brummel, J. Libuda, Angew. Chem. Int. Ed. 2022, 61, e202202957
[2]   M. Kastenmeier, E. Franz, F. Waidhas, T. Yang, N. Taccardi, P. Wasserscheid, J. Libuda, accepted J. Phys. Chem. C.
[3]   M. George, G.-R. Zhang, N. Schmitt, K. Brunnengräber, D. J. S. Sandbeck, K. J. J. Mayrhofer, S. Cherevko, B. J. M. Etzold, *ACS Catalysis* 2019, *9*, 8682-8692.
[4]   J. Yang, F. Hilpert, Y. Qiu, E. Franz, V. Briega-Martos, S. Cherevko, K. J. J. Mayrhofer, O. Brummel, J. Libuda, submitted.

Drift Correction and Calibration of High-Resolution SPM Image Data with *un*Drift

T. Dickbreder, Bielefeld/DE, F. Sabath, Bielefeld/DE, L. Höltkemeier, Bielefeld/DE, R. Bechstein, Bielefeld/DE, A. Kühnle, Bielefeld/DE
Tobias Dickbreder, Physical Chemistry I, Bielefeld University, Universitätstr. 25, 33615 Bielefeld

Scanning probe microscopy (SPM) techniques are widely used in material science to obtain high-resolution insights into the structure and properties of surfaces and interfaces. For the evaluation of this high-resolution experimental data, a most accurate and artifact-free analysis is crucial. One of the major artifacts in SPM is (thermal) drift, an unintended movement of the sample relative to the probe, which causes a distortion of the recorded SPM data [1]. Literature holds a multitude of strategies to compensate for drift during the measurement (online drift correction) or afterwards (offline drift correction). With the currently available software tools, however, offline drift correction of SPM data is often a tedious and time-consuming task. This is particularly disadvantageous when analysing long image series. Here, we present *un*Drift, an easy-to-use scientific software for fast and reliable drift correction of SPM images [2]. *un*Drift provides three algorithms to determine the drift velocity based on two consecutive SPM images without the need of any additional reference. We demonstrate the performance and reliability of *un*Drift using three challenging examples: images distorted by a very high drift velocity, only partly usable images and images exhibiting an overall weak contrast. Moreover, we show that our software can be applied to long series containing hundreds of images.
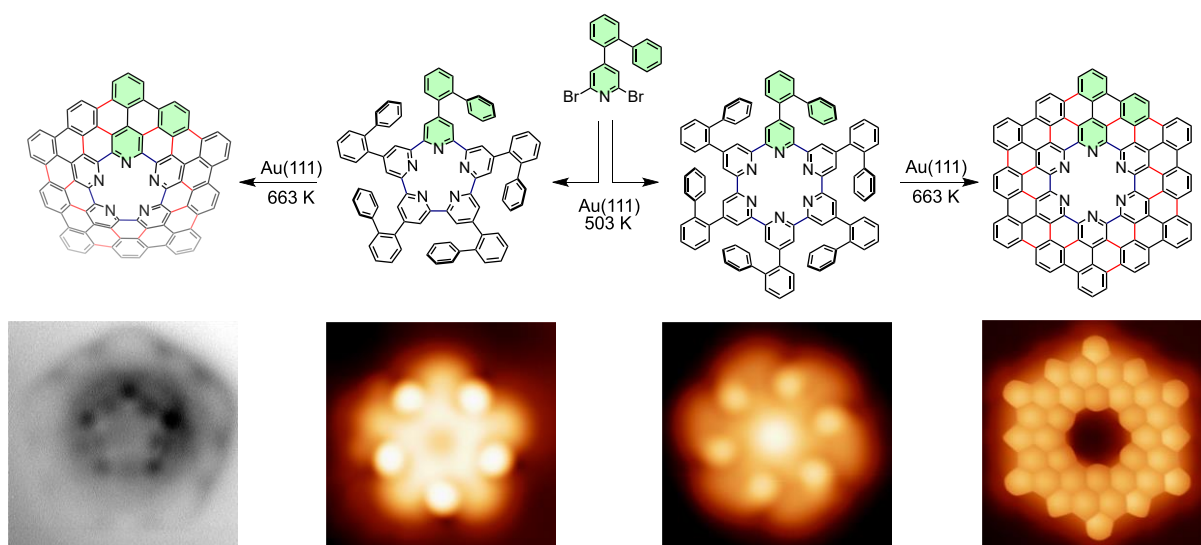
Literature:
[1] P. Rahe *et al.*, J. Vac. Sci. Technol. B 2010, 28.
[2] T. Dickbreder *et al.*, submitted to the Beilstein Journal of Nanotechnology 2023.

On-surface Synthesis of Nitrogen-Doped Carbon Nanostructures

T. Naumann, Marburg/DE, Z. Ruan, Marburg/DE, O. Kleykamp, Marburg/DE,
A. Kaczmarek, Gießen/DE, E. Sharikow, Marburg/DE, J. Sundermeyer, Marburg/DE,
D. Mollenhauer, Gießen/DE, J. M. Gottfried, Marburg/DE
Tim Naumann, Philipps Universität Marburg, Hans-Meerwein-Straße 4, 35043
Marburg

The electronic and magnetic properties of carbon-based nanomaterials can be tailored by altering the topology, introducing defect sites like vacancies, or doping with heteroatoms.[1] Here, we present an on-surface synthesis route to a variety of nitrogen-containing 0D and 1D carbon nanostructures starting from one single precursor. Annealing 4-([1,1'-biphenyl]-2-yl)-2,6-dibromopyridine on a Au(111) substrate leads to Ullmann-coupling of the precursor molecules followed by dehydrocyclization to yield cycloarenes with different cavity sizes as well as a nitrogen-doped gulf-edge graphene nanoribbon. A nitrogen containing derivative of the C108 graphene ring is formed by a ring closure of six precursor molecules.[2] Its central cavity can host a metal atom. By filling the cavity, an energetic shift of the cycloarene's frontier orbitals is caused, where the direction of the shift depends on the metal used. A curved cycloarene emerges from a ring formed by five precursor molecules, whereas a higher surface coverage favors chain formation. The electronic and geometric properties of the products were investigated by scanning tunneling microscopy/spectroscopy (STM/STS) and non-contact atomic force microscopy (nc-AFM).

Literature:

[1] F. Banhart *et al.*, ACS Nano 2011, 5, 26. [2] Q. Fan *et al.*, J. Am. Chem. Soc. 2020, 142, 894.

High Resolution GHz and THz Spectroscopy for Tunneling Structure and Dynamics of Chiral Molecules Including Parity Violation

G. Wichmann, K. Keppler, E, Miloglyadov, G. Seyfang, and M. Quack

Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland

When including only the parity conserving electromagnetic force the ground states of isolated chiral molecules would have a well-defined parity being delocalized due to tunneling and being effectively achiral. Chiral states would arise from superposition of parity states and could be very long lived, if the tunneling splittings are very small. When including the parity violating electroweak nuclear force in the framework of 'electroweak quantum chemistry' the ground states are localized, chiral and separated by a very small 'parity violating' energy difference $\Delta_{pv}E$ between the enantiomers, provided that the tunneling splitting in the symmetric case would be much smaller. Following our theoretical breakthrough in 1994-2000 predicting $\Delta_{pv}E$ in the sub-feV to feV range for 'light' molecules, two orders of magnitude larger than previously calculated, these new values have in the meantime been confirmed by numerous theory groups, but experimental confirmation is still lacking. Such experiments are a major challenge and are important for the fundamental 'standard model of particle physics (SMPP), for the structure and dynamics of chiral molecules and for the evolution of biomolecular homochirality in the origin of life (see reviews [1, 2]). In the experimental approach following [3] we have demonstrated with the achiral test molecule NH_3 [4] that our current experimental set up has the possibility of detecting values of $\Delta_{pv}E$ as small as 100 aeV (or larger). The experiment requires analyzing relevant rotation-vibration-tunneling quantum structures and here we report on our recent results developing high resolution spectroscopic experiments in the GHz and THz range for polyatomic molecules, including benzene, thiophene, aniline (NHD), CF_4, $CH^{37}Cl^{35}ClF$ [5] and the chiral candidate molecule, 1,2- dithiine.

References:

[1] M. Quack, G. Seyfang, G. Wichmann, *Proc. Nobel Symposium* 167 on Chiral Matter, Stockholm **2021,** pp 207−266 (World Scientific, Singapore 2023).
[2] M. Quack, G. Seyfang, G. Wichmann, *Chemical Science*, **2022**, 13, 10598−10643
[3] Quack, M., *Chem. Phys. Lett.*, **1986**, 132, 147−153.
[4] P. Dietiker, E. Milogyadov, M. Quack, A. Schneider, and G. Seyfang, *J. Chem. Phys.*, **2015**, 143, 244305. G. Wichmann, E. Miloglyadov, G. Seyfang and M. Quack, *Mol. Phys.*, **2020**, 118, e1752946.
[5] M. Caviezel, V. Horká-Zelenková, G. Seyfang and M. Quack, *Mol. Phys.*, **2022,** 120, e2093285; J. Agner,S. Albert, P. Allmendinger, U. Hollenstein, A. Hugi, P. Jouy, K.Keppler, M. Mangold, F.Merkt, and M.Quack, *Mol. Phys.,* **2022,** 120, e2094297.

Structural and compositional investigation of a marine worm 'tooth'

N. Oehlsen, Freiberg/Germany
J. von Döhren, Bonn/Germany
S. Weiner, Rehovot/Israel
L.Stegbauer, Freiberg/Germany

Nina Oehlsen, TU Bergakademie Freiberg, Gustav-Zeuner-Str. 3,09599 Freiberg, Germany

Amorphous calcium phosphate (ACP) is a transient precursor phase in bone and teeth, transforming into crystalline carbonated hydroxyapatite. Some rare organisms like the Nemertean worm *Amphiporus lactifloreus* produce ACP that is stable throughout the organism's lifetime in its stylet [1]. The stylet is a 100-micron long nail-shaped "tooth" at the end of the proboscis and is used to capture and pierce prey. ACP, although transient under aqueous conditions, could be a valuable mineral phase for tissue-engineering of bone due to its similar elemental composition to carbonated apatite in bone. We aim to study the worm's ACP stability mechanisms to develop methods to stabilize synthetic ACP. We study the 3D structure using x-ray nano computer tomography and focused ion beam scanning electron microscopy (FIB/SEM), as well as the elemental composition and distribution of stylets extracted from *A. lactifloreus.*

The stylet consists of an inner core region, surrounded by an outer lamellar structured layer. In both regions, Ca and P are the main elements. Surprisingly, the concentrations of Ba and Sr are high with Ca/Ba 5:1 by atoms and Ca/Sr 10:1. The outermost layer, only a few tens of nanometer thick, exhibits elemental contrast of heavier elements in nano-CT and is enriched in S and Ba according to EDS. Raman detected SO_4^{2-} . Nanoindentation results showed an elastic modulus of 10–28 GPa and a Vickers hardness of 30-160.

We carry out syntheses with different elemental compositions and monitor the ACP stability by FTIR. The addition of Ba at atomic ratio Ca/Ba = 9:10 is capable of stabilizing ACP and with Ca/Ba = 3:1 and 19:1 can delay crystallization. By substituting Ca in the ACP synthesis with different ratios of Ba and Sr, the crystalline transformation of ACP can be slowed down for weeks. This result shows that Ba can be used to modulate ACP stability. In the future this might lead to ACP that can be tailored to various industrial and medical applications in the field of bone repair and replacements.

Literature:
[1] S. A. Stricker and S. Weiner, *Experientia*, **1985**, *vol. 41*, no. 12, pp. 1557–1559

On-Surface Synthesis of Non-Alternant Nanographenes

L. Heuplick, Marburg/DE, Q. Fan, Marburg/DE, A. Ihle, Gießen/DE, P. Liu, Tianjin/CN, X.-Y. Chen, Tianjin/CN, J. Cao, Tianjin/CN, J. Herritsch, Marburg/DE, D. Ebeling, Gießen/DE, X.-Y. Wang, Tianjin/CN, A. Schirmeisen, Gießen/DE, J.M. Gottfried, Marburg/DE
Lukas Heuplick, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg

In contrast to benzenoid and alternant structures, molecules with non-alternant binding motifs, like azulene, show drastic changes in their electronic and optical properties. Acepleiadylene (APD), a constitutional isomer of pyrene consists of 5-, 6-, and 7-membered rings and shows such a non-alternant structure. So far, its complex synthesis led to only few further experiments. However, a new synthetic route - developed only recently [1] - makes it possible to investigate surface reactions based on APD.

Here, we report the successful on-surface synthesis of a non-alternant nanographene based on 1,2-dibromoacepleiadylene (DBA) on Ag(111), studied by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), gas phase density functional theory (DFT), and non-contact atomic force microscopy (nc-AFM).

Upon annealing DBA on Ag(111), depending on the coverage, high yields of dimer or trimer products can be obtained. At medium coverage (≈0.3-0.45 monolayers) nearly only dimers were observed. These can further be classified into the trans-dimer and the cis-dimer. At coverages close to a monolayer, the formation of the trimer is favored. Depending on the temperature, the organometallic intermediate as well as the covalent nanographene were formed, as shown by nc-AFM measurements.

Literature:
[1] P. Liu, J. Am. Chem. Soc. 2021, 143, 5314-5318.

High Resolution THz (FTIR) Spectroscopy for Tunneling Structure and Dynamics of the Hydrogen Fluoride Dimer (HF-HF)

H. Hollenstein, M. Hippler, G. Seyfang, and M. Quack

Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland

High resolution Spectroscopy in the THz range covering essentially all of the infrared and visible part of the spectrum, and even beyond, is among the most powerful techniques for the study of the structure and dynamics of matter (see reviews [1, 2]). In this context the study of prototypical molecular systems is of particular interest and the hydrogen fluoride dimer HF-HF can be considered to be one of the simplest and highly characteristic prototype systems for the structure and dynamics of the hydrogen bond, as it shows a binding strength (about 12 kJ/mol) intermediate between weak van der Waals bonding and strong covalent or ionic bonding. We have studied its high resolution spectroscopy for decades from the far infrared rotational-vibrational-tunneling spectrum to the near infrared HF stretching overtone range extending into the visible part of the spectrum, but there still remain important gaps in our knowledge. We have recently completed the analysis of the N=2 HF stretching overtone polyad spectrum demonstrating highly mode selective tunneling rearrangement and dissociation dynamics (see [3] and references cited therein). Here we report the analysis of the far infrared spectrum in the range of the two fundamentals situated at 417.505 and 486.944 cm^{-1} , comparing also with calculated results on the SO-3 surface [4], which agree well, and further recent theoretical calculations, which show similar or slightly less good agreement. Our analysis fills an important gap in the knowledge of vibrational-rotational-tunneling dynamics and hydrogen bond structure in a range, where the first high resolution analyses started decades ago [5], but which remains challenging even today.

References:

[1] M. Quack and F. Merkt (eds.), Handbook of High Resolution Spectroscopy, **2011**, 3 Volumes. (Wiley, Chichester and New York 2011).

[2] R. Marquardt and M. Quack (eds.), *Molecular Spectroscopy and Quantum Dynamics*, **2021**, 1st edition (Elsevier, St. Louis and Amsterdam 2021)

[3] M. Hippler, L. Oeltjen, M. Quack, *Isr. J. Chem.*, **2023**, 63, e202300092

[4] W. Klopper. M. Quack, M. Suhm, *J. Chem. Phys.*, **1998**, 108, 10096-10115.

[5] K. von Puttkamer and M. Quack, *Mol. Phys.,* **1987**, 62, 1047-1064, 10e2093285; K. von Puttkamer, M. Quack, M. Suhm, *Mol. Phys.*, **1988,** 65, 1025-1045; M. Quack and M. Suhm, *J. Chem. Phys.*, **1991**, 95, 28-59.

Electrospray Ionization Ion Beam Deposition of Organic Molecules

F. Münster, Marburg/DE, L. Heuplick, Marburg/DE, G. Pasko, Marburg/DE,
J. Herritsch, Marburg/DE, J. M. Gottfried, Marburg/DE
Florian Münster, Philipps-Universität Marburg,
Hans-Meerwein-Straße 4, 35032 Marburg

When studying large molecules on surfaces, the deposition process can often be a limiting factor. While small molecules can usually be thermally evaporated using a Knudsen cell, the vapor deposition of larger molecules may be hindered by their low vapor pressure, especially if the molecules have labile functional groups. One approach to overcome these preparation-related limitations is electrospray ionization ion beam deposition (ESI-IBD, see Figure 1).
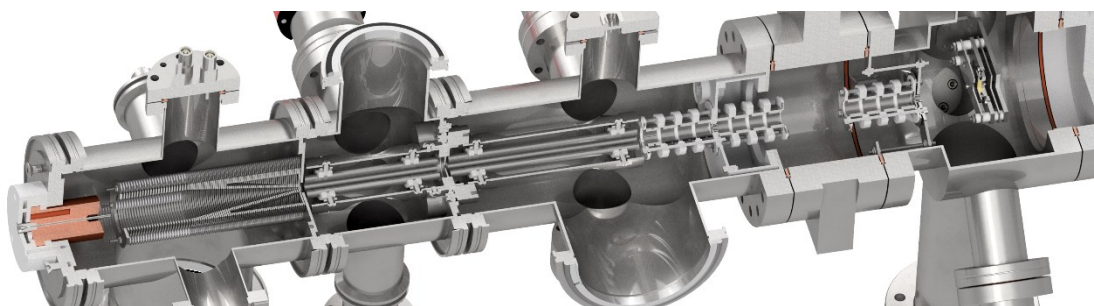
Figure 1: CAD model illustrating the placement of the electronic components for ion guidance and filtering in the experimental setup.

While this technique is becoming increasingly popular, for example in the preparation of large biomolecules, the precise chemical state of the deposited molecules is often unknown. For this study, we chose meso-tetraphenylporphyrin (2H-TPP) as a well-known model system to investigate the chemical state of the molecule after deposition via ESI-IBD. X-ray photoelectron spectroscopy (XPS) indicates the presence of an N-protonated species. By utilizing scanning tunneling microscopy (STM), we observed self-assembled islands

Figure 2: STM image of 2H-TPP islands composed of multiple distinguishable species after the deposition via ESI-IBD.

composed of multiple distinguishable species (see Figure 2), in agreement with the existence of N-protonated porphyrin molecules.

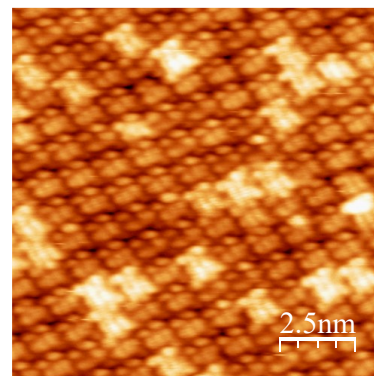# High resolution infrared spectroscopy and ro–vibrational analysis of the v_6 fundamental of $^{13}CHF_3$: Line positions, energy structure, absolute line strengths

O.N. Ulenikov, O.V. Gromova, E.S. Bekhtereva, A.L. Fomchenko,
Tomsk Polytechnic, University, Tomsk 634050, Russia

M. Quack, H. Hollenstein, D. Zindel,
ETH-Zürich, Zürich, CH-8093, Switzerland

V. Ilyushin,
Institute of Radio Astronomy of NASU, 61002 Kharkiv, Ukraine

C. Sydow, C. Maul, S. Bauerecker,
TU Braunschweig, 38106, Braunschweig, Germany

We present the high resolution infrared spectrum of $^{13}CHF_3$, recorded with the Zürich prototype ZP2001 (Bruker IFS125 HR) Fourier transform infrared spectrometer at a resolution of 0.001 cm^{-1} and analyzed in the region of 450–750 cm^{-1} (v_6 bending fundamental centered at v_0 =506.75189 cm^{-1}). A total of 6332 transitions with J_{max}= 80, K_{max}= 79 were assigned to this band. The weighted fit of 3159 upper energy values obtained from the experimentally recorded transitions was made with a Hamiltonian which takes into account different types of ro–vibrational effects in doubly degenerate vibrational states of C_{3v}−symmetric molecules. As the result, a set of 33 fitted parameters was obtained which reproduces the initial 3159 upper "experimental" ro–vibrational energy values with a root mean square deviation d_{rms}= 4.7×10^{-5} cm^{-1}. Absolute strengths of 1679 transitions (1083 lines) were obtained from the fit of their shapes with the Hartmann–Tran profile and parameters of the electric dipole transition moment of the v_6 band were determined by the computer code SYMTOMLIST (SYMmetric TOp Molecules: LIne Strengths), created on the basis of a newly derived theoretical approach resulting in five effective dipole moment parameters reproducing the initial experimental strengths of 1679 transitions with a relative d_{rms}= 5.5%. The results are discussed in relation to the current interest in ^{13}C isotope effects in quantum dynamics and due to the role of this molecule as an atmospheric trace gas.

References

S. Albert, E.S. Bekhtereva, I.B. Bolotova, Z. Chen, C. Fábri, M. Quack, O.N. Ulenikov: Isotope effects on the resonance interactions and vibrational quantum dynamics of fluoroform $^{12,13}CHF_3$, Phys. Chem. Chem. Phys. (2017) 19(39), 26527–26534

I.B. Bolotova, O.N. Ulenikov, E.S. Bekhtereva, S. Albert, Z. Chen, H. Hollenstein, D. Zindel, M. Quack: High resolution Fourier transform infrared spectroscopy of the ground state, v_3, $2v_3$ and v_4 levels of 13CHF3, J. Mol. Spectr. (2017), 337, 96–104

Water Influence on Cathodic Corrosion of Au(111) in Ionic Liquids: an *in situ* STM study

M.-K. Heubach, Ulm/DE, F. M. Schuett, Ulm/DE, A. Abdelrahman, Ulm/DE, L. A. Kibler, Ulm/DE, T. Jacob, Ulm/DE

Maren-Kathrin Heubach, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm.

Noble metals can be reductively dissolved at potentials negative of 0 V *vs.* NHE.[1] This process is called 'cathodic corrosion' and made possible by the adsorption of hydrogen on the electrode, high pH-values, and stabilising cations.[1] Due to these requirements, the presence of water seems to be an essential requirement for the observation of cathodic corrosion.[2] Nevertheless, this phenomenon can also be observed in some non-aqueous electrolytes.[3] Ionic liquids (ILs) are particularly suitable to study the initial stages of cathodic corrosion since they have much broader electrochemical stability windows than water.[4,5]

In this study, the initial stages of cathodic corrosion of a Au(111) surface in an IL with different amounts of residual water were studied by *in situ* scanning tunnelling microscopy (STM). It could be shown that corrosion started at the so-called 'elbows' of the herringbone reconstruction. With increasing water content, the number of pits on the surface increased.
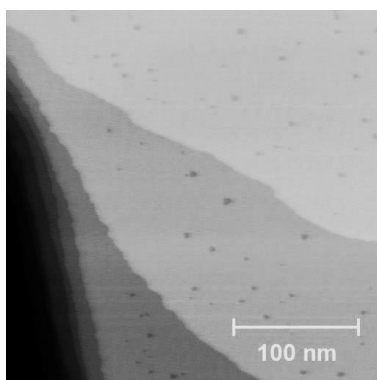

Figure 1: Pits formed by cathodic corrosion of the Au(111) surface in [MPPip][TFSI] at -1.3 V vs. Al/AlPO$_4$ and 20 ppm water.

Literature:
[1] T. J. P. Hersbach, *et al. Curr Opin Electrochem* **2021**, *26*, 100653. [2] M. M. Elnagar, *et al. Electrochemical Science Advances* **2022**, *2*, e2100175. [3] J. Simonet, *et al. Electrochem commun* **1999**, *1*, 252–256. [4] F. Lu, *et al. RSC Adv* **2013**, *3*, 18791. [5] Z. Liu, *et al. The Journal of Physical Chemistry C* **2021**, *125*, 26793–26800.

Solid State Electrolyte $Li_7P_2S_8I$ – Structural investigations for the amorphous and heat-treated phase

H. M. Wenzel Marburg/DE, B. Paulus Marburg/DE, J. R. Stellhorn Kyoto/JP,
V. Miß Marburg/DE, B. Roling Marburg/DE, W.-C. Pilgrim Marburg/DE
Philipps-Universität Marburg, Hans-Meerwein-Str. 4, 35032 Marburg

Impedance spectroscopy shows an increase in Li^+ ion conductivity in the solid electrolyte $Li_7P_2S_8I$ of 0.8 mS/cm up to 4.6 mS/cm when heat-treated at 180 °C. [1] Even though the melting temperature of 190 °C is not exceeded, significant differences between the two states are revealed by X-ray diffraction pattern (Figure 1). It is assumed that these differences are the reason for conductivity increase.
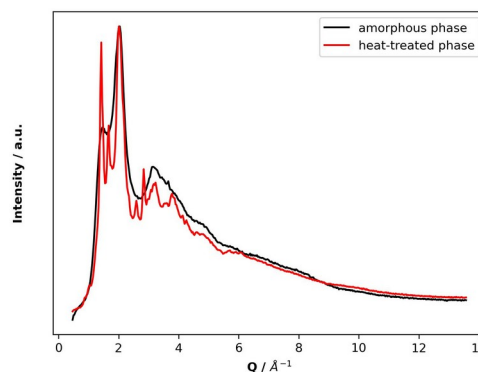

Figure 1: XRD patterns of the amorphous and the heat-treated $Li_7P_2S_8I$.

For structure determination, Reverse Monte Carlo (RMC) simulations are used with X-ray scattering and extended X-ray absorbtion fine structure (EXAFS) data as boundary conditions. [2] The simulations are performed with atomic moves as well as taking into account additional substructures containing the P surrounding (as PS_4^{3-}) obtained by ^{31}P NMR. [3, 4]

RMC results suggest that tempering induces structural changes occurring in the first coordination sphere around S. As the P-S atomic distance increases, a widening in the PS_4^{3-} tetrahedrons is measured.

Literature:
[1] S. Spannenberger; V.. Miß; E. Klotz.; J. Kettner; M. Cronau; A. Ramanayagam; F. Di Capua; M. Elsayed; R. Krause-Rehberg; M. Vogel; B. Roling, Solid State Ionics 2019, 341, 115040.
[2] R. L. McGreevy; L. Pusztai, Molecular Simulations 1988, 6, 359 – 367.
[3] V. Miß; S. Neuberger; E. Winter; J. O. Weiershäuser; D. Gerken; Y. Xu; S. Krüger; F. Di Capua; M. Vogel; J. Schmedt auf der Günne; B. Roling, Chem. Mater 2022, 34, 7721 - 7729.
[4] B. D. Klee; B. Paulus; S. Hosokawa; M. T. Wharmby; E. Dornsiepen; S. Dehnen; W.-C. Pilgrim, Journal of Physics Communications 2020, 4, 035004.

Estimation of water content in microgels using super-resolution fluorescence microscopy

H. Höche, Aachen/DE, S. Jana, Aachen/DE, O. Nevskyi, Göttingen/DE,
E. Siemes, Aachen/DE, J. Enderlein, Göttingen/DE, A. Fürstenberg, Geneva/CH,
D. Wöll, Aachen/DE
Hannah Höche, RWTH Aachen University, Landoltweg 2, 52074 Aachen

Although numerous environmentally sensitive (fluorescent) probes are able to report on physicochemical properties, such as viscosity or polarity,[1] few fluorophores can detect changes in the local water content. This shortage presents an issue because many processes occur in aqueous environments – and water quenches the fluorescence of many molecules. Indeed, it has been demonstrated that red-emitting dyes are particularly susceptible to the quenching ability of H_2O, and it has been postulated that this is due to an effective transfer of energy from the electronically excited dye to the surrounding water molecules.[2] When replacing H_2O with D_2O, however, there is an increase in both the fluorescence quantum yield and the excited-state lifetime. Thus, the amount of water molecules can be estimated using fluorescence lifetime imaging microscopy (FLIM). In our study, the fluorescence lifetime of ATTO 655, which was covalently embedded into microgels, was measured. These cross-linked polymer networks display intriguing characteristics that possess high potential for application in medicine and biochemistry.[3] We recorded FLIM images of such labelled microgels in different H_2O:D_2O ratios in their swollen state (22 °C) and in their collapsed state (40 °C), Scheme 1. A Stern-Volmer analysis was conducted to determine the local water content in microgels at different temperatures. Furthermore, the combination of FLIM with localization-based super-resolution microscopy enables the estimation of the spatial distribution of water within microgels.[4]

Scheme 1: Estimation of water content in ATTO 655-labelled microgels in their swollen and collapsed state by measuring τ_{fl}.

Literature:

[1] A. S. Klymchenko, Acc. Chem. Res. 2017, 50, 366. [2] J. Maillard, C. A. Rumble, A. Fürstenberg, J. Phys. Chem. B 2021, 125, 9727. [3] F. A. Plamper, W. Richtering, Acc. Chem. Res. 2017, 50, 131. [4] J. C. Thiele, D. A. Helmerich, O. Nevskyi, J. Enderlein et al., ACS Nano 2020, 14, 14190.

An in Depth Study of the Bonding Situation for the Many-Electron Bonds in N_2 and C_2H_2 with Probability Density Analysis

Michel V. Heinz, **Emma Gorgas, Nicole Maser, and Arne Lüchow**

Institute of Physical Chemistry, RWTH Aachen University, Germany

A century ago, Lewis introduced the concept of electron sharing and the famous Lewis structures[1], shaping the chemical language. Recently, it was shown that, by studying the electron positions maximizing the many-electron probability density $|\Psi|^2$ via probability density analysis (PDA), Lewis structures can be retrieved from *ab initio* calculations for most two center, two electron bonds.[2] For two center, many-electron bonds however, the maxima of $|\Psi|^2$ diverge from the familiar Lewis picture. While the maxima for acetylene correspond to the Lewis structures, the maxima for N_2 do not. A thorough investigation, using Jastrow-correlated[3,4] Slater determinant wave functions, was conducted for both systems.

The topology for the N_2 wave function drastically differs from the topology of the C_2H_2 wave function, by only having two maxima, unrelated to Lewis structures. Acetylene however, has a multitude of maxima, of which the majority corresponds to Lewis structures. Expanding the analysis to the maximum probability paths, connecting the maxima, differences in the electron delocalization were revealed: the electrons in N_2 move more freely than those in C_2H_2. These difference were traced primarily to the presence of hydrogen atoms, which was further compounded by a study of C_2H_6, C_2H_4, HCN, and HCC^-. Considering the different chemical behaviors of both molecules, different topologies of their wave functions, should be expected.

---

[1] G. N. Lewis, THE ATOM AND THE MOLECULE., *J. Am. Chem. Soc.*, **1916**, *38*, *4*, 762–785

[2] A. Lüchow, Maxima of $|\Psi|^2$ A connection between quantum mechanics and Lewis structures, *J. Comput. Chem.*, **2014**, *35*, 854–864

[3] A. D. Güçlü, G. S. Jeon, C. J. Umrigar, J. K. Jain, Quantum Monte Carlo study of composite fermions in quantum dots: The effect of Landau-level mixing, *Phys. Rev. B*, **2005**, *72*, 205327

[4] A. Lüchow, A. Sturm, C. Schulte, K. H. Mood, Generic expansion of the Jastrow correlation factor in polynomials satisfying symmetry and cusp conditions, *J. Chem. Phys*, **2015**, *142*, 084111

1

Mechanism Investigation of the Cation-Exchange Reaction on CdSe/CdS-Dot-in-Rods with Lead Halides in Oleylamine

V. Mittag, Hamburg/DE, L.-F. Mochalski, Hamburg/DE, C. Strelow, Hamburg/DE, T. Kipp, Hamburg/DE, A. Mews, Hamburg/DE, University of Hamburg, Institute of Physical Chemistry, Grindelallee 117, 20146 Hamburg

Complex hetero-semiconductor nanoparticles can exhibit unique optical properties that are not achievable for single-material nanostructures. Nanoparticles consisting of a spherical CdSe core embedded into a rod-like CdS shell, so called dot-rods (DRs), represent a kind of heterostructure whose complexity can still be enhanced when one tip of the structure is composed of a third material. To obtain these tipped nanoparticles, reactions or post-synthetic treatments on pre-synthesized DRs must be understood. A possible post-synthetic treatment is a partial and anisotropic cation exchange (CE) that modifies one tip of the elongated nanoparticle. CE on elongated CdSe nanoparticles has been exploited to transform them into spherical PbSe nanoparticles. However, a partial CE on DRs leading to tipped nanoparticles has not been reported, yet.

Here, we report the CE mechanism on CdSe/CdS DRs using lead halides in oleylamine. By carefully adjusting the amount of lead halide, it is possible to isolate PbS-tipped CdSe/CdS DRs as an intermediate of the CE reaction. The size of the tip depends on the kind of halide used; it increases from chloride over bromide to iodide. X-ray diffraction and high-resolution transmission electron microscopy reveal that the PbS tips have a reorganized crystal structure as compared to the CdS crystal before CE. The optical properties of the PbS-tipped CdSe/CdS DRs exhibit characteristics of all three materials and revealed dual-wavelength emission from excitons confined in both, the CdSe and the PbS material. Besides tipped DRs, also elongated nanoparticles without tips as well as spherical nanocrystals occurred as side products of the reaction. Their different yields depend on the amount of lead halide but also on the kind of halide used. Excess of lead halide leads to a strong excess of spherical nanoparticles, in line with what has been reported before. Based on the findings we suggest a reaction mechanism for the tailored synthesis of the complex nanoparticle system of PbS-tipped CdSe/CdS DRs.

Free Energy Based Quantum Chemical Microsolvation in Arbitrary Solvents

Lukas B. Magenheim[1], Radu A. Talmazan[1] and Maren Podewitz[1]

[1] *Technische Universität Wien, Institut für Materialchemie, Vienna, Austria*

Much of chemistry takes place in solution. The physical and chemical behavior of the dissolved solute largely depends on the nature of the surrounding solvent. For an accurate description of the system at hand, it is therefore vital that solvent effects are taken into account. In quantum chemical descriptions, this can be done either by treating solvents implicitly, accounting only for bulk properties such as the electrical permittivity, or explicitly by describing an extended condensed phase system. As the latter strategy is often too computationally expensive, quantum chemical microsolvation, also termed cluster approach, has emerged, where only the most important solvent molecules around the solute are considered.

This, however, raises two issues:

- Where should those solvents be placed?
- How many are needed to capture the most relevant interactions?

We have developed a computational protocol that quantifies solute-solvent interactions using molecular dynamics simulations and Grid Inhomogeneous Solvation Theory (GIST). [1] Our algorithm automatically places and orients solvent molecules based on free energy solvation thermodynamics.[2]

Here, we present the completely revised and extended methodology, which is now capable of identifying favorable solvation sites for the most common (rigid) solvents, such as dichloromethane or DMSO.[3] We demonstrate the applicability of our method in a number of examples, from organic molecules to transition-metal complexes.

References:

[1] C. N. Nguyen, T. Kurtzman Young and M. K. Gilson, *J. Chem. Phys.,* **2012**, *137*, 044101.

[2] M. Steiner, T. Holzknecht, M. Schauperl, M. Podewitz, *Molecules* **2021**, *26*, 1793.

[3] L. B. Magenheim, R. A. Talmazan, M. Podewitz, *manuscript in preparation* (**2024**).

Biophysical Chemistry and Biophotonics

A trick of the tail: computing the entropic contribution to the energetics of quinone-protein unbindung

Jetmir Haxhija, Felix Guischard and Thorsten Koslowski

Albert-Ludwigs-University Freiburg, Albertstrasse 21, 79104

Freiburg, Germany.

We estimate the entropic contributions to the free energy of quinone unbinding in bacterial and mitochondrial respiratory chains using molecular dynamics (MD) and Monte Carlo (MC) computer simulations. For a varying length of the isoprenoid side chain, MD simulations in lipid bilayers and in unpolar solvents are used to assess the dihedral angle distributions along the chain. These form the basis of a MC estimate of the number of molecular structures that do not exhibit steric self-overlap and that are confined to the bilayer. We obtain an entropy drive of $T\Delta S = 1.4$ kcal/mol for each isoprene unit, which in sum is comparable to the redox potential differences involved in respiratory chain electron transfer. We postulate an entropy-driven zipper for quinone unbinding and discuss it in the context of the bioenergetics and the structure of complex I, and we indicate possible consequences of our findings for MD-based free energy computations.

Label-free surface plasmon resonance detection of SARS-CoV-2 proteins with biofunctionalized 1 nm thick carbon nanomembranes

Ghazaleh Eshaghi[1], David Kaiser[1], Hamid Reza Rasouli[1], Rania Ennaciri[1], Martha Frey[1], Christof Neumann[1], Dominik Gary[2], Tobias Fischer[2], Katrin Frankenfeld[2], Andrey Turchanin[1]

[1]Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena, Germany
[2]Forschungszentrum für Medizintechnik und Biotechnologie (fzmb) GmbH, 99947 Bad Langensalza, Germany

In the ongoing pursuit of improving global health outcomes, there is a high demand for the accurate detection of severe acute respiratory syndrome corona virus 2 (SARS-CoV-2). We report a novel platform for the detection of the nucleocapsid protein and spike protein receptor binding domain (RBD) – two key targets for the rapid diagnosis and monitoring of individuals with COVID-19 – using surface plasmon resonance (SPR) technique. In this study, we underscore the significant influence of a 1 nm-thick carbon nanomembrane (CNM) as a novel 2D molecular material for the functionalization of SPR gold sensor chips greatly to enhance the specific immobilization of targeted SARS-CoV-2 proteins. To this end, we employ an amino-terminated carbon nanomembrane with azide linker (N_3-CNM) on the SPR gold sensor chips with covalently bonded SARS-CoV-2 antibodies for specific immobilization of the targeted proteins. The successful immobilization of each functionalization step is confirmed by X-ray photoelectron spectroscopy (XPS), polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) and multiparametric SPR measurements. The monoclonal antibodies for binding SARS-CoV-2 nucleocapsid protein (N-protein) and spike protein (S-protein) are attached to the N_3-CNM with high surface coverages and high stability. The kinetic study shows that the equilibrium dissociation constants (K_D) for the N-protein and the S-protein are 570 ± 30 pM and 22 ± 3 pM with the detection limits (LODs) of 190 pM and 5 pM, respectively. The high specificity of the N-protein antibody to SARS-CoV-2 N-protein is demonstrated by its negligible cross-reactivity to SARS-CoV-1 and MERS-CoV N-proteins. Finally, specific detection of SARS-CoV-2 S-protein in nasopharyngeal swab samples is successfully confirmed with the limit of detection down to 30 pM.

Snapshot hyperspectral imaging in the NIR

J. Stegemann, Duisburg/DE, F. Gröniger, Duisburg/DE,
S. Kruss, Bochum/DE

Fraunhofer Institute for Microelectronic Circuits and Systems IMS, Germany
Department of Chemistry, Ruhr University Bochum, Germany

Materials and molecules have specific vibrational overtones and combination modes in the near infrared (NIR) region of the spectrum. NIR absorption spectra can therefore be used as a chemical fingerprint. By combining the NIR spectroscopy with imaging technologies, it is possible to gain analytical information and spatial resolution. In hyperspectral imaging the image is either scanned spatially or spectrally, but these procedures are very slow. Hyperspectral snapshot cameras would be a solution but so far the optical approaches have reduced spectral or spatial resolution. We present a novel optical approach to generate hyperspectral snapshot images in the NIR. The design makes use of a regular NIR camera, which is transformed into a hyperspectral camera by the addition of an optical module that encodes the spectral information in an intensity difference. The spectral range is tunable, and it can be adjusted for unique measurements. To show the potential NIR fluorescent carbon nanotubes (CNT), which show emission from 800 to 1200 nm depending on their chirality, were imaged. Additionally, mixtures of CNTs with different emission peaks were unmixed. This can be used to achieve spectral multiplexing, which is interesting for biosensing applications. Additionally, the potential for chemical fingerprinting is demonstrated with NIR hyperspectral image analysis of micro-plastic and skin tissue.

Fluorescence lifetime imaging of membrane tension during immune cell function

J. M. Mohr, Bochum/DE, L. Sistemich, Bochum/DE, J. Gretz, Bochum/DE, S. Jung, Bochum/DE, L. Erpenbeck, Münster/DE, S. Kruss, Bochum/DE

Jennifer Mohr, Ruhr-Universität Bochum, Universitätsstr. 150, 44801 Bochum

Cells are constantly exposed to mechanical forces that act on the plasma membrane and change membrane tension. Additionally, processes inside the cells affect both membrane structure and tension. Imaging of mechanical membrane properties would therefore provide valuable insights into the spatiotemporal organization of cells. Here, we use the mechanosensitive fluorescence probe FlipperTR to image membrane tension in immune cells. We use time correlated single photon counting (TCSPC) in a confocal microscope for fluorescence lifetime imaging (FLIM) of this mechanosensitive dye. It enables us to observe and analyze the physical forces acting on the plasma membrane of human neutrophils. As a key component of the immune system, neutrophil granulocytes migrate along chemical gradients and through confined spaces, phagocytose microorganisms and particles, and release net-like structures of DNA during NETosis. We image dynamic changes in membrane tension and correlate it with biological functions. Thus, FLIM enables us to to better understand the biophysical basis of these processes with high spatiotemporal resolution and obtain insights into the mechanobiology of NETosis and phagocytosis.

NrfH in external electric fields: Protonation and dielectrics

Z. Rahimi, J. Haxhija, M. Castellano, Thorsten Koslowski, Insitute of Physical Chemistry,University of Freiburg, Albertstr. 21, 79104 Freiburg

The study of the interaction between external electric fields and biological molecules has attracted increasing attention because of its potential implications for understanding and manipulating cellular processes [1,2]. The present study focuses on investigating the response of NrfH, a key participant in cellular homeostasis and redox regulation, to external electric fields. Specifically, the effect of these fields on the pKa of amino acids in NrfH was investigated using molecular dynamics simulations. The results obtained indicate that electric fields induce changes in the protonation patterns of selected amino acids.

Subsequently, the proton-electron interactions in NrfH was then carried out using continuum dielectric theory, which revealed a small electron-proton interaction in NrfH. Furthermore, the voltage distribution along NrfH was computed using the numerical solution of the Laplace equation. After studying various parameters such as system geometry, humidity and membrane thickness, it was found that the primary voltage drop occurs within the membrane.

This study provides valuable insights into the molecular mechanisms underlying the response of NrfH to external electric fields. In addition, our findings contribute to a broader understanding of the electrostatic modulation of biological macromolecules, thereby providing the basis for future research efforts in the fields of bioelectricity, medicine and biotechnology.

[1] Z. Rahimi, A. Lohrasebi, Phys. Chem. Chem. Phys., 2020, 22, 25859-25868
[2] Z. Rahimi, A. Lohrasebi, Eur. Phys. J. E. 2023 46, 3.

Protein Adsorption on Smart Switchable Germanium Interfaces

A. Das, 40237 Düsseldorf, M. Rabe, 40237 Düsseldorf

Ankita Das, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str.1, 40237 Düsseldorf, Germany

Smart surfaces that are responsive to electrochemical triggers and change in hydrophobicity offer exciting possibilities for applications in microfluidics, separation systems, biosensors and analytics. When coupled with spectroscopy, they act as an analytical tool to observe the reaction and provide a deeper understanding of the dynamics occurring during the adsorption of proteins onto the smart surfaces. [1;2]

The main focus of this research work, is on controlling adsorption of proteins by reversibly switching between hydrophobic –H terminated surface and hydrophilic –OH terminated surface of germanium (100) crystal which is induced through an applied electrode potential [3]. The adsorption of different proteins – albumin and lysozyme – is studied in deuterated phosphate buffer solution (pH 7.4) *in situ* using an electrochemical cell combined with polarized attenuated total reflection infrared (ATR-IR) spectroscopy. These proteins differ in regards to their size, charge and unfolding tendencies which gives an insight into the effect of these properties on the adsorption dynamics of proteins. Changes in the conformational structure of the protein structure is observed along with reversible adsorption while switching between the hydrophobicity of the surface. Our work studying adsorption control of proteins on smart surfaces will further contribute in understanding and designing bioanalytical tools which are simple in application and easy to control.

Literature: -

[1] J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, and G.M. Whitesides, *Chem. Rev.,* 2005, 105, 1103-1169. [2] H. Nandivada, A. M. Ross, and J. Lahann., *Prog. Polym. Sci.*, 2010, 35, 141-154. [3] L. Baumgartner, A. Erbe, A. L. Boyle and M. Rabe, *Phys. Chem. Chem. Phys.*, 2022, 24, 4809.

in cellulo investigation of the excited state dynamics of biologically relevant photoactive compounds

A. Valavalkar, Jena/ DE, A. Chettri, Jena/ DE, T. Yang, Jena/ DE H. Cole, Arlington/ USA, G. Shi Arlington/ USA, C. Cameron, Arlington/ USA, U. Pischel, Huelva/ Spain, S. McFarland, Arlington/ USA

Prof. B. Dietzek-Ivanšić, Friedrich Schiller University of Jena, Helmholtzweg 4, 07743 Jena/ DE and Leibniz Institute of Photonic Technology, Albert Einstein Strasse 11, 07745 Jena/DE

Biologically relevant chromophores are ubiquitously employed in sensing, imaging, and therapy. Certain organic fluorophores as well as metal coordinated compounds find application as photoactive functional colorants. They exhibit photobiological activity due to their tunable excited state and electron or energy transfer processes. While the target site of application for these small molecule functional colorants is the human body, there exists a gap in current state of the art, in elucidating the photophysical processes that they undergo in biologically relevant surrounding. A step in this direction is to measure the photophysical properties of these dyes and relevant functional molecules in live human cells.[1,2] In our study, we employ *in cellulo* transient absorption spectroscopy, buttressed by microscopy to understand if it is the chemistry of the molecule that determines its excited state behaviour, or its local environment. We report *in cellulo* kinetics of borylated arylisoquinolines with different terminal groups and investigate Ruthenium based photosensitisers in live human cancer cells to understand the therapeutic action they deliver in an environment that resembles the target site. We also believe this study will further aid rational design of functional molecules, which could be tailored with specificity to a cellular microenvironment.

1. Yang, T. *et al.* Monitoring excited-state relaxation in a molecular marker in live cells-a case study on astaxanthin. *Chemical communications (Cambridge, England)* **57,** 6392–6395; 10.1039/D1CC01907D (2021).

2. Yang, T. *et al.* Excited-State Dynamics in Borylated Arylisoquinoline Complexes in Solution and in cellulo. *Chemistry - A European Journal*; 10.1002/chem.202203468 (2022).

Magnetic bio-nanohybrid materials based on T. maritima encapsulin

N. Mucke, Hamburg/DE, M. Rütten, Hamburg/DE, T. Beck, Hamburg/DE

Prof. Dr. Tobias Beck, Universität Hamburg, Institute of Physical Chemistry, Grindelallee 117, 20146 Hamburg

Encapsulin, a natural protein container with a diameter of 24 nm found in bacteria such as *Thermotoga maritima*, provides an interesting platform for bioengineering. Our goal is to use the encapsulin container to encapsulate superparamagnetic iron oxide nanoparticles (SPIONs) for potential biomedical applications.

To achieve encapsulation, we will follow a multi-step approach based on established methods for encapsulating inorganic particles established recently in our group.[1] Initially, spherical oleic acid-stabilized SPIONs are modified on the surface, following by coupling to a maleimide-conjugated cargo-loading peptide (CLP), which is then used to direct the modified SPIONs within the 18 nm large cavity of the protein container.

The modification and encapsulation processes are thoroughly characterized using techniques such as transmission electron microscopy (TEM), dynamic light scattering (DLS), and fluorescence spectroscopy. The encapsulation of the cargo is further evaluated through SEC (size exclusion chromatography) and IEC (ion exchange chromatography).

The encapsulation of SPIONs within encapsulin offers opportunities for diverse biological applications, including targeted hyperthermia treatment of cancer cells and their potential use as contrast agents in magnetic resonance imaging (MRI).

Literature:

 [1] M. Künzle, J. Mangler, M. Lach, T. Beck, Nanoscale 2018, 10, 22917-22926.

Investigation of synthesis parameters and characterization of protein-templated semiconductor quantum dots

T. Katenkamp, Hamburg/DE, H. Böhler, Hamburg/DE, T. Beck, Hamburg/DE

Prof. Dr. Tobias Beck, University of Hamburg, Institute of Physical Chemistry, Grindelallee 117 20146 Hamburg, Germany

Due to the quantum confinement effect, quantum dots (QDs) have unique tunable optical properties that can be used for example in optical devices, displays or light emitting diodes. Conventional semiconductor quantum dot syntheses rely on organic solvents, precursors and ligands and are usually carried out at high temperatures. They are difficult to scale up and the used chemicals are hazardous for the environment. Water-based QD syntheses are eco-friendlier than the organic syntheses but still ligands and other additives are used at high temperatures. Here, a new synthesis method of homogeneous Mn-doped ZnSe nanoparticles is established using the cavity of a protein cage acting as a size-restrictive template with Ftn(neg), a supercharged human heavy chain variant, as a scaffold.[1] The inner cavity of ferritin is ideally suited to mineralize inorganic material, also non-natural nanoparticles such as CeO_2 or Co_3O_4.[1] The synthesis of ZnSe QDs inside the cavity of ferritin was published using a slow chemical reaction in the inner cavity of Ftn(neg) at ambient temperature.[2] An overview of the synthesis of Mn-doped ZnSe QDs is shown in Figure 1. Here, the optimal synthesis parameters for maximum protein recovery and fluorescent monodisperse spherical QDs inside the protein containers were investigated. Modification of the QDs after synthesis to create a ZnS shell around the nanoparticles could improve the fluorescence properties of the QDs. Furthermore, attaching a Mn-binding peptide to the C-terminus of the protein container could improve the reproducibility of the optical properties of the QDs. The outer surface of the protein cage is modified to construct binary protein superlattices, opening the route to highly ordered assemblies of Mn-doped ZnSe QDs in combination with other materials, such as plasmonic nanoparticles or dyes to investigate possible emerging effects.
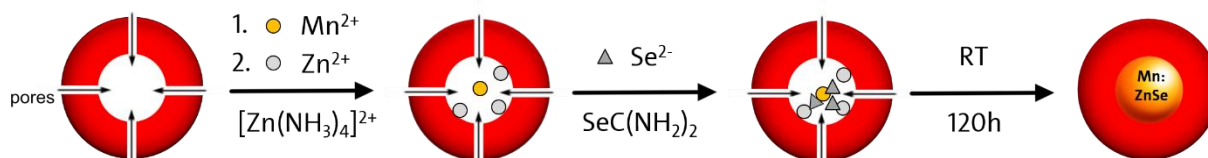

Figure 1: Schematic overview for the synthesis of Mn-doped ZnSe QDs in ferritin.

Literature:
[1] M. Künzle, T. Eckert, T. Beck *J. Am. Chem. Soc.* **2016**, *138*, 12731.
[2] K. Iwahori, K. Yoshizawa, M. Muraoka, I. Yamashita *Inorg. Chem.* **2005**, 44, 18, 6393-6400.

Hofmeister Effects Cause Hydrophobic Interaction Driven Biomolecular Condensate Formation

A. Czajkowski, Dresden/DE,
Dr. E.M. Adams, Dresden/DE,
Physics of Life Excellence Cluster, TU Dresden, Arnoldstraße 18, 01307 Dresden,
Helmholtz Zentrum Dresden Rossendorf, Bautzner Landstraße 400, 01328 Dresden

Many proteins containing disordered regions are known to form structures called biomolecular condensates. These biomolecule-rich phases form through multivalent interactions, and allow the cell to compartmentalize its contents without lipid membranes.[1] For a complete picture of these structures, the role of hydration effects must be considered, as it has been shown to play a key role in the formation of multiple other macromolecular structures.[2] It is possible to study the hydration within condensates using Terahertz (THz) spectroscopy, a method using electromagnetic waves on the cusp of infrared and microwave radiation. Radiation in this range is resonant with the vibrations of hydrogen bonds between water molecules.[3]

In the presented work, THz spectroscopy has been used to study the effects of a range of monovalent and multivalent salt ions on the solvation changes happening during condensate formation. Typically, biomolecular condensation is inhibited by salts due to the screening of electrostatic interactions. However, the protein used in this study, Fused in Sarcoma (FUS), shows a reentrant phase transition at very high salt concentrations, where the threshold concentration depends on the type of ion present[4]. Droplets forming under these conditions show unique spectral features corresponding to the changes in the hydration of hydrophobic residues. These results seem to corroborate the hypothesis that the return of phase separation under high salt conditions is caused by the ion induced enhancement of hydrophobic interactions.

Literature:
[1] Hyman et al. Annu Rev Cell Dev Biol. 2014;30:39-58. [2] Privalov, P. L., & Crane-Robinson, C. European Biophysics Journal, 2017:46(3):203–224. 21 [3] Ahlers, J. et al. Biophysical Journal, 2021;120(7):1266–1275. [4] Krainer, G. et al. (2021). Nature Communications 2021;12(1):1–14.

Commented [EA1]: Two sentences is not a paragraph. Would suggest to combine with paragraph below.

Commented [CA(-12R1]:

Characterization of FUS Condensate Dissolution by Isothermal Titration Calorimetry

Likhitha Pulibandla[1,2], Dr. Jana Oertel[2],
Prof. Dr. Karim Fahmy[2], Dr. Ellen M. Adams[1,2],
[1]Technische Universität Dresden, DFG Cluster of Excellence "Physics of Life" (PoL), [2]Helmholtz Zentrum Dresden Rossendorf, Dresden/ Germany

Liquid-liquid phase separation (LLPS) of macromolecules stimulates the formation of biomolecular condensates. The RNA-binding protein fused in sarcoma (FUS) undergoes phase separation, which is associated with intrinsically disordered regions (IDRs), and is enhanced in the low salt regime.[1] Although the mechanism of FUS LLPS is understood, its thermodynamic properties are known to a lesser extent. Previous studies on the thermodynamic properties of FUS were conducted using MD simulations, which do not directly measure heat. [2] Isothermal titration calorimetry (ITC) measures the heat of reactions of FUS as it undergoes LLPS in the low salt conditions. Results showed that the heat produced for FUS phase separation is temperature dependent. At the lowest temperature studied, the molar enthalpy suggests an exothermic process. As temperature increased, the process became endothermic. Upon phase separation, the thermal equilibrium baseline was not recovered, indicating a change in energetics.

Furthermore, combining ITC and microscopy, the effects of ATP concentration on the thermodynamic properties and morphological studies of FUS condensates were explored. Previous studies showed that ATP dissolves the previously formed condensates at average cellular concentrations. [3] However, the microscopy images revealed that the condensates assume fibril-like shapes rather than their usual spherical form when ATP was added. This distortion in shape may be due to the absence of Mg^{2+} ions in the solution. Furthermore, the impact of temperature on FUS condensate thermodynamics was explored, and it was observed that exothermic properties decrease as the temperature rises. The binding between ATP and FUS is estimated to be weaker because of the lower k_D (binding affinity) values. These findings provide valuable insights into the thermodynamics of FUS and highlight the crucial role that temperature plays in phase separation.

Literature:

[1] J. Wang, Cell, vol. 174, pp. 688-699, 2018. [2] Y. Ji, Journal of materials chemistry B, pp. 8616-8628, 2022. [3] K. Jian, Biochemical and Biophysical Research Communications, vol. 504, no. 2, 2018, pp. 545–551.

Establish protein containers as building blocks for the assembly of anisotropic nanorods into optical hybrid nanomaterials

V. Yadav, Hamburg/DE, T. Beck, Hamburg/DE
Prof. Dr. Tobias Beck, Universität Hamburg, Institut für Physikalische Chemie,
Grindelallee 117, 20146 Hamburg

Creating functional, biocompatible and stimuli-responsive crystalline arrays from nanoscale building blocks is a growing interest and aims to develop new nanotechnology applications. Biomolecules such as DNA or proteins have the ability to act as functional templates for the organization of nanomaterials. Structural and functional diversity of protein cages, such as virus capsids, and encapsulin nano-compartments are often combined with unique properties of inorganic nanomaterials to create new biohybrid materials with tunable physical and chemical properties. Protein containers present a viable building block for the synthesis of higher-order superlattices because (a) they have an atomically precise shape defined by their molecular composition, and (b) their inner cavity can be loaded with a range of organic and inorganic materials.[1][2][3]

We study the encapsulation of plasmonic gold nanorods and fluorescent dot rods in different protein containers. The main goal is to establish protein containers as building blocks for the assembly of anisotropic nanorods into optical hybrid nanomaterials. Binary anisotropic materials will be constructed using protein-encapsulated gold nanorods and CdSe/CdS dot rods. The CdSe/CdS dot rods have several advantageous properties such as high quantum yield, strong and tunable light emission and a high degree of linear polarization. The protein containers will form a defined ligand shell around the dot rod and thus enable the precise position of the cargo in subsequent assemblies. After the encapsulation of dot rods into the protein containers, the composites will be assembled using layer-by-layer approaches. The interactions between the plasmonic gold nanorods and the fluorescent dot rods will be studied. The properties will be exploited to enable new possible applications in biomedical and nanotechnology applications.

Literature:
[1] M. Künzle, T. Eckert, T. Beck, Journal of the American Chemical Society 2016, 138(39), 12731-12734. [2] M. Künzle, J. Mangler, M. Lach, T. Beck, Nanoscale 2018,10(48), 22917-22926. [3] M. Lach, C. Strelow, A. Meyer, A. Mews, T. Beck, ACS Applied Materials & Interfaces 2022, 14(8), 10656-10668

Convergence of SERS with CRISPR/Cas: towards real-time, multiplexed and amplification-free detection of nucleic acids

H. Giesler, Essen/DE, Dr. N. Choi Essen/DE, L. Supovec, Essen/DE,
Prof. Dr. S. Schlücker, Essen/DE
Helene Giesler, University of Duisburg-Essen (UDE), Universitätsstr. 5, 45141 Essen

The gene-editing CRISPR/Cas complex is rapidly emerging as a powerful tool in molecular diagnostics. The CRISPR/Cas-based detection of nucleic acids involves the production of amplicons (PCR products), activation of the Cas protein, and the release of a fluorophore upon enzymatic cleavage.[1-2] Fluorescence detection has limitations with respect to quantification and sensitivity due to photobleaching; the number of targets that can be simultaneously detected is usually limited to 2-3 due to the broad emission profiles of fluorescent dyes. Surface-enhanced Raman scattering (SERS) overcomes these limitations.[3-4]

The combination of CRISPR/Cas and SERS has the potential to enable multiplexed, amplification-free molecular diagnostics via real-time monitoring. To this end, we combine bright and photostable SERS nanotags conjugated to magnetic beads via oligonucleotides that are continuously cleaved by activated CRISPR/Cas for signal amplifcation rather than target amplification. We developed a home-built laser setup and a custom-made temperature-controlled sample chamber for analyzing very small sample volumes of ca. 35-70 µL. Multiplexed detection is achieved by employing spectrally distinct Raman reporter molecules on the surface of plasmonically active nanoparticles.

Literature:
[1] M. J. Kellner et al., Nat. Protoc. 2019, 14, 2986-3012. [2] M. M. Kaminski et al., Nat. Biomed. Eng. 2021, 5, 643-656. [3] E. Stepula et al., ACS Appl. Mater. Interfaces 2020, 12, 32321-32327. [4] K. Faulds et al., Angew. Chem. Int. Ed. Engl. 2007, 46, 1829-1831.

Surface-enhanced Raman scattering identifies a systematic error in conventional one-step lateral flow assays

Dr. N. Choi, Essen/DE, Dr. R. Grzeschik, Essen/DE, Dr. A. Hoffmann, Essen/DE, Prof. Dr. Sebastian Schlücker, Essen/DE

Dr. Namhyun Choi, University of Duisburg-Essen (UDE), Universitätsstr. 5, 45141 Essen

Lateral Flow Assay (LFA) is the most widely used platform in point-of-care testing, such as pregnancy tests, diagnosis of infectious diseases, and food inspection.[1] However, LFAs face challenges such as false-negative results due to their limited sensitivity. To improve sensitivity, gold nanoparticles (AuNP) responsible for the red colour on the test and control line are chemically modified by chemisorption of Raman reporter molecules for optical detection based on surface-enhanced Raman scattering (SERS). This approach provides access to the low-concentration regime that is not accessible with conventional LFA.[2]

Despite these improvements in sensitivity by SERS readout, the conventional one-step LFA scheme with parallel immuno-reactions suffers from inherent systematic response errors such as i) the well-known hook effect at high antigen concentrations[3] and ii) non-quantitative capturing at low antigen concentrations. In the case of separated immuno-reactions, computer simulations and experiments demonstrated unfavourable results in terms of detection sensitivity.[4] However, in the low-concentration regime, despite the limits in chances of reactions, the two-step scheme should show an improved quantification because of the formation of more accurate '1:1' immuno-complexes. Due to the limited sensitivity of conventional LFA, this effect cannot be detected by the naked eye. We hypothesized that SERS-based LFA will be capable of revealing this systematic error of one-step LFA and that it may be overcome by separating immuno-reactions in a two-step similar to ELISA. Overall, our SERS-based two-step approach surpassed the conventional way by over 100 times in limits of detection. It highlights the significance of the separated immuno-reaction in mitigating errors and improving the detection sensitivity of SERS-LFA.

Literature:
[1] C. Parolo et al., Nat. Protoc. 2020, 15, 3788-3816. [2] V. Tran et al., Angew. Chem. Int. Ed. Engl. 2019, 58, 442-446. [3] E. G. Rey et al., Anal. Chem. 2017, 89, 5095-5100 [4] D. Gasperino et al., Annu. Rev. Anal. Chem. 2018, 11, 219-244.

Vibrational spectroscopy (IR, Raman, UV Resonance Raman) of isotopically labelled (^{13}C,^{15}N, ^{18}O) *N*-methylacetamide: a model system for site-specific probing of peptides

L. Supovec, Essen/DE, Prof. Dr. S. Schlücker, Essen/DE
Luca Supovec, University of Duisburg-Essen (UDE), Universitätsstraße 5, 45141 Essen

N-Methylacetamide (NMA) is a widely accepted simple model system for peptides that has been extensively studied.[1-2] Isotopic labelling of amide groups in peptides and proteins provides a non-invasive and site specific approach to probe local structures and intermolecular interactions by vibrational spectroscopic methods.[3-4] Among them, UVRR provides both high sensitivity by exploiting signal enhancement via electronic resonances combined with high selectivity for the peptide chromophore. In case of the model system NMA, numerous studies on deuterated NMA species are known, but only few reports on ^{13}C, ^{18}O or ^{15}N isotopically labelled NMA are published.

We synthesized three isotopically edited NMA derivatives and characterized them by IR, Raman and UVRR spectroscopy: N-^{13}C=O, N-^{13}C=^{18}O, and ^{15}N-^{13}C=^{18}O. Experimentally observed isotope-induced shifts of the amide I, II & III vibrations agree well with those predicted by computer simulations employing density functional theory. The advantage of a triple substituted ^{15}N-^{13}C=^{18}O Amide bond is that all amide vibrations exhibit characteristic wavenumber shifts and become spectrally well separated from unlabelled peptide bonds. Our proof of concept study paves the way for applying triple isotope labelling to oligopeptides in combination with UVRR spectroscopy for obtaining information about local structures and intermolecular interactions.

Literature:
[1] X. G. Chen et al., J. Phys. Chem. 1995, 99, 10, 3074–3083. [2] W. A. Herrebout et al., J. Phys. Chem. A 2001, 105, 20, 4865–4881. [3] C. Fang et al., J. Phys. Chem. B 2004, 108, 29, 10415–10427. [4] H. Maekawa et al., J. Phys. Chem. C 2014, 118, 50, 29448–29457.

Thermodiffusion of Aqueous Solutions of Guanidinium Salts

B. Rudani, Jülich/Germany, A. Jakubowski, Jülich/ Germany
Prof. Dr. S. Wiegand, FZJ Jülich, 52425 Jülich und Universität zu Köln,
Luxemburger Str. 116, 50939 Cologne

Thermodiffusion, or the Ludwig-Soret effect, refers to the motion of solute molecules induced by a thermal gradient. This phenomenon is quantified by the Soret coefficient (S_T), in aqueous solutions S_T is highly sensitive to the nature of solute-water interactions [1]. It is being used as a tool to probe molecular interactions, mainly protein-ligand binding [2,3]. Guanidinium ions play a pivotal role in the exploration of protein folding, denaturation, and the hydration of biological molecules owing to its rigid and symmetric structure [4]. Despite its significance, there is a dearth of information on their thermophoretic behaviour. Recent research by our group has delved into the thermodiffusion of similar non-ionic organic solutes [1] and simple ionic inorganic salts [5] in aqueous solutions, revealing distinctive temperature and concentration dependencies of the S_T. In our present research, we utilize thermal diffusion forced Rayleigh scattering (TDFRS) to scrutinize guanidinium salt solution with various anions (carbonate, chloride, iodide and thiocyanate), spanning the entire range of the Hofmeister series from hydrophilic to hydrophobic. We performed systematic measurements of S_T in a temperature range of 15 to 35°C and concentrations ranging from 0.5 to 2 m. The change of S_T with temperature as a function of increasing concentration becomes weaker for aqueous guanidinium salt solutions. We assume that fewer hydrogen bonds are present at higher concentrations reducing the change of the Soret coefficient and indicating that the hydration of the salt plays an important role [6]. Overall, this systematic study helps to gain a fundamental understanding of thermodiffusion in protein-ligand systems.

Literature:
[1] D. Niether and S. Wiegand, J. Phys. Condens. Matt., 2019, 31, 503003. [2] J. Colombani et al., J. Chem. Phys., 1999, 110, 8622. [3] Jerabek-Willemsen et al., Assay Drug Dev Technol., 2011, 4, 342. [4] V. Balos et al., Phys. Chem. Chem. Phys., 2017, 19, 9724 [5] S. Mohanakumar et al. J. Chem. Phys, 2021, 154, 84506. [6] G. Gannoner et al., J. Phys. Chem. B, 2008, 112, 8906–8911.

Structural dynamics of the intrinsically disordered SNARE protein SNAP25a in its pre-fusion conformation

T. Stief, K. Vormann, L. Gremer, R. Biehl, N.-A. Lakomek, Forschungszentrum Jülich, Wilhelm-Johnen-Straße, 52428 Jülich

Á. Pérez-Lara, University of Granada, Campus Universitario de Cartuja, 18071 Granada

S. Pribicevic, D. F. Espinueva, R. Jahn, Max-Planck Institute for Multidisciplinary Sciences, Am Faßberg 11, 37077 Göttingen

The release of neurotransmitters in presynaptic vesicles into the synaptic cleft is essential for signal transmission between neurons. The assembly of the SNARE (soluble N-ethylmaleimide-sensitive-factor attachment receptor) complex provides the energy required for vesicular membrane fusion with the pre-synaptic plasma membrane. Important molecular transitions of the SNARE proteins and their membrane interactions have not yet been well understood at the molecular level.

The neuronal SNARE protein SNAP25a (isoform 2) is one of those SNARE proteins comprising the SNARE complex. While the post-fusion cis-SNARE complex is relatively well understood, only a few details are known about the pre-fusion conformation of SNAP25a.

We used three-dimensional NMR backbone assignment experiments, NMR relaxation measurements, and other biophysical methods, such as SAXS and CD spectroscopy, to investigate the secondary structure and backbone dynamics of SNAP25a. Large regions of SNAP25a are highly disordered and exhibit high internal flexibility, while the N-terminus of SNAP25a is α-helical [1]. We speculate that this region is a nucleation site for initiating the so-called SNARE zippering process.

Literature:

[1] Stief, T. et al. Intrinsic disorder of the neuronal SNARE protein SNAP25a in its pre-fusion conformation. J. Mol. Biol. 435, 168069 (2023)

Protein-based Adsorbents for Uremic Toxin Clearance in Chronic Kidney Disease Patients

H Wagler, Hamburg/DE, H. Böhler, Hamburg/DE, S. O. Alampour, Aachen/DE, M. Riedner, Hamburg/DE, J. Jankowski, Aachen/DE, T. Beck, Hamburg/DE
Prof. Dr. Tobias Beck, University of Hamburg, Grindelallee 117, 20146 Hamburg

Chronic kidney disease (CKD) affects nearly one-tenth of the global population. In advanced CKD stages, protein-bound uremic toxins (PBUTs) accumulate in the blood due to impaired kidney function. Elevated PBUT levels contribute to renal and cardiovascular issues. Renal replacement therapies, such as dialysis, become necessary. However, PBUTs are challenging to remove using dialysis membranes due to their partially hydrophobic character and plasma protein binding. To address this, a bio- and hemocompatible adsorbent with high PBUT affinity is crucial for effective treatment.

We present an innovative approach utilizing ferritin, an intrinsically biocompatible protein cage, as a scaffold to develop an adsorbent for PBUT removal.[1] Whereas the small PBUTs can enter the cage and bind at the inner surface, larger molecules and blood cells will be excluded. To enhance PBUT adsorption we genetically modify the amino acid sequence of the ferritin protein cage based on computational approaches using the Rosetta software. First experiments showed that by changing the amino acid side chains at the inner surface of the protein cage, overall binding affinity can be improved and distinct binding sites be created. Further optimization of the inner surface as well as the pores and the overall morphology of the material needs to be done in order to develop a promising adsorbent for PBUT removal.

Literature:
[1] H. Böhler, S. Orth-Alampour, C. Baaten, M. Riedner, J. Jankowski, T. Beck, J. Mater. Chem. B 2022, 11, 55-60.

NV⁻ qubit in nanodiamond for precise sensing of rotational and translational mobilities of active proteins

I. Pérez, L. Spantzel, F. Rashidi, T. Heitkamp, M. Börsch.

Jena University Hospital, Nonnenplan 2-4, 07743 Jena.

Nitrogen-vacancy (NV) centers in nanodiamonds (10 to 100 nm diameter) can be applied in biotechnology as single fluorescent quantum sensors. The surface of nanodiamonds can be tailored for specific binding to biological targets. The extraordinary photo-physical properties such as very high photo-stability and non-blinking behaviour allow for optical detection of magnetic resonance due to the NV triplet spin states [1] and nanoscale distance measurements. Taking advantage of the extended observation times of single nanodiamonds in solution using our version of a confocal anti-Brownian electrokinetic trap (ABEL trap), we determined molecular brightness, spectral ratio, diffusion coefficient, surface charge and multiexponential fluorescence lifetimes for each nanodiamond one by one in solution [2].

The goal of our quantum-sensing project is to exploit the single-spin properties of the luminescent NV⁻ center in nanodiamonds to reveal the dynamics of an active biological protein complex. We have studied the membrane enzyme F_oF_1-ATP synthase at physiological conditions with highest spatio-temporal resolution using intramolecular single-molecule FRET for about a second in the ABELtrap [3]. Now, monitoring fluorescence lifetime changes of the NV⁻ center due to the effect of local magnetic fields [4] makes it possible to observe conformational changes of a single protein for tens of seconds in solution.

[1] C. Laube, et al. Nanoscale, 2019, **11**, 1770-1783.

[2] A. E. Cohen and W. E. Moerner, Proc. Natl. Acad. Sci. U. S. A., 2006, **103**, 4362–4365.

[3] I. Pérez, et al. Intl. J. Mol. Sci. 2023, **24**, 8442.

[4] F. M. Stürner, et al. Appl. Phys. Lett., 2021, **119**, 134001.

Catalysis

(Photo)electrochemical Characterization of Cocatalyst-decorated CdS Nanorods for Oxygen Evolution Catalysis

J. Voss, Hamburg/DE, Prof. Dr. Alf Mews, Hamburg/DE

Institute of Physical Chemistry, University of Hamburg, Grindelallee 117,

20146 Hamburg, Germany

Due to the demand for efficient production of green hydrogen, photocatalytic overall water splitting has become of interest. CdS nanorods with platinum tips as reduction cocatalyst were found to drive photocatalytic hydrogen evolution in the presence of sacrificial agents. [1] This study aims to add oxygen evolution cocatalysts to this structure to overcome the need for sacrificial agents and enable overall water splitting. Oxygen evolution is a complex four-electron transfer process, exhibiting a high activation barrier, which makes the development of suitable materials challenging. Here, (photo)electrocatalysis is be employed to characterize possible candidates for photocatalysis.

CdS nanorods were decorated with Ir, RuO_2 and IrO_2 nanoparticles (NPs), which are known to be the state of the art catalysts for electrocatalytic oxygen evolution. IrNPs were deposited by reduction of Na_3IrCl_6 with sodium borohydride in the presence of CdS nanorods in alkaline media. The deposition of RuO_2 and IrO_2 NPs followed two literature known procedures by Grätzel *et al.* and Amirav *et al.*, respectively. [2][3]

To enable photocatalytic oxygen evolution, cocatalyst-semiconductor composites need to exhibit sufficiently low overpotentials and high photovoltages. [4] The overpotential was determined in electrocatalytic tests. The photovoltage should become apparent as a shift in the overpotential upon irradiation, which could not be observed. Nevertheless, the impact of irradiation on the measured current densities and stabilities of the prepared catalysts was studied.

Literature:
[1] Y.Yuan, J. Mater. Chem. A, 2018, 6, 11606. [2] K. Kalyanasundaram, Helv. Chim. Acta, 1981, 64, 35. [3] P. Kalisman, J. Mater. Chem. A, 2015, 3, 3261. [4] C. Ding, ACS Catal. 2017, 7, 675−688

Tailor-made ordered mesoporous silicates and metallosilicates prepared by directly templating lyotropic liquid crystals

S. Itzigehl, T. Ott, Ch. Vogler, S. Naumann, J. R. Bruckner
University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart

Performing chemical reactions in confined spaces may lead to a dramatically increased product selectivity, if the confinement conditions, e.g. dimension and polarity of the cavity, match the requirements of the catalysed reaction. [1] To study this effect further, it is necessary to design surroundings, which provide continuously changeable as well as precisely addressable confinement conditions. We will show that mesoporous silicates prepared by directly templating the hexagonal phase of lyotropic liquid crystals are ideal for this purpose since they exhibit a narrow pore size distribution, accessible pores with low tortuosity and a high reproducibility. [2] We utilize commercial surfactants to fabricate mesopores down to 2.5 nm and tailor-made polymers to generate rationally addressable pore diameters up to 20 nm. [3] We will demonstrate that direct templating of lyotropic liquid crystal phases is especially well suited for the synthesis of ordered mesoporous metallosilicates with high metal loading as well as tailorable pore size and acidity. We study the effect of metal concentration and synthesis temperature on the nanostructure as well as the Lewis- and Brønsted acidity by SAXS, N_2 physisorption, TEM, ICP-OES, EDX, NMR and IR spectroscopy with probe molecules, revealing fundamental differences between the different types of mesoporous materials.

Literature:
[1] F. Ziegler, H. Kraus, M. J. Benedikter, D. Wang, J. R. Bruckner, M. Nowakowski, K. Weißer, H. Solodenko, G. Schmitz, M. Bauer, N. Hansen, M. R. Buchmeiser, ACS Catal. 2021, 11, 11570. [2] J. R. Bruckner, J. Bauhof, J. Gebhardt, A.-K. Beurer, Y. Traa, F. Giesselmann, J. Phys. Chem. B 2021, 125, 3197. [3] C. Vogler, S. Naumann, J. R. Bruckner, Mol. Syst. Des. Eng. 2022, 7, 1318.

Synthesis of metal-alloy tipped CdSe/CdS dot-in-a-rod nanostructures

C. Frost, Hamburg/DE, A. Mews, Hamburg/DE

Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany

CdSe/CdS dot-in-a-rod nanostructures have unique properties that can be further modified when a tip of a different material is attached to the rod-shaped nanostructure. The rod material CdS is a good absorber of sunlight. If, after absorption, the separation of photoexcited electron-hole pairs is achieved, the holes can serve to oxidize water, while the electrons can reduce water to hydrogen. To facilitate the separation of the charge carriers, metal tips on the semiconductor nanoparticles can be used. It has been already reported that Pt tips on CdSe-dot/CdS-rod nanoparticles leads to a catalytic enhancement of the hydrogen evolution reaction. Here, we concentrate on capturing photoexcited holes for the oxygen evolution reaction. For this we use different alloy materials such as Ni/Ir (Nickel/iridium).

We report on the synthesis of CdSe/CdS dot-in-a-rod nanostructures that are tipped with Ni-Ir material. Starting point is the synthesis of well-known CdSe seeds followed by the growth of the elongated CdS shell. Then Ni domains are synthesized at the tips of the rod-shaped nanostructureds before Ni-Ir alloys are formed. The CdSe/CdS/Ni-Ir dot-in-a-rod nanostructures were investigated by TEM and optical methods such as UV/Vis. Due to the different surface energies, the tips of the dot-in-a-rod nanostructures are mainly located on one side of the rod. XRD measurements were performed to determine the crystal structures. EDX was used to investigate the composition and distribution of the elements. In the future, we plan to investigate the synthesis of different alloy materials on the tip.

Effect of subsurface hydrogen on formation and stabilization of enol form of 2-acetylpyridine

P. Hubert, Kiel/DE, P. Haugg, Kiel/DE, J. Smyczek, Kiel/DE, C. Schröder, Kiel/DE

Prof. Dr. S. Schauermann, Institute of Physical Chemistry, Kiel University, Max-Eyth-Straße 2, 24118 Kiel, Germany

The stability of the C=O bond makes hydrogenation of carbonyl compounds challenging and thus requires effective catalysts. There is an ongoing discussion on a possible low-temperature hydrogenation pathway proceeding via formation of enol form of a carbonyl compound followed by H insertion into the newly formed olefinic bond. This two-step process was theoretically predicted to proceed via significantly lower activation barriers as compared to the direct hydrogen insertion into the C=O bond. The major challenge of this mechanism is the low stability of enol species that – if not deliberately stabilized – would readily convert to ketone under the reactive conditions.

In this contribution, we present a mechanistic study on keto-enol tautomerization of a carbonyl compound 2-acetylpyridine (APy) performed by a combination of infrared reflection absorption spectroscopy (IRAS), molecular beam techniques and scanning tunneling microscopy (STM) to investigate its adsorption behaviour and formation of the enol form on Pd(111) in presence of hydrogen. The main focus lies on the understanding of the role of different hydrogen species – H_{surf} adsorbed on the surface vs. H_{sub} absorbed in the subsurface region of Pd – on the formation and stabilization of enol form of APy. Particularly, we show spectroscopically that APy can readily convert to the enol form on all types of Pd surfaces, however, the largest amounts of the enol species were detected in the presence of subsurface H_{sub}. Complementarily, the STM results indicate that the enhanced evolution of enol species on H_{sub}-containing Pd is accompanied by formation of the specific acetyl-acetyl dimers, interacting via the acetyl groups. This specific interaction is most likely responsible for the efficient formation and stabilization of the enol species.

HR-XPS Study on the Adsorption of CO on Graphene-Supported Co Clusters

N. J. Waleska-Wellnhofer, Erlangen/DE, F. Düll, Erlangen/DE, U. Bauer, Erlangen/DE, P. Bachmann, Erlangen/DE, J. Steinhauer, Erlangen/DE, C. Papp, Erlangen/DE

Natalie J. Waleska-Wellnhofer, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Cobalt plays an important role as catalytic active material for the industrial production of hydrocarbons by Fischer-Tropsch synthesis. To overcome the material gap, we investigated graphene-supported Co clusters as model catalyst by HR-XPS to gather more information about the catalysts' properties. Using CO as a probe molecule, we were able to determine the available adsorption sites on the as-prepared clusters which are edge/top and bridge/hollow sites. The desorption temperatures of CO from these sites were determined by temperature-programmed XPS to be 360 and 240 K, respectively. Additionally, CO dissociation was observed. The dissociation products were used to study the influence of C and O on the reactivity of the clusters. For the precovered clusters, no CO adsorption at edge sites was observed due to site blocking. Furthermore, no CO dissociation was found. Thus, the edge sites are determined to be the most active sites. Moreover, the desorption temperature of CO decreased as a result of a change in the adsorption energy on the precovered clusters.

Catalytic activity of ligand-stabilised platinum nanoparticles towards the hydrogenation reaction of citral

O. Schmidt, Oldenburg/DE, N. Brinkmann, Oldenburg/DE, M. Osmic, Oldenburg/DE

Prof. Dr. Katharina Al-Shamery, University of Oldenburg,

Carl-von-Ossietzky-Straße 9-11, 26131 Oldenburg

Metal nanoparticles have become a promising approach for modern heterogenic catalysis, due to their large surface-to-volume ratio and many catalytic active sites relative to their mass. The control of size and shape is crucial as selectivity and activity strongly depend on the surface properties.[1]

One way for preparation is by colloidal synthesis method, which allows precise control of the shape and size of the metal nanoparticles. Furthermore, previous experiments by the working group have shown that the catalytic activity of Pt nanoparticles stabilised with dodecylamine is increased compared to ligand-free Pt nanoparticles.[2] Citral is an acyclic monoterpene that contains an isolated and a conjugated double bond as well as a carbonyl group. Due to the many functionalities of the molecule, the hydrogenation of citral is a favourable model reaction for the investigation of catalyst properties in terms of selectivity and activity.[3]

In this work, various TiO_2 supported dodecylamine-stabilised Pt nanoparticles are synthesised by a colloidal pathway and investigated for their reactivity for the catalytic hydrogenation reaction of citral. For this purpose, the reaction is carried out in liquid phase under atmospheric hydrogen pressure in a temperature-controlled double-walled tank reactor. The reaction progress is determined by gas chromatography. The particles are characterised and checked for possible electronical and structural changes by using transmission electron microscopy and X-ray photoelectron spectroscopy. Several influences, such as particle shape and size as well as temperature, are analysed. Interestingly, smaller particles show a higher conversion rate, while the selectivity is independent of the particle size. The conjugated double bond is preferentially hydrogenated.

[1] C. Jia, F. Schüth, Phys. Chem. Chem. Phys., 2011,13, 2457-2487.
[2] N. Brinkmann, A. Damps, M. Siemer, J. Kräuter, F. Rößner, K. Al-Shamery, J. Vis. Exp., 2022, 184, e63936. [3] M. Steffan, M. Lucas, A. Brandner, P. Claus, M. Wollny, N. Oldenburg, *Chem. Ing. Tech.* 2006, *78*, 923.

Interaction between CdSe@CdS nanorods and Ru-based water-oxidation catalysts

S. Lander, Kaiserslautern/DE, A. Mengele, Ulm/DE, K. Siewerth, Ulm/DE, S. Rau, Ulm/DE, M. Wächtler, Kaiserslautern/DE
Sarah Lander, Chemistry Department and State Research Center OPTIMAS, RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern

Artificial photosynthetic approaches are highly desirable solutions to convert solar energy and offer a source for clean and sustainable fuels and feedstock for chemical industry. In this regard, the light-driven production of molecular hydrogen from water has been heavily investigated and successfully demonstrated in various photocatalytic schemes. Colloidal semiconductor nanocrystals such as CdSe@CdS nanorods have shown great promise as light-harvesting entities in hydrogen evolution reactions (HER) due to their unique geometry enabling efficient and long-lived charge separation via trapping of the holes in the CdSe core while electrons can be transferred to surface bound HER catalysts. However, the reduction of protons needs to be accompanied by an oxidation reaction, e.g. oxygen evolution reaction (OER) in a full water-splitting scheme. This oxidation reaction is still a bottleneck in the development of functional artificial photosynthetic devices due to its kinetic and energetic complexity. This process requires efficient charge separation and transfer of four holes to the reactive center. In this context, we investigate the interaction of CdSe@CdS nanorods with Ruthenium complexes, which are potential water-oxidation catalysts. Applying steady-state and time-resolved absorption and photoluminescence spectroscopy comparing Ruthenium complexes with and without the capability to bind via an anchoring group to the surface of the nanocrystals we will elucidate the role of surface binding groups present in the catalyst to enable efficient interaction and their effect on the mechanistic interplay between the two components of the system.

UHV-studies of adsorbed CO_2 on Cu and Cu_2O at Rutile (110)

J. Klimek Oldenburg/DE, M. Grebien, Oldenburg/DE, Prof. Dr. K. Al-Shamery, Oldenburg/DE
University of Oldenburg, Carl-von-Ossietzky-Straße 9–11, 26129 Oldenburg/DE

Carbon dioxide (CO_2) is one of the major greenhouse gases causing the worldwide climate change thus making it desirable to recycle carbon dioxide as a contribution to remove anthropogenic produced CO_2.[1] Therefore it is desirable to capture and use anthropogenic CO_2 as an organic feedstock for various products like methanol, which is already synthesized from H_2 and CO_2 (syngas) using a $Cu/ZnO/Al_2O_3$ catalyst. But studies have shown that the use of CO_2 affords lower yields than the use of CO, thus, showing the need for the development and investigation of new, more efficient catalysts.[2]

Interesting systems are mixed oxides such as TiO_2/WO_3 [3] as well as Au or Cu on TiO_2 which have shown high reactivity towards methanol reactions due to Ti^{3+} as reactive center for interaction with oxygen.[4] Literature has also shown that formation of methanol from syngas using Cu-based nanocatalysts is possible.[5]

In this work we present the preparation of nanoparticulate copper and cuprous oxide on Rutile (110) of different reduction degrees, prepared via electron beam evaporation under UHV conditions and high-pressure oxidation in a chamber connected to the UHV-system. These systems were characterized with X-ray photoelectron spectroscopy (XPS) and the reaction behaviour of CO_2 and coadsorbates was investigated with temperature programmed desorption spectroscopy (TPD). The performed experiments show cluster-size-dependent formation of carbon monoxide and CO_2-coverage-dependent adsorption-site-sensitive desorption of CO_2.

[1] IPCC, *IPCC Special Report on the Impacts of Global Warming of 1.5 °C - Summary for Policy Makers*; Incheon, **2018**. [2] B. Lacerda de Oliveira Campos, et al., *Processes* **2022**, *10*, 1535. [3] L. Mohrhusen et al., *Phys. Chem. Chem. Phys.* **2021**, *23*, 12137, [4] F. Boccuzzi et al., *Applied Catalysis B: Environmental* **2004**, *57*, 201–209 [5] J Huang et al., *Energy Fuels* **2021**, 35, 10, 8558–8584.

SERS-based Kinetic Monitoring of the Pt-catalyzed Reduction of the three Nitrothiophenols Isomers on Gold Nanorods

D. Schäfer, Essen/DE, Dr. Jesil Jose, Essen/DE, Dr. Roland Grzeschik, Essen/DE and Prof. Dr. Sebastian Schlücker, Essen/DE

Daniel Schäfer, University of Duisburg-Essen (UDE), Universitätsstraße 5, 45141 Essen, Germany

4-Nitrothiophenol (4-NTP) has been widely used in surface-enhanced Raman scattering (SERS)-based studies for testing the catalytic performance of a variety of noble metal nanoparticles using hydride or hydrogen as reducing agent.[1,2] The catalytic conversion of 4-NTP to 4-aminothiophenol (4-ATP) proceeds via a Langmuir-Hinshelwood mechanism, involving the formation of active Pt-H species. In principle, two alternative reaction pathways are possible. The first possible pathway describes the direct transfer of a hydrogen radical or hydride to the molecule (hypothesis 1), while the second pathway describes an electron transfer from the platinum to the 4-NTP followed by a proton transfer from the active species (hypothesis 2). To falsify one of these two contradicting hypotheses, we varied the position of the nitro group relative to the thiol groups and thereby the distance of the nitro group to the metal surface. The reduction kinetics of the three isomers of NTP (2-NTP, 3-NTP, and 4-NTP) on platinum-coated gold nanorods was monitored by SERS with molecular hydrogen as the reducing agent. First-order rate constants were determined by analysis of the experimental SERS kinetic data, yielding $k_{2\text{-NTP}} > k_{3\text{-NTP}} > k_{4\text{-NTP}}$. We draw the conclusion that the reduction does not proceed via an electron transfer mechanism, but via a hydrogen/hydride transfer.[3]

Literature:
[1] W. Xie et al., J. Am. Chem. Soc. 2011, 133,19302-19305. [2] W. Xie et al., Angew. Chem. Int. Ed. 2016, 55, 13729-13733. [3] D. Schäfer et al., J. Phys. Chem C. 2023, 127, 1015-1022.

Creating Artificial Photosystems in Lipid Bilayers

A. Pannwitz, Ulm/D and Jena/D

Jun.-Prof. Dr. Andrea Pannwitz, Universität Ulm Albert-Einstein-Allee 11, 89081 Ulm and Friedrich-Schiller Universität Jena,

In nature, solar light energy conversion takes place within the thylakoid membrane during photosynthesis. Biomimetic lipid bilayers can be used as supramolecular scaffold to mimic concepts of photosynthesis to eventually generate fuels and high value chemicals using solar light as principal energy resource.[1,2] In the here presented work, lipid bilayer membranes of liposomes assemble chromophores for light harvesting energy transfer cascades, light induced transmembrane electron transfer, and (compartmentalized)[3] light driven conversions such as NADH conversion and CO_2 reduction providing new directions for artificial photosynthesis and solar fuels generation.

Time resolved transient absorption and emission spectroscopy gives insights about light driven charge transfer dynamics and allows to derive mechanistic information about light energy conversion at the membrane-water interface.[4]

Literature:
[1] Pannwitz, A.; Klein, D. M.; Rodríguez-Jiménez, S.; Casadevall, C.; Song, H.; Reisner, E.; Hammarström, L.; Bonnet, S. Chem. Soc. Rev. 2021, 50, 4833–4855.
[2] Sinambela, N.; Bösking, J.; Abbas, A.; Pannwitz, A ChemBioChem 2021, 22, 3140–3147.
[3] R. E. P. Nau, J. Bösking, A. Pannwitz, ChemPhotoChem 2022, 6, e202200158.
[4] Abbas, A.; Oswald, E.; Romer, J.; Lenzer, A.; Heiland, M.; Streb, C.; Kranz, C.; Pannwitz, A., Chemistry – A European Journal 2023, e202302284.

Dealing with high pressure infrared gas phase contributions: A new and novel method to subtract unwanted gas phase interactions for more accurate IR band assignments on metal decorated catalysts.

L. Caulfield, Karlsruhe/+49, E. Sauter, Karlsruhe/+49

Prof. Dr. Christopf Wöll, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1, Karlsruhe/+49

Metal decorated powders (Pd, Pt, Cu, etc.) facilitate many important industrial processes such as the water-gas shift reaction, toxic gas oxidation, and Fisher-Tropsch-reaction, all of which we rely on in the modern world. It is therefore of great importance that the reactivity and active sites of such catalysts are fully understood. Using the so called CO-SLIR

method such surface structures can be investigated in great detail, particularly for model systems in UHV conditions. However, difficulties tend to arise when studying these catalysts under realistic conditions. At higher pressures and temperatures gas phase interactions become incredibly problematic and

lead to the obstruction of data for both the support material and metal particles, which can lead to incorrect or incomplete data analysis. Therefore, a sophisticated subtraction method is needed to remove these interactions so such surface features can be studied. We employ such a system by using a KBr reference material to subtract the CO gas phase interactions from M/CeO_2 catalysts so that a detailed and accurate assignment of the CO surface-ligand vibrational bands is possible.

Electronic structure analysis for understanding spectroscopic features of hexadecafluoro iron phthalocyanine

Roman Kornievskii, Justin Krampe,
Prof. Dr. Vera Krewald, Technische Universität Darmstadt, Quantenchemie,
Peter-Grünberg-Str. 4, 64287 Darmstadt.
Timon Zankel, Kilian Heckenberger,
Prof. Dr. Christina Thiele, Technische Universität Darmstadt, Organische
Chemie, Peter-Grünberg-Str. 16, 64287 Darmstadt.

Iron phthalocyanine [FePc] is a promising complex for replacing established palladium catalysts in cross-coupling or Wacker-type oxidation reactions due to its non-toxicity, stability, low price, and accessibility on a large scale.[1] The solubility of the complex in donor solvents can be increased by perfluorination, yielding hexadecafluoro iron phthalocyanine [FePc^{F16}].[2]

Although in many cases iron catalyzed reactions yield the same products as palladium catalyzed ones, the exact mechanisms can differ fundamentally, since iron can undergo not only two electron, but also one electron transfer processes.[3] A further complication for establishing the reaction mechanisms arises specifically for [FePc^{F16}], because it can react with oxygen to form a mono-μ-oxo bridged dinuclear complex (μ-O)[FePc^{F16}]$_2$ which may contain linear or bent Fe(III)–μ-O–Fe(III) units in analogy to (μ-O)[FePc]$_2$.[1,4] Thus, it is not clear what the catalytically active species is: the mononuclear or the dinuclear complex. Furthermore, because of the possible multireference character of [FePc^{F16}] and (μ-O)[FePc^{F16}]$_2$, their magnetic properties need to be analysed.

To determine the catalytically active species, the experimentally predicted oxidation mechanism of [FePc^{F16}] is verified using density functional theory (DFT) by calculating the reaction enthalpies, the UV/VIS and the ^{19}F-NMR spectra of the species potentially participating in the mechanism. The magnetic properties of the dinuclear species are studied using broken symmetry DFT.

Literature:
[1] A. B. Sorokin, *Chem. Rev.* **2013**, 113, 8152-8191.
[2] J. G. Jones, M. V. Twigg, *Inorg. Chem*. **1969**, 8, 2018-2019.
[3] A. Fürstner, *ACS Cent. Sci*. **2016**, 2, 778–789.
[4] A. Purtsas, O. Kataeva, H.-J. Knölker, *Chem. Eur. J.* **2020**, 26, 2499–2508.
[5] C. Iwanov, M. Hopp, D. Lorenz, J. Ballmann, M. Enders, *Chem. Eur. J.* **2023**, e202302761.

Electrochemistry

Investigation of OER Activity Enhancement of "Fe-Effect" on Nickel-based Electrodes through Solution Immersion

S. Zhang[1, 2], I. Efthimiopoulos[1], M. Rabe[1]

[1]College of Chemistry, Nankai University, Weijin Rd. 94, 300071, Tianjin, China;
[2]Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

Ni-based materials are promising OER electrocatalysts owing to their high activity, durability, and low cost [1]. There have been many efforts to enhance the activity of Ni-bearing electrodes, the most typical being with the introduction of iron [2]. Even though there are many ways to incorporate iron in Ni-based electrodes, the immersion of the nickel substrate in an Fe-bearing solution is one of the simplest and direct preparation methods [3].

Here the effect of different Fe(II/III) solutions on the catalytic activity of Ni foams and meshes is investigated (Fig.1). The $Fe(NO_3)_3$ and $FeCl_2$ treatments exhibited the lowest overpotentials, with the $FeCl_2$-treated sample showing higher stability, indicating a joint effect of the iron
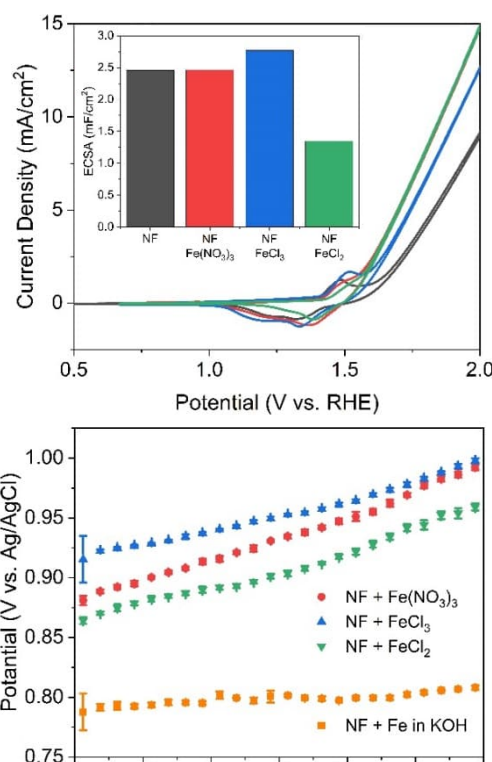

Figure 1: Cyclic voltammetry, ECSA and corrosion plots of Ni foam treated in different solutions. Black lines are results of pure Ni foam tested in iron-free 0.1 M KOH as the blank reference.

valence and the anion. Immersion in different ionic solutions was additionally tested, with the Zn^{2+}-treatment yielding similar activity to that of Fe^{3+}. The best activity and stability of the Ni electrode, however, resulted from the direct addition of Fe^{3+} into the electrolyte. The correlation between the structural and electrochemical properties will be investigated from *in-situ/operando* Raman spectroscopy.

Literature:
[1] A. Peugeot, C. Cressen, D. Karapinar, H. Tran, M. Schreiber, M. Rontecave, *Joule* **2021**, 5, 1281. [2] S. Anantharaj, S. Kundu, S. Noda, *Nano Energy* **2021**, 80, 100514. [3] H. Yin, L. Jiang, P. Liu, A. Al-Mamun, Y. Wang, Y. Zhong, H. Yang, D. Wang, Z. Tang, H. Zhao, *Nano Res.* **2018**, 11, 3959.

Operando-XRD of electrochemical reactors for selective Li+ extraction from brines and seawater

A. Kuhlmann, M. Huck, E. Skrentny, Paderborn/DE
V. Vinci, J. Drnec, European Synchrotron Radiation Facility, Grenoble/FR
H.-G. Steinrück, Paderborn University, Warburger Str. 100, 33098 Paderborn, Germany

In times of rising demand of Li for use in Li-ion batteries (LIBs), and ensuring its supply for aluminum electrolysis, ultralight alloys, optics, synthesis, nuclear research, and pharmaceuticals, it is essential to simplify the processing of Li sources in a sustainable manner. Current extraction from ores is complex and requires large energy input while generating high amounts of waste. This causes the danger of making Li a limited resource and even more expensive.[1]

A new promising way is the electrochemical extraction of Li by desalination batteries (DBs) from brines or seawater[2]. Thereby, selective extraction of ions can be promoted by the chemistry of the electrode material, e.g., by using $FePO_4$. To further enhance the selectivity, potentiostatic application proved to be useful[3]. DBs are superior to other extraction methods in terms of energy efficiency, and waste generation. Still, varying Li^+ concentrations in brines[1b], competitive intercalation of other cations with similar size - especially $Na^{+[2]}$ -, and degradative effects of anions[4], H_2O, and O_2[5] are major challenges to overcome for DBs with $FePO_4$.

In this contribution, we focus on the selective extraction of Li^+ using $FePO_4$ electrodes by specifically-designed multi-step potentiostatic application. Results are shown for salt solutions containing a mixture of Na^+/Li^+, and artificial seawater. It is vital to understand the atomic-scale processes so that the electrodes, and electrochemical parameters can be optimized. Therefore, we used *operando* high-energy X-ray diffraction (HEXRD) microscopy to investigate the crystal structure of $FePO_4$ during the electrochemical process. The experiments showed that the energy barrier for Na^+ (de)intercalation was higher than that of Li^+ during galvanostatic cycling, i.e., $FePO_4$ is selective for Li^+. Using a multi-step potentiostatic procedure, the (de)intercalation process could be enhanced, as evident from our HEXRD results and simultaneous conductivity measurements. Our tentative interpretation is that Li^+ is highly selectively (de)intercalated, although electrochemical signatures hinted on a two-step process during deintercalation, which may indicate the intercalation of Na^+. To selectively deintercalate the remaining Na^+ over Li^+, we further optimized the applied potentials. During galvanostatic cycling in artificial seawater, the (de)intercalation potentials were at more positive and more negative potentials, respectively, likely caused by the variety of cations. We expect that our results contribute to the design of high-performance DBs and inspire the exploration of further systems based on our proposed multi-step process.

References:
[1]   a) Tarascon, *Nat. Chem.* **2**, 510 (2010); b) Han et al., *J. Electrochem. Soc.* **170** (2023).
[2]   Pasta et al., *Energy Environ. Sci.* **5**, 9487 (2012).
[3]   Srimuk et al., *ChemSusChem* **11**, 2091-2100 (2018).
[4]   Easton et al., *Carbon* **162**, 502-509 (2020).
[5]   a) Porcher et al., *Ionics* **14**, 583-587 (2008); b) Luo et al., *Nat. Chem.* **2**, 760-765 (2010).

A solid proton conductor realized by the encapsulation of ionic liquids in the metal-organic framework ZIF-8

W. Yang[a], Jülich/DE, Dr. C. Rodenbücher[a], Jülich/DE, Prof. Dr. JS Luo[b], Sichuan/CN,PD Dr. Korte[a] Jülich/DE,

a Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-14), 52425 Jülich, Germany
b Sichuan University, Institute of materials science and technology, 610000 Chengdu, PR China

The synergy between ionic liquids (ILs) and metal-organic frameworks (MOFs) has attracted considerable scholarly attention as an innovative hybrid ionic conductor [1-2]. The incorporation of ionic liquids into the nanomaterial structure of MOFs has led to the successful synthesis of a novel solid electrolyte characterized by exceptional thermal stability and high ionic conductivity [3]. Here, we use an efficient capillary action method to introduce a proton conductive ionic liquid, namely diethylmethylammonium triflate ([dema][TfO]), into the pores of ZIF-8. Our investigation focuses on the influence of varying IL quantities on pore volume, thermal stability, microstructure, and proton conductivity. The cages of ZIF-8 expand, and the decomposition temperature decreases following the encapsulation of [dema][TfO] molecules. Notably, when the pores of the ZIF-8 material are entirely saturated with [dema][TfO], the composite material exhibits an impressive ionic conductivity of 0.23 mS·cm^{-1} (at 0 % RH and 160 °C). The activation energy for this particular composite is 0.35(4) eV, which is notably low when compared to other IL@MOF conductive composites. These findings underscore the significant promise of IL@MOF hybrid composites as potential ionic conductors, attributable to their elevated electrical conductivity and relatively low activation energy. Additional, this composite can be used as electrolytes of High-Temperature Proton Exchange Membrane Fuel Cells, which are a type of fuel cell that operates at higher temperatures compared to traditional proton exchange membrane fuel cells (PEMFCs).

Literature:
[1] Achieving High Intrinsic Proton Conductivity via Functionalization of MOF-808 by Ionic Liquid. J. Jia et al, ACS Sustain. Chem. Eng. 2023, 11, 13502-13507.
[2] Bunching and Immobilization of Ionic Liquids in Nanoporous Metal−Organic Framework. A. B. Kanj et al, Nano Lett. 2019, 19, 2114-2120.
[3] MOF-Directed Synthesis of Crystalline Ionic Liquids with Enhanced Proton Conduction. W. L. Xue et al, Angew. Chem. Int. Ed. Engl. 2021, 60, 1290-1297.

Electrochemically triggered back-conversion of (*Z*)-4,4'-(diazene-1,2-diyl)bis(N,N-diethylaniline)

Zarah Hussain, Erlangen/DE, Dominic Schatz, Gießen/DE, Nils Oberhof, Heidelberg/DE, Evanie Franz, Erlangen/DE, Andreas Dreuw, Heidelberg/DE, Hermann A. Wegner, Gießen/DE Olaf Brummel, Erlangen/DE, Jörg Libuda, Erlangen/DE

Zarah Hussain, FAU Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Molecular solar thermal (MOST) systems are switchable photosystems that store absorbed solar energy directly in the form of chemical energy.[1] Their operation principle is based on the photochemical conversion of an energy-lean valence isomer to an energy-rich, meta-stable isomer. One approach to control the release of the stored energy is to use electrochemical triggers.[2], [3]

In this work, we investigate the electrochemically triggered energy release in the (*E/Z*)-azobenzene-based MOST system 4,4'-(diazene-1,2-diyl)bis(N,N-diethyl-aniline) (AZO*) using photoelectrochemical infrared reflection absorption spectroscopy (PEC-IRRAS). AZO* can be oxidized reversibly and we identified spectroscopically two oxidized AZO* species, namely a singly oxidized and a doubly oxidized one. Oxidation of the energy-rich *Z*-isomer triggers the energy release to the energy-lean E-isomer and, thus, allows us to initiate the energy release electrochemically.

References:

[1] Z. Wang *et al.*, "Storing energy with molecular photoisomers," *Joule*, vol. 5, no. 12, pp. 3116–3136, 2021, doi: 10.1016/j.joule.2021.11.001.

[2] O. Brummel *et al.*, "Energy Storage in Strained Organic Molecules: (Spectro)Electrochemical Characterization of Norbornadiene and Quadricyclane," *ChemSusChem*, vol. 9, no. 12, pp. 1424–1432, Jun. 2016, doi: 10.1002/cssc.201600127.

[3] E. Franz *et al.*, "How Adsorption Affects the Energy Release in an Azothiophene-Based Molecular Solar-Thermal System," *J. Phys. Chem. Lett.*, vol. 14, no. 6, pp. 1470–1477, Feb. 2023, doi: 10.1021/acs.jpclett.2c03732.

Electrochemically controlled Hydrogen Bonding 1,4-dinitrobenzene as redox-dependent Receptors for Diphenyl Urea containing co-polymer

Jyoti Bisht[a], Benjamin Dietzek-Ivansic[a]*

[a]Institute of Physical Chemistry Helmholtzweg 4 Friedrich Schiller University Jena Germany

Controlled, switchable reactions in supramolecular chemistry create dynamic materials that enable precise modulation of molecular structure and improve functionality for applications in drug delivery, sensing, and nanotechnology. External stimuli, like applied potential in electrochemical systems, play a crucial role in controlled switchable reactions in supramolecular chemistry. In this work, we employed electrochemical stimuli to direct and control the assembly and disassembly of redox redox-responsive diaryl urea-containing polymer (as donor) and a 1,4-dinitrobenzene (as acceptor). In the first step, the switchable assembly between the donor and acceptor unit is investigated by sequentially introducing diphenyl urea-containing monomer to 1,4-dinitrobenzene. Cyclic voltammetry measurements under this condition reveal positive shifts of the half-wave potential of the reduction wave of 1,4-dinitrobenzene derivative that varies with the concentration of added donor units. The observed positive shift signifies a significant enhancement in the stabilization of the reduced state of the 1,4-dinitrobenzene derivative in the presence of diphenyl urea units. The enhanced stabilization can be explained by the increased hydrogen bonding interaction of the reduced acceptor with the diaryl urea unit that drives the assembly or complexation process which is evidently controlled by applied potential and can be reversed by reversal of applied stimuli. This work along with further experimentation involving UV-vis Spectro-electrochemistry, and resonance-Raman Spectro-electrochemistry will contribute to the understanding of the bond-restoring properties of the urea-containing polymer under controlled potentials.
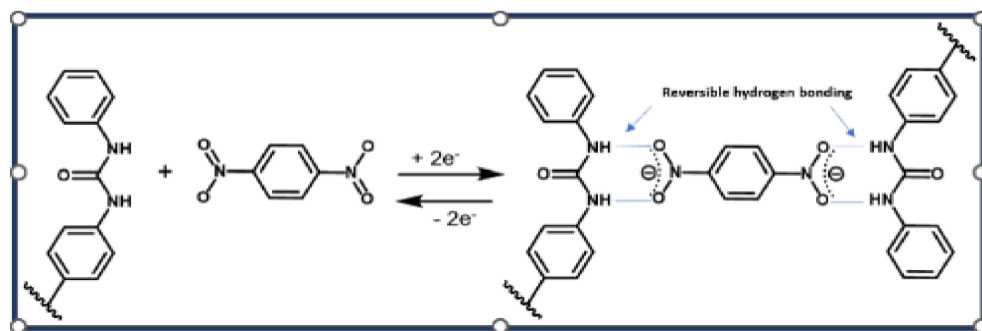
Scheme 1. Electrochemically controlled assembly and disassembly of di nitrobenzene with diaryl-ureas

Photoelectrochemical Investigation of Different Semiconductor Nanoparticles in Cross-linked Gel Structures

P.J. Thomsen, Hamburg/DE; J. Schlenkrich, Hannover/DE; F. Lübkemann-Warwas, Hannover/DE; R.T. Graf, Hannover/DE; J.G. Eckert, Hannover/DE; C. Wesemann, Hannover/DE; M. Rosebrock, Hannover/DE; N. C. Bigall, Hamburg/DE

N. C. Bigall, University of Hamburg, Institute of Physical Chemistry, Grindelallee 117, 20146 Hamburg, Germany

The potential of gel-like networks based on semiconductor nanoparticles lies in their capacity to convey the exceptional characteristics of nanoscale building blocks into porous assemblies. These macroscopic architectures preserve or even enhance nanoscale-specific properties, such as a tunable band gap. The the wet-chemical synthesis of different nanocrystals, followed by the assembly of macroscopic structures tailors the material for specific applications, such as photocatalysis.[1]

The colloidal dispersions of semiconductor heterostructures were deliberately destabilized to form interconnected assemblies. Further exploration of individual network structures, along with their optical and photoelectrochemical properties, unveiled remarkable differences based on particle shapes. Techniques such as linear sweep voltammetry and intensity-modulated photocurrent spectroscopy were employed to delve into the dynamics of charge carriers and electron pathways, shedding light on the electrochemical kinetics within the gel structures and their correlation with the morphologies of the building blocks.

Moreover, the photocatalytic activity of the diverse gel structures displayed significant variations in hydrogen production rates, suggesting a connection with the outcomes of the electrochemical investigations. This comprehensive approach provides valuable insights into the complex interaction between nanoscale structures, macroscopic gel properties, and their functional performance in potential applications.

[1] J. Schlenkrich, F. Lübkemann-Warwas, R.T. Graf, C. Wesemann, L. Schoske, M. Rosebrock, K. Hindricks, P. Behrens, D. Bahnemann, N.C. Bigall, Small, 2023, 2208108

Influence of oxidation state and vacancies on low transition metal migration barriers during in situ exsolution

A. Bonkowski, Aachen/DE, A. Klein, Darmstadt/DE, R. A. De Souza, Aachen/DE
Alexander Bonkowski, Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52074 Aachen

To overcome the limitations of conventional deposition methods, *in situ* exsolution processes have been developed to produce heterogeneous supported metal nanoparticles. Upon reduction, transition metal ions emerge from the host material to form metallic clusters on the surfaces. Although the thermodynamic aspects of this process have been studied to a certain extent, a comprehensive understanding of the migration is still lacking, and not all experimental observations can be explained by current theoretical considerations.

In this study, we propose, with a simple model system, why transition metal cations exsolve from perovskite hosts upon reduction, and why exsolution occurs at relatively low temperatures. This involves different charge states of the transition metal ions as well as the abundant *A*-site vacancies: The perovskite-based host materials show high electronic conductivities, allowing appropriate energy levels in the band gap to be occupied due to Fermi level shifts.[1] Additionally, the experimentally observed dependence of *A*-site vacancies is explained in terms of migration path energetics.

Literature:
[1] A. Klein, K. Albe, N. Bein, O. Clemens, K. A. Creutz, P. Erhart, M. Frericks, E. Ghorbani, J. P. Hofmann, B. Huang, B. Kaiser, U. Kolb, J. Koruza, C. Kübel, K. N. S. Lohaus, J. Rödel, J. Rohrer, W. Rheinheimer, R. A. De Souza, V. Streibel, A. Weidenkaff, M. Widenmeyer, B.-X. Xu, H. Zhang, J. Electroceram. 2023.

Electrochemical redox behavior of Pt(II)-N-heterocyclic carbene complexes: An in-situ IR spectroscopy study

J. Yang, Erlangen/DE, A. Bergen, Erlangen/DE, C. Wick, Erlangen/DE, A. Smith, Erlangen/DE, K. Meyer, Erlangen/DE, O. Brummel, Erlangen/DE, J. Libuda, Erlangen/DE
Juntao Yang, Interface Research and Catalysis, ECRC, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstraße 3, 91058 Erlangen, Germany

Transition metal complexes with N-heterocyclic carbene (NHC) ligands show unique steric and electronic properties and are applied in fields such as (electro)catalysis and materials science.[1,2] In this work, we characterize a $Pt^{II}(NHC)_2Cl_2$ complex in which the NHC ligands form a square planar coordination environment. The redox behavior of $Pt^{II}(NHC)_2Cl_2$ on polycrystalline Pt electrodes was monitored by in-situ electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) combined with density functional theory (DFT). The study was complemented by cyclic voltammetry (CV) and nuclear magnetic resonance (NMR) spectroscopy measurements. The reduction of the complex occurs in two steps at -2.30 and -2.43 V_{fc} and is reversible. We observe reduced species showing a clear redshift (115 cm^{-1}) in the IR spectrum and an increase in intensity of the nitrile band. By comparing experimental spectra with modelling, we identify the formation of $[Pt(NHC)_2Cl_x]^{z-}$ complexes with mesomeric charge delocalization on the two NHC ligands. This leads to an elongation of the CN bond and, as a result, induces the observed redshift of the nitrile band and the increase in the dynamic dipole. Our result demonstrates the important role which the NHC ligands play for the electrocatalytic behavior.

Literature:
[1] D. Broere et al., Chem. Soc. Rev., 2015, 44, 6886. [2] I. Mikhailov et al., Catalysts, 2023, 13, 1291.

X-ray Absorption Microscopy to Measure Concentration Profiles in Battery Electrolytes

E. Skrentny[1,2], Marten Huck[1,2], Andreas Kuhlmann[1,2], H.-G. Steinrück[1,2]

[1]Forschungszentrum Jülich, Institute for a Sustainable Hydrogen Economy (INW), Am Brainergy Park 4, 52428 Jülich, Germany

[2]RWTH Aachen University, Institute of Physical Chemistry, Landoltweg 2, 52074 Aachen, Germany

Toward lifetime and performance predictions of batteries, foundational and quantitative understanding of ion and electrolyte transport is imperative. During the polarization of electrochemical cells, the ions and the solvent move and concentration profiles of the species are formed. The understanding of electrolyte transport and quantification of associated transport parameters historically relied on interpreting macroscopic voltage (or current) measurements. Recently, imaging and spectroscopic methods were employed to directly probe velocity and concentration profiles, providing significant new insight.[1]

In this context, we are currently developing novel X-ray microscopy setups to *operando* and directly measure concentration profiles in electrochemical cells upon their polarization and during subsequent relaxation. The setup is based on a laboratory X-ray source coupled with a micrometer resolution X-ray camera. The methodology uses the general relationship between salt concentration and X-ray absorption for binary electrolytes.[2] In addition, we designed a dedicated electrochemical cell.

We will present first results for several electrolyte formulations. These are primarily non-aqueous Li-ion battery electrolytes, with a particular focus on the Lithium bistrifluoromethanesulfonimide (LiTFSI) in poly(ethylene oxide) (PEO) polymer electrolyte system. While LiTFSI/PEO has been investigated over decades[3], researchers still debate the values and nature of the corresponding transport parameters.[4] In particular, two recent studies show qualitatively and quantitatively different concentrations profiles upon polarization of Li|LiTFSI/PEO|Li symmetric cells, using two different measurement methods.[5][6] We hope to shed light on this discrepancy with our new X-ray absorption microscopy data set of the concentration profiles. We anticipate that the novel methodology can contribute to the efficient determination of electrolyte transport properties and thereby support knowledge-based optimization of electrolytes.

References:
[1]   A. Mistry et al., *Adv. Energy Mater.* **13**, 2203690 (2023).
[2]   H.-G. Steinrück, *AIP Adv.* **11**, 115119 (2021).
[3]   D. T. Hallinan & N. P. Balsara, *Annu. Rev. Mater. Res.* **43**, 503 (2013).
[4]   M. P. Rosenwinkel & M. Schönhoff, *J. Electrochem. Soc.* **166**, A1977 (2019).
[5]   H.-G. Steinrück et al., *Energy & Environmental Science* **13**, 4312 (2020).
[6]   Z. J. Hoffman et al., *J. Electrochem. Soc.* **170,** 090517 (2023).

Proton migration in doped barium zirconate from a computational point of view

S. Neitzel-Grieshammer, Steinfurt/DE

G. Winterhoff, Aachen/DE

FH Münster University of Applied Sciences, Stegerwaldstr. 39, Steinfurt, Germany

Barium zirconate demonstrates significant potential as a solid electrolyte in ceramic fuel cells due to its elevated protonic conductivity, particularly when doped with trivalent oxides like yttria. The intricate dynamics at the atomic level are accessible through density functional theory, with various researchers in recent years calculating energy parameters relevant for mobility. The present study offers a comprehensive summary of existing literature, focusing on the interaction energies between protons and dopant ions, along with the migration barriers of proton motion in bulk $BaZrO_3$, with emphasis on Y-doping.[1]

The outcomes reveal a notable range of energy values, coming from diverse calculation parameters and fluctuations in the ionic lattice due to defects, with cell size significantly influencing results. Yttrium, compared to other dopants, demonstrates comparable proton trapping in both nearest and second nearest neighbor positions, fostering conductivity through overlapping trapping zones and moderate barriers for the detrapping jump to a third nearest neighbor position.

Utilizing the collected data, we estimate protonic conductivity employing kinetic Monte Carlo simulations. The simulations underline the variation of the conductivities depending on the energy values within the literature range.

[1] G. Winterhoff & S. Neitzel-Grieshammer, Solid State Ionics, 2023, 397, 116231.

A direct observation of the influence of nitrogen-doping on ion dynamics for electric double layer capacitor performance

H. R. N. B. Enninful, Leipzig/Germany; M. Hermesdorf, Jena/Germany; Desirée Leistenschneider, Jena/Germany; Martin Oschatz, Jena/Germany; Alex Forse, Cambridge/United Kingdom; Rustem Valiullin, Leipzig/Germany.

Dr. Henry R. N. B. Enninful, Faculty of Physics and Earth Sciences, Felix Bloch Institute for Solid State Physics, Universität Leipzig, Linnéstraße 5, 04103, Leipzig, Germany.

Substantial improvements in the design of Electric Double Layer Capacitors (EDLC) have led to increased performance in both power and energy densities. To obtain comparable energy densities to those of batteries, EDLC electrode materials have been doped with nitrogen to yield very high specific capacitances and energy densities.

In what some researchers call pseudocapacitors, the mechanisms that underlie the improved capacitances due to electrode-electrolyte surface interactions is still rarely understood. This work sheds light on ion transport and motion at the pore surface and within the pore interior.

We show that for carbon electrodes synthesized from cellulose and potassium carbonate, increased melamine content - which results in an increase in the amount of nitrogen-doping - leads to a sacrifice of the pore surface area and volume, resulting in reduced specific capacitances. Furthermore, the substitution of melamine with urea in the same ratio produces reduced nitrogen content in the resulting material. The effect thereof, is an attendant reduction in specific capacitance regardless of the comparable surface area. Lastly, we show that electrodes with a certain threshold of nitrogen content are able to store ions from a pure water "electrolyte". The phenomena resulting in the produced performances are explained and future prospects in this work are shown.

Reaction Kinetics and Dynamics

Exploring the Influence of Environmental Factors on the Photoinduced Activation of Ru^{II}tpphzRh^{III}Cp*Cl

L. Blechschmidt, Friedrich-Schiller University Jena, Helmholtzweg 4, D-07743 Jena; L. Zedler, B. Dietzek-Ivanšić

The dyad [(tbbpy)$_2$RutpphzRhCp*Cl]Cl(PF$_6$)$_2$ (RutpphzRhCp*Cl) consists of a catalytic rhodium centre for NAD$^+$-reduction and a Ru^{II}-bpy type photosensitizer (PS) connected by a tetrapyridophenazine (tpphz) bridge ligand.[1] Excitation of the PS causes the reduction of the Rh^{III}-centre accompanied by the dissociation of the chloro ligand. Femtosecond transient-absorption (fs-ta) spectroscopy enabled the investigation of this process. An intermediate species in which the negative charge is centred at the bridge ligand is formed. This intermediate has a lifetime of about half a microsecond, despite the fully conjugated π-system.[2] Here, we would like to present our investigations into the environmental conditions during this process. We conducted additional fs-ta experiments, where we adjusted either the sample temperature or the concentration of Cl$^-$ or PF$_6^-$ in the solution. The experiments revealed that lowering the temperature and increasing the chloride concentration both result in an extended lifetime of the intermediate mentioned. Conversely, the presence of PF$_6^-$ had no significant impact on this decay. Other decay components remained generally unaffected. These results suggest an association between the dissociation of the chloro-ligand and an energy barrier.
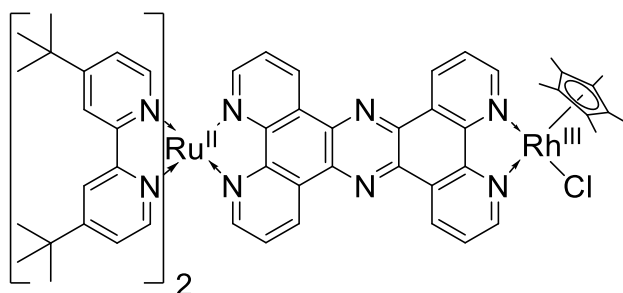

Figure 1: Molecular structure of RutpphzRhCp*Cl.

Literature:
[1] A. K. Mengele, S. Kaufhold, C. Streb, S. Rau, Dalton Trans. 2016, 45, 6612;
[2] L. Zedler, A. K. Mengele, K. M. Ziems, Y. Zhang, M. Wächtler, S. Gräfe, T. Pascher, S. Rau, S. Kupfer, B. Dietzek, Angew. Chem., Int. Ed. 2019, 58, 13140.

On the so-called Hydrophobic Cavity Around Anions in Bulk Aqueous Solution

A. Jindal, Bochum/DE, **P. Schienbein, London/UK**,
Prof. Dominik Marx, Bochum/DE,
Dr. Aman Jindal, Ruhr-Universität Bochum, 44780 Bochum, Germany

Recently, there has been some debate about the similarity between the local solvation structure of anions in bulk water and at the air-water interface [1, 2, 3]. This discussion has been stimulated by pioneering simulation results that proposed a hydrophobic cavity around anions in bulk, which is analogous to air at the interface, thus providing a similar short-range solvation environment[4]. Using extensive ab initio molecular dynamics simulations of an aqueous Cl^- solution, we now unveil an anisotropic arrangement of H-bonded versus interstitial water molecules. The associated electronic polarization and charge transfer effects align the induced dipole moment of the anion which explains the observed effects without invoking the concept of a hydrophobic cavity.

[1] Smith, J. D.; Saykally, R. J.; Geissler, P. L. *J. Am. Chem. Soc.* **2007**, *129*, 13847–13856.

[2] Wick, C. D.; Xantheas, S. S. *J. Phys. Chem. B* **2009**, *113*, 4141–4146.

[3] Fulton, J. L.; Schenter, G. K.; Baer, M. D.; Mundy, C. J.; Dang, L. X.; Balasubramanian, M. *J. Phys. Chem. B* **2010**, *114*, 12926–12937.

[4] Paul, S. K.; Herbert, J. M. *J. Am. Chem. Soc.* **2021**, *143*, 10189–10202.

Unusual shell morphologies of responsive amino core-shell microgels induced by pH during shell synthesis

M. Annegarn, 33615 Bielefeld, T. Hellweg, 33615 Bielefeld
Marco Annegarn, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld

While cationic nano- and microgels are potentially useful for the transfection of cells or the immobilization of biomacromolecules, their synthesis often has certain drawbacks regarding size, polydispersity, yield and incorporation of the cationic comonomer.[1,2] Since many cationic comonomers like primary or secondary amines are pH-responsive, their charge relies on the surrounding pH. It has been shown, that the reaction pH has a tremendous impact on the feasibility of the synthesis and the properties of the resulting microgels.[3]

To investigate the influence of the reaction pH on the synthesis of pH-responsive amino core-shell microgels, a series of core-shell microgels were synthesized at different pH values. The results show a strong influence on the morphology of the resulting shells. While very fuzzy shells were obtained at acidic pH, alkaline shell synthesis leads to a larger and more dense shell together with another byproduct. The results highlight the possibility of utilizing the reaction pH in order to influence the network morphology of the core-shell microgels. In general, the necessity of pH control during microgel synthesis is shown regarding the reproducibility of microgel synthesis.

Moreover, these multiresponsive core-shell microgels can be loaded with an anionic drug. By using the pH as an external trigger, the drug is released from the microgel network in a nearly quantitative manner.

Literature:
[1] P. Kodlekere, A. L. Cartelle, L. A. Lyon, RSC Adv. 2016, 6, 31619–31631.
[2] K. Mai-ngam, K. Boonkitpattarakul, M. Sakulsombat, P. Chumningan, B. Mai-ngam, Eur. Polym. J. 2009, 45, 1260–1269.
[3] M. Annegarn, M. Dirksen, T. Hellweg, Polymers 2021, 13, 827.

Elucidating the Dissociation Behaviour of Cationic Caesium Iodide Clusters Through Multiple-Isomer RRKM Theory

G. Schöpfer, Innsbruck/AT, M. Salzburger, Innsbruck/AT, M. Juanes, Innsbruck/AT, Valladolid/ES, M. K. Beyer, Innsbruck/AT, M. Ončák, Innsbruck/AT
Gabriel Schöpfer, Leopold-Franzens-Universität Innsbruck, Technikerstraße 25/3, Innsbruck/AT

Determining rate constants for chemical reactions from theoretical calculations only is still very challenging. A common approach to calculate unimolecular rate constants is based on RRKM theory. Recently, we have proposed a multiple-isomer modification to the usual RRKM approach to successfully describe dissociation kinetics of sodium chloride clusters. Now, we want to apply it to caesium iodide clusters to verify that the modified version is a powerful tool that can be used to reliably calculate rate constants of various systems.

To be specific, we performed ultraviolet photodissociation mass spectrometry on cationic caesium iodide clusters. We explain the measured mass spectra by theoretical calculations, modelling microscopic unimolecular dissociation rates with RRKM theory. However, we go away from the description where the global minimum structure of the reactant reacts to the global minimum structures of the products. Instead, we use many different isomers both for the reactant and the products and allow for fast interconversion between the reactant isomers before dissociation. This delivers a model much closer to the experimental conditions where a UV laser provides an energy of several electron volts to the clusters, and therefore gives the clusters the possibility to explore large parts of the potential energy surface, much more than only the region around the global minimum.

The dissociation rates for the different reaction channels are calculated as a function of the available energy. These are used to calculate product branching ratios, which can be compared to the wavelength-dependent mass spectrum in the experiment.

OH Radical Kinetics of Lactic Acid, Glyceric Acid and Methylmalonic Acid in the Aqueous Phase as a Function of Temperatur and pH value

T. Schaefer, Leipzig/D, Y. Hu, Leipzig/D, Y. Zhang, Leipzig/D
Prof. Dr. Hartmut Herrmann, Leibniz Institute for Tropospheric Research
(TROPOS), Atmospheric Chemistry Department (ACD), Permoserstraße 15,
04318 Leipzig

Carboxylic acids are compounds frequently found in the atmosphere. [1] Formed during the decomposition and conversion of volatile organic compounds (VOCs). And are often initiated by gas-phase radical reactions leading to oxidation products such as carboxylic acids. In this study, the •OH radical kinetics of carboxylic acids in the aqueous phase (cloud droplets, fog, rain or hygroscopic particles) were investigated. Rate constants were determined by using the competition kinetics method with the laser flash photolysis-laser long path absorption (LFP-LLPA) technique as a function of T and pH. [2] The Arrhenius equations for oxidation by the •OH radical are as follows (unit in L mol^{-1} s^{-1}): Lactic acid: $k(T, HA) = (1.26 \pm 0.04) \times 10^{10} \times \exp[(-910 \pm 160 \text{ K})/T]$ and $k(T, A^-) = (1.26 \pm 0.02) \times 10^{10} \times \exp[(-800 \pm 80 \text{ K})/T]$, glyceric acid: $k(T, HA) = (5.95 \pm 0.17) \times 10^{10} \times \exp[(-1100 \pm 170 \text{ K})/T]$ and $k(T, A^-) = (3.58 \pm 0.06) \times 10^{11} \times \exp[(-1500 \pm 100 \text{ K})/T]$ and methylmalonic acid: $k(T, H_2A) = (5.49 \pm 0.97) \times 10^{10} \times \exp[(-1750 \pm 100 \text{ K})/T]$, $k(T, HA^-) = (1.37 \pm 0.02) \times 10^{9} \times \exp[(-530 \pm 80 \text{ K})/T]$ and $k(T, A^{2-}) = (9.58 \pm 0.42) \times 10^{10} \times \exp[(1500 \pm 270 \text{ K})/T]$.

Gibbs energy barriers of the •OH radical reaction and thus the most probable position of H-atom abstraction were also calculated with density functional theory (DFT) simulations, indicating a change in the Gibbs energy barrier of the protonated and deprotonated acid, which corresponds to the change in reactivity. The oxidation process can act as sink in the aqueous phase, and results allow a better description of the degradation of carboxylic acids.

Literature:
[1] K. Kawamura, E. Tachibana, K. Okuzawa, S.G. Aggarwal, Y. Kanaya, Z.F. Wang, Atmos. Chem. Phys. 2013, 13, 8285−8302. [2] L. Wen, T. Schaefer, Y. Zhang, L. He, O.N. Ventura, H. Herrmann, Phys. Chem. Chem. Phys. 2022, 24, 11054-11065.

Colloidal synthesis of 2D copper chalcogenides and their optical properties

U. Parekh, Rostock/DE, R. Piehler, Rostock/DE R. Lesyuk, Rostock/DE

Prof. Dr. Christian Klinke, Insititut für Physik,
Universität Rostock, Albert-Einstein-Str. 23, 18059 Rostock

The family of copper chalcogenides is currently of significant interest in optoelectronic research, owing to their unique combination of semiconducting and metallic properties. These materials exhibit very strong ang highly tuneable surface plasmon bands in the near-infrared (NIR) region due to their exceptionally large conductivity and, at the same time, excitonic absorption in the visible range. This allows for a widely tuneable set of combinations of plasmonic and excitonic properties in one monolithic system, and thus for adjustable nonlinear coupling. The ability to tailor these properties is achievable through careful manipulation and control of the synthesis conditions.

In our work, we use a one-pot hot injection based colloidal synthesis method to synthesize 2D copper sulphide (CuS) and copper selenide (CuSe) nanomaterials. We manipulate the various synthesis conditions like concentration of precursors used, synthesis temperature, reaction time, etc. to achieve specific geometries of nanosheets and investigate how this affects the optical properties of the resulting nanomaterials. The key study of work is to show broad plasmon-tunability in both CuS and CuSe. We successfully show that different shapes of CuS nanosheets can give us tunable plasmonic band from 1100 nm to 1600 nm. Additionally, in case of CuSe we have plasmon tunability in range of 1000 nm to 1200 nm. Moreover, we will also present our results on in-situ phase transition of CuS and its effects on the optical and electrical properties.

Comprehensive Analysis of ignition properties and Reaction Mechanism in Lean Premixed Prevaporized (LPP) Combustion of tetrahydrofuran (THF) and isopropanol Blends

G. Wang Braunschweig/DE, S. Nadiri Braunschweig/DE, B. Shu Braunschweig/DE, Ravi X. Fernandes Braunschweig/DE
Guanyu Wang, Department of Physical Chemistry, Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, 38116 Germany

To reach sustainable and energy-efficient aviation, transitioning from conventional fossil fuels to renewable energies becomes imperative. Liquid energy carriers in combustion-based propulsion systems play a crucial role, with e-fuels emerging as a promising strategy to achieve both high energy density and carbon-neutral aviation. Nevertheless, challenges in reducing non-CO2 emissions including CO, soots, and NOx still exist. This has prompted a concentrated investigation into lean pre-vaporization premix (LPP) combustion [1]. The aim is to address emission challenges and enhance the overall environmental performance of the aviation industry.

This study focuses on the ignition properties of a composite e-fuels blend consisting of tetrahydrofuran (THF) (C_4H_8O) and isopropanol (iC_3H_8O), specifically under lean combustion conditions at equivalence ratio equal to 0.25, 0.5, and 0.9. Shock tube experiments were conducted at 1 bar, within a temperature range of 1250 to 1700 K. By Employing Tunable Diode Laser Absorption Spectroscopy (TDLAS), we measured the key species such as CO and water vapor during the ignition process to get insights into the combustion chemistry. Furthermore, a kinetics mechanism for ignition delay time (IDT) and CO mole fraction prediction of the THF/isopropanol blends was developed based on literature mechanisms, while the undefined reaction pathways were estimated using Reaction Mechanism Generator (RMG) software.

Literature:

[1] Brehm et al./ISABE 99-7163, 1999 from R. Fink, Diss TU-München 2001.

Radical yields and temperature dependence of Fenton-like reactions in the presence of oxalic acid

D. Scheres Firak, Leipzig/D, T. Schaefer, Leipzig/D, P. Senff, Leipzig/D, Prof. Dr. Hartmut Herrmann, Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Permoserstraße 15, 04318 Leipzig

Reactions between Fe and H_2O_2, known as Fenton reactions, play important roles in the aqueous particle phase oxidation. In this environment, Fe is complexed by organic ligands originating from the chemical oxidation of volatile organic compounds and combustion processes [1]. Dicarboxylic acids, particularly oxalic acid (OXL), are significant components of aerosol particles [1,2] and modify the reactivity of Fe towards H_2O_2. Rate constants for the Fenton-like reaction in the presence of OXL range from 10^3 to 10^4 L mol^{-1} s^{-1} [4], much higher than those measured in the absence of this ligand (40 to 80 L mol^{-1} s^{-1}) [5].

Herein the kinetics and radical yields of Fenton-like reactions were investigated in the presence of OXL complexes using the phenanthroline method for Fe (II) quantification and electron paramagnetic resonance (EPR) spectroscopy. The measured rate constant for the Fenton-like reaction was 2.8 ± 0.3 (x10^3) M^{-1} s^{-1} at 298.15 K and pH 3, and a decrease in the formation of HO$^{\bullet}$ was observed with the increase in the concentration of iron complexes. Thermochemical parameters calculated for the Fenton-like reaction exhibited similar enthalpies of activation but significantly different entropies of activation if compared to the reaction in the absence of ligands ($\Delta H^{\ddagger}$ 52 ± 10 vs. 36 ± 5 kJ mol^{-1} and $\Delta S^{\ddagger}$ - 6.0 ± 0.8 vs. - 87 ± 9 J K^{-1} mol^{-1}, for Fenton-like and Fenton respectively).

Literature:
[1] S. Myriokefalitakis et al., Atmos. Chem. Phys. 2011, 11, 5761–5782.
[2] S. Scheinhardt, et al., Atmos. Environ. 2013, 74, 102–109. [3] A. G. González et al, Sci. Total Environ. 2022, 829, 154642. [4] J.S.B. Park et al., Free Rad. Res. 1997, 27, 447–458. [5] J.J Pignatello, E. Oliveros and A. Mackay, Crit. Rev. Environ. Sci. Technol. 2006, 36, 1-84.

Direct observation of ring-puckering in monosaccharides with 2D-IR spectroscopy

T. Stensitzki/Potsdam/DE, P.Gasse/Potsdam/DE, Y.Mai-Linde/Potsdam/DE, T.Linker/Potsdam/DE, T.Jansen/Groningen/NL, H.Müller-Werkmeister/Potsdam/DE

Dr. Till Stensitzki, Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Deutschland

Ring-puckering of carbohydrates is believed to play a fundamental role in many chemical reactions. However, quantifying and observing ring-puckering poses challenges due to the similar properties of the different conformers. In our recent work we presented and characterised [1] SCN-labelled carbohydrates. Here, the SCN-group acts as a vibrational reporter group which can be readily observed with FTIR and 2D-IR spectroscopy. By comparing our spectroscopic findings to MD simulations, we demonstrate that the vibrational spectrum is modulated by the ring-conformation. This allows us to directly observe the ring-puckering dynamics by measuring the spectral diffusion using 2D-IR.

Literature:
[1] P. Gasse, T. Stensitzki, Y. Mai-Linde, T. Linker, H. M. Müller-Werkmeister; *J. Chem. Phys.* 14 April 2023; 158 (14): 145101.

GC-MS studies of Reactive Oxygen Species (ROS) and the pH impact on the Iron Catalytic Cycles

E. Poschart, Leipzig/D, D. Firak, Leipzig/D, T. Schaefer, Leipzig/D
Prof. Dr. Hartmut Herrmann, Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Permoserstraße 15, 04318 Leipzig

Reactive oxygen species (ROS) include hydrogen peroxide (H_2O_2) and organic hydroperoxides (ROOH), as well as radicals such as hydroxyl ($^\bullet OH$), hydroperoxyl ($HO_2^\bullet$) and organic radicals. These ROS can contribute significantly to the formation of atmospheric secondary organic aerosols (SOAs). [1] By oxidizing volatile organic compounds (VOCs) with atmospheric reactants, such as ozone (O_3) and/or radicals ($^\bullet OH$, NO_3), semi-volatile compounds known as ROOH are produced. [2] Due to their significant hydrophilicity, ROOHs have a rapid uptake into the aqueous phase of the troposphere and may undergo decomposition via Fenton reaction [3] by dissolved iron (II). [4]

Here, we investigate the decomposition of atmospherically relevant peroxides such as H_2O_2 and isoprene hydroxy hydroperoxides (ISOPOOH), by the Fenton reaction, in terms of the amount of the radical products formed at different pH values. Furthermore, k_{2nd} was determined for the reaction between Fe(II) and ISOPOOH. The yield of OH radicals was determined by using 2-propanol-d_8 as a radical scavenger, and the resulting formation of acetone-d_6 from the mixtures of ISOPOOH and Fe(II) and mixtures of H_2O_2 and Fe(II) were measured by GC-MS analysis. The second-order reaction constant of reaction between Fe(II) and ISOPOOH at pH = 4.5-4.9 was determined to be $k_{2nd} = 65.1 \pm 9.2$ L mol^{-1} s^{-1}. The results obtained will contribute to a better understanding of the decomposition of atmospherically relevant peroxides in aqueous-phase by the Fenton reaction, in terms of the yield and composition of ROS products under cloud and aerosol conditions.

Literature:

[1] B. Bonn, R. von Kuhlmann, M. G. Lawrence, Geophys. Res. Lett. 2004, 31, 10, L10108.
[2] H. Herrmann, T. Schaefer, A. Tilgner, S.A. Styler, C. Weller, M. Teich and T. Otto, Chem. Rev. 2015, 115, 10, 4259-4334. [3] K. Barbusiński, Ecol. Chem. Eng. S. 2009, 16, 3, 347-358.[4] L. Deguillaume, M. Leriche, K. Desboeufs, G. Mailhot, C. George, and N. Chaumerliac, Chem. Rev. 2005, 105, 9, 3388-3431.

Introducing Hyperreactor Dynamics for Efficient Reaction Space Exploration

A. Stan-Bernhardt, Munich/DE, L. Glinkina, Munich/DE, A. Hulm, Munich/DE
Prof. Dr. Christian Ochsenfeld, University of Munich (LMU), Butenandtstr. 5 (B),
81377 Munich, Germany

In recent years, first-principles exploration of chemical reaction space has provided valuable insights into intricate reaction networks. Here, we introduce *ab initio* hyperreactor dynamics, which enables rapid screening of the accessible chemical space from a given set of initial molecules, predicting new synthetic routes that can potentially guide subsequent experimental studies. Inspired by the computational nanoreactor introduced by Martínez and coworkers [1], *ab initio* molecular dynamics simulations of a periodically contracting spherically-confined molecular system are enhanced by different hyperdynamics bias potentials to increase reactivity [2]. Hereby, mild conditions are employed to circumvent the problem of thermal decomposition of products as observed before [3].

The advantages and flexibility of the hyperreactor approach are first showcased on an HCN toy model, where the interplay between the two biasing strategies is investigated and excellent temperature control is achieved. Furthermore, we apply this method to prebiotic systems on the formation of glycinal and acetamide in interstellar ices [4], as well as on an aqueous non-enzymatic DNA nucleoside synthesis [5], and retrieve results in line with recent experimental findings.

Literature:
[1] Wang, L. P.; Titov, A.; McGibbon, R.; Liu, F.; Pande, V. S.; Martínez, T. J. *Nature Chem.* **2014**, *6*, 1044–1048.
[2] Stan-Bernhardt, A.; Glinkina L.; Hulm, A.; Ochsenfeld, C. *submitted* **2023**.
[3] Stan, A.; von der Esch, B.; Ochsenfeld, C. *J. Chem. Theory Comput.* **2022**, *18*, 6700–6712.
[4] Marks, J. H.; Wang, J.; Kleimeier, N. F.; Turner, A. M.; Eckhardt, A. K.; Kaiser, R. I. *Angew. Chem. Int. Ed.* **2023**, *62*, e202218645.
[5] Teichert, J. S.; Kruse, F. M.; Trapp, O. *Angew. Chem. Int. Ed.* **2019**, *58*, 9944–9947.

The role of phenylnitrene in the formation of polycyclic aromatic nitrogen containing hydrocarbons

R. Arns, Paderborn/DE, R. McClish, Boulder/USA, P. Hemberger, Villigen/CH, A. Bödi, Villigen/CH, J. Bouwman, Boulder/USA, T. Kasper, Paderborn/DE, D. Schleier, Paderborn/DE

Dr. Domenik Schleier, University of Paderborn, Warburger Str. 100, 33098 Paderborn

Chemical energy storage in the form of biofuels is essential for the energy economy of the future. In fields like heavy-duty machines, aviation, or shipping, it is difficult to replace fuels by batteries. Polycyclic aromatic hydrocarbons (PAHs) are a toxic and unwanted side product of combustion processes and understanding their formation is crucial to mitigate their effects. While PAH formation is well studied, potential reactions of nitrogen-rich biofuels[1] leading to polycyclic aromatic nitrogen heterocycles (PANHs) are thus far unknown.

To improve our understanding of the nitrogen chemistry in combustion environments, we investigated the reaction of phenylnitrene with propargyl radicals. Nitrenes are more stable than carbenes, because of their larger singlet-triplet gap[2], and they have been detected in pyrrole and pyridine flames.[3,4] Phenyl azide and 3-iodopropyne were used as precursors to generate the reactive species in a heated tubular microreactor and the products are identified by mass-selected threshold photoelectron spectra (ms-TPES) using double imaging photoelectron photoion coincidence (i^2PEPICO) spectroscopy. We performed quantum chemical calculations to gain insights into the chemical pathways leading to reaction products.

We identified the C_9H_7N isomers quinoline, 1H-inden-1-imine and 3-methylene-3H-indole as products in the experiment. The potential energy surface confirms that all of them are formed via addition-elimination reactions that proceed without an entrance barrier. Interestingly, all of the reaction pathways leading to stable products pass through wells that are lower in energy than the final products. While quinoline is the thermodynamically most favourable product, the formation of 3-methylene-3H-indole is kinetically favoured.

Our results show that phenylnitrene is an important precursor for the formation of PANHs. In the comparable reaction of benzyl radicals with propargyl radicals, the only product is naphthalene, the isoelectronic equivalent to quinoline.[5] The presence of the two indene-like products demonstrates the influence of the nitrogen atom.

Literature:
[1] L. Petrus et al, Green Chem. 2006, 861-867. [2] C. Wentrup, Chem. Rev. 2017, 117, 4562−4623 [3] Z. Tian et al, J Chem. Phys. 2007, 20, 425-430. [4] Z. Tian et al, J. Phys. Chem. 2008, 112, 13549-13555 [5] A. M. Mebel et al, J. Phys. Chem. A 2017, 121, 5, 901-926

Dissociative Photoionization of Quinoxaline, Quinazoline and Cinnoline

Gülben Sariyar Paderborn/DE , D. Schleier, Paderborn/DE, H. Hrodmarsson Paris/FR, A. Boedi, Villigen/CH, P. Hemberger, Villigen/CH, J. Bouwman, Boulder/USA

Prof. Dr. Jordy Bouwman, University of Colorado, 80309 Boulder, USA

Polycyclic aromatic hydrocarbons (PAHs) and their nitrogen-containing counterparts (PANHs) are ubiquitous in extraterrestrial environments ranging from planetary atmospheres to the interstellar medium.[1] After photoexcitation by the interstellar radiation field, they cascade back to the ground state emitting their IR photons on which their presence is based. However, only large PA(N)Hs with more than 50 carbon atoms survive the extreme conditions, whereas smaller ones are destroyed. Their dissociation mechanisms give insights into the cycle of matter in the universe, but so far only singly substituted PANHs have been investigated.[2]

In this work, three nitrogen-containing PANH isomers of $C_8H_6N_2$ composition, quinoxaline, quinazoline and cinnoline, have been studied by dissociative photoionization in a double imaging photoelectron photoion coincidence (i²PEPICO) apparatus at the VUV beamline of the Swiss Light Source. The experimental findings are supported by quantum chemical calculations providing insights into the dissociation mechanism and barriers. To characterize the dissociation kinetics, energy-dependent unimolecular dissociation rates for each channel were calculated as a function of internal energy based on Rice-Ramsperger-Kassel-Marcus (RRKM) statistical rate theory.

The isomers show characteristic dissociation pathways that lead to the elimination of HCN fragments from quinoxaline and quinazoline with barriers of 2.86 and 2.58 eV, respectively. The latter also shows a competing hydrogen loss channel, which occurs not directly at the parent molecule, but instead from the first intermediate on the HCN loss reaction pathway, exhibiting a barrier of 2.56 eV. Even though the H-loss barrier is lower in energy than the HCN loss, the latter is still the main product, which can be explained by a tight transition state leading to a highly constrained hydrogen loss coordinate. In contrast the third isomer, cinnoline, eliminates N_2 instead of HCN, most likely due to the two adjacent nitrogen atoms in its aromatic ring. This route has a barrier of 3.04 eV, which is the highest of all three isomers.

Literature:

[1]   A. G. G. M. Tielens, *Ann. Rev. Astron. Astrophys.* **2008**, *46*, 289-337.
[2]   J. Bouwman, B. Sztáray, J. Oomens, P. Hemberger, A. Bodi, *J. Phys. Chem. A* **2015**, *119*, 1127-1136.

Dissociative Photoionization of Quinoxaline, Quinazoline and Cinnoline

Gülben Sariyar Paderborn/DE , D. Schleier, Paderborn/DE, H. Hrodmarsson Paris/FR, A. Boedi, Villigen/CH, P. Hemberger, Villigen/CH, J. Bouwman, Boulder/USA

Prof. Dr. Jordy Bouwman, University of Colorado, 80309 Boulder, USA

Polycyclic aromatic hydrocarbons (PAHs) and their nitrogen-containing counterparts (PANHs) are ubiquitous in extraterrestrial environments ranging from planetary atmospheres to the interstellar medium.[1] After photoexcitation by the interstellar radiation field, they cascade back to the ground state emitting their IR photons on which their presence is based. However, only large PA(N)Hs with more than 50 carbon atoms survive the extreme conditions, whereas smaller ones are destroyed. Their dissociation mechanisms give insights into the cycle of matter in the universe, but so far only singly substituted PANHs have been investigated.[2]

In this work, three nitrogen-containing PANH isomers of $C_8H_6N_2$ composition, quinoxaline, quinazoline and cinnoline, have been studied by dissociative photoionization in a double imaging photoelectron photoion coincidence (i²PEPICO) apparatus at the VUV beamline of the Swiss Light Source. The experimental findings are supported by quantum chemical calculations providing insights into the dissociation mechanism and barriers. To characterize the dissociation kinetics, energy-dependent unimolecular dissociation rates for each channel were calculated as a function of internal energy based on Rice-Ramsperger-Kassel-Marcus (RRKM) statistical rate theory.

The isomers show characteristic dissociation pathways that lead to the elimination of HCN fragments from quinoxaline and quinazoline with barriers of 2.86 and 2.58 eV, respectively. The latter also shows a competing hydrogen loss channel, which occurs not directly at the parent molecule, but instead from the first intermediate on the HCN loss reaction pathway, exhibiting a barrier of 2.56 eV. Even though the H-loss barrier is lower in energy than the HCN loss, the latter is still the main product, which can be explained by a tight transition state leading to a highly constrained hydrogen loss coordinate. In contrast the third isomer, cinnoline, eliminates N_2 instead of HCN, most likely due to the two adjacent nitrogen atoms in its aromatic ring. This route has a barrier of 3.04 eV, which is the highest of all three isomers.

Literature:

[1]   A. G. G. M. Tielens, *Ann. Rev. Astron. Astrophys.* **2008**, *46*, 289-337.
[2]   J. Bouwman, B. Sztáray, J. Oomens, P. Hemberger, A. Bodi, *J. Phys. Chem. A* **2015**, *119*, 1127-1136.

Identification of critical process parameters in the synthesis of gold nanoparticles using a home-built synthesis robot

Dr. R. Grzeschik, Essen/DE, A. Dankov, Essen/DE, L. Hensen, Essen/DE,
Prof. Dr. S. Schlücker, Essen/DE
Dr. Roland Grzeschik, University of Duisburg-Essen (UDE),
Universitätsstr. 5, 45141 Essen

The wet-chemical synthesis of gold nanoparticles (NPs) is performed manually in nearly all laboratories worldwide. In a few exceptions, robots such as HERMAN[1] and an AI-controlled pipetting machine[2] are employed. These robots focus on the production and/or processing of NPs by adjusting synthesis protocols, i.e., by varying the chemical reaction space.

An underestimated yet crucial issue to be considered is that, depending on the particle composition and morphology, manual syntheses are rarely reproducible. The origin of this lack of reproducibility is poorly understood. One potential candidate is the merely qualitative
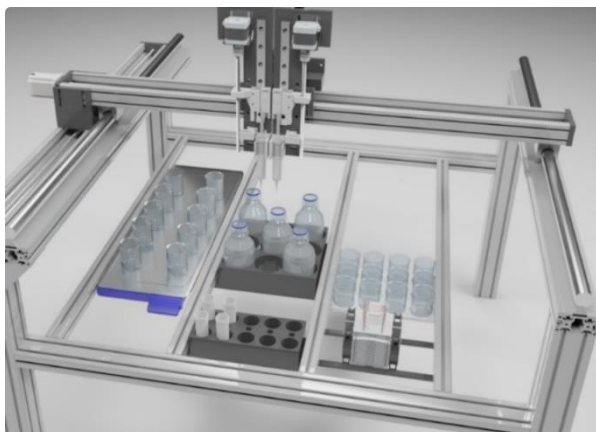
description of process parameters such as: How fast and where with respect to the center of the vessel have the reagents to be added? What are optimum mixing conditions? Poor reproducibility, in turn, complicates the production of NPs with specific physicochemical properties required for applications (e.g., catalysis, photothermal therapy etc.). Our home-built synthesis robot BOttom-up NAnoPARTiclE synthesis robot (BONAPARTE) was designed to perform highly reproducible synthesis of NPs by controlling the process parameters space including parameters such as pipetting speed/volume flow and pipetting position. The goal of our research is to identify critical process parameters and utilize this knowledge to improve the quality of various NPs.

Literature:
[1] https://foundry.lbl.gov/2017/03/16/science-in-360-herman-the-nanoparticle-robot/ (2023). [2] Jiang et al., Sci. Adv., 2022, 8, eabo2626.

Cation exchange on 2D CdSe nanoplatelets: where, why and what for?

Volodymyr Shamraienko, Subakti Subakti, Rico Friedrich, Axel Lubk, Arkady Krasheninnikov, Alexander Eychmüller

Technische Universität Dresden, Chair of Physical Chemistry, Zellescher Weg 19, 01069 Dresden, Germany

Two-dimensional (2D) zincblende CdSe nanoplatelets (NPLs), despite their remarkable optical properties, are attractive platform for production of various metal chalcogenides via cation exchange (CE) reaction, especially when this is the only currently available way to achieve precise thickness control over the resulting structure maintaining lateral dimensions. Diverse synthetic conditions of CE reactions on cadmium-based zinc blende NPLs made the production of 2D near-infrared active lead and mercury chalcogenides possible, however, only a few amounts of effort were done to understand how this transformation works and where it begins. Investigation of defects and single cation exchanged sites on CdSe NPLs during this cation exchange procedure needed to be done, in order to understand the nature of this reactions.

In this work, we investigate the process of mercury selenide formation in cadmium selenide NPLs, focusing our attention on determining the weakest spot in the CdSe NPL structure where the opening gambit of the metal exchange reaction should occur. Our study of $Cd_xHg_{1-x}Se$ NPLs with HAADF-STEM indicates a formation of exchanged species on NPL corners and edges where the amount of accumulated Hg can be quantified by z-contrast evaluation. Calculation of Hg substitution energies in 4 monolayer CdSe NPL stabilized with acetate ligands reveals that energetically preferred exchange positions are corners of the platelet, which are consequently representing the weakest spots in the system.

Understanding light-induced reaction dynamics of molecular systems in polar and non-polar solvents using ultrafast pump-probe methods

M. Sekkal [1,2], C. Bömer [2,3], M. Busi [4], T. Choi [2], S. J. Goodner [5], Z. Nurekeyev [1,2], F. Otte [2,3,6], R. D. Schaller [7,8], K. Haldrup [4], D. J. Gosztola [7], M. Kushniyarov [5], C. Bressler [2,3,1], and K. Kubicek [1,2]

Many of the light-induced processes of direct relevance to efficient photoswitching, photocatalysis and photosensitization occur on the femto- to picosecond time scale. They involve both electronic and nuclear structure changes on the Ångström length scale[1]. We present herein results from ultrafast pump-probe experiments which enlarge our understanding of such photo-chemical transformations. Explicitly, utilizing femto- and picosecond pulses from X-ray and optical sources we have investigated the electronic excited state dynamics after photo-absorption events for two classes of transition metal coordination compounds: novel Fe(II)-based spin state photoswitches with room-temperature stability [2,3] and mixed-ligand Cu(I) photosensitizers[4,5].

For the Fe(II) compounds, we will discuss results on the excited state dynamics associated with their photoswitching from our femtosecond time-resolved transient absorption spectroscopy experiments. More precisely, we have investigated the response of the system after 275 nm or 375/570 nm in acetonitrile and cyclohexane solution respectively, triggering an open- to closed-ring transformation (or vice versa) in its photocyclizable ligand [2,3]. Our data gives the first indication about the time scales and processes involved in this reaction, which we prepare to investigate in more detail using (ultrafast) X-ray based (pump-probe) techniques.

For the Cu(I) photosensitizers we will discuss results from our picosecond time-resolved Wide-Angle X-ray Scattering experiments at the APS synchrotron mapping the structural details of their energetically lowest lying triplet excited states in coordinating and non-coordinating solvents. More accurately, we have elucidated the changes in the nuclear configuration after initial metal-to-ligand charge transfer excitation and intersystem crossing in these compounds, in particular including the interaction between the metal center in the flattened excited state compound geometry and the surrounding solvent molecules. The results show how molecular properties and steric hindrance can dictate excite state structures for these systems which in turn correlate to excited state lifetimes relevant to their functionality.

[1] K. J. Gaffney, Chem. Sci. **12**, 8010 (2021)
[2] M. Milek et al., Inorg. Chem. **52**, 11585 (2013)
[3] M. M. Khusniyarov, Eur. J. Chem. **22**, 15178 (2016)
[4] S.-M. Kuang et al., Inorg. Chem. **41**, 3313 (2002)
[5] K. Kubicek et al., Polyhedron **124**, 166 (2017)

Spectroscopy

Excited state dynamics of molecular dyads for light driven catalysis

M. Semwal, Jena/DE, M. Lämmle, Ulm/DE, E. Brohmer, Jena/DE, A. Mengele, Ulm/DE, G.Shillito, Jena/DE, L.Zedler, Jena/DE, S.Kupfer, Jena/DE, S.Rau, Ulm/DE, B. Dietzek-Ivanšić Jena/DE

Mohini Semwal, Institute of Physical Chemistry, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany

Supramolecular photocatalyst consisting of a photosensitizer, a bridging ligand, and a catalyst to carry out hydrogen evolution reaction in presence of sacrificial electron donor, plays a crucial role in providing artificial photosynthesis which has drawn immense attention to meet the problem of climate changes and energy crisis. By irradiation with visible light, Ru-based photocatalysts were found as efficient systems to carry out catalysis and as suitable models to study the individual electron transfer steps within a single molecule.[1]

Previous studies have shown that the bridging ligands play an important role as electron relay and affect the electron transfer reactions along with their fast catalytic activity.[2] Herein, we investigated the photophysics of two Ruthenium-Rhodium complexes as [(tbbpy)$_2$Rup(L)pRh(Cp*)Cl]$^{3+}$ (L=none or Ph) (tbbpy = 4,4´-tert-butyl-2,2´ bipyridine, Cp* = pentamethyl-cyclopentadienyl, p=phenanthroline Ph = phenyl) by time-resolved absorption spectroscopy and resonance Raman spectroscopy studies in combination with TD-DFT studies. According to our observations a long-lived charge separated state is being formed upon photoexcitation at the MLCT along with the molecular rotation around the bridge in the complex that tends to localize the electron in the bridging site but not sufficiently towards the catalytic center. Our studies together with TD-DFT gave us a new approach towards the discussion of molecular rotation within the complex when photoexcited and a basis to synthesize a highly conjugated planar and more electron accepting systems in the bridging side to promote forward reactions in future.

Literature:
[1] Zedler, L., Müller, C., Wintergerst, P., Mengele, A., Rau, S., Dietzek-Ivanšić, B., *Chem. Eur. J.* **2022**, *28*, e202200490 [2] Zedler, L., Mengele, A., Ziems, K., Zhang, Y., Wächtler, M., Gräfe, S., Pascher,T., Rau, S.,Kupfer, S., Dietzek-Ivanšić, B., *Angew. Chem. Int. Ed.* **2019**, *58*, 13140-13148.

Spectroelectrochemical methods for the elucidation of photoredox processes

N. Hagmeyer, Jena/DE, F. Weick, Karlsruhe/DE, H.-A. Wagenknecht, Karlsruhe/DE, B. Dietzek-Ivanšić, Jena/DE, N. Mroweh, Grenoble/FR, M. Chavarot-Kerlidou, Grenoble/FR
Nina Hagmeyer, Friedrich Schiller University Jena, IPC, Helmholtzweg 4, 07743 Jena

In the field of solar light to energy conversion, the storage of the harvested energy with the help of molecular charge accumulating units[1] as well as the use of sunlight for driving catalytic reactions have become key interests. In the corresponding photoredox cycles, a reduced or oxidized intermediate is often involved. Spectroelectrochemical methods are extremely valuable to identify these intermediates as well as their photophysical properties and to determine their role in the reaction. In here, two examples for molecular systems with application in photocatalysis are presented.

In the context of light-driven charge accumulation, two ruthenium complexes with a flavin-type ligand were investigated. To assess their ability to store electrons upon irradiation in the presence of a sacrificial electron donor, spectroscopic/electrochemical methods were employed. These allowed to characterize the complexes and their spectral features in different redox and protonation states. Hence, the photoproducts as well as the reaction pathway towards charge accumulation were identified.

N-aryl phenothiazines, on the other hand, are a promising class of compounds that has been successfully applied as photoredoxcatalysts. They are purely organic and show a high reducing power in their excited state. [2,3] We tested different N-aryl phenothiazines as catalyst in the activation of aryl chlorides and found different product yields. Steady-state and transient absorption spectroelectrochemical methods gave valuable mechanistic insights as they suggest that it is not the photophysics of the neutral phenothiazines but of the radical cations which determine the efficiency. These radical cations are generated in the first half of the catalytic cycle and show strikingly different behavior across the three compounds under investigation.

Literature:
[1] Y.-J., Yuan, Z.-T. Yu, D.-Q. Chen, Z.-G. Zou, Chem. Soc. Rev. 2017, *46*, 603–631.
[2] D. Rombach, H-A. Wagenknecht, ChemCatChem 2018, 10, 14, 2955-2961. [3] E. H. Discekici, J. R. de Alaniz, Chem Commun. 2015, 51, 11705-11708.

Formation of Nanoplasma by Spatially Inhomogeneous Light Fields inside NaCl Particles

Hanchao Tang, Zurich/CH, Loren Ban, Zurich/CH, Jonas Heitland, Zurich/CH, Christopher W. West, Zurich/CH, Bruce L. Yoder, Zurich/CH, Ioannis Thanopulos, Patras/GR, Ruth Signorell, Zurich/CH

Hanchao Tang, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

Particles with diameters in the submicrometer to few-micrometer range can significantly alter the light field inside and around themselves. [1–3] Because of this unique property compared to bulk phase, the light-matter interaction becomes especially intriguing for the formation process of nanoplasma. An acceleration mechanism for the electrons and ions originating from surface adsorbates in intense NIR fields has been proposed [3,4]. However, the precise mechanism of ion emission including the role of Coulomb explosion and hydrodynamic expansion is still not fully understood.

To further understand the ion ejection mechanism, our study focuses on nanoplasma formation inside NaCl particles by intense NIR and UV pulses. A moderate NIR pulse intensity ($<2\cdot10^{13}$ W/cm^2) was employed to investigate the transition regime between direct photoemission (MPI) and plasma formation [5,6]. With UV pulses at an intensity of $\sim2\cdot10^{12}$ W/cm^2, we can exclude the influence of collisional ionization on ion emission. We recorded mass-gated velocity map images (VMIs) of electrons, cations, and anions on a shot-to-shot basis. First, both NIR and UV pulses generate the same ion fragments. Secondly, different effects on electron acceleration were observed with UV and NIR pulses. Since electrons can only gain a negligible amount of pondermotive energy in UV fields, the effect of charge interaction on electron acceleration can therefore be isolated. Correspondingly, photoions from NIR and UV pulses show similar kinetic energy distributions, while ion emission after UV pulses shows a strong directionality, indicating a stronger light confinement effect. Finally, we further examine the angular distribution of ion-VMIs to determine the particle orientation during laser ionization.

Literature:
[1] R. Signorell et al., Chem. Phys. Lett. **658**, 1 (2016). [2] L. Ban et al., Annu. Rev. Phys. Chem. **71**, 315 (2020). [3] L. Seiffert et al., Adv. Phys. X **7**, (2021). [4] P. Rosenberger et al., ACS Photonics **7**, 1885 (2020). [5] J. Reif et al., Appl. Phys. A Mater. Sci. Process. **79**, 1229 (2004).[6] M. Hada et al., **1**, 1 (2014).

Investigating the microsolvation of TEMPO by large halogenated alcohols

E. Sennert, Göttingen/GER, M. A. Suhm, Göttingen/GER

Georg-August-Universität Göttingen, Institut für Physikalische Chemie,
Tammannstr. 6, 37077 Göttingen

Motivated by a large dynamical nuclear polarization effect observed for nitroxyl radicals combined with halogenated solvents [1] and the investigation of the microhydration of TEMPO in the gas phase by Brás et. al. [2] the present work investigates the microsolvation of TEMPO by benzyl alcohol and its halogenated derivatives [3].

Considering possible hydrogen bonding, the OH stretching vibration of the alcohol is used as a sensitive indicator for the presence of a specific heterodimer (1:1) conformation by comparing slit jet FTIR-spectra with the results of harmonic DFT calculations. By varying the halogenation of the alcohols the role of polarity and polarizability for the conformational solvation preferences is explored.

For the combination of TEMPO with benzyl alcohol, two signals of 1:1-complexes can be observed and assigned. Switching to halogenated benzyl alcohols with chlorine, bromine or iodine at the *para*-position these signals are also visible but slightly shifted to lower wavenumbers which agrees with the DFT calculations.

Literature:

[1] G. Liu, M. Levien, N. Karschin, G. Parigi, C. Luchinat, M. Bennati, *Nat. Chem.* **2017**, 9, 676.

[2] E. M. Brás, T. L. Fischer, M. A. Suhm, *Angew. Chem. Int. Ed.* **2021**, 60, 19013.

[3] M. Lange, E. Sennert, M. A. Suhm, *Synlett* **2022**, 33, 2004.

Microhydration of tertiary amines:
Robust resonances in red-shifted water

E. Lwin, Göttingen/GER, T. L. Fischer, Göttingen/GER,
M. A. Suhm, Göttingen/GER
Georg-August-Universität Göttingen, Institut für Physikalische Chemie,
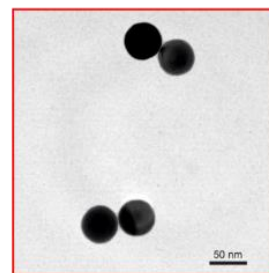Tammannstr. 6, 37077 Göttingen

Tertiary amines are strong hydrogen bond acceptors. When a water molecule donates one of the OH groups, its in-phase stretching vibration wavenumber is lowered to such an extent that it comes close to the water bending overtone. This gives rise to anharmonic phenomena such as classical Fermi resonance, resonance with multiple-quantum dark states, or combination transitions with low frequency intermolecular modes. These effects, which contribute to the spectral breadth of room temperature hydrogen-bonded amine complexes, are disentangled by FTIR spectroscopy in pulsed supersonic slit jet expansions. [1] Monohydrates of the amines quinuclidine, *N*-methylpyrrolidine, *N*-methylpiperidine, and dimethylcyclohexylamine exhibit systematic mode coupling signatures. These suggest relatively fast energy flow out of the excited OH stretching fundamental into intra- and inter- molecular degrees of freedom of the hydrogen-bonded water molecule. [2] Trimeric complexes are spectroscopically separated from the amine monohydrates.

[1] A. Kjaersgaard, E. Vogt, A. S. Hansen, H. G. Kjaergaard, *J. Phys. Chem.* A **2020**, 124, 7113–7122.
[2] E. Lwin, T. L. Fischer, M. A. Suhm, *J. Phys. Chem. Lett.* **2023**, 14, 10194–10199.

Particle Size-Dependent Onset of the Tunneling Regime in Ideal Dimers of Gold Nanospheres

Prof. Dr. S. Schlücker, Essen/D, Dr. J. Jose, Essen/D, Dr. L. Schumacher, Essen/D, Dr. M. Jalali, Duisburg/D, Dr. J.-T. Svejda, Duisburg/D, Prof. Dr. D. Erni, Duisburg/Dr, Physical Chemistry and Theoretical Electrical Engineering, University of Duisburg-Essen (UDE)
Dr. G. Haberfehlner, Graz/A, Institute for Electron Microscopy and Nanoanalysis, Graz University of Technology (TU Graz)

Dimers of spherical gold nanoparticles are the simplest system for which plasmon hybridization is observed, conceptually similar to the LCAO method for describing energy levels and MOs in homonuclear diatomic molecules. We addressed two research questions: 1. At which gap distance between the two spheres does the transition from classical electromagnetism to quantum effects such as tunneling occur? 2. Does this transition depend on particle size and if so why? We resolved them by precision plasmonics in a joint experimental and theoretical effort.[1] Specifically, we employed dimer assembly with sub-nm precision, characterization by single-particle dark-field scattering microspectroscopy and cryo-HAADF-HRTEM as well as computer simulations using a quantum-corrected model. Our study constitutes the closest experimental result to the theory for a 3D sphere dimer system and offers a reference data set for comparison with theory/simulations.

Literature:

[1] Schlücker, Erni, and co-workers, ACS Nano 2022,16,21377−21387.
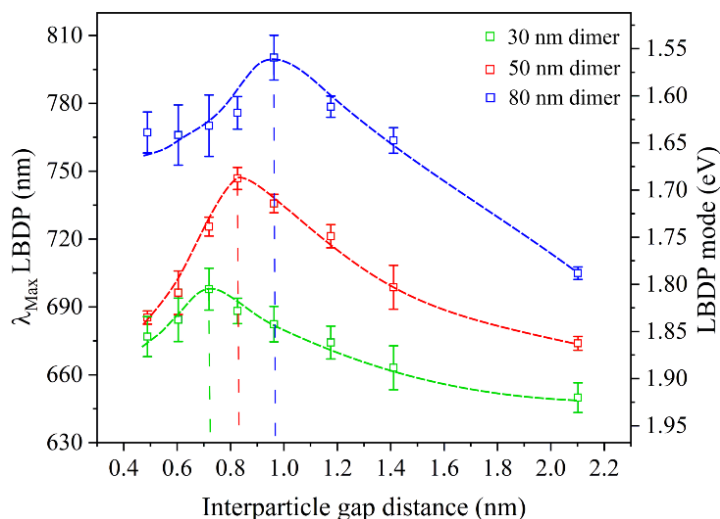
h-BN in the Making – The Surface Chemistry of Borazine on Rh(111)

<u>E. M. Freiberger, Erlangen/DE</u>, F. Düll Erlangen/DE, P. Bachmann Erlangen/DE, J. Steinhauer Erlangen/DE, H.-P. Steinrück, Erlangen/DE, C. Papp, Berlin/DE

Eva Marie Freiberger, FAU Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen

The intriguing properties of two-dimensional materials (2DM) gave rise to a vivid research field. In the last two decades, numerous 2DM were predicted and synthesized. One of the most-studied representatives of this class is hexagonal boron nitride (*h*-BN). In ultra-high vacuum (UHV), *h*-BN can be grown on a metal support via chemical vapor deposition (CVD) using suitable precursors, such as ammonia borane or borazine. [1] *h*-BN grown on a lattice-mismatched substrate undergoes a buckling, leading, in the case of Rh(111), to the formation of a so-called nanomesh. [2]

In this UHV study, we investigated the evolution of the *h*-BN nanomesh from borazine on Rh(111) using synchrotron radiation-based high-resolution X-ray photoelectron spectroscopy (XPS). The adsorption of borazine at 130 K was followed *in situ*, showing that borazine adsorbs mainly as an intact molecule. By studying borazine on Rh(111) with NEXAFS, we were able to identify a flat-lying adsorption geometry. For a better understanding regarding the formation of *h*-BN, the thermally-induced reaction of borazine on Rh(111) was investigated by temperature-programmed XPS. We find that borazine multilayers already desorb below 200 K. At ~ 300 K, dehydrogenation of the remaining monolayer occurs, and boron nitride starts to grow in a disordered fashion. Above 600 K, the formation of the nanomesh sets in and, at about 1100 K, the conversion to *h*-BN is complete.

Literature:

[1] P. Bachmann et al., J. Chem. Phys. 2018, 149, 164709. [2] M. Corso et al., Science 2004, 303 (5655), 217 – 220.

Surface Science Investigations of Oxanorbornadiene/ Oxaquadricyclane Ester Derivatives as MOST Systems on Pt(111)

F. Hemauer, Erlangen/DE, V. Schwaab, Erlangen/DE, E. M. Freiberger, Erlangen/DE, N. J. Waleska-Wellnhofer, Erlangen/DE, D. Krappmann, Erlangen/DE, H.-P. Steinrück, Erlangen/DE, C. Papp, Berlin/DE
Felix Hemauer, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

The harvesting and storage of solar power is feasible in a chemical manner with so-called molecular solar thermal (MOST) systems. In one-photon one-molecule processes, the conversion of the energy-lean norbornadiene (NBD) into its strained quadricyclane (QC) isomer takes place upon irradiation. On demand, the energy-releasing back reaction is triggered. To ensure higher efficiencies through an improved overlap of the absorption profile with the solar spectrum, an appropriate molecular design of the NBD framework is required. Additionally, for a sustainable storage and release cycle, the catalytic release needs to occur without loss of the MOST molecules. Since the methylene bridgehead group was found to be the weakest link, the surface chemistry of derivatized hetero-NBD/QC pairs was assessed on Pt(111). [1, 2]

Specifically, synchrotron radiation-based XPS experiments were performed on 2,3-bis(methylester)-oxa-NBD/QC derivatives and its extended 2,3-bis(benzylester) substitution. Next to qualitative information on adsorption motifs, respective reaction pathways were deduced by means of temperature-programmed measurements. That is, the energy release in the cycloreversion reaction from the energy-rich isomers was studied, as well as competing desorption and decomposition steps determined. [3]

Literature:
[1] J. Orrego-Hernández, A. Dreos, K. Moth-Poulsen, Acc. Chem. Res. 2020, 53, 1478-1487. [2] H. Prinzbach, Pure Appl. Chem. 1968, 16, 17-46. [3] F. Hemauer, D. Krappmann, V. Schwaab, Z. Hussain, E. M. Freiberger, N. J. Waleska-Wellnhofer, E. Franz, F. Hampel, O. Brummel, J. Libuda, A. Hirsch, H.-P. Steinrück, C. Papp, J. Chem. Phys. 2023, 159, 074703.

Aerogel lined capillaries as liquid core waveguides for real time spectroscopy in aqueous systems.

L. Jakob, Freiberg/GER, M. Lippold, Freiberg/GER, F. Spiske, Freiberg/GER, Prof. Dr. A. S. Braeuer, Freiberg/GER, Prof. Dr. Y. Joseph, Freiberg/GER, Technische Universität Bergakademie Freiberg, Gustav-Zeuner-Straße 3, 09599 Freiberg

We report the reproducible production of hydrophobic aerogel lined capillaries, which -when filled with an aqueous solution- serve as optofluidic waveguides. Due to the confinement of the aqueous solution and the light all along the length of the capillary, the number of signal-producing light/matter-interactions is increased. The potential of these capillaries for the increasement of Raman signals has already been demonstrated by our group [1]. Here we emphasize the effect of the properties of the lining suspension and the coating parameters as well as the drying parameters onto the quality of the obtainable aerogel lining. The quality of the aerogel lining was characterized by their ability to increase the Raman signal of an aqueous solution contained inside the respective capillaries and via contact angle measurements and scanning electron microscopy (SEM) measurements. The engineered aerogel lined capillaries show long-term stability and reproducible signal enhancement. The advantages compared with already existing optofluidic waveguides and the wide range of scientific and industrial applications in spectroscopy-based sensing methods will be described.

Literature:

[1] Spiske, F.; Dirauf, M.P.; Braeuer, A.S. Aerogel-Lined Capillaries for Raman Signal Gain of Aqueous Mixtures. Sensors 2022, 22, 4388.

Acknowledgement:

Two-Dimensional IR Spectroscopy of Bifunctional Vibrational Probes

C. Gräve, Bonn/DE, S. Flesch, Bonn/DE, L. I. Domenianni, Bonn/DE, J. Lindner, Bonn/DE, P. Vöhringer, Bonn/DE

Claudia Gräve, Clausius-Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, 53115 Bonn, Germany

The nitrile group is a superb vibrational probe for the dynamics of biomolecular systems such as proteins, nucleic acids, and complexes thereof.[1] Unfortunately, the CN-group exhibits a relatively small transition dipole moment, which causes sensitivity issues in IR-spectroscopic studies of biosystems.

Here, we study the vibrational dynamics of small organic nitriles featuring an azide residue, which can later be exploited for purposes of protein incorporation. The two nitriles studied here are 3-(4-azidophenyl)propiolonitrile ($N_3 - C_6H_4 - C \equiv C - C \equiv N$) and 4-azidobenzonitrile ($N_3 - C_6H_4 - C \equiv N$).

We report on the linear Fourier-transform infrared spectra, as well as on the femtosecond pump-probe and 2DIR spectroscopy. The linear spectra in the azide and nitrile stretching region are highly complex due to Fermi resonances involving the N_3-fundamental. Furthermore, the 2DIR spectra reveal the detailed vibrational energy flows between the azide and the nitrile groups separated by the phenyl ring. Finally, coherent oscillations resulting from the impulsive excitation of the Fermi multiplets associated with N_3 were observed by means of pump-probe measurements. Our results suggest that propiolonitrile is a superior vibrational probe as compared to the bare CN.

Literature:

[1] H. Kim and M. Cho, *Chem. Rev.* **2013**, *113*, 5817-5847.

Tailoring the composition of ultrathin colloidal 2D MoS$_2$/WS$_2$ alloyed nanoplatelets

M. Fröhlich Tübingen/DE, M. Kögel Tübingen, Reutlingen/DE, L. Kahlmeyer Tübingen/DE, J. Meyer Tübingen, Reutlingen/DE , J. Lauth Tübingen, Hannover/DE

University of Tübingen, Institute of Physical and Theoretical Chemistry, Auf der Morgenstelle 18, D-72076, Tübingen, Germany.

Transition metal dichalcogenides (TMDCs) such as MoS$_2$ and WS$_2$ are well studied van der Waals materials forming stable layers without dangling bonds. Recently, we obtained colloidal, phase-pure mono- and few-layered semiconducting MoS$_2$ and WS$_2$ nanoplatelets (NPLs).[1] The wet-chemical approach allows for the formation of scalable amounts of TMDC NPLs with different lateral sizes, each with a highly monodisperse size distribution.[1,2] By confining the 2D NPLs not only in z-direction but also in the lateral dimension, the excitonic features can be shifted to higher energy, allowing a limited extend of band tuning.[1] Expanding on these findings, we show, that besides changing the morphology of the NPLs, it is possible to further tune the band structure of colloidal TMDC NPLs via the composition of MoS$_2$ and WS$_2$ content of the structure. The study of the optical transitions shifting in dependence of elemental composition is backed up with microscopic and macroscopic structural information from scanning transmission electron spectroscopy (STEM) and Raman spectroscopy.

This wet chemical synthesis protocol is designed to be adapted also for other combinations of TMDCs in the future. Alloying is the next step for tailoring colloidal TMDCs towards optoelectronics, catalysis and sensing.[3]

[1] Niebur A., Söll A. et al. Nanoscale, 2023,15, 5679-5688**.** [2] Frauendorf A., Niebur A. et al. J. Phys. Chem. *C* 2021, 125, 34, 18841–18848. [3] Xie L.M. Nanoscale, 2015,7, 18392-18401. Fröhlich M., et. al., 2023, manuscript in preparation

High Resolution Spectroscopy of *trans-c*-2,3-di-deutero-oxirane and additional isotopomers

S. Albert, Zürich/CH, Z. Chen, Lanzhou/China, K. Keppler, Zürich/CH,
C. Manca Tanner Zürich/CH, G. Wichmann, Zürich/CH, J. Stohner, Wädenswil/CH
V. Schurig, Tübingen/D, O. Trapp, München/D
M. Quack, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

The concept of isotopic chirality introduces a completely new isotope effect arising from the parity violating weak nuclear force, has possible astrophysical applications, and is of fundamental interest [1−3]. Oxirane (c-C_2H_4O), detected in Sgr B2N [4], has two isotopically chiral isotopomers, monodeuterooxirane (c-C_2H_3DO) and *trans-c*-2,3-dideuterooxirane (c-CHD-CHDO). We have previously reported the analysis of the GHz and THz spectra of c-C_2H_3DO in the context of a possible first astrophysical observation of an isotopically chiral species [5]. Based on this work Müller et al have recently reported a tentative detection of monodeuterooxirane and the achiral c-CD_2CH_2O toward IRAS 16293-2422B [6]. We have previously analyzed the GHz and THz spectrum of trans-c-CHD-CHDO [7], and report here the analysis of features in its infrared spectrum, recorded at room temperature with an instrumental resolution of 0.0015 cm^{-1} using the ZP2001 prototype Bruker IFS125 FTS [8]. Molecular parameters have been determined using the Watson Hamiltonian. The results will be discussed as they pertain to isotopic chirality and molecular parity violation.

[1] M. Quack, *Angew. Chem. Int. Ed.*, 1989, 28, 571.
[2] R. Berger, G. Laubender, M. Quack, A. Sieben, J. Stohner, M. Willeke, *Angew. Chem. Int. Ed.,* 2005, 44, 3623.
[3] M. Hippler, E. Miloglyadov, M. Quack and G. Seyfang, "Mass and Isotope Selective Infrared Spectroscopy," in Handbook of High-resolution Spectroscopy Vol. 2, p. 1069, M. Quack and F. Merkt, eds, Wiley, Chichester, 2011. See also the recent review by M. Quack, G. Seyfang, G. Wichmann, *Chem. Science* 2022, 13, 10598.
[4] J. E. Dickens, W. M. Irvine, M. Ohishi, M. Ikeda, S. Ishikawa, A. Nummelin, A. Hjalmarson, *ApJ,* 1997, 489, 753.
[5] S. Albert, Z. Chen, K. Keppler, P. Lerch, M. Quack, V. Schurig, O. Trapp, *PCCP,* 2019, 21, 3669.
[6] H.S.P. Müller, J.K. Jørgensen, J.-C. Guillemin, F. Lewen, S. Schlemmer, *JMS,* 2023, 394, 111777; H.S.P. Müller, J. K. Jørgensen, J.-C. Guillemin, F. Lewen, S. Schlemmer, *Monthly Notices of the Royal Astronomical Society*, 2023, 518(1), 185.
[7] Z. Chen, S. Albert, K. Keppler, M. Quack, V. Schurig, and O. Trapp, Proc. 2021 ISMS, Urbana, IL, USA, paper WJ01, p. 182 (2021) and in preparation.
[8] S. Albert, K. Albert and M. Quack, *Trends in Optics and Photonics* 2003, 84, 177; Handbook of High-resolution Spectroscopy Vol. 2, p. 965, Wiley, Chichester, 2011.

Environmental Shifts of Hydrogen Bond Vibrations in Ne Cryomatrices and He Nanodroplets - Filling Gaps in the Vacuum Reference Data Base

M. Bödecker, Göttingen/GER 37077, M. A. Suhm, Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße 6, 37077 Göttingen/GER

Cold rare gas matrices and superfluid He nanodroplets are commonly used in vibrational spectroscopy to cool molecules and molecular clusters in order to simplify the IR spectrum by reduction of the rotational structure and suppression of hot vibration bands. Measurements in cryomatrices and nanodroplets are thus an alternative to cooling via supersonic jet expansions. Furthermore, not only global but also local minimum conformers are stabilized by kinetic trapping in He nanodroplets, which gives access to the spectroscopic analysis of metastable structures. Ne matrices are known for causing small shifts of vibrational wavenumbers compared to gas phase measurements and He nanodroplet shifts are often considered to be even smaller. However, for hydride stretching vibrations in hydrogen bonds larger He solvent shifts have been observed. Based on experimental data of around one dozen hydrogen bonded complexes, Miller and coworkers [1] postulated a linear correlation between the He solvent shift and the redshift originating from complexation. In this work, this hypothesis is reviewed by creating further data pairs of experimental gas phase wavenumbers and existing He nanodroplet wavenumbers. In the same spirit, the data set of gas phase and Ne matrix wavenumber pairs is, in cooperation with the group of René Wugt Larsen, extended in order to look for empirical correlations and outliers.

If reliable correlations can be established, this could provide a powerful tool for isomer assignments in IR spectra or for predictions of cold gas phase wavenumbers from He nanodroplet or Ne matrix values, respectively. Additionally, the compilation of these data pairs may serve as a base for future theoretical studies on matrix effects.

Literature: [1] M.Y. Choi, G. E. Douberly, T. M. Falconer, W. K. Lewis, C. M. Lindsay, J. M. Merritt, P. L. Stiles, R. E. Miller, Int. Rev. Phys. Chem., 2006, 25:1-2, 15–75.

Chiral Recognition from NMR and Computational Studies

T. L. Gomes Cabral, Magdeburg/DE, C. F. Tormena, Sao Paolo/BR, Matthias Stein, Magdeburg/DE
Tadeu Luiz Gomes Cabral, Max Planck Institute for Dynamics of Complex Technical Systems, Molecular Simulation and Design Group, Sandtorstr. 1, 39106 Magdeburg, Germany.

The separation of enantiomers is critical for the pharmaceutical, agricultural and food industries. The Matrix-Assisted DOSY (MAD) uses a chiral matrix to separate racemic mixtures via Nuclear Magnetic Resonance (NMR) spectroscopy. However, this method lacks detailed insight into the chiral recognition modes and the complexation process at molecular level. [1] Here, we integrate computational methods with experimental investigations to explain the differences in complexation between mandelic acid enantiomers and (*R*/*S*)-BINOL as a chiral matrix. ^{1}H and diffusion NMR measurements in $CDCl_3$ were carried out using *Oneshot* pulse sequence [2] at 25 °C on a 600 MHz spectrometer. DFT and molecular dynamics (MD) studies were performed to support experimental findings. [3] The results show that the most shielded mandelic acid enantiomer has the same chirality as the employed BINOL. The enantiomer that interacts more strongly and has a lower diffusion coefficient is of opposite stereochemistry to the BINOL. DFT studies confirm the preferred formation of enantioselective binding and highlight the role of intermolecular hydrogen bonding. Moreover, the MD simulations are able to give dynamic properties such as diffusion coefficients in good agreement with experimental data. This illustrates the feasibility of enantiodiscrimination through NMR and the importance of theoretical studies to provide insights into molecular recognition processes.
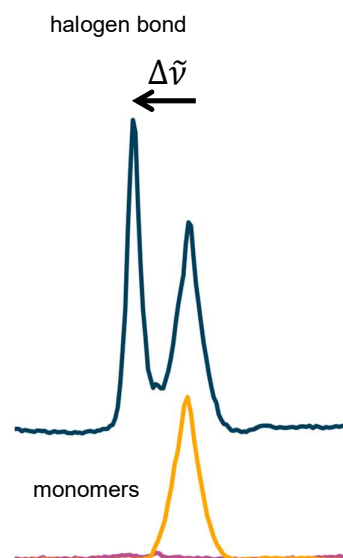
Literature:
[1] K. Salome, Chem. Commun. 2019, 55, 8611. [2] M. Pelta, Magn. Reson. Chem. 2002, 40, 13. [3] J. Hayes, J. Phys. Chem. A 2004, 16, 3572.

Filling the gaps: Raman jet spectroscopy of halogen bonds

J. N. Hasselhorn, S. Lambert-Klemme, B. Hartwig,
M. A. Suhm (msuhm@gwdg.de), University of Göttingen, Göttingen, Germany.

The first halogen bonded complexes were synthesized as early as the 19th century. [1] In recent years halogen bonds attracted interest due to possible applications regarding the design of drug-target-binding in pharmacology [2] as well as the enzyme catalysed synthesis of drugs. [3] There also exists a lot of work on halogen bonds in solid state chemistry. [1]

Although a multitude of microwave experiments have structurally characterized halogen bonds in the gas phase little to no vibrational data is available. [1] We employed Raman jet spectroscopy which posed multiple experimental challenges. Aided by DFT calculations (B3LYP-D3(BJ,abc) and CAM-B3LYP-D3(BJ,abc)), we were able to find spectral evidence of halogen bond formation for a variety of donor/acceptor pairs. We found that CX (X=Cl, Br, I) stretching frequencies were less adequate to judge halogen bond strength but other modes showed more systematic correlation with dissociation energies. We also discuss our results in the context of the Badger-Bauer rule [4] which has been established for OH stretching vibrations.

Literature:
[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, Chem. Rev. 2016, 116, 2478–2601.
[2] Z. Xu, Z. Yang, Y. Liu, Y. Lu, K. Chen, W. Zhu, J. Chem. Inf. Model. 2014, 54, 69–78.
[3] S. Jiang, L. Zhang, D. Cui, Z. Yao, B. Gao, J. Lin, D. Wei, Sci. Rep. 2016, 6, 34750
[4] R. M. Badger, S. H. Bauer, J. Chem. Phys. 1937, 5, 839–851.

Designing an electro-optical modulator with quantum dot supercrystals

R. Thalwitzer, Tübingen/Germany, J. Hiller, Tübingen/Germany,
Prof. Dr. Marcus Scheele, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen

In our work, we investigate the self-assembly of lead halide perovskite (LHP) nanocrystals into three-dimensional supercrystals from solution by a special evaporation technique.

The aim is to investigate the electro-optical modulation capability of those supercrystals to overcome the drawbacks of existing materials in terms of energy consumption and size limitations [1]. The modulation of the optical signal will be based on the quantum confined Stark effect, in which the application of an external electric field shifts the valence- and conduction bands and thus changes the absorption frequency.

For contacting the previously prepared supercrystals we have implemented two different techniques. On the one hand the lines as well as the capacitor plates made of platinum can be deposited precisely besides the supercrystals by means of a gas injection system. On the other hand, with a microgripper system, individual supercrystals can be picked up and placed accurately between prefabricated capacitor plates. Another application resulting from the latter technique is the stacking of supercrystals with different emission wavelengths or different materials to gain adjustable optical properties.

Literature:

[1] G. Sinatkas, J. Appl. Phys. 2021, 1302, 010901.

Spectroscopic investigations of reactive selenium intermediates

C. Allacher[1], Regensburg/DE, D. Grenda[1], Regensburg/DE, E. Harrer[1], Regensburg/DE, F. Bergemeier[2], München/DE, Dr. R.J. Kutta[1], Regensburg/DE, Prof. Dr. A. Breder[1], DE/Regensburg, Prof. Dr. J. Rehbein[1], Regensburg/DE, Prof. Dr. E. Riedle[2], München/DE, Prof. Dr. P. Nuernberger, Regensburg/DE.

[1] Fakultät für Chemie und Pharmazie, Universität Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany.

[2] Fakultät für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, 80538 München, Germany

Organoselenium compounds have gained the status of versatile reagents and catalysts in organic synthesis due to their ability to facilitate efficient and selective bond-forming reactions [1]. The low bond energy of selenium-selenium bonds enables the cleavage with near-UV light [2] or under photo-oxidative conditions [3].

We utilized diphenyl diselenide (Ph_2Se_2) as a precursor, which may homolytically dissociate upon irradiation [4] generating reactive selenium intermediates. As evidenced by transient absorption of Ph_2Se_2 after exciting with UV light, initial Se-Se bond cleavage leads to phenylselenyl radical (PhSe•) formation, from which partially another intermediate builds on a ps-timescale. Both, the initial PhSe• and the newly formed intermediate persist over 100 µs, depending on solvation environment.
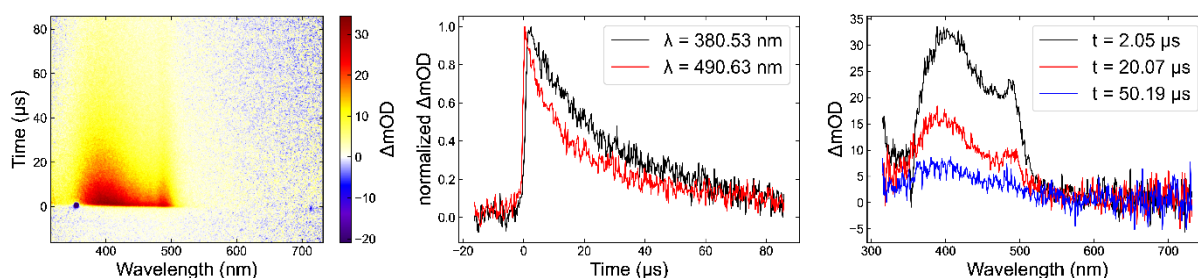

Figure 1: Transient absorption data of Ph_2Se_2 in tetrachloromethane after the excitation at 355 nm (left) with selected temporal (middle) and spectral (right) slices as indicated.

We explored the photodynamics of the selenium compounds and their potential photointermediates in different solvents and the presence of additives on a timescale from nano- to milliseconds probing their electronic absorption spectra in the UV/Vis/NIR [5].

[1] Sonawane, A. D.; Sonawane, R. A.; Ninomiya, M.; Koketsu, M, *Dalton Trans.* **2021**, *50*, 12764-12790.

[2] Ji, S.; Cao, W.; Yu, Y.; Xu, H., *Angew. Chem. Int. Ed* **2014**, *53*, 6781–6785.

[3] Park, S.; Dutta, A. K.; Allacher, C; Abramov, A.; Dullinger, P.; Kuzmanoska, K.; Fritsch, D.; Hitzfeld, P.; Horinek, D.; Rehbein, J.; Nuernberger, P.; Gschwind, R. M.; Breder, A. *Angew. Chem. Int. Ed.* **2022**, e202208611.

[4] O. Ito, *J. Am. Chem. Soc.* **1983**, *105*, 850.

[5] Kutta, R.-J.; Langenbacher, T.; Kensy, U.; Dick, B. *Appl. Phys. B* **2013**, *111*, 203–216.

Model Catalytic Studies on the Thermal Dehydrogenation of Alcohol-Based Liquid Organic Hydrogen Carrier Systems

V. Schwaab, Erlangen/DE, F. Hemauer, Erlangen/DE,
N. J. Waleska-Wellnhofer, Erlangen/DE, E. M. Freiberger, Erlangen/DE,
H.-P. Steinrück, Erlangen/DE, C. Papp, Berlin/DE
Valentin Schwaab, Friedrich-Alexander-Universität Erlangen-Nürnberg,
Egerlandstr. 3, 91058 Erlangen

The transition to a sustainable, renewable-based energy system requires novel energy storage technologies. Hydrogen production through electrolysis is a promising approach, however, under standard conditions the gas has a low volumetric energy density and is difficult to handle. So-called liquid organic hydrogen carriers (LOHCs) enable safe storage of hydrogen at high volumetric energy densities through the reversible hydrogenation of organic compounds. [1] Alcohols are particularly interesting systems, as they often exhibit exceptionally low dehydrogenation temperatures in their reaction to the respective hydrogen-lean carbonyl compounds. [2]

We investigated the dehydrogenation reactions of two alcohol-based LOHC pairs, namely, benzaldehyde/cyclohexylmethanol and acetophenone/1-cyclohexylethanol, on a Pt(111) model catalyst. [3] The adsorption and the thermal evolution of the compounds was monitored in situ in synchrotron radiation photoelectron spectroscopy (SRPES) experiments at BESSY II, Helmholtz-Zentrum Berlin (HZB).

Literature:

[1] P. Preuster, C. Papp, P. Wasserscheid, Acc. Chem. Res. 2017, 50, 74-85.
[2] V. Yadav, G. Sivakumar, V. Gupta, E. Balaraman, ACS Catal. 2021, 11, 14712-14726.
[3] V. Schwaab, F. Hemauer, E. M. Freiberger, N. J. Waleska-Wellnhofer, H.-P. Steinrück, C. Papp, J. Phys. Chem. C 2023, 127, 11058-11066.

Expanding the toolbox of *in cellulo* transient absorption spectroscopy

A. Valavalkar, Jena/DE, Markus Müller, Munich/DE, Dr. Oliver Thorn-Seshold, Munich/DE

Prof. B. Dietzek-Ivanšić, Friedrich Schiller University of Jena, Helmholtzweg 4, 07743 Jena/ DE and Leibniz Institute of Photonic Technology, Albert Einstein Strasse 11, 07745 Jena/DE

Biologically relevant chromophores are ubiquitously employed in sensing, imaging, and therapy. Certain organic fluorophores as well as metal coordinated compounds find application as photoactive functional colorants. They exhibit photobiological activity due to their tunable excited state and electron or energy transfer processes.[1] While the target site of application for these small functional molecules is the human body, there exists a gap in current state of the art, in elucidating the photophysical processes that they undergo in biologically relevant surrounding. A step in this direction is to measure the photophysical properties of these molecules in live human cells. Previous works in the group address these concerns for fluorophores, and for photosensitisers in live human cancer cells. [2,3] In this work, "dark" but "loud" photoacoustic agents[4] were measured *in cellulo*, thus obtaining temporal information environment specific information for non-emissive molecules.

1. Jaswal, S. & Kumar, J. Review on fluorescent donor–acceptor conjugated system as molecular probes. *Materials Today: Proceedings* 26, 566–580; 10.1016/j.matpr.2019.12.161 (2020).

2. Chettri, A. *et al.* Using Biological Photophysics to Map the Excited-State Topology of Molecular Photosensitizers for Photodynamic Therapy. *Angewandte Chemie International Edition* 62, e202301452; 10.1002/anie.202301452 (2023).

3. Yang, T. *et al.* Excited-State Dynamics in Borylated Arylisoquinoline Complexes in Solution and in cellulo. *Chemistry (Weinheim an der Bergstrasse, Germany)*; 10.1002/chem.202203468 (2022).

4. Müller M. *et al*. Merged molecular switches excel as optoacoustic dyes: azobenzene-cyanines are loud and photostable NIR imaging agents. ChemRxiv. Cambridge: Cambridge Open Engage (2023)

Traceable hydrogen measurement using laser absorption spectroscopy

Sumit Agarwal, Denghao Zhu, Bo Shu, Ravi Fernandes, <u>Zhechao Qu</u>
Physikalisch-Technische Bundesanstalt, Braunschweig, Germany

The European Union set a target to reduce carbon emissions by 55 % by 2030 and become carbon neutral by 2050. Hydrogen is a versatile and promising energy carrier, with various applications ranging from fuel cells to power generation. Decarbonisation of the gas grids by replacing natural gas with hydrogen is one of the promising solutions to meet the climate change targets and reduce CO_2 emissions. The precise, and reliable measurement of hydrogen is of utmost importance to accurately control blending within target tolerances. Hydrogen quality assessment is necessary for custody transfer and fair trade.

New purity specifications have been published in gas quality standards (such as OIML R140, ISO 14687, ISO/AWI 19880-9) for alternative gases to natural gas including hydrogen and hydrogen-enriched natural gas. Although gas standards and analytical methods have been developed, but further effort is required before gas industries can verify the quality of gases as specified in published standards. This work aims to develop the metrological method to ensure reliable and traceable measurement necessary to apply appropriate quality control on hydrogen using laser absorption spectroscopy (LAS). High sensitivity and selectivity LAS techniques offer several advantages for hydrogen purity analysis. They are non-intrusive, allowing online in-situ monitoring. The developed spectrometer is based on tunable diode laser absorption spectroscopy (TDLAS). As a diatomic homonuclear molecule without dipole moment, H_2 absorption lines are extremely weak in the infrared region. Optical pathlength enhanced method (multipass or cavity enhanced gas cell) was employed to increase the sensitivity of the H_2-TDLAS system. The performance of the spectrometer was evaluated and the applicability for H_2 measurement was demonstrated. The H_2 absorption line broadening and narrowing effects was also investigated. The outcomes of this research will contribute to the development of standardized approaches for hydrogen purity analysis.

In-situ measurements of Prussian Blue as cathode material for sodium ion batteries

Y. Hu, Jülich/DE, C. Rodenbücher, Jülich/DE, C. Korte, Jülich/DE,
Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Str., 52425 Jülich/DE

Sodium-ion batteries (NIB) area competitive alternative to lithium-ion batteries for large-scale electric energy storage, needed for power grid stabilisation and in a for electric vehicles, because of lower costs, environmental benignity and the higher natural abundance of sodium resources. Prussian Blue (PB) $Na_xFe[Fe(CN)_6]_y$ and Prussian blue analogues (PBA) $Na_xMe[Fe(CN)_6]_y$ (Me = Mn, Ni, Cu, V, etc.) are promising as cathode materials for Na-ion batteries due to their high-theoretical capacity of about 170 mAh/g [1].

The presence of interstitial water and vacancies in PB and PBA influence the structure and electrochemical properties [2]. Herein, we investigate the change of PB's structure by different synthesis conditions using X-ray diffraction. Moreover, the cyanide stretching vibration mode v(CN) is sensitive to the oxidation state of coordinating iron ions [3]. The mechanism of reversible sodiation and de-sodiation is verified by *in-situ* Raman techniques. It is found that the peaks of cyanide stretching vibration shift reversible, which indicates the structural transformation to the cell potential and sodium uptake.

Literature:

[1] D. O. Ojwang, ACS applied materials & interfaces 2021, 13, 10054–10063.
[2] F. M. Maddar, J. Mater. Chem. A, 2023, 11, 15778–15791.
[3] W. Ren, Adv Funct Materials, 2019, 29.

Accurate Small Molecule Property Data from Theory

D. Andrae, Berlin/DE
Freie Universität Berlin, Arnimallee 22, 14195 Berlin, Germany

Data for properties of isolated small molecules in their electronic ground state, like molecular structure (r_e, r_0, r_g, … structure) or fundamental frequencies, are of fundamental interest in many branches of science, e. g. astrochemistry, atmospheric chemistry, heterogeneous catalysis, matrix isolation vibrational spectroscopy under cryogenic conditions, to name just a few.

It is well established that calculated property data compare very well with experimental data (for the latter see, e. g., [1,2] and references therein), if (i) the system under study – the molecule in a given electronic state – is composed of only few and of only light atoms (say, $Z < 10$) and if (ii) the calculated property data derive from a sufficiently high level of quantum chemical theory (typically from an explicitly correlated coupled-cluster method like CCSD(T)-F12).

This contribution shows that accurate property data for many small molecules containing heavier atoms (up to, say, $Z = 80$ [Hg]) can be obtained, at least in favourable cases, with good success from a valence-only treatment.

Literature:
[1] J. Rumble (ed.), CRC Handbook of Chemistry and Physics, 103rd ed., Routledge, 2022, Sec. 9. [2] NIST Chemistry WebBook (NIST Standard Reference Database No. 69).

Towards plasmon-enhanced Raman spectroscopy of single molecular adsorbates with defined surface orientation

S. Mennicken, Essen/DE, D. Schäfer, Essen/DE, Dr. D. Ohm, Essen/Mainz/DE,
Dr. S. Mehrpavar, Essen/DE, J. Neumann, Essen/DE,
Prof. Dr. G. Haberhauer, Essen/DE, Prof. Dr. K. F. Domke, Essen/Mainz/DE,
Prof. Dr. S. Schlücker, Essen/DE,
Simon Mennicken, University of Duisburg-Essen (UDE), Universitätsstr. 5,
45141 Essen

Surface- and tip-enhanced Raman scattering (SERS/TERS) are capable of detecting single molecules via very high local electric fields that are generated by optical excitation of metal nanostructure supporting localized surface plasmon resonances. The observation of single molecules over extended periods of time necessitates their immobilization on substrates to minimize Brownian motion. Triphenyl (trityl)-substituted carbon centers, also termed molecular tripods, fulfill this requirement: i) The three phenyl substituents contain sulfur atoms for strong multivalent binding to gold surfaces and ii) the fourth ligand attached to sp^3-hybridized central carbon atom, also termed tail group, has a well-defined perpendicular orientation to the gold surface.[1] To this end, we have synthesized and characterized a molecular tripod with three acetyl-protected sulfur atoms in *meta* position to the central carbon center and an alkyne tail for spectroscopic analysis. The terminal alkyne moiety exhibits a strong and isolated Raman peak in the Raman-silent region around 2100-2300 cm^{-1}.[2] Furthermore, for the analysis of other tail groups, the alkynes can be converted into other moieties via click chemistry. We present preliminary Raman-spectroscopic results of this molecular tripod adsorbed on gold surfaces. We compare conventional Raman scattering of the tripod in solution with nanogold-based SERS in order to confirm chemisorption through vibrational spectroscopic differences. Monolayers of the tripod on Au(111) single crystals were prepared for spectroscopically probing the surface orientation of the alkyne tail with both conventional Raman scattering and TERS.

Literature:
[1] M. Lindner et al., Chem. Eur. J. 2016, 22, 37. [2] Y. Chen et al., Anal. Chem. 2016, 88, 6115.

Structure and dynamics of the Sars-CoV-2 NSP3 Ubiquitin-like domain 1 characterized by NMR spectroscopy and further biophysical methods

Katharina Vormann [1,2], Tobias Stief [1,2], Ralf Bartenschlager [3],
Nils-Alexander Lakomek [1,2]

[1] Forschungszentrum Jülich, Institute of Biological Information Processing
(IBI-7: Structural Biochemistry), Jülich, Germany

[2] Heinrich Heine University Düsseldorf, Institute of Physical Biology, Düsseldorf, Germany

[3] Deutsches Krebsforschungszentrum (DKFZ), Division Virus-Associated Carcinogenesis, Heidelberg, Germany

Novel anti-viral agents are needed in response to the severe acute respiratory syndrome coronavirus 2 (Sars-CoV-2) pandemic. One potential drug target is the multi-domain non-structural protein 3 (nsp3). Nsp3 is involved in forming the Sars-Cov-2 replication organelle (RO), which drives the coronavirus replication in the host cell. Nsp3 is one major constituent of molecular pores embedded in the Double Membrane Vesicles (DMVs) bilayer. These DMV pores allow the import and export of viral RNA. As the largest protein encoded by the coronavirus, nsp3 comprises 16 domains, including the N-terminal Ubiquitin-like domain 1 (Ubl1), forming the cytosolic-faced prongs of the crown-like pore. Considering that ubiquitin-like domains are involved in the regulation of diverse biological processes, the list of potential viral and host cell interaction partners is numerous.

Currently, information on the structure, dynamics, and binding partners of nsp3 is limited. Thus, our in vitro studies aim for structural and dynamic information on nsp3-Ubl1 by nuclear magnetic resonance (NMR) spectroscopy and other biophysical methods. For this purpose, we have expressed and purified the ^{15}N, ^{13}C isotopically labeled Ubl1 domain and characterized its internal and conformational dynamics by NMR spectroscopy. Additionally, circular dichroism (CD) spectroscopy was performed to analyze the secondary structural elements of Ubl1. Dynamic binding interactions by nsp3-Ubl1 with viral RNA and the N-protein will be investigated using bio-layer interferometry (BLI) and microscale thermophoresis (MST).

Room-temperature luminescence from a dinuclear Cr^{III} complex

D. Fritzler, Osnabrück/DE,
Jun.-Prof. Dr. Cui Wang, Osnabrück University, Barbarastr. 7, 49076 Osnabrück

Multinuclear Cr[III] complexes are of certain interests due to their unique optical and magnetic properties.[1] Particularly, numerous hydroxo- and oxo-bridged dinuclear Cr[III] complexes have been explored with respect to their electron exchanges and photoinduced properties. These dinuclear complexes are usually non-luminescent at room temperature and exhibit mostly antiferromagnetic coupling.[1-2]

In this work, we present a novel dinuclear Cr[III] complex showing phosphorescence emission at 748/825 nm with a quantum yield of 0.01% in acetonitrile at room temperature, which is comparable to mononuclear Cr[III] tris(bipyridine) or terpyridine complexes. Single crystal X-ray diffraction analysis of the complex gives a symmetric butterfly-like structure with the Cr[III] centres being bridged by one acetate and two hydroxyl groups. These bridging units are found responsible for the ferromagnetic coupling in dinuclear Cr[III] complexes.[3] This luminescent dinuclear Cr[III] complex could expand the few examples of luminescent single-molecular magnets, which rely mostly on lanthanide ions.[4]
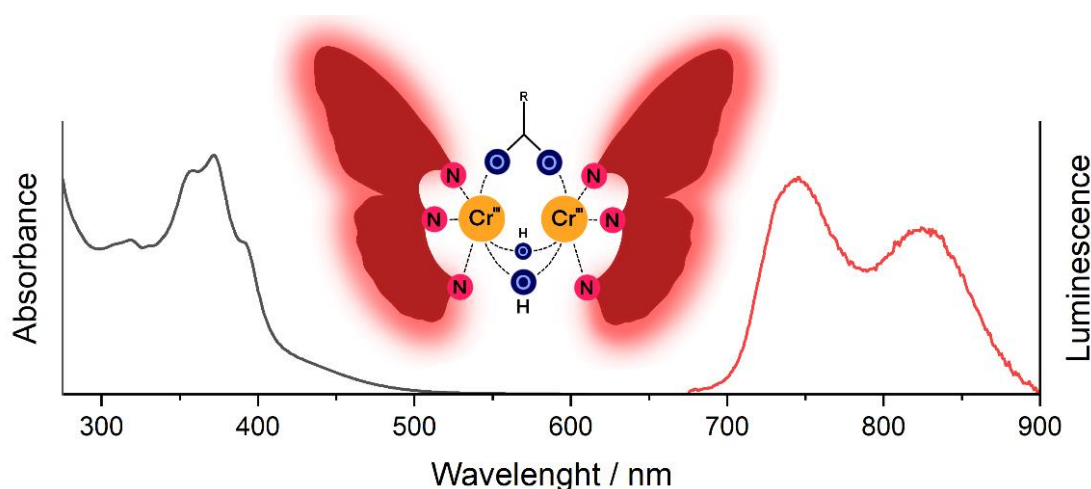
Literature:

[1] A. Døssing, Coord. Chem. Rev. 2014, 280, 38-53. [2] a) T. J. Morsing, J. Bendix, H. Weihe, A. Døssing, Inorg. Chem. 2014, 53, 2996-3003; b) H. W. L. Fraser, G. S. Nichol, G. Velmurugan, G. Rajaraman, E. K. Brechin, Dalton Trans. 2017, 46, 7159-7168. [3] H. W. L. Fraser, L. Smythe, S. Dey, G. S. Nichol, S. Piligkos, G. Rajaraman, E. K. Brechin, Dalton Trans. 2018, 47, 8100-8109. [4] a) J.-H. Jia, Q.-W. Li, Y.-C. Chen, J.-L. Liu, M.-L. Tong, Coord. Chem. Rev. 2019, 378, 365-381.

Ru^{II}-triad enables one-component photon upconversion and initiates photopolymerization with red light

<u>H. Hammecke, Osnabrück/DE</u>,
Jun.-Prof. Dr. Cui Wang, Osnabrück University, Barbarastr. 7, 49076 Osnabrück

Photoactive Ru^{II} polypyridene complexes are long known photosensitizers used for photocatalysis or solar cells.[1] Efficient green-to-blue photon upconversion is well established with Ru^{II} complexes due to their long-lived triplet excited states, which are favoured for sensitizing triplet-triplet annihilation upconversion (sTTA-UC) with annihilators, e.g. anthracene derivates.

In this work, we present a Ru^{II} polypyridine complex conjugated with two anthracene moieties on the ligand backbones, which leads to an elongation of the triplet excited state lifetime by a factor of 30 compared to the prototype Ru^{II} complex without anthracene units, hinting a triplet-reservoir effect.[2] Selective photoexcitation of the Ru^{II}-triad in solution under air with green (532 nm) or red (638 nm) cw-lasers leads to blue upconversion luminescence (~ 430 nm) indicating a self-sTTA-UC event. This one-component sTTA-UC enables a blue-light requiring photo-polymerization of acrylamide under ambient conditions with red (638nm) light excitation.
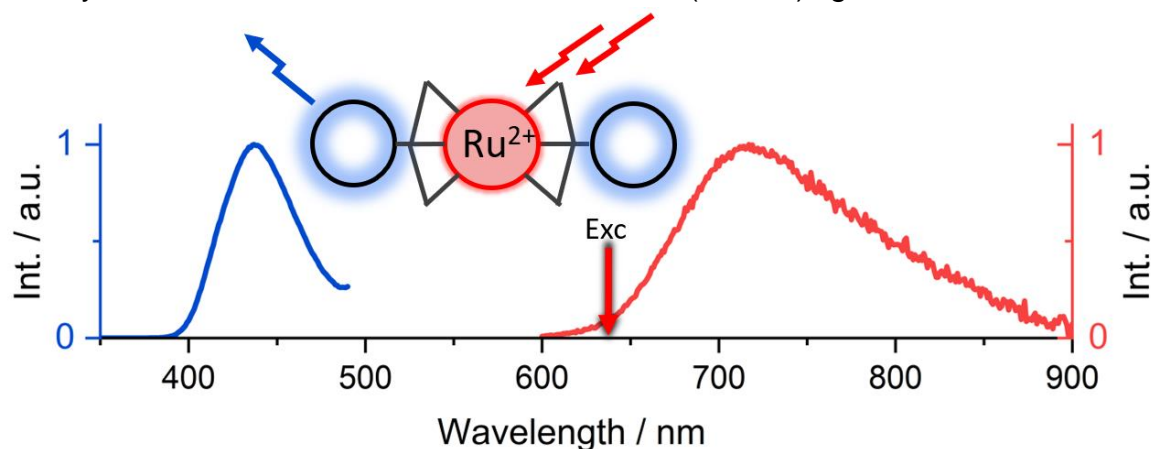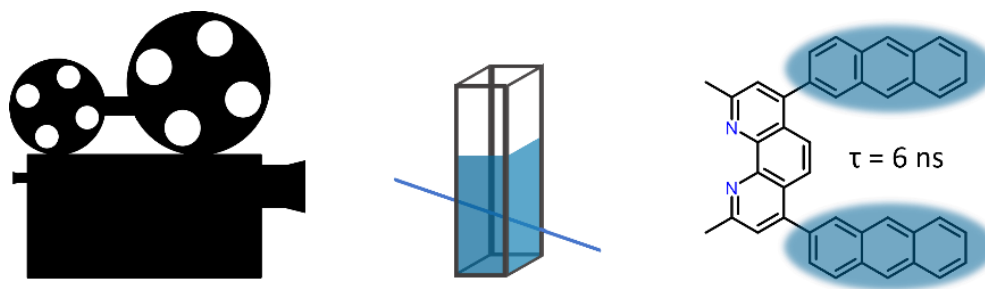

Literature:

[1] (a) N. Armaroli and V. Balzani, Energy for a Sustainable World, Wiley-VCH Verlag GmbH & Co. KGaA, 2010; (b) M. Gratzel, Acc. Chem. Res., 2009, 42, 1788–1798; (c) H. Imahori, Y. Mori and Y. Matano, J. Photochem. Photobiol., C, 2003, 4, 51–83.
[2] a) H. Li, C. Wang, F. Glaser, N. Sinha, O. S. Wenger, J. Am. Chem. Soc. 2023, 145, 11402–11414; b) C. Kerzig, O. S. Wenger, Chem. Sci. 2018, 9, 6670-6678.

Polyaromatic Hydrocarbon substituted phenanthroline ligands for Cu(I) Photosensitizer: Migration of the Excited State

Johannes P. Zurwellen, Braunschweig/DE, O. Lange, Braunschweig/DE, F. Doettinger, Braunschweig/DE, M. Karnahl, Braunschweig/DE, S. Tschierlei*, Braunschweig/DE
TU Braunschweig, Department of Energy Conversion, Institute of Physical and Theoretical Chemistry, Rebenring 31, 38106 Braunschweig

Heteroleptic Cu(I) photosensitizers of the type [Cu(N^N)(P^P)]$^+$ (where N^N = diimine and P^P = diphosphine ligand) are of great interest as an alternative to precious metal complexes for photocatalytic applications such as the reduction of H_2O or CO_2.[1] Many studies have focused on 2,9-dimethyl-1,10-phenanthroline (**dmp**) derived diimine ligands containing an additional organic chromophore like naphthalimide to enhance various photophysical properties.[2,3] Here, the well-known organic dyes phenanthrene (**P**), 9,9-dimethyl-9*H*-fluorene (**F**) and anthracene (**A**) were covalently linked in the 4,7-positions of **dmp**. The effects on the photophysical properties were then investigated in detail using various steady-state and time-resolved spectroscopic methods. While the properties of the ligands and Cu(I) complexes are significantly improved by the substitution, the system containing anthracene behaves quite differently. A migration of the excited state from **dmp** to anthracene was identified as a major reason.

Literature:

[1] E. Mejía, S.-P. Luo, M. Karnahl, A. Friedrich, S. Tschierlei, A.-E. Surkus, H. Junge, S. Gladiali, S. Lochbrunner, M. Beller, *Chem. Eur. J.*, **2013**, *19*, 15972 – 15978.
[2] F. N. Castellano, *Acc. Chem. Res.*, **2015**, *48*, 828-839.
[3] Y. Yang, F. Doettinger, C. Kleeberg, W. Frey, M. Karnahl and S. Tschierlei, *Front. Chem.*, **2022**, *10*, 936863.

Photorearrangement reaction of theophylline derivatives

T. Rittner, Regensburg, R. E. Rodríguez-Lugo, Regensburg, K. Heilmeier, Regensburg, F. Arp, Regensburg, S. Dietzmann, Regensburg, S. Wortmann Regensburg, R. Kutta, Regensburg, E. Riedle, München, R. Wolf, Regensburg, P. Nuernberger, Regensburg

Thomas Rittner, University of Regensburg, Universitätsstr. 31, 93053 Regensburg

8-Pyridiyl substituted theophylline derivatives bearing an aryl substituent on the oxopurine-scaffold, such as **NN-7-ArOMe** and **NN-9-ArOMe**, exhibit a remarkable photoreaction, similar to a recently reported aryl transfer in related systems [1]. Upon excitation with ultraviolet light, the aryl moiety migrates from the 7- or 9-nitrogen on the theophylline-based skeleton to the 1'-nitrogen of the pyridine fragment, forming the zwitterionic species **NN-1-ArOMe**.
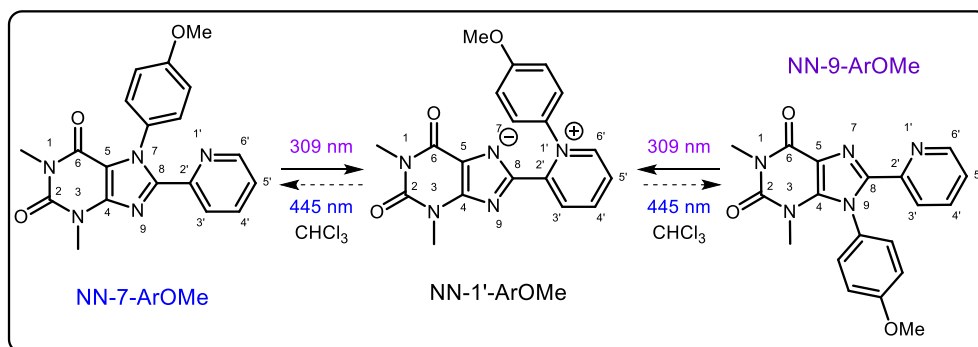

Figure 1 Chemical structure and photoisomerization of NN-7-ArOMe, NN-1'-ArOMe and NN-9-ArOMe

The quantum yield [2] for the photoisomerization of **NN-7-ArOMe** to **NN-1'-ArOMe** is 0.1 % in acetonitrile. In contrast, for **NN-9-ArOMe** the quantum yield of the light-induced aryl shift is 1 %. The back-reaction was demonstrated in chloroform under irradiation with blue light. Ultrafast fluorescence up-conversion and transient absorption accompanied by quantum chemical calculations gave a detailed insight into the reaction mechanism. It was further demonstrated that the photoisomerization reaction proceeds in many solvents, including water, and that the protonation of NN-7-ArOMe inhibits the isomerization. In principle, this detailed mechanistic study enables a general design for alternative photoswitchable molecular structures with prospective applications ranging from catalysis to biology.

[1] T.-C. Chou *et al.*, *J. Am. Chem. Soc.* 2023, **145**, 18104 – 18114.
[2] U. Megerle *et al.*, *Photochem. Photobiol. Sci.* 2010, **9**, 1400 – 1406.

Quantum Cascade Laser in IR Difference Spectroscopy: Exploring Protein Photoreactions

M. Diedrich, T. Kottke, Biophysical Chemistry and Diagnostics, Bielefeld University, Universitätsstr. 25, 33615 Bielefeld, DE

Time-resolved infrared spectroscopy represents an effective tool for the structural and kinetic investigation of proteins and became an integral component for resolving mechanisms of photoreactions in proteins. By analyzing the prominent amide I and amide II bands, questions about dynamic changes of secondary structures can be addressed. Established FT-IR instruments rely on globars as broadband infrared radiation source, characterized by low radiant power that limits the optical path length of the sample and, consequently, signal strength. Quantum Cascade Lasers (QCLs) were established and are nowadays used as a high-power radiation source with a tunable wavelength spanning from mid-IR to the submillimeter wave region. Various time-resolved methods implemented QCLs in recent years. These methods provide vibrational information about protein secondary structure at lower sample concentrations and achieve time resolutions across extensive time scales from nanoseconds up to seconds [1, 2 ,3].

We introduce a novel EC-QCL transmission setup, showcasing its application in studying the kinetics of protein photoreactions in aqueous solution by time-resolved vibrational spectroscopy in a flow cell. The setup is specialized for handling protein samples in flow swith a low sample consumption of nanoliters per minute. In investigations on the model protein bacteriorhodopsin, we resolved various intermediates in different time scales. We furthermore performed characterization measurements on flavin mononucleotide in aqueous solution which yielded a time resolution of 20 nanoseconds. We present an overview about the complexities of measurement procedures, the utilization of diverse components, and encountered challenges like measurement cycle timing or coping with the acquisition and evaluation of large amounts of data. Our goal will be the unraveling of protonation mechanisms of the blue light receptor protein cryptochrome, featuring the chromophore flavin as a cofactor.

[1] Alcaráz, M. R., Schwaihofer, A., Kristament, C., Ramer, G., Brandstetter, M., Goicoechea, H., Lendl, B., Anal. Chem. 2015, 87, 6980.
[2] Klocke, J.L., Mangold, M., Allmendinger, P., Hugi, A., Geiser, M., Jouy, P., Faist, J., Kottke, T., Anal. Chem. 2018, 90, 10494
[3] Klocke, J.L., Kottke T., Phys. Chem. Chem. Phys., 2020, 22, 26459.

Markov Chain Monte Carlo methods to model multiexciton dynamics in CdSe quantum dots

R. Baruah, Kaiserslautern/DE, K. Kumar, Jena/DE, M. Wächtler, Kaiserslautern/DE

Raktim Baruah, Chemistry Department and State Research Center OPTIMAS, RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern

Quantum dots (QDs) are semiconductor nanocrystals possessing exceptional optoelectronic properties resulting from size dependent spatial confinement of their electronic wavefunctions. Photoexcitation of QDs generates electron-hole pairs called excitons. With high excitation intensity (i.e., high photon flux) several pairs of confined excitons, known as multiexcitons (MX, e.g., biexciton, triexciton…), can be generated. Multiexcitons are of interest for applications such as lasing, or photovoltaics and photocatalysis. In QDs, MXs undergo fast non-radiative Auger recombination (AR) on the ps to 10s of ps time-scale due to strong spatial overlap of electron and hole wavefunctions. For potential applications, a sufficient lifetime of MX needs to be achieved. Understanding the relation between structural parameters of the nanocrystals and lifetimes of MX is necessary for the development of systems exploiting MX states.

In this contribution we explore multiple exciton processes in CdSe quantum dots, applying transient absorption spectroscopy in dependence of excitation intensity. We not only evaluate the dynamics at the bleach feature of the lowest excitonic transition to unravel multiexciton dynamics, which is prone to misinterpretation due to additional contributions of e.g. charge-carrier trapping processes. In our approach we evaluate spectral and temporal changes in the collected data set in dependence on excitation intensity applying a Markov Chain Monte Carlo method. This allows to determine spectral characteristics of the contributing species, hence distinguish between multiexcitons and surface traps, and determine their respective population dynamics and determine their lifetimes. We demonstrate this approach on a series of CdSe quantum dots with varying size and surface functionalization, to modify the nature and density of available trap states, to test the capability of our approach to discriminate between multiexciton decay and trapping processes.

Investigation of energy flow in COFs by 2D-IR spectroscopy

Y. Pfeifer, Potsdam/GER, A. Thomas, Berlin/GER
Prof. Dr. Henrike Müller-Werkmeister, Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam

Covalent organic frameworks (COFs) showed up as a new and proposing material mimicking the biological characteristics of DNA or proteins by merging covalent as well as non-covalent bonds. A significant porosity and high functionality [1] opens possible applications as a metal-free photocatalyst [2]. Depending on the scaffold of the organic building blocks the utilization changes drastically [3].

We are studying the influence of different linkers and COF materials trying to understand the catalytic process and photoreaction mechanism. In particular, we use transient spectroscopy in IR as well as UV-Vis to follow the photoreaction pathway. Furthermore, upon assignment of vibrations by FTIR, IVR/VET can efficiently be tracked by cross peak dynamics in 2D-IR spectroscopy.

Literature:
[1] K. Tan, Nat Rev Methods Primers. 2023, 3, 1
[2] A. Thomas, Chem. Eur. J. 2023, 29, 4
[3] J. Yang, Nat. Commun 2022, 13, 6317

Temperature-dependent NMR data reveal a "dark state" in the interaction of a-synuclein with the aggregation inhibitor AS69

Sophia Werner[1,2], Melinda Jaspert[1,2], Celina Schulz[2], Tobias Stief[1,2], Maximilian Burmeister[2], Fabian Russak[2], Wolfgang Hoyer[2], Nils-Alexander Lakomek[1,2]

[1] Institute of Biological Information Processing (IBI-7), Forschungszentrum Jülich, Jülich, Germany
[2] Institute of Physical Biology, University of Düsseldorf, Düsseldorf, Germany

Parkinson's disease (PD) is the second most widespread neurodegenerative disease in humans. When the otherwise intrinsically disordered human protein α-synuclein (α-syn) misfolds and aggregates, fibrils get formed, and Lewy bodies can arise. A general treatment of Parkinson´s disease is not possible yet.

In biotechnology, as well as diagnostics and therapy, so-called Affibody proteins have become increasingly established over the past decade. Such engineered proteins are also being considered for use in the therapy of Parkinson's disease. A promising therapeutic approach is the inhibition of fibril growth or the prevention of aggregation of monomeric α-syn itself. The Affibody protein AS69 binds with a K_d of 240 nM to α-syn. AS69 is a homodimer linked by a cysteine bridge. During the interaction with α-syn, a β-hairpin of the otherwise intrinsically disordered α-syn is induced. The formation of the β-hairpin in α-syn takes place between the amino acids V37 and K43 (β1) and V48 and T54 (β2), which are connected by a β-turn (T44-G47). Interestingly, this structural change, induced by the binding of AS69, prevents the aggregation of α-syn (Mirecka *et al.,* 2014).

We have conducted temperature-dependent liquid NMR measurements to examine the interaction between AS69 and α-syn. In particular, the formation of the α-syn β-hairpin is investigated. While at physiological temperatures of 37 °C, NMR resonances of V37 to T54 of the disordered α-syn disappear in the presence of (NMR unlabelled) AS69, and several new resonances appear, indicating β-sheet conformation of those respective residues; at 10 °C, none of those NMR resonances, neither of the folded or the unfolded state, remain visible, suggesting a "dark state" of α-synuclein. This argues for complex internal dynamics of α-syn manifested or induced by AS69. We aim to investigate the dynamic binding equilibrium of AS69 and α-syn in more detail using NMR spectroscopy. A deeper understanding of these dynamic binding interactions will help to identify improved aggregation inhibitors of α-synuclein.

References

Mirecka EA, Shaykhalishahi H, Gauhar A, Akgül Ş, Lecher J, Willbold D, Stoldt M, Hoyer W. Sequestration of a β-hairpin for control of α-synuclein aggregation. Angew Chem Int Ed Engl. 2014 Apr 14;53(16):4227-30. doi: 10.1002/anie.201309001. Epub 2014 Mar 12. PMID: 24623599.

Ultrafast photoisomerization dynamics of protonated azobenzene and azobenzene containing complexes in an ion trap

M. J. P. Schmitt[1], P. Weber[1], R. I. Petrikat[2], J. Hornbogen[3], R. Diller[3], S. Becker[2], C. Riehn[1]

FB Chemie[1,2]/ FB Physik[3], RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Str. 52[1]/54[2]/46[3],67663 Kaiserslautern, Germany.

The photochemical properties and in particular the E/Z-photoisomerization process of azobenzene and its derivatives are an ongoing topic of research.[1,2] Their broad range of applications as molecular photoswitches in biological or optical materials is based on the elucidation of their efficient ultrafast dynamics, which are determined both by intrinsic factors and by interaction with the environment. Thus, disentangling both dynamic contributions is a valuable task. Here, we report the gas phase ultrafast dynamics of E and Z isomers of protonated azobenzene (ABH$^+$) by static ultraviolet and visible (UV-PD) and transient photodissociation action spectroscopy (т-PD) using an electrospray ionization quadrupole ion trap mass spectrometer.[3,4] The resulting dynamics reveal a multiexponential electronic decay with lifetimes in sub-ps and ps time regimes. Remarkably, the observed parent and fragment ion decays exhibit rapidly damped oscillatory signals with a period of ca. 0.4 ps and phase shifted transients for specific fragments.[5,6] Additionally, we present gas phase experiments on azobenzene derivatives, in particular a cyclic Cu(I) complexed pyridyl-substituted azobenzene and compare their dynamics with condensed phase results. Experimental results were supported by DFT/TD-DFT calculations of structures, energies and electronic spectra.

Literature:
[1] S. Crespi, N. A. Simeth, B. König, *Nat. Rev. Chem.* **2019**, 3, 133-146. [2] S. Megow, H.-L. Fitschen, F. Tuczek, F. Temps, *J. Phys. Chem. Lett.* **2019**, *10*, 6048–6054. [3] G. Féraud, C. Dedonder-Lardeux, C. Jouvet, E. Marceca, *J. Phys. Chem. A* **2016**, 120, 3897-3905. [4] D. Imanbaew, J. Lang, M. F. Gelin, S. Kaufhold, M. G. Pfeffer, S. Rau, C. Riehn, *Angew. Chem. Int. Ed.* **2017**, *56*, 5471–5474. [5] K. Munkerup, D. Romanov, T. Bohinski, A. B. Stephansen, R. J. Levis, T. I. Sølling, *J. Phys. Chem. A* **2017**, 121, 8642-8651. [6] J.-W. Ho, W.-K. Chen, P.-Y. Cheng, *J. Chem. Phys.* **2009**, 131, 13408.

Nanodisc reconstitution and NMR analysis of the vesicular SNARE protein Synaptobrevin-2

Mirko Kraus[1,2], Katharina Vormann[1,2], Moritz Lemke[3], Henrike Heise[1,2], Nils-Alexander Lakomek[1,2]

[1]*Institute of Physical Biology, Heinrich Heine University Düsseldorf, Düsseldorf, Germany.*

[2]*Institute of Biological Information Processing (IBI-7: Structural Biochemistry), Forschungszentrum Jülich, Jülich, Germany.*

[3]*Institute of Biochemical Plant Physiology, Heinrich Heine University Düsseldorf, Düsseldorf, Germany.*

Membrane proteins fulfill important functions in various cellular processes, such as intercellular signaling or the transport of metabolites. The neuronal SNARE complex induces membrane fusion between vesicles filled with neurotransmitters and the pre-synaptic plasma membrane. The SNARE complex consists of the three SNARE proteins SNAP25, Syntaxin-1a and Synaptobrevin-2 (Syb2). The latter is a membrane protein that is located on the vesicular surface. Syb2 is intrinsically disordered in its monomeric pre-fusion state but forms an α-helix during the SNARE complex formation.

Large amounts of isotopically labeled protein can be produced (here using *E.coli*), which is a requirement for structural studies by Nuclear Magnetic Resonance (NMR). The expression is done in a minimal media supplemented by the addition of ^{13}C glucose and ^{15}N ammonium chloride. The Syb2, comprising a C-terminal transmembrane region, is reconstituted into lipid nanodiscs to study the SNARE protein in a near-physiological lipid environment.

The SNARE protein is investigated by solution and fast MAS solid-state NMR. The solution NMR is used to get the first insides into the dynamic and interactive region of the protein with the lipid environment. The fast MAS solid-state NMR measurements are not limited by the weight limitation that solution NMR faces. Using fast MAS solid-state NMR, it is possible to detect protons and compare their chemical shifts to the solution NMR spectra. The first measurements indicated an influence of the phospholipids used for the lipid nanodisc and on the conformation of Syb2.

We aim for detailed structural and dynamic insights into the SNARE motif and linker domain region interacting with the lipid bilayer membrane. Further we want to gain currently unavailable experimental structural insights on the C-terminal transmembrane region of Syb2 in the lipid membrane environment.

Investigations on light-driven processes in novel biomimetic [FeFe]-hydrogenase complexes

K. Rediger, Kaiserslautern/DE, C. Kasahara, Jena/DE, I.Basma Jena/DE,
S. Kupfer, Jena/DE, H. Abul-Futouh, Zarqa/JO, M. Micheel, Kaiserslautern/DE,
W. Weigand, Jena/DE, M. Wächtler, Kaiserslautern/DE
Katharina Rediger, Chemistry Department and State Research Center OPTIMAS,
RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern

[FeFe]-hydrogenases are enzymes with the ability of hydrogen formation by the reduction of protons. This functionality inspired the development of various biomimetic complexes for the synthesis of green hydrogen. These artificial systems can be activated via electrochemical reduction of the [FeFe]-center or in a light-driven mechanism by activation with a photosensitizer in presence of a sacrificial electron donor. By linkage of sensitizer and catalyst systems can be designed which can be activated by absorption of visible light. [1] Usually an electron transfer from the reductively quenched sensitizer to the [FeFe]-center is discussed.

In this work three novel biomimetic hydrogenase complexes each consisting of a catalytic active diiron center directly linked to light-harvesting oligothiophene units are characterized by steady-state absorption and emission and time-resolved transient absorption spectroscopy. Calculations indicate two potential mechanisms, one based on an electron transfer step, the other involving an energy transfer from the excited sensitizer to the [FeFe]-center. Our results show that the investigated biomimetic complexes all revealed different pathways of the formation of the activated [FeFe]-center. Depending on the exact nature of the sensitizer either the energy transfer or the electron transfer is preferred. The third investigated sensitizer-catalyst dyad contains an additional electron donating functionality. In this species a fast intramolecular reductive quenching of the sensitizer supports the electron transfer pathway.

Literature:

[1] P. Buday, Angew. Chem. Int. Ed. 2022, 61, 20.

Zero-field splittings in photo-generated high-spin main group compounds studied by THz-EPR

T. Al Said, Berlin/GER, M. Neben, Göttingen/GER, K. Holldack, Berlin/GER, S. Schneider, Göttingen/GER, A. Schnegg, Mülheim an der Ruhr/GER
Tarek Al Said, Department Spins in Energy Conversion and Quantum Information Science, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Straße 16, 12489 Berlin

In contrast to transition metal or lanthanide ions, that often exist in a high-spin state with $S > 1/2$ due to ferromagnetic coupling of multiple electrons in their d or f orbitals, respectively, such strongly coupled high-spin systems are rare in main group compounds. Subvalent main group species, such as nitrenes, frequently have triplet ground states [1,2], but are usually highly reactive transient species. Only recently, the higher homologues of group 15, i.e., triplet phosphinidene [3] and bismuthinidene [4] species could be stabilized and characterized. The coupling of electrons in high-spin states results in a zero-field splitting (ZFS) caused by the spin-orbit coupling that scales with the atomic number. The detection of large ZFS is optimally performed by high-field / high-frequency electron paramagnetic resonance (EPR) methods, such as field-domain Fourier-transform THz-EPR (FD-FT THz-EPR) spectroscopy [5].

Here, we report the spectroscopic characterization of a series of light-generated metallopnictinidenes MPn (M=Pd, Pt; Pn=N, P, As, Sb) with a triplet ground state, generated by photolysis of precursor molecules at cryogenic temperatures. The photoreaction is followed by mid-infrared spectroscopy showing different yields of the photoproduct depending on the precursor. FD-FT THz-EPR studies on the photo-generated molecules show a high ZFS, that is correlated with the atomic number. The results will help to reveal the impact of spin-orbit coupling on the reactivity of this largely unexplored class of molecules and to benchmark quantum chemical calculations of relativistic effects.

Literature:
[1] Sun et al., Nat. Chem. 2020, 12, 1054 – 1059. [2] Schmidt-Räntsch, T. et al., Angew. Chem. Int. Ed. 2022, 61, e202115626. [3] Akimov et al., Angew. Chem. Int. Ed. 2017, 56, 7944 – 7947. [4] Pang et al., Science. 2023, 380, 1043 – 1048. [5] Nehrkorn, J. et al., J. Magn. Reson. 2017, 280, 10 – 19.

Probing mechanochemical racemic-crystal formation by solid-state NMR spectroscopy

S. Moos, Mülheim (Ruhr) & Aachen/D, C. Quaranta, Aachen/D, I. d'Anciães Almeida, Mülheim (Ruhr)/D, E. Bartalucci, Aachen/D & Mülheim/D, C. Bolm, Aachen/D, T. Wiegand, Aachen/D & Mülheim (Ruhr)/D
Sven Moos, Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim/Ruhr, Germany & Institute for Technical and Macromolecular Chemistry Worringerweg 2, 52074 Aachen, RWTH Aachen University, Germany

Chirality of molecules plays an important role, as the properties of the enantiomers can change in a chiral medium. An essential phenomenon is their mutual molecular recognition, where the physical properties of the enantiopure compounds can be altered due to a change in the crystal structure.[1,2]

The attention towards the implementation of chemical reactions aligned with the principles of "green chemistry" has increased over the past years. Consequently, there is a growing interest in mechanochemistry due to its capability to circumvent the requirement for solvents in conventional organic reactions, thereby unlocking novel reaction pathways.[3] Molecular recognition processes of enantiomers can be promoted through the use of ball milling. This approach combines a synergistic interplay of mixing, pressure, and reduction in particle size, each of which affects reactions in the solid state and thus the formation of racemic crystals. To disentangle these effects, techniques such as Resonant Acoustic Mixing (RAM) can be employed. RAM leads only to the oscillation-induced mixing of reactants without inducing an increase of the pressure or temperature or leading to particle-size reduction.[4] Solid-state NMR is well-suited for analyzing mechanochemical reactions, as samples can be investigated without changing their aggregation state by dissolving the material.

We have investigated various formations of racemic crystals from mixtures of the enantiomeric compounds using mechanochemical approaches. Primarily, the formation of racemic crystals of trifluoromethyl lactic acid (TFLA) was examined. By mixing equimolar ratios of TFLA enantiomers and reacting them in the ball mill, racemic crystals are formed. The formation of such phases can then be followed by solid-state NMR ^{13}C cross-polarization (CP) experiments, as the carboxyl group of TFLA exhibits detectable chemical-shift changes upon racemic-crystal formation compared to their enantiopure counterpart. Racemic-crystal formation was also performed using RAM, which allowed for a more detailed investigation of the influence of pure mixing on such molecular-recognition events.

Literature:
 [1] (a) S.H. Wilen et al., *Stereochemistry of Organic Compounds*, John Wiley & Sons: **1995**; pp 179-183. (b) J. Jacques, A. Collet, S.H. Wilen, H. Krieger, *Enantiomers, Racemates, and Resolutions;* **1994**, pp 162-165.
[2] R. Breslow, Z.-L. Cheng, Proc. *Natl. Acad. Sci.* **2009**, *106*, 9144.

[3] S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413-447.
[4] A. L. Michalchuk, K. S. Hope, S. R. Kennedy, M. V. Blanco, E. V. Boldyreva, C.R. Pulham, *Royal Soc. of Chem.* **2018**, *54*, 4033-4036.

Amplified Spontaneous Emission in Colloidal Nanoplatelets: Towards Lasing in Hollow Core Glass and Polymer Fibers

D. A. Rudolph, D-30167 Hannover, L. F. Klepzig, D-30167 Hannover, S. Spelthann, D-30167 Hannover, V. Adolfs, D-30167 Hannover, D. H. Chau, D-30167 Hannover, S. L. Hachmeister, D- 38106 Braunschweig, F. Li, D- 38106 Braunschweig, Dr. H. H. Johannes, Dr. M. Steinke, D-30167 Hannover Germany, Prof. Dr. W. Kowalsky, D-38106 Braunschweig, Prof. Dr. D. Ristau, D-30167 Hannover Germany Hannover, Prof. Dr. H. Menzel, D-38106 Braunschweig

Jun.-Prof. Dr. Jannika Lauth Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen and Leibniz Universität Hannover, Callinstr. 3A, D-30167

Colloidally synthesized cadmium chalcogenide-based 2D nanoplatelets (NPLs), especially core-crown heterostructures, display a high photoluminescence quantum yield and large absorption and gain cross sections [1] as well as low Auger recombination rates. [2] This makes these colloidal nanoemitters promising for optical applications e.g., in lasing and LEDs. [3] Due to an anisotropic emission pattern of the NPLs along their lateral surface normal, many current applications, which rely on a flat-on orientation of the NPLs in deposited thin films, are limited in making full use of the light-matter interactions in the nanostructures, e.g., light redirection. [4]

Here we investigate two fiber-based approaches to incorporate bright CdSe/CdS core-crown NPLs in optical applications for amplified spontaneous emission (ASE) towards lasing. The first method is based on colloidally dispersing NPLs inside a micrometer scaled core of hollow core glass fibers. By choosing solvents with a sufficient refractive index, the light emitted by the NPLs is waveguided to the ends of the fiber. Our custom-built setup also allows for the incoupling of a light source into the fiber on the longitudinal axis. By pumping the NPLs with an in-core pump fluence of 360 μJ/cm^2 at an excitation wavelength of 480 nm we observe the onset of a slightly redshifted amplified spontaneous emission (ASE) at 532.5 nm. [5]

In the second approach, we use stable-jet electrospun PMMA fibers with encapsulated bright CdSe/CdS core-crown NPLs. Here, the NPLs align perpendicular to the fiber axis during the fiber formation [6]. The fixed alignment inside the polymer in combination with an isotropic absorption of the NPLs allows for efficient perpendicular or longitudinal excitation. Both approaches are investigated towards ASE and lasing behavior.

Literature:
[1] A. Yeltik et al., J. Phys. Chem. C 2015, 119, 47, 26768–26775.
[2] A. Poloyitsyn et al., Chem. Mater. 2017, 29, 13, 5671–5680.
[3] Q. Zhang et al., ACS Photonics 2023, 10, 5, 1397-1404.
[4] F. Li et al., Langmuir 2022, 38, 37, 11149–11159.
[5] S. Spelthann et al., arXiv:2303.09624.
[6] X. Liu et al., Macromol. Mater. Eng. 2023, 308, 2300027.

146

Surfaces and Interfaces

Formation of {111} oriented defects in heteroepitaxial Ir/YSZ/Si(001) layers

Dr. Jürgen Weippert, Freiburg im Breisgau/D

Dr. Lutz Kirste, Freiburg im Breisgau/D

Dr. Patrik Straňák, Freiburg im Breisgau/D

MSc. Balasubramanian Sundarapandian, Freiburg im Breisgau/D

Dr. Jan Engels, Freiburg im Breisgau/D

Dipl.-Ing. Sabine Oeser, Freiburg im Breisgau/D

Dr. Andreas Graff, Halle an der Saale/D

Dr. Vadim Lebedev Freiburg im Breisgau/D

Main author address:

Fraunhofer-Institut für Angewandte Festkörperphysik IAF

Tullastraße 72

D-79108 Freiburg im Breisgau

Heteroepitaxial Ir/YSZ/Si(001) layers, in which YSZ stands for Yttria-Stabilized Zirconia, are required for the preparation of wafer-scale heteroepitaxial diamond films. In the fabrication of these Ir films by magnetron sputtering epitaxy (MSE), two types of {111} oriented defects are observed:

(a) direct processes, i.e. processes in which Ir and YSZ deposited onto the wafers while these remain placed on the same carrier in uninterrupted vacuum, predominantly lead to fjord-shaped {111} oriented defects with an internal lamellar structure. They occur in four rotational variants in which the longitudinal axis of the fjord follows the [100], [010] and reverse directions.

(b) separated processes, i.e. processes in which the two epilayers are deposited in fully separated sequences using different carriers for each of the materials, thus having to interrupt the vacuum in between the depositions, predominantly lead to {111} defect islands with less defined borders. These islands occur in eight rotational variants.

In this talk, we present analyses of these defects using scanning electron microscopy, X-ray diffraction, electron backscatter diffraction, secondary ion mass spectrometry and high-resolution transmission electron microscopy followed by our layer preparation strategy to avoid the formation of these defects.

Layer-by-Layer Deposition of Thin Films based on Polyoxometalate-Composites

R. Frigge, Freiberg/GER, Prof. Dr. Y. Joseph, Freiberg/GER, Technische Universität Bergakademie Freiberg, Gustav-Zeuner-Straße 3, 09599 Freiberg

Polyoxometalates (POM) are a promising class of materials for several fields of application. They can be used as catalysts, for energy storing applications, active sensor materials, as dyes, in medicine and for hole transport layers in organic solar cells. In the field of sensors, they can be used to detect gases, high energy light, pH-value and changes in the redox potential. Especially for the latter, many POMs react with a change in their colour. Thus, they are interesting for electrochromic devices. [1], [2] For these applications it is necessary to produce thin layers containing POM, which is usually achieved by layer-by-layer dip coating, even if the coating process and the used relevant parameters are only poorly understood. [3]

Thus, in this work the deposition of POM-polymer-composites on substrates was studied with automated in-situ quartz-microbalance measurements (QCM-D) and the resulting layers were characterised by optical microscopy, laser scanning microscopy, XPS and AFM. In particular, $(NH_4)_6[H_2W_{12}O_{40}]$, $(NH_4)_3H_6[CrMo_6O_{24}]$ and $(NH_4)_6[MnMo_9O_{32}]$ in combination with polyethylenimine and three generations (G1-G3) of polypropylenimine-dendrimers were deposited based on electrostatic forces between the poly-anions of the POMs and the polymers. The effects of the deposition time, flow-rate, concentrations and the ionic strength in the solutions were optimized to get homogenous thin films with metal-like conductivity. Furthermore, these investigations provide an insight into the deposition process and the possibilities to improve the deposition by adjusting the ionic strength in the solutions to fabricate thin films for advanced applications in the future.

Literature:

[1] Toshihiro Yamase, Chem. Rev. 1998, 98, 307-325. [2] M. Ishaque Khan, Cryst. Growth Des. 2013, 13, 4667−4672. [3] Shaoqin Liu, Journal of Cluster Science, Vol. 14, No. 3, 2003.

Silver-Based Semiconductor Nanoparticles for Novel Transistor Structures

N. Metzkow, Dresden/+49, Prof. Dr. Alexander Eychmüller
Technical University Dresden, Zellescher Weg 19, 01069 Dresden

Smartphones, computers, televisions, radios, power chargers - transistors can be found in almost every electronic device. Nowadays, such electronic components are expected to become smaller, flexible, and more powerful. However, a high-performance, flexible, thin-film transistor technology is still missing.

Semiconductor nanocrystals (NCs) have the potential to achieve a breakthrough in transistor performance, as they are processed solution-based and can overcome the intrinsic low carrier mobility of organic semiconductors. In the last decades, different functional NCs have been successfully fabricated. It is possible to precisely control the physical and electronic properties of NCs via parameters such as size, shape and composition. Using them in different transistor architectures is promising, as studies with CdSe NCs have shown recently.[1]

In this work, we strive to use different NCs for transistors, which allow to easily realize high-performance devices without nanostructuring. Therefore, NCs like Ag_2S or $AgInS_2$ are synthesized to replace the widely studied but more toxic Cd- or Pb-containing materials. To improve the electronic communication, the insulating organic ligands necessary for the synthesis are exchanged with inorganic ligands (I^-, Br^-, S^{2-}, SCN^-) in simple solution-based phase transition ligand exchanges. The materials are then characterized in terms of their film-forming properties and electronic parameters. [2,3]

Literature:
[1] Fan, X., J. Phys. Chem. Lett., 2019, 10(14), 4025–4031. [2] Stroyuk, O., J. Phys. Chem. C, 2018, 122, 25, 13648–13658. [3] Sayevich, V., Chem. Mater., 2015, 27, 12, 4328–4337.

Nanostructure of Metal Nanoparticle Covered Supported Ionic Liquids Studied by Nano-IR Spectroscopy

C. Mehrmann, Düsseldorf/DE; J. Johny, Mülheim a. d. Ruhr/DE; P. Ebbinghaus, Düsseldorf/DE; A. Das, Düsseldorf/DE; M. F. Tesch, Mülheim a. d. Ruhr/DE; M. Rabe, Düsseldorf/DE

Carolin Mehrmann, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf

Preparation of imidazolium-based supported ionic liquid phases (SILPs) on ultra-flat Si/SiO2 substrates followed by deposition of Ru metal nanoparticles (NPs) is investigated. This system serves as a model for NP@SILP systems on silica used as hydrogenation catalysts [1] and the study aims to promote a fundamental understanding of the interplay between the NP@SILP nanostructure and its catalytic properties. Each fabrication step was followed by spectroscopic

Fig. 1: *Nano-IR image of NP@SILP imaged at $v_{as}(CH_3)$ = 2956 cm^{-1} showing metal NP in dark and IL aggregates in lighter color.*

ellipsometry and infrared spectroscopy (IRRAS and ATR-IR) which yielded a quantitative assessment of the SILP thickness and insight into the molecular order of the IL monolayer at the interface. In addition, photothermal nano-IR spectroscopy studies of the SILP and NP@SILP provided insight into their nanostructures. The SILPs were found to be composed of continuous monolayers with thicknesses in the range of the expected molecular length, indicating low tilt angles of the molecules. Nanoscopic heterogeneities in the form of circular features were detected, which can be attributed to adsorbed molecular aggregates of the ILs, as shown by nano-IR spectroscopy. The subsequent deposition of metal NPs on the SILPs led to the formation of a complex heterogeneous material, on which nano-IR spectroscopy allows to clearly distinguish between metal NP and IL aggregates by chemical imaging (Fig. 1). Depending on the method of NP deposition, either by organometallic synthesis or direct sputtering, different morphologies and NP distributions were observed and it was found that the SILP stabilizes the NP attachment on the surface. This work sheds light on important details of the NP@SILP system and opens a path for future nanoscopic studies on catalysts, based on molecular modified surfaces.
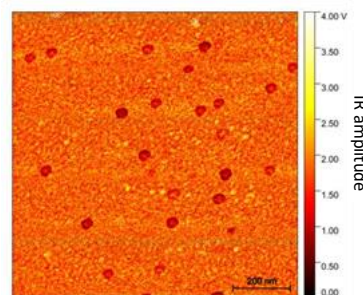
[1] A. Bordet, W. Leitner, *Acc. Chem. Res.* **2021**, *54*, 2144–2157.

Controlled Growth of Two-Dimensional SnSe/SnS Core/Crown Heterostructures by Reactivity of the Precursors

J. Schulz, Hamburg/DE, A. Mews, Hamburg/DE

Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany

Tin(II)selenide (SnSe) and tin(II)sulfide (SnS) are promising materials due to their optoelectronic properties and their low toxicity. They have great potential for applications in solar cells because of a high absorption coefficient, high electrical conductivity and because the energies of the direct bandgaps coincide with the spectral range required for these applications. Moreover, there is an increasing interest in the formation of two-dimensional (2D) heterostructured nanosheets, where many different possible material combinations allow for extending the range of properties in 2D systems.

We report on the synthesis of SnSe/SnS nanosheets. Starting from SnSe nanosheets, which we synthesized using a one-pot reaction technique with tin(II)chloride, hexamethyldisilazane and selen precursor in oleylamine, we produced two-dimensional heterostructures by continuously adding various amounts of sulfur precursor to a hot solution of the SnSe nanosheets. The structure of the final heterostructure can be controlled by the variation of the precursors. We can therefore control the number and position of the crowns in a core/crown heterostructure system and synthesize different kinds of heterostructures, for example SnSe wires with a SnS tip.

The SnSe/SnS nanosheets were investigated via TEM, AFM and optical methods, e.g., Raman spectroscopy. EDX and XRD measurements were utilized to determine the elemental composition and the crystal structure of the nanosheets.

Investigating the phase behavior of polymer blends at the air-water interface at the molecular level

B. Kővágó, Vienna/AT, Z. Peng, Cergy/FR, A. el Haitami, Cergy/FR, S. Cantin, Cergy/FR and E. H. G. Backus, Vienna/AT
Bence Kővágó, University of Vienna, Währinger Straße 42, 1090 Vienna

In numerous cases (e.g., paints, adhesives), polymer blends offer improved properties compared to pure polymers, but they often undergo phase separation in three-dimensional blends. In order to avoid this phase separation, the idea of cross-linking monomolecular-thick Langmuir polymer film networks has been shown to be a successful approach [1]. Transferring these cross-linked networks onto a solid substrate is considered one of the most effective ways for tailoring nanometer-thick films with well-defined properties.

As a first step to design such films, the miscibility properties of non-cross-linked polymer blends have to be understood. In this presented study, we aim to understand the miscibility behavior of amphiphilic poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (PEG-PPG-PEG) triblock copolymer and hydrophobic poly(dimethylsiloxane) (PDMS). Both polymers are insoluble in water and form a Langmuir monolayer at the air-water interface.

Brewster angle microscopy (BAM) and compression isotherms are used to determine the mixing behavior on the macroscopic and mesoscopic scales, respectively. With sum frequency generation spectroscopy (SFG), an interface specific technique, we obtain the vibrational spectrum of the polymer mixtures present at the water surface.

By varying the compositions, we measured the surface pressure and obtain BAM images in order to establish the pressure-composition phase diagram of the polymer mixtures. Complete miscibility was observed at low surface pressure regardless of the composition. At high surface pressure, phase separation was noted for given composition. On a molecular level, the SFG results obtained at different composition and surface pressure provide information about the orientation and interaction strength. With these results, we aim to gather a thorough microscopic and macroscopic understanding of the PEG-PPG-PEG/PDMS system.

Literature:
[1] A.-S. Vaillard, A. el Haitami, L. B. Drecker, P. Fontaine, F. Cousin, P. Gutfreund, M. Goldmann, E.H.G. Backus, S. Cantin, Langmuir, 2022, 38, 8, 2538-2549.

Metalworking influence on the
corrosion behaviour of sterling silver and silver-coated copper

V. Ljubić Tobisch, Vienna/A, A. Selimović, Vienna/A, <u>W. Kautek, Vienna/A</u>
Prof. Dr. Wolfgang Kautek, University of Vienna, Währinger Straße 42,
A-1090 Vienna, Austria

Metalworking methods of silver and silver-plated copper artefacts may strongly influence their corrosion behaviour [1,2]. Various surface states were generated on sterling silver dummy coupons as well as silver-plated copper to simulate surface finishing procedures on historical silver artefacts. Coupons were either polished by hand, by a fabric disc on a polishing machine, or submitted to a hammering process in reference to the as-received state. All samples were subjected to various aging protocols, such as natural aging, a thioacetamide (TAA) gas test (NBN EN ISO 4538:1995) and a Na_2S immersion test (NBN EN ISO 8891:1998). The tarnishing and morphology evolution were evaluated by colorimetry, optical microscopy and scanning electron microscopy. The various surface finishing procedures led to marked differences in the tarnishing behaviour. The evaluation of these phenomena can aid the development of techniques to mitigate corrosion on such metal artefacts such as selective reductive treatment by means of an electrolytic pencil [3].

Literature:
[1] Scott DA., Ancient metals : microstructure and metallurgy, Los Angeles: Conservation Science Press, 2011. [2] Novakovic J, Vassiliou P, Georgiza E., Int. J. Electrochem. Sci. 2013, 8, 7223–32. [3] Ljubić Tobisch V, Selimović A, Kautek W., Stud. Conserv, 2023, 68, 657-668.

Graphene coating generation by femtosecond Laser-assisted reduction of Graphene Oxide

M. Pfaffeneder-Kmen, Vienna, Aida Naghilou, Vienna, A, Ignacio Falcón Casas, A,
<u>Wolfgang Kautek, Vienna, A</u>
Prof. Dr. Wolfgang Kautek, University of Vienna, Währinger Straße 42, A-1090
Vienna, Austria

Graphene oxide is a potential precursor for graphene. The mechanism of the electrochemical [1,2] as well as of a femtosecond laser-assisted reduction to reduced graphene oxide have been the focus of this present study. An electrochemical quartz crystal microbalance was utilized to perform mass-sensitive measurements during the electrochemical deposition of graphene oxide. The mechanism of the electrochemical reduction was investigated by in-situ attenuated total reflection FTIR spectroscopy. A multivariate method was applied for evaluating the spectra. It could be shown that the reduction occurs in two steps. At first graphene oxide is reduced to □reduced graphene oxide. In a second step, it is reduced to □reduced graphene oxide.

Literature:
[1] M. Pfaffeneder-Kmen, F. Bausch, G. Trettenhahn, W. Kautek, J. Phys. Chem. C 2016, 120, 15563-15568. [2] M. Pfaffeneder-Kmen, I. Falcon Casas, A. Naghilou, G. Trettenhahn, W. Kautek, Electrochim. Acta 2017, 255, 160-167.

Surface Chemistry of a (Sub-)monolayer [C$_2$C$_1$Im][OTf] Film on Pt(111): A Combined XPS, IRAS, and STM Study

Hanna Bühlmeyer, Erlangen/DE, Timo Talwar, Erlangen/DE, Roman Eschenbacher, Erlangen/DE, Jade Baretto, Erlangen/DE, Jonas Hauner, Erlangen/DE, Florian Maier, Erlangen/DE, Hans Peter Steinrück, Erlangen/DE, Jörg Libuda, Erlangen/DE

Hanna Bühlmeyer, FAU Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, DE

In a solid catalyst with ionic liquid layer (SCILL), ionic liquid (IL) coatings are used to modify noble metal catalysts to improve their selectivity. In order to understand the origins of this selectivity control, we performed model studies by surface science methods in ultrahigh vacuum (UHV). We investigated the growth and thermal stability of an ultrathin IL film by infrared reflection absorption spectroscopy (IRAS) and X-ray photoelectron spectroscopy (XPS) in time-resolved and temperature-programmed experiments. We combined these spectroscopy experiments with scanning tunneling microscopy (STM) to obtain detailed insights into the orientation and adsorption geometry of the ions, and the wetting behavior in the first IL layer. Furthermore, we propose a mechanism for the thermal evolution of the IL 1-ethyl-3-methyl-imidazolium trifluormethanesulfonate [C$_2$C$_1$Im][OTf] on Pt(111).

In specific, we studied [C$_2$C$_1$Im][OTf] on a Pt(111) single crystal surface. We observe an intact IL layer on the surface at temperatures below 200 K. The adsorbed [C$_2$C$_1$Im][OTf] forms islands, which are evenly distributed over the surface with no preferential adsorption site. The [OTf]$^-$ anion adsorbs via the SO$_3$ group with the molecular axis perpendicular to the surface. Anions and cations are arranged next to each other, alternating on the Pt(111) surface. Upon heating to 250 K, we observe changes in geometry and structural distribution. Whereas, at low temperature, the ions are arranged alternately for electrostatic reasons, this driving force is no longer decisive at 250 K. Here, a phase separation of two different species are discernible in STM. We propose that this effect is due to a surface reaction, which changes the charge of the adsorbates. We assume that the IL starts to decompose around 250 K and, thus, pristine IL and decomposition products coexist on the surface. Also, IRAS and XPS show indication of IL decomposition. Further heating leads to increased IL decomposition. The reaction products associated with the anions are volatile and leave the surface. In contrast, the cation fragments remain on the surface up to temperatures above 420 K.

Spectroscopic and microscopic study of (car)borane-based 2D materials

M. Frey[1], J. Picker[1], J. Višňák[2], C. Neumann[1], T. Baše[2], A. Turchanin[1]

*[1]Friedrich Schiller University Jena, Institute of Physical Chemistry,
Lessingstraße 10, 07743 Jena, Germany*
*[2]The Czech Academy of Sciences, Institute of Inorganic Chemistry,
250 68 Husinec-Rez, c.p. 1001, Czech Republic*

Boron hydride clusters (also referred to as boranes) represent a special class of molecular materials with several features that distinguish them from their carbon-based counterparts. These boron and hydrogen containing molecules show high structural diversity and unique electronic properties, both a consequence of the electron deficiency of boron. The cage-like molecules feature three-center two-electron bonds, enabling the formation of hydrogen bridges between boron atoms, μ-BHB. Among larger macropolyhedral boranes, obtained by the fusion of smaller cluster precursors, two isomers of $B_{18}H_{22}$ (docosahydrooctadecaboranes) have received significant attention due to their luminescent properties. Their structural and chemical characteristics, together with their interactions with light, make them promising candidates for a wide range of applications, including energy storage, semiconductor doping, and nano- and optoelectronic devices. Here we present the preparation of novel boron-based and completely carbon-free two-dimensional (2D) nanomembrane material using electron irradiation-induced crosslinking of borane-based self-assembled monolayers (SAMs). To accomplish this goal, the SAMs of two isomeric HS-$B_{18}H_{21}$ thiol derivatives were prepared by physical vapor deposition on Ag(111) substrates and subsequently irradiated with low-energy electrons in ultra-high vacuum. The self-assembly, its electron-induced crosslinking, and the mechanical stability of the formed nanosheets (nanomembranes) were studied by complementary surface sensitive techniques including X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), low-energy electron diffraction (LEED) as well as by scanning tunneling and electron microscopies (STM, SEM). Furthermore, the results were compared with the carborane-based 2D nanomaterials studied previously in our labs. The data clearly demonstrate that properties of the ~1 nm thick (car)borane nanosheets can be adjusted and tailored by the respective SAM constituents and that these structurally diverse cluster molecules open up new avenues for engineering novel functional 2D materials. [1]

Literature:
[1] D. K. Patel, B. S. Sooraj, K. Kirakci, J. Macháček, M. Kučeráková, J. Bould, M. Dušek, M. Frey, C. Neumann, S. Ghosh, A. Turchanin, T. Pradeep, T. Baše, *J. Am. Chem. Soc.* 145 (**2023**) 17975-17986.

Antimicrobial 2D materials for bone implants

R. Ennaciri[1], C. Neumann[1], S.H. Han[1], Z. Gan[1], A, George[1], G. Gupta[2],
L. Tuchscherr de Hauschopp[2], A. Turchanin[1]

[1]*Friedrich Schiller University Jena, Institute of Physical Chemistry,
Lessingstraße 10, 07743 Jena*
[2]*Jena University Hospital Institute of Medical Microbiology Am Klinikum 1 07747 Jena*

Antibiotic resistance presents an important issue in the medicine field particularly in the context of bone replacement surgeries, where infections from antibiotic-resistant bacteria can lead to severe health complications and even fatalities. Therefore, it is crucial to design new biomaterials that, on the one hand, prevent bacterial adhesion or proliferation and, on the other hand, promote osteoblast growth.

While titanium serves as the conventional choice for bone implants, there is a clear need for further improvements of this material to enhance its antimicrobial resistance. In this regard, hybrids based on two-dimensional (2D) materials, such as molybdenum disulfide (MoS_2) and graphene present a great promise due to their intrinsic antimicrobial activity and biocompatibility.

In this work, we focus on the functionalization of titanium surfaces with MoS_2 nanowalls and graphene derivates to enhance their antimicrobial properties. Scanning electron microscope (SEM), Raman spectroscopy and X-ray electron microscopy (XPS) are used to characterize the structural and chemical properties. Additionally, surface plasmon resonance (SPR) is employed to study the adhesion and interaction of bacteria with the formed hybrid surfaces.

The antimicrobial property of the functionalized titanium surfaces was investigated by exposing the material to *S. aureus* strain USA300. After bacterial attachment, adherent and non-adherent bacteria were counted. The effect of each material on the bacterial phenotype was also investigated. Bacterial adhesion was visualized by fluorescence microscopy.

Dissipative supramolecular equilibrium-balanced actuation and motion of messenger droplets

Lukas Zeininger, Potsdam/D

Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam/D

Autonomous chemo-mechanical signal transduction is an inherent feature by which natural systems exert control over complex biological functions and is therefore essential for the emulation and delineation of complex emergent behaviors in artificial dissipative material systems. In this contribution, the design of a synthetically minimal, artificial, complex emulsion platform that, regulated by interfacial supramolecular recognition events, is capable to autonomously and reversibly adapt to its chemical environment will be presented. Surfactant stabilized droplets intrinsically persist in a thermodynamically out-of-equilibrium state and are highly dynamic. Interface-selective sensitization of droplets with supramolecular motifs allows such systems to exhibit programmed up- and down-regulating capabilities and reversible interfacial host–guest complexation can trigger morphological reconfigurations of the complex droplets, which mediate their ability to selectively present, or hide liquid–liquid interfaces.[1] These droplets thereby can serve as messenger colloid to visualize, measure and to report force gradients in temperature, chemistry, and concentration quantitatively, and with up to femtomolar sensitivity.[2]

In addition, an exploration of basic physico-chemical stability parameters of these novel types of complex fluids enables the creation of artificial soft matter systems that exhibit chemo-intelligence in that they are capable to autonomously operate in response to (bio-) chemical cues.[3] To this end, we have realized messenger droplets that move chemotactically and reversibly in response to interfacial tension differentials,[4] tilt out of gravitational alignment, caused by multivalent chemical interactions or intra-droplet thermocapillary fluid convections,[1,2] and combining a series of these separate responsive modalities as well as having control over the dynamic partitioning of solutes provides as a tool to characterize multiple supramolecular interactions independently. Building on these findings, collaborative effects form the basis for the realization of droplets that exhibit unprecedented decentralized chemo-intelligence, where dynamic and triggerable supramolecular events can balance a reversible tactile response of all-liquid matter, with significant implications for future soft robotic and sensing technologies.

[1] S. Djalali, P. Simón Marqués, B. D. Frank & L. Zeininger, *Adv. Funct. Mater.* **2022**, 2107688. [2] B. D. Frank, M. Antonietti, P. Giusto & L. Zeininger, *J. Am. Chem. Soc.* **2023**, *145*, 24476. [3] A. W. Baryzewska, C. Roth, P. H. Seeberger & L. Zeininger, *ACS Sens.* **2023**, *8*, 4143. [4] B. D. Frank, S. Djalali, A. W. Baryzewska, P. Giusto, P. H. Seeberger & L. Zeininger, *Nat. Commun.* **2022**, *13*, 2562.

Novel fast-X-ray Reflectivity setup for studying electrochemical interfaces

W. Corts, S. Frücht, X. Ge, T. Matar, Prof. H.-G. Steinrück, Jülich/DE
F. Bertram, M. Lippmann, Deutsches Elektronen-Synchrotron DESY, Hamburg/DE
Forschungszentrum Jülich, Institute for a Sustainable Hydrogen Economy (INW),
Am Brainergy Park 4, 52428 Jülich, Germany

A fundamental understanding of atomic scale processes occurring at electrochemical interfaces is crucial for advancing the development of energy-related electrochemical systems such as ion batteries or fuel cells. For this purpose, *operando* experiments are imperative. X-ray reflectivity (XRR) is a non-destructive technique that enables *operando* analysis of buried structures with atomic resolution [1,2]. However, the time-resolution of typical XRR setups of minutes per XRR scan is limited by diffractometer motor motion and detector read-out times; this resolution is in many cases too slow to observe interfacial electrochemical phenomena [1,2].

To overcome these limitations, we developed a novel fast-XRR setup, which employs a fast quasi-continuous rotation stage in combination with a stationary, high frame rate area detector. With this setup, the sample can be rotated with a frequency of up to 10 Hz, yielding sub-second time resolution for an individual XRR scan. In contrast to complementary fast-XRR setups [3,4], the presented setup can easily be combined with complex sample environments, as typically required for the investigation of electrochemical interfaces.

We present first fast-XRR results obtained at PETRA III beamline P08 at DESY using 18 keV and a Dectris Eiger1M detector. We reached a time resolution below one second for an incident angular range between $0° - 6°$ ($\triangleq 0 - 2$ 1/Å). We measured several multilayer samples and benchmarked the results to "standard" XRR measurements, where the measurements took several minutes. We find good agreement and conclude, that our novel setup provides significant XRR data within less than one second, demonstrating its usability for *operando* XRR measurements.

Literature:
[1] C. Cao, H.-G. Steinrück, Encyclopedia of Solid-Liquid Interfaces, 391–416, Elsevier, 2024.
[2] C. Cao, H.-G. Steinrück et al., Nano Letters, 16, 12, 7394–7401, 2016.
[3] M. Lippmann et al. Review of Scientific Instruments, 87, 113904, 2016.
[4] H. Jorres et al., Applied Physics Letters, 114, 081904, 2019.

Magnetic Aerogels from FePt and CoPt$_3$ directly from Organic Solution

L. Schoske, Hannover/DE, F.Lübkemann-Warwas, Hannover/DE, I. Morales, Hannover/DE, C.Wesemann, Hannover/DE, J.G.Eckert, Hannover/DE, R.T.Graf, Hannover/DE, N.C. Bigall, Hannover/DE

M.Sc. Larissa Schoske, Prof. Dr. Nadja C. Bigall, Leibniz Universität Hannover,

Institute of Physical Chemistry and Electrochemistry, Callinstr. 3A, D-30167

Hannover

Magnetic nanoparticles are applied in different fields such as biomedicine, data storage, catalysis or hyperthermia.[1] To the present day mainly the not connected magnetic nanoparticles are used for applications while combining the magnetic properties with the high surface area and porous structure of aerogels[2] is beneficial.

Within this work magnetic assemblies were synthesized and characterized. The assemblies were formed in organic solution without a previous phase transfer to aqueous medium. Subsequently a characterization with the help of Transmission Electron Microscopy, Scanning Electron Microscopy and measurements on a Super Conducting Quantum Interference Device were performed to investigate the structure and the influence of the gelation process on the magnetic properties.

[1] A.-H. Lu, E. L. Salabas, F. Schüth *Angew. Chem. Int. Ed.* **2007**, 46, 1222-1244.

[2] P. Rusch, D. Zámbó, N. C. Bigall, *Acc. Chem. Res.* **2020**, 53, 10, 2414-2424.

Laser Direct Ink Writing of TMDC-based Photodetectors from Atomically Precise Gold Nanoclusters

W. Roberts, Tübingen/DE, M. Strienz, Tübingen/DE, A. Schnepf, Tübingen/DE, K. Braun, Tübingen/DE, M. Scheele, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen

Printed electronics is a quickly emerging concept in the manufacturing of microelectronic devices due to high compatibility with a large range of substrates and materials, low chemical waste production as well as highly customizable circuit manufacturing with numerous potential applications including wearable electronics, food packaging or sensor technology. [1]

Recently, Geladari et al. introduced a method for laser assisted direct ink writing of electrically conductive Au micro- and nanostructures utilizing the photolysis of atomically precise $Au_{32}(^nBu_3P)_{12}Cl_8$ gold nanoclusters [2] under laser illumination. [3] The method employs a low level of laser power, enabling sub-micrometer printing with diffraction-limited resolution.

By applying this technique to transition metal dichalcogenide (TMDC) monolayers, 2D semiconductor materials excellently suited for photosensing due to their optoelectronic properties, we aim to fabricate TMDC-based photodetectors with printed top contact gold electrodes to investigate their photogain as well as temporal response towards laser illumination, compared to devices from conventional metal evaporation. Through this research, we reveal the influence of the fabrication method on the structural and electrical transport properties of the formed metal-semiconductor interfaces. Our aim is to improve the detectivity and electrical bandwidth of TMDC-based photodetectors, which will be crucial for high frequency optical switching in future electronic applications.

Literature:
[1] D. Lupo, W. Clemens, S. Breitung, OE-A Roadmap for Organic and Printed Electronics in *Applications of Organic and Printed Electronics* (Ed.: E. Cantatore), Springer, Boston, **2013**, pp. 1–26. [2] S. Kenzler, F. Fetzer, C. Schrenk, N. Pollard, A. R. Frojd, A. Z. Clayborne, A. Schnepf, *Angew. Chem., Int. Ed.* **2019**, *58*, 5902. [3] O. Geladari, M. Eberle, A. Maier, F. Fetzer, T. Chassé, A. J. Meixner, M. Scheele, A. Schnepf, K. Braun, *Small Methods* **2023**, e2201221.

In-situ AFM Imaging of photocatalytically active semiconducting microcrystals

M. Voigtmann, Dresden/Germany, I. Siretanu, Enschede/Netherlands,
M. Wittmann Dresden/Germany J. Simmchen, Dresden/Germany & Glasgow/United Kingdom,
F. Mugele Enschede/Netherlands
M. Voigtmann, Technische Universität Dresden, Zellescher Weg 19, 01069 Dresden

$BiVO_4$ is a promising material for photocatalytic water splitting, as it shows a well-suited bandgap and is at the same moment producible from earth abundant and inexpensive materials. However, the material faces also various problems, such as stability issues and low efficiency.

To get a deeper understanding of such systems, we characterized the surface properties of hydrothermally synthesized faceted $BiVO_4$ micro crystals [1] *in situ* (i.e. in ambient electrolyte) on the nanometre scale using high resolution Atomic Force Microscopy (AFM) [2]. By that we were able to identify the crystallographic orientation. (Figure 1 a) From local force measurements we extracted surface charges to get insights in internal electric fields which are crucial for the electron hole separation. (Figure 1 b)
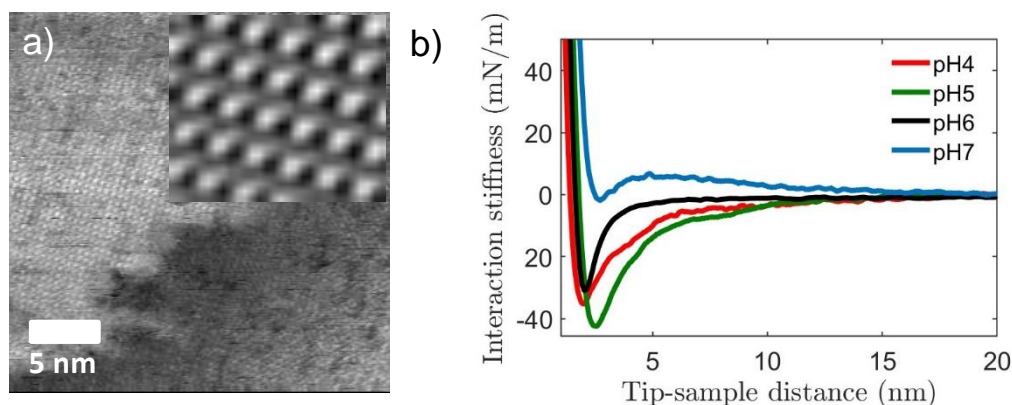

Figure 1: a) High resolution phase image (surface of a $BiVO_4$ crystal) Inset shows FFT filtered image. b) Interaction stiffness measured at different pH on $BiVO_4$.

Literature:

[1] Heckel, S., Adv. Sci. 2022, 9, 2105009.
[2] Su, S., Adv. Mater. 2021, 33, 2106229.

Defect engineering at MoS$_2$ interfaces by ion sputtering and heterostructuring

E.Juriatti, 72076 Tübingen DE, P.Haizmann, 72076 Tübingen DE,
apl. Prof. Heiko Peisert, University of Tübingen, Auf der Morgenstelle 18, 72076
Tübingen, Prof. Dr. Marcus Scheele, University of Tübingen, Auf der Morgenstelle
18, 72076 Tübingen.

To satisfy Moore's law new materials which allow a further miniaturization of semiconducting devices are highly anticipated. One promising candidate is the group of transition metal dichalcogenides (TMDCs) due to their exceptional physical and electronical properties.[1] By e.g., chemical doping and heterostructuring those properties can be further modified.[2] In this project, defects were selectively introduced in a bulk MoS$_2$ crystal by noble gas sputtering using both, argon and neon. The influence of these defects on interface properties to essentially physisorbed phthalocyanine molecules is studied. By sputtering, the formation of monosulfur vacancies is observed primarily which leads to a n-type doping of the system.[3] On the defect-rich surface, thin layers of one of the transition metal phthalocyanines CoPc and CoPcF$_{16}$ were deposited to form heterostructures. By fluorination, a tuning of the ionization potential of the phthalocyanine is possible which can lead to a change in the donor/acceptor characteristics of the given phthalocyanine as shown by Greulich *et al.*[4] for MoS$_2$/FePcF$_x$ (x= 0, 4, 16) interfaces with differently fluorinated iron phthalocyanines. To analyze the electronic properties of the heterostructure, XPS and UPS measurements were performed. The obtained data proves that both, Ne- and Ar-sputtering lead to a n-type doping of the system. A decrease in sulfur concentration in the crystal is observed which proves the formation of sulfur vacancies. While the deposition of CoPc does not show any charge-transfer processes localized on the Co-atom, the heavily n-type doped CoPcF$_{16}$/MoS$_2$ interface provides such an interaction for Co-atoms. With these results it is shown that defect engineering at MoS$_2$ is possible, and it can lead to interesting new structures, well-suited for semiconducting devices.

Literature:
[1] P. Haizmann, E. Juriatti et al., **2023**, DOI 10.26434/chemrxiv-2023-tj7m0.
[2] A. Chaves et al. *npj 2D Mater Appl* **2020**, *4*, 1–21.
[3] H. Qiu et al., *Nat Commun* **2013**, *4*, 2642.
[4] K. Greulich et al., *J. Phys. Chem. C* **2020**, *124*, 16990–16999.

Structure and chemical reactivity of clean and Pt-decorated oxide surfaces

Shuang Chen, Zairan Yu, Eric Sauter, Alexei Nefedov, Christof Wöll and Yuemin Wang

Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Metal oxides and oxide-supported noble metal catalysts have attracted enormous attention from both fundamental and technological perspectives due to their unique catalytic properties. Here, we present our recent work on systematic infrared spectroscopic investigations of pure and Pt-deposited Y-stabilized ZrO_2 (YSZ) and CeO_2 surfaces in the form of both well-defined single crystals (polarization-resolved IRRAS) and differently shaped nanoparticles (temperature-dependent IR transmission, and in-situ DRIFTS). The surface ligand IR (SLIR) approach using various probe molecules (in particular CO) was complemented by X-ray photoelectron spectroscopy, microscopic spectroscopy (STEM), atomic force microscope and density functional theory calculations. This surface-sensitive and non-destructive SLIR approach using a sophisticated UHV apparatus is well-suited to investigate the surface chemistry of metal/oxide catalysts.[1-3]

We report the first polarization-resolved IRRAS data of CO adsorption on the polar YSZ(100) single-crystal surface. The combined results demonstrated that the YSZ(100) surface is dominated by low-coordinated Zr^{4+} cations) in the presence of O vacancies generated by Y^{3+}-doping. The high chemical activity of the YSZ(100) surface was validated through the water dissociation reaction at 250 K. These reliable reference data allow for fundamental insights into the surface chemistry and CO-induced reduction of YSZ powders measured by in-situ DRIFTS in the CO atmosphere (1 bar) at 295 K. For Pt/CeO_2, the comprehensive spectroscopic data enabled to provide a thorough insight into the structural and electronic properties of both Pt and ceria support under different conditions.[4-7] We focused on the local structure, chemical coordination and reactive properties of oxide-supported Pt catalysts that vary strongly in charge state and size ranging from single atoms to small clusters and nanoparticles.

Literature:

[1] Y. Wang, C. Wöll, *Chem. Soc. Rev.* **2017**, *46*, 1875.
[2] A. Chen, X. Yu, Y. Zhou, S. Miao, Y. Li, S. Kuld, J. Sehested, J. Liu, T. Aoki, S. Hong, M. Farnesi Camellone, S. Fabris, J. Ning, C. Jin, C. W. Yang, A. Nefedov, C. Wöll, Y. Wang, W. Shen, *Nat. Catal.* **2019**, *2*, 334.
[3] S. Liu, Y. Li, X. Yu, S. Han, Y. Zhou, Y. Yang, H. Zhang, Z. Jiang, C. Zhu, W. Li, C. Wöll, Y. Wang, W. Shen, *Nat. Commun.* **2022**, *13*, 4559.
[4] C. Yang, X. Yu, S. Heisler, A. Nefedov, S. Colussi, J. Llorca, A. Trovarelli, Y.Wang, C. Wöll, *Angew. Chem., Int. Ed.* **2017**, *56*, 375.
[5] C. Yang, M. Capdevila-Cortada, C. Dong, Y. Zhou, J. Wang, X. Yu, A. Nefedov, S. Heissler, N. López, W. Shen, C. Wöll, Y. Wang, *J. Phys. Chem. Lett.* **2020**, *11*, 7925.
[6] F. Maurer, J. Jelic, J. Wang, A. Gänzler, P. Dolcet, C. Wöll, Y. Wang, F. Studt, M. Casapu, J.-D. Grunwaldt, *Nat. Catal.* **2020**, *3*, 824.
[7] J. Wang, E. Sauter, A. Nefedov, S. Heißler, F. Maurer, M. Casapu, J.-D. Grunwaldt, Y. Wang, C. Wöll, *J. Phys. Chem. C* **2022**, *126*, 9051.

Surface Space-Charge Potential and Oxygen Surface Exchange Coefficient of SrTiO$_3$: The Effect of Surface Orientation

J. Kler, Aachen/DE, J. M. Börgers, Aachen/DE, R. A. De Souza, Aachen/DE
Joe Kler, RWTH Aachen University, Institute of Physical Chemistry, 52074 Aachen

Oxygen transport through the best mixed ionic−electronic conducting oxides is often governed by the transfer of oxygen across the material's surfaces rather than oxygen diffusion through the bulk phase. This transfer process is rather complex, involving oxygen molecules becoming oxide ions (or vice versa) in a multistep reaction with various reaction intermediates. Generally, the surface is simply taken as the planar interface between the gas phase and the solid. This simplification is problematic because it ignores that the surface has its own structure, which depends on the surface orientation, and that the surface may be charged, with an attendant space-charge zone within which charge-carrier concentrations are drastically altered.

Taking the prototypical perovskite SrTiO$_3$ as a model system, the influence of the surface orientation on the surface exchange process and the surface space-charge potential was investigated. [1] We employed a single experiment to investigate both parameters: an $^{18}O_2$ / $^{16}O_2$ isotope exchange followed by determination of the isotope diffusion profile with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). We obtained data for single-crystal samples of SrTiO$_3$ with three different surface orientations, (100), (110) and (111). A huge surprise was that the difference in isothermal surface exchange coefficients was less than an order of magnitude. A further surprise was that the (110) and (111) surfaces exhibited a clear change in activation enthalpy, whereas the (100) surface did not. The third surprise was that the behaviour of the surface exchange coefficients was similar to that for the surface space-charge.

For two of these surprising results (the latter two), we found a single explanation. We started with a careful analysis of the surface exchange data, attributing the high activation enthalpy at high temperatures to a mechanism limited by charge transfer and the low activation enthalpy at lower temperatures to a mechanism involving adsorbed water species (due to trace amounts of water present in the oxygen exchange gas). The

common behaviour of the two parameters is then linked to the presence of charged OH surface species at lower temperatures.

Literature:
[1] J. Kler, J. M. Börgers, R. A. De Souza, *Adv. Mater. Interfaces* **10** (2023), 2201434.

Exploring Reactivity of Oxygen Radicals, O_2^- and O_3^-, on MgO Nanocubes in the Presence of Water

F. Kloiber-Tollinger, Innsbruck/AT, M. Belina, Prague/CZ, E. Muchová, Prague/CZ, M. Ončák, Innsbruck/AT
Felix Kloiber-Tollinger, BSc, Institut für Ionenphysik und Angewandte Physik, University of Innsbruck, Technikerstraße 25, 6020 Innsbruck

Electronic structure of neat and defected metal oxides surfaces, electron transfer to adsorbed molecules and their further reactivity are of fundamental interest in nanotechnology and catalysis. Here, we investigate the fate of oxygen radicals, O_2^- and O_3^-, in an attempt to understand the intricate reactivity dynamics of these radicals when interfaced with MgO nanocubes in the presence of water. To elucidate the underlying mechanisms, we employed two distinct models: periodic surfaces and nanocubes in the gas phase, combining density functional theory with semi-empirical methods for proper description of electronic structure and reactivity (Figure 1). Using the elastic band method, we probed reaction pathways and associated energy barriers. The proposed reaction schemes show how defects influence the surface reactivity and electron transfer to adsorbed oxygen molecules.
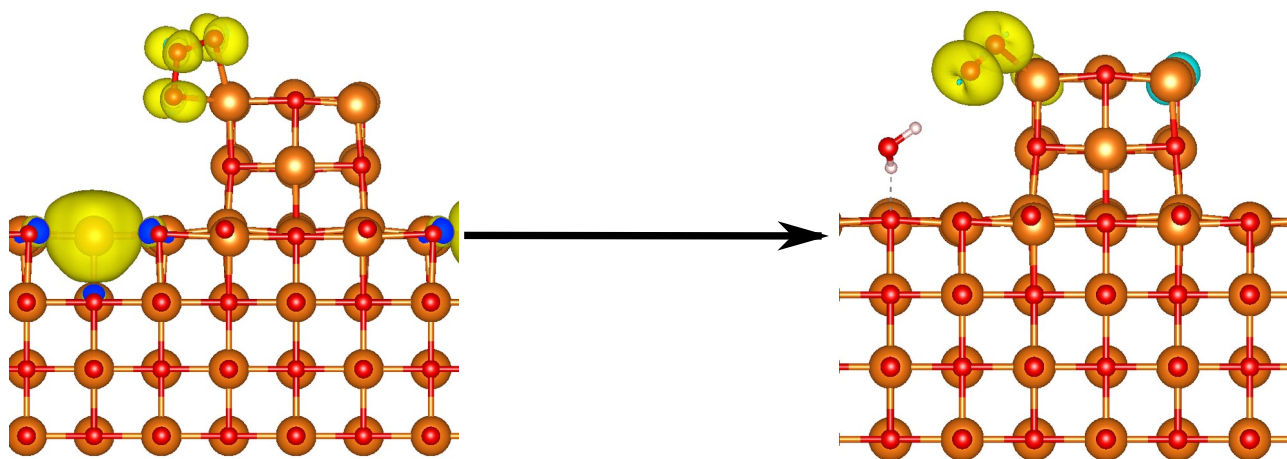
Figure 1: An observed reaction of an O_3^- radical reacting with water under periodic boundary conditions.

Toward High-throughput Surface-sensitive X-ray Scattering Studies of Electrochemical Interfaces

T. Matar, W. Corts, Prof. H.-G. Steinrück, Jülich/DE
Forschungszentrum Jülich, Institute for a Sustainable Hydrogen Economy (INW), Am Brainergy Park 4, 52428 Jülich, Germany

Lithium-ion batteries (LIBs) are recognized as essential parts of portable electronics, electric vehicles, grid storage, and are a fundamental component in sustainable energy systems development [1]. However, several scientific questions still puzzle researchers, including interfaces and interphases [2]. For instance, the structure and speciation of the potential- and surface-dependent electric double layer (EDL) (especially in advanced concentrated electrolytes) are not fully understood yet. Basic knowledge of multiple properties of the solid electrolyte interphase (SEI), a passivation layer formed on anode surfaces by electrolyte reduction products, needs to be unraveled to predict electrolyte behavior as well as cell kinetics and lifetime [3].

To understand the structural properties of these solid-liquid interfaces and interphases, X-ray reflectivity (XRR) is a powerful method that employs model electrodes such as single crystals or thin films [4,5]. Non-destructive XRR provides surface sensitivity with sub-Ångström resolution and allows probing buried nanoscale layers and can be carried out in operando modality [3]. However, XRR is typically employed for a single electrochemical cell at a given time and an experiment takes several hours up to one day. In this scenario, the experiments are not photon-limited and continuous data collection is not necessary to obtain meaningful results because changes are slow towards later stages of the experiment (even though initial processes occur relatively fast). To overcome this limitation, we designed a high-throughput setup and corresponding experimental workflow, in which up to ten electrochemical cells can be measured via XRR and other surface-sensitive X-ray scattering methods (e.g., GISAXS and GIWAXS) quasi-simultaneously in an interleave fashion. We will present our novel experimental setup and first results will be discussed.

Literature: [1] Zubi et al., Renew. Sust. Energ. Rev., 89, 292, 2018. [2] Xu, Journal of Power Sources, 559, 232652, 2023. [3] Cao, Steinrück, Encyclopedia of Solid-Liquid Interfaces, 391, Elsevier, 2024. [4] Fister et al. Chem. Mater., 28, 47, 2016. [5] Cao et al., Nano Lett., 16, 7394, 2016.

Porous Thin Films with Large Specific Surface Area on the Basis of Spray-Coated Metal Aerogels

Pavel Khavlyuk, Volodymyr Shamraienko, Fiona Tenhagen, Johannes Kresse, Nelli Weiß, Nikolai Gaponik, and Alexander Eychmüller

Physical Chemistry, TU Dresden, Zellescher Weg 19, 01069 Dresden, Germany

The preparation of aerogels in the form of thin films deposited on a substrate (e.g., as an electrode material) is an attractive but challenging task. Such thin films are expected to combine the highly porous gel nanostructure, good mechanical stability, and a remarkably high specific surface area with efficient charge-carrier transport via the interconnected nanoparticle chains. All together, they make them attractive for the fabrication of (electro)catalysts or sensors for microfluidics, flexible electrodes for microelectronics, soft electrodes compatible with a stress-sensitive bioenvironment, etc.

In our work, thin aerogel films of colloidal Pd and PtNi building blocks were prepared from the corresponding wet gels using a spray technique. The films were fabricated on substrates of around 1.5 cm^2. During the modification of the substrates, the film thickness can be adjusted by controlling the ink content (flow rate, gas pressure, and temperature) and the number of spray cycles. In this way, both the electrical (down to R_s = ~0.2 kOhm/sq) and optical parameters of the thin porous films can be tuned. Comparative studies of the pore and surface structures of the films have confirmed their integrity and the highly porous structure typical for aerogels. In perspective, spray-coated aerogels can be easily adapted to industrial applications because upscaling is possible and expensive equipment such as supercritical or freeze-dryers is not required. It is important to note that the spray-coating technique is applicable through a mask or can be converted to inkjet printing, which allows for the desired micropatterning of aerogel thin films.

Microphase separation of copolymeric architectures for gas separation membranes

D. Kösters, Göttingen/GER, S. C. Wendler, Göttingen/GER
Prof. Dr. Philipp Vana, Georg-August-Universität, Institut für Physikalische Chemie,
Tammannstraße 6, 37077 Göttingen

Block copolymers can covalently link otherwise incompatible polymers. Microphase separation of these incompatible domains leads to well defined morphologies on the nano scale.[1] Both these characteristics can be used in the preparation of gas permeability membranes. The combination of highly permeable and highly selective materials regardless of their intrinsic compatibility, as well as the microphase separation of the domains have a significant effect on the gas permeability and selectivity of polymeric materials.[2,3] In more complex polymeric architectures like bottlebrush block copolymers, the microphase separation can be used for even more diverse and defined morphologies.[4,5]

This work aims to combine a 4,4′-(Hexafluoroisopropylidene)-diphthalic anhydride (6FDA) based polyimide as a solution-selective polymer with poly(dimethylsiloxane) (PDMS) as a highly diffusive 'gutter' polymer in a densely packed bottlebrush block copolymeric architecture. Covalent combination of these two, usually incompatible, materials has high potential for improved membrane design through microphase separation.

Literature:

[1] D. J. Lohse, N. Hadjichristidis, *Current Opinion in Colloid & Interface Science* **1997**, *2*, 171–176.
[2] P. A. Gurr, J. M. P. Scofield, J. Kim, Q. Fu, S. E. Kentish, G. G. Qiao, *Journal of Polymer Science Part A: Polymer Chemistry* **2014**, *52*, 3372–3382.
[3] G.-L. Zhuang, M.-Y. Wey, H.-H. Tseng, *Journal of Membrane Science* **2017**, *529*, 63–71.
[4] A. Halim, P. A. Gurr, A. Blencowe, G. Bryant, S. E. Kentish, G. G. Qiao, *Polymer* **2013**, *54*, 520–529.
[5] A. Chremos, P. E. Theodorakis, *ACS Macro Lett.* **2014**, *3*, 1096–1100.

The Effect of Doping in Inelastic H Atom Scattering from Silicon

M. Opfermann, Göttingen/DE, S. Tödter, Göttingen/DE, K. Krüger, Göttingen/DE, O. Bünermann, Göttingen/DE

Malte Opfermann, Georg August University of Göttingen, Tammannstraße 6, 37077 Göttingen

Recent inelastic H atom scattering experiments from the semiconducting Ge(111)c(2x8) surface have shown a bimodal energy loss distribution. One of the components was narrow with a small energy loss. The other component has shown a broad and large energy loss with an onset equal to the surface band gap. The high energy-loss channel was explained by the excitation of electrons over the surface band gap. [1] While the low energy loss channel could be explained by an adiabatic molecular dynamics simulation, the high-energy loss component is not described theoretically yet.

To gain a better understanding of the underlying mechanism, we extended our studies to silicon, another semiconductor. Depending on the surface facet and reconstruction, surfaces exhibit different electronic structures. The Si(100)2x1 surface is semiconducting while the Si(111)7x7 surface exhibits a metallic band structure. Despite their different electronic structure, both surfaces exhibit similar energy-loss distributions. To understand if doping has an influence on the energy loss, we carried out scattering experiments from samples with various doping levels. The results indicate a doping effect.

Literature:

[1] Krüger et al., Nat. Chem., DOI:10.1038/s,41557-022-01085-x (2022)

This study is focused on the degradation of metal-organic frameworks (MOFs) in the presence of volatile organic compounds (VOCs). MOFs, known for their high surface area and tunable porosity, have shown promise in various applications, but their stability under real-world conditions, especially in the presence of VOCs, remains a critical concern. The investigation employs operando diffuse reflectance infrared spectroscopy (DRIFTS) as a powerful tool for real-time monitoring of the degradation process. Unlike traditional characterization methods, operando DRIFTS allow for the simultaneous analysis of structural changes and chemical transformations during MOF exposure to VOCs. The study aims to elucidate the dynamic nature of MOF degradation and its correlation with the presence of specific VOCs. The insights gained from this study have implications for the design and optimization of MOFs for use in gas storage, separation, and sensing technologies.

This study is focused on the degradation of metal-organic frameworks (MOFs) in the presence of volatile organic compounds (VOCs). MOFs, known for their high surface area and tunable porosity, have shown promise in various applications, but their stability under real-world conditions, especially in the presence of VOCs, remains a critical concern. The investigation employs operando diffuse reflectance infrared spectroscopy (DRIFTS) as a powerful tool for real-time monitoring of the degradation process. Unlike traditional characterization methods, operando DRIFTS allow for the simultaneous analysis of structural changes and chemical transformations during MOF exposure to VOCs. The study aims to elucidate the dynamic nature of MOF degradation and its correlation with the presence of specific VOCs. The insights gained from this study have implications for the design and optimization of MOFs for use in gas storage, separation, and sensing technologies.

Colloidal Synthesis of Two-Dimensional MoTe$_2$ and WTe$_2$

O. Strolka, Tübingen/DE, A. Niebur, Hannover/DE, D. Rudolph, Hannover/DE
Prof. Dr. J. Lauth, Tübingen, Hannover/DE, University of Tübingen, Institute of
Physical and Theoretical Chemistry, Auf der Morgenstelle 18, 72076 Tübingen

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) of the form MX$_2$ (M = Mo,W; X = S, Se, Te) exhibit highly interesting optoelectronic properties including a strong spin-orbit coupling, [1] and successive opening of the indirect band-gap with decreasing layer thickness down to the monolayer with a direct band-gap. [2] TMTellurides possess a small direct band gap of 1.10 eV and 0.74 eV in monolayers for Molybdenum and Tungsten respectively, which extends the range of optical applications of TMDCs from UV-Vis to near infrared wavelengths. [3,4] Proposed applications of TMDCs range from sensors, nanoelectronics, superconductors and energy harvesting to catalysis. While the main synthetic routes for 2D TMDCs are still exfoliation and chemical vapor deposition-based, since recently, wet-chemical bottom-up syntheses offer a scalable approach to processable 2D TMDC mono- and bilayers as inks in larger quantities. [5,6]

Up to now, 2D TMSulfides and TMSelenides from colloidal syntheses have been the primary focus of research, [6-8] while colloidally synthesized TMTellurides remained virtually unexplored. [9] Here we present the application of our synthetic route to the colloidal synthesis of 2D MoTe$_2$ and WTe$_2$.

Literature:
[1] A. Kormányos, G. Burkard, M. Gmitra, J. Fabian, V. Zólyomi, N. D. Drummond, V. Fal'ko, 2D Mater. 2015, 2, 022001. [2] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, Phys. Rev. Lett. 2010, 105, 136805. [3] C. Ruppert, B. Aslan, T. F. Heinz, *Nano Lett.* 2014, 14, 11, 6231–6236. [4] P. Liu, B. Xiang, Science Bulletin, 62, 16, 2017, 1148-1161. [5] J. R. Brent, N. Savjani, P. O'Brien, Prog. Mater. Sci. 2017, 89, 411–478. [6] A. Niebur, A. Söll, P. Haizmann, O. Strolka, D. Rudolph, K. Tran, F. Renz, A. P. Frauendorf, J. Hübner, H. Peisert, M. Scheele, J. Lauth, Nanoscale 2023, 15, 5679-5688. [7] A. P. Frauendorf, A. Niebur, L. Harms, S. Shree, B. Urbaszek, M. Oestreich, J. Hübner, J. Lauth, J. Phys. Chem. C. 2021, 125, 18841-1884. [8] M. Fröhlich, *in preparation* 2023 [9] Y. Sun, Y. Wang, D. Sun, B. R. Carvalho, C. G. Read, C.-h. Lee, Z. Lin, K. Fujisawa, J. A. Robinson, V. H. Crespi, M. Terrones, R. E. Schaak, Angew. Chem. Int. Ed. 2016, 55, 2830.

Theory and Data Science

Where the Schrödinger equation works and where it does not

I. Frank, Hannover/D,, University of Hannover, Theoretical Chemistry,
Callinstr. 3A, 30167 Hannover

The Schrödinger equation writes an incredible success story since almost hundred years. It is less known, that this is true for the time-independent description of the structure of bound electrons only. Since the electronic cloud determines the structure of all kind of matter, the Schrödinger equation has a wide range of applications. The electronic wavefunction is responsible for all kinds of interactions within atomic systems, that is, for covalently bound molecules, hydrogen-bonded systems, metals, salts, solutions, solids, etc. If, however, one wants to study the dynamics of such systems, it turns out that assigning a wavefunction to nuclear structure and motion leads to nonsense. In contrast, taking the nuclei as point particles and describing nuclear motion with Newton dynamics leads to a convincing description of chemical reactions and of spectra [1, 2, 3]. This is even true for photoreactions as we have shown in many applications. We investigate cases where quantum mechanical motion was assumed to be essential and show that using the Schrödinger equation is not necessary or is even wrong.

Literature:
[1] R. C. Büchel, D. A. Rudolph, I. Frank, Int. J. Quantum Chem. 2021, 121, e26555. [2] E. Rohloff, D. A. Rudolph, O. Strolka, I. Frank, Int. J. Quantum Chem. 2022, 122, e26902. [3] I. Frank, Hydrogen 2023, 4, 287.

MolBar: A Molecular Identifier for Inorganic and Organic Molecules with Full Support of Stereoisomerism

N. van Staalduinen, Aachen/DE, C. Bannwarth, Aachen/DE
Nils van Staalduinen, RWTH Aachen University, Melatener Str. 20,
52074 Aachen

Data uniqueness is critical to the integrity of data sets and the longevity of databases. Quality data sets contain a limited number of duplicates. Duplicate identification helps maintain data uniqueness, while data cleansing and deduplication can eliminate redundant records. The Simplified Molecular Input Line Entry Specification (SMILES) and the International Chemical Identifier (InChI) are widely used as molecular identifiers in databases for deduplication tasks [1]. Both representations describe molecules by a sequence of bonded atoms. They can distinguish between diastereomers and enantiomers based on local chirality.

Yet, the description of metal complexes remains a challenging task. For complex metal structures with η-bonds, this holds particularly true. Furthermore, the representation of chirality beyond chiral centers is important for the description of metal complexes, e.g. for chiral planar ferrocene derivatives. Widely used identifiers cannot describe axial and planar chirality due to the atom-centered description of a molecule [2].

Here, a chemical identifier is introduced based on a fragmentary approach instead of an atomistic description. The fragments are idealized based on a special-purpose force field and described by physically inspired indices using only atomic positions. A permutation invariant representation is obtained from the spectra of several Hückel-like adjacency matrices containing bonding information and stereoisomerism indices. This novel representation is robust and superior to the aforementioned representations as demonstrated for a large number of organic and inorganic test cases. A Python implementation named Molecular Barcode (MolBar) is available as open source [3].

Literature:
[1] T. Engel, J. Gasteiger, O. Sacher, E. Zass, *Chemoinformatics*, John Wiley & Sons, Ltd, **2018**, p. 14.
[2] F. Strieth-Kalthoff, F. Sandfort, M. H. S. Segler, F. Glorius, **Chem. Soc. Rev.**, 2020, **49**, 6154-6168.
[3] MolBar implementation: https://git.rwth-aachen.de/bannwarthlab/molbar

Utilizing Machine Learning for the Approximation of Hessian Matrices based on GFN2-xTB derived Features

G. Feldmann, Aachen/DE, Prof. Dr. C. Bannwarth, Aachen/DE

RWTH Aachen University, Melatener Straße 20, 52074 Aachen

The computation of seminumerical nuclear Hessian matrices is a cost-intensive bottleneck for the evaluation of e.g. thermodynamical corrections in the widely used rigid rotor harmonic oscillator (RRHO) approximation in electronic structure theory (EST). Various approaches use lower-level theory methods e.g. force fields to approximate the Hessian.[1,2,3] It could already be shown, that machine learning (ML) models provide through their architecture the opportunity to circumvent costly computations in EST methods.[4] Hence, Hessian matrices show a high potential for ML-based computation.

In our introduced ML model, atomistic features derived from the semiempirical tight-binding method GFN2-xTB[5] are utilized to maintain a consistent feature vector length, ensuring independence from molecular size. Moreover, the Hessian is deconstructed into atom pairwise block matrices as targets. In contrast to various other approaches, the Cartesian Hessian is used, as it allows for a significant reduction of required targets for the computation of the complete Hessian matrix concluding in a higher training performance. The Hessian is rotational variant and thus it is critical to address this behavior in the model. In order to utilize straightforward ML architecture, a rotation routine is devised to establish an invariant feature-target relation. The developed model is trained on a data set including molecules with all elements in the spd-blocks. For the GDB7[6] data set, it can be shown that the thermodynamic corrections computed with the RRHO approximation from the ML model Hessian are within chemical accuracy in comparison to the GFN2-xTB quantities.

Literature:
[1] R. Lindh, A. Bernhardsson, G. Kalström, P. Mamqvist, *Chem. Phys. Lett.* **241,** 423 (1995). [2] S. Spicher, S. Grimme, *J. Chem. Theory Comput.* **17**, 1701 (2021). [3] S. Grimme, *J. Chem. Theory Comput.* **10**, 4497 (2014). [4] J. Behler, M. Parrinello, *Phys. Rev. Lett.* **98,** 146401 (2007). [5] C. Bannwarth, S. Ehlert, S. Grimme, *J. Chem. Theory Comput.* **15***,* 1652 (2019). [6] L. Blum, J. Reymond, *J. Am. Chem. Soc.* **131***,* 8732*,* (2009).
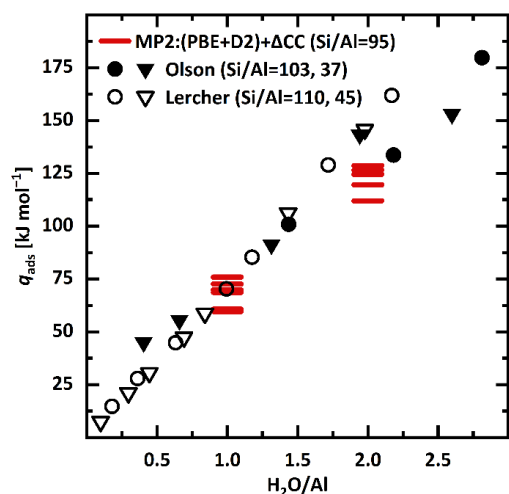
Next Generation Quantum Chemistry of Water Adsorption in Acidic Zeolites

H. Windeck, Berlin/DE, F. Berger, Cambridge/UK
Joachim Sauer, Humboldt–Universität zu Berlin, Unter den Linden 6, 10099 Berlin

Water is ubiquitous in zeolite catalysis, yet its effect is poorly understood and converged computational simulations are still missing. We study the interaction of Brønsted acid sites (Al–O(H)–Si, BAS) with one to three water molecules in the zeolite H–MFI. Considering that BAS can be in different topological regions of the MFI framework (site heterogeneity), we define a representative set of six BAS positions. We predict chemically accurate (± 4 kJ mol^{-1}) heats of water adsorption. Going beyond commonly used methodology, we couple second–order Møller–Plesset perturbation theory (MP2) with dispersion–corrected density functional theory (PBE+D2) and optimise structures with hybrid MP2:PBE+D2. To reach chemical accuracy, we add coupled–cluster corrections (MP2:(PBE+D2)+ΔCC).[1]

For the first water molecule per BAS (1 H$_2$O/BAS), we predict heats of adsorption between 60–73 kJ mol^{-1}. The figure shows excellent agreement with calorimetric (open symbols)[2] and isotherm (full symbols)[3] measurements. The predictions for three of six BAS positions agree with experiment (70 kJ mol^{-1})[2] within chemical accuracy limits (± 4 kJ mol^{-1}). For 2 H$_2$O/BAS, however, our predictions show significantly weaker adsorption (112–129 kJ mol^{-1}) than indicated by the experimental values. This discrepancy between predictions and experiment indicates an effect that goes beyond our model of ideal, isolated BAS and leads to stronger adsorption of the second water molecule.

Literature: [1] J. Sauer, Acc. Chem. Res. 2019, 52, 3502. [2] J. Lercher and co–workers, Angew. Chem., Int. Ed. 2019, *58*, 3450-3455. [3] D. Olson and co–workers, Micropor. Mesopor. Mat. 2000, 35-36, 435-446.

Application of a tensor train based global optimization algorithm to conformer sampling of large molecules

C. Zurek, Aachen/DE, C. Bannwarth, Aachen/DE
Christopher Zurek, RWTH Aachen University, Melatener Str. 20, 52074 Aachen

Since a molecule's properties are directly related to its predominant three-dimensional structure, the search for the global minimum geometry is crucial for the quantum chemical prediction of physical properties and chemical reactivity.

Due to its fundamental importance, manifold conformer search approaches have been proposed over the past decades, ranging from early systematic grid search algorithms to extensive molecular dynamic (MD) simulations, primarily relying on force field methods for energy evaluation. [1] In the recent years, metadynamic (MTD) simulations have been established as one of the most effective tools, providing reliable coverage of the relevant conformational space in a reasonable amount of time. However, the huge amount of required geometry optimizations inherently associated with MTD simulations generally limits the approach to system sizes of about 200 atoms, depending on the molecule's flexibility. [2]

Large interconformational energy barriers, that typically hinder MD and MTD simulations, can be circumvented via a systematic search on a relatively coarse grid of dihedral angles in combination with an efficient dimensionality reduction strategy. For this purpose, we utilize a tensor train based global optimization algorithm in combination with local gradient optimizations. [3] This allows typical conformer search tasks to be performed more than one order of magnitude faster than MTD based algorithms. Furthermore, it is a promising technique to extend conformer sampling at a quantum mechanical level to significantly larger molecules.

Literature:
[1] P. C. D. Hawkins, J. Chem. Inf. Model. 2017, 57, 8, 1747−1756.
[2] P. Pracht, Phys. Chem. Chem. Phys., 2020, 22, 7169-7192.
[3] K. Sozykin, Adv. Neural Inf. Process. Syst., 2022, 35, 26052-26065.

Volume phase transition of copolymer microgels with non-thermoresponsive comonomers
A Hill-like adaptation of the Flory-Rehner theory

J. Krüger, Bielefeld / Germany, Prof. Dr. Thomas Hellweg, University of Bielefeld, Universitätsstraße 25, 33615 Bielefeld

The Flory-Rehner theory is a common model for describing the volume phase transition of swollen 3D polymer networks which was found to work reasonably well for macroscopic polyacrylamide networks. D.C. Leite *et al.* introduced a Hill-like model for the Flory-Huggins interaction parameter χ_{Hill} (eq. 1), analogous to the Hill transition in cooperative thermotropic transitions. This model accurately fits the swelling data of poly(N-isopropylacrylamide) (PNIPAM) microgels. [1] The present contribution highlights the advantages of employing the Hill-like model in studying copolymer microgels.

$$\chi_{Hill} = \chi_0 + a \cdot (T - T_a) + b \cdot \frac{(T - T_a)^\nu}{(T - T_a)^\nu + (VPTT - T_a)^\nu}$$

The Hill-like model provides the Hill parameter ν, representing the number of water molecules per network chain leaving the microgel during the phase transition. S. Friesen *et al.* observed a linear decrease in ν with the N,N′-methylene-bisacrylamide (BIS) crosslinker content, attributed to a constant presence of adsorbed water molecules on the crosslinker during the phase transition, caused by the absence of a lower critical solution temperature (LCST) in BIS. [2] The Hill-like-model yields good fit results of copolymer microgel swelling curves. [3] To assess its applicability to non-thermo-responsive components, N-*tert*-butylacrylamide (NtBAM) was used as a comonomer in PNIPAM-*co*-NtBAM copolymer microgels. By combining the original Flory-Huggins interaction parameter with the Hill-like model, we achieved an excellent description of the swelling curves, outperforming other methods.

Literature:

[1] D. C. Leite, S. Kakorin, Y. Hertle, T. Hellweg, N. P. Da Silveira, Langmuir **2018**, *34*, 10943. [2] S. Friesen, Y. Hannappel, S. Kakorin, T. Hellweg, Gels **2021**, 7, 42. [3] S. Friesen, S. Kakorin, T. Hellweg, Polymers 2022, *14.*

Temperature Dependence of the Conformational Landscape and Methyl-Group Dynamics of 2-13C-Ethyl-1-13C-Acetate in a Glycerol-Water Environment

M. Brandt, Rostock/DE, E. R. Bensons, Rostock/DE, Prof. B. Corzilius, Rostock/DE, D. Paschek, Rostock/DE

Marcel Brandt, Universität Rostock, Albert-Einstein-Str. 27, 18059 Rostock

Methods which induce site-specificity and sensitivity enhancement in solid-state magic-angle spinning NMR spectroscopy become increasingly important for structural biology applications due to the size of the molecules under investigation. Recently, several strategies have been developed to improve site specificity and thus reduce signal overlap. Under dynamic nuclear polarization (DNP) for NMR signal enhancement, it is possible to use cross-relaxation transfer induced by select dynamic groups within the molecules which is exploited by SCREAM-DNP (Specific Cross Relaxation Enhancement by Active Motions under DNP).[1] Here ^{1}H DNP-based transfer with site-specific heteronuclear transfer is used, resulting in a fast build-up of polarization sufficiently distant to the radical and thus avoiding paramagnetic broadening. Here we study the intramolecular [13]C-^{1}H interaction in 2-13C-ethyl-1-13C-acetate in a glycerol-water environment as a simplified test case. For a better understanding of the mechanistic details of polarization transfer, the knowledge of the population of the conformational space of the 2-13C-ethyl-1-13C-acetate is equally important as a proper description of the methyl-group dynamics. We use molecular dynamics simulations of 2-13C-ethyl-1-13C-acetate in a glycerol-water environment to study the temperature dependence of its conformational landscape as well as the methyl group dynamics, thus bringing us in the position to be able to compute polarization transfer from a first-principles based approach.

Literature:
[1] T. Biedenbänder, E. R. Bensons, B. Corzilius. ChemPhysChem 2023, 24, e202300206.

OrthoBoXY: A Simpler Way to Compute *True* Self-Diffusion Coefficients and Viscosities from Molecular Dynamics Simulations

Dr. D. Paschek, Rostock/DE, J. Busch Rostock/DE
Dr. Dietmar Paschek, Universität Rostock, Albert-Einstein-Str. 27, 18059 Rostock

Recently, an analytical expression for the system size dependence and direction-dependence of self-diffusion coefficients for liquids, liquid mixtures and ionic liquids due to hydrodynamic interactions in periodic systems has been derived for molecular dynamics (MD) simulations using orthorhombic unit cells. Based on this description, we show that for systems with "magic" box length ratios of $L_z/L_x = L_z/L_y = 2.7933596497$ the computed self-diffusion coefficients D_x and D_y in the x- and y-direction become system-size independent and thus represent the *true* self-diffusion coefficient $D_0 = (D_x + D_y)/2$.[1] Moreover, by using this particular box geometry, the viscosity can be determined with a high degree of accuracy from the difference of components of the diffusion coefficients in x-, y-, and z-directions using the simple expression $\eta = k_BT \times 8.1711245653/[3\pi L_z(D_x+D_y-2D_z)]$, where k_B denotes Boltzmann's constant and T represents the temperature.[1] MD simulations of TIP4P/2005 water for various system sizes using both orthorhombic and cubic box geometries are used to test the approach. Our simulations show that the OrthoBoXY method provides accurate self-diffusion and viscosity data even for system sizes as small as 96 water molecules, thus making it an ideal candidate to determine viscosities and true self-diffusion coefficients from computationally expensive calculations such as *ab initio* molecular dynamics simulations.

Literature:
[1] J. Busch, D. Paschek. J. Phys. Chem. B 2023, 127, 7938.

A First Principles Based Approach to Determine the Frequency-Dependent Dipolar ^{19}F-NMR Relaxation in an Ionic Liquid from Molecular Simulations

A. M. Chiramel Tony, Rostock/DE, L. Kruse Rostock/DE, Dr. A. Strate, Rostock/DE, Prof. R. Ludwig, Rostock/DE, Dr. Dietmar Paschek, Rostock/DE
Angel Mary Chiramel Tony, Universität Rostock, Albert-Einstein-Str. 27, 18059 Rostock

By using Fast Field Cycling (FFC) NMR spectroscopy, dynamical processes can be studied over many orders of magnitude, ranging from 10 kHz to about 100 MHz. However, interpreting FFC-NMR data often requires motional models that are specific to certain systems and assume often simplified analytical forms of the relevant time correlation functions. Here we propose a novel approach for computing the inter- and intramolecular contribution to the magnetic dipolar relaxation from molecular dynamics (MD) simulations, enabling us to predict NMR relaxation rates addressing the full FFC frequency range, covering many orders of magnitude, while also avoiding influences due to limitations in system size and the accessible time interval. Our approach is based on combining the analytical theory of Hwang and Freed (HF) [1] for the long-range intermolecular contribution of the magnetic dipole-dipole correlation function with MD simulations. We show that the correlation functions due to the HF-theory do asymptotically converge with our MD simulation results at long times. Here we apply this approach to compute the inter- and intramolecular NMR relaxation of ^{19}F nuclei in the ionic liquid n-pentyl-pyridinium bis-(trifluoromethyl-sulfonyl)imide (C$_5$Py-NTf$_2$) to study the dynamics of the NTf$_2$ anion. Thus, we are able to study both the influence of the translational dynamics and the rotational dynamics of the anions. Moreover, by using our MD simulation-based approach, we are able to disentangle the different contributions to the intramolecular ^{19}F-NMR relaxation rate due to the complex intramolecular dynamics of the anion.

Literature:
[1] L.-P. Hwang, J.H. Freed. J. Chem. Phys. 1975, 63, 4016.

"50 Ways" of Computing the Viscosity of Poly(Ethylene Glycol) Ethers from Molecular Dynamics Simulations

F. Freytag, Rostock/DE, J. Busch, Rostock/DE, Dr. D. Paschek, Rostock/DE, Prof. Dr. R. Ludwig, Rostock/DE,
Franka Freytag, Universität Rostock, Albert-Einstein-Str. 27, 18059 Rostock

We explore various ways to compute viscosity data of liquids from molecular dynamics (MD) simulations. From the fluctuation of the off-diagonal components of the stress tensor, the viscosity can be determined by using the Green-Kubo-approach.[1] However, for viscous liquids, the fluctuation-based methods converge poorly due to the slow relaxation processes in the liquid. Recently, an alternative approach has been proposed, utilizing the effect of the hydrodynamic (self) interactions on the direction-dependent self-diffusion coefficients in systems with an orthorhombic unit cell with "magic" box dimensions $L_z/L_x=L_z/L_y=2.793359$.[2] For such a system, the diffusion coefficients in x- and y- direction represent the system size independent true self-diffusion coefficient D_0, while the viscosity can be obtained from diffusion coefficients in x-, y-, and z-direction with $\eta=k_B T \times 8.171125 / [3\pi L_z(D_x+D_y-2D_z)]$. The advantage of this approach is the good predictability of the uncertainty of the computed data and its applicability to systems of rather small size.[2] A rapidly converging alternative way of computing the viscosity are, of course, nonequilibrium simulations. Here we utilize the periodic perturbation method as implemented in GROMACS.[3] This approach has, however, the disadvantage of a shear-rate dependence of the computed viscosity. Therefore, an extrapolation towards a zero-shear rate is required. In this contribution, we test the consistency of all three methods by using poly (ethylene glycol) ether oligomers as a model system. Our aim is to rank the efficiency of the different methods in their ability to compute viscosity data with a targeted uncertainty level.

Literature:
[1] D.J. Tildesley, M.P. Allen. "Computer Simulation of Liquids", Clarendon Press, 1987
[2] J. Busch, D. Paschek. J. Phys. Chem. B 2023, 127, 7983.
[3] B. Hess. J. Chem. Phys. 2002, 116, 209.

Combining low-cost electronic structure theory and low-cost parallel computing architecture

Pit Steinbach, Christoph Bannwarth

Institute for Physical Chemistry, RWTH Aachen University, Melatener Str. 20, 52074 Aachen, Germany

The potential of low-cost electronic structure methods can be further accentuated by leveraging heterogenous computing architectures. The software package TeraChem[1,2] has been developed since 2008 to make use of graphical processing units (GPUs) for the acceleration of quantum chemical calculations. We choose to implement three low-cost methods, namely HF-3c[3], PBEh-3c[4] and the recently introduced wB97X-3c[5]. We show that the performance of "consumer grade" GPUs can be leveraged by using the mixed precision[6] formalism integrated in TeraChem. These methods can be combined with the *hh*-TDA[7,8] formalism to give new and efficient low-cost excited states methods, whose performance is benchmarked in this work. By combining affordable electronic structure theory methods and affordable computing hardware, we present an optimal computational and monetary cost to accuracy ratio.
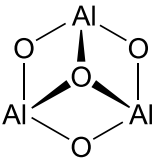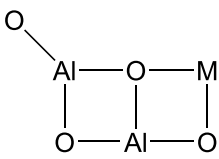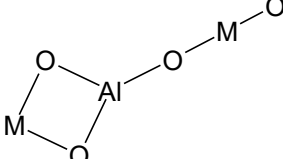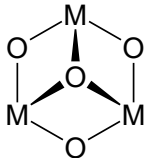
[1] Seritan, S.; Bannwarth, C.; Fales, B. S.; Hohenstein, E. G.; Kokkila-Schumacher, S. I. L.; Luehr, N.; Snyder, J., James W.; Song, C.; Titov, A. V.; Ufimtsev, I. S.; Martínez, T. J. *J. Chem. Phys.* **2020**, *152*, 224110.
[2] Seritan, S.; Bannwarth, C.; Fales, B. S.; Hohenstein, E. G.; Isborn, C. M.; Kokkila-Schumacher, S. I. L.; Li, X.; Liu, F.; Luehr, N.; Snyder Jr., J. W.; Song, C.; Titov, A. V.; Ufimtsev, I. S.; Wang, L.-P.; Martínez, T. J. *WIREs Comput. Mol. Sci.* **2021**, *11*, e1494.
[3] Sure, R.; Grimme, S. *J. Comput. Chem.* **2013**, *34*, 1672-1685.
[4] Grimme, S.; Brandenburg, J. G.; Bannwarth, C.; Hansen, A. *J. Chem. Phys.* **2015**, *143*, 054107.
[5] Müller, M.; Hansen, A.; Grimme, S. *J. Chem. Phys.* **2023**, *158*, 014103.
[6] Luehr, N.; U mtsev, I. S.; Martínez, T. J. *J. Chem. Theory. Comput.* **2011**, *7*, 949-954.
[7] Bannwarth, C.; Yu, J. K.; Hohenstein, E. G.; Martínez, T. J. *J. Chem. Phys.* **2020**, *153*, 024110.
[8] Yu, J. K.; Bannwarth, C.; Hohenstein, E. G.; Martínez, T. J. *J. Chem. Theory Comput.* **2020**, *16*, 5499-5511.

Structure and Reactivity of
First Row Transition Metal Substituted Aluminum Oxide Cluster
A Gas-Phase Study Combining Experiment and Theory

W. Schwedland, Berlin/DE, F. Müller, Berlin/DE, H. Windeck, Berlin/DE, S. Leach, Berlin/DE, Y. Li, Leipzig/DE, A. Chakraborty, Leipzig/DE, F. Berger Berlin/DE

Prof. Dr. K. Asmis, University of Leipzig, Linnéstraße 2, 04103 Leipzig,

Prof. Dr. J. Sauer, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

Methane, as the most stable alkane with generally low reactivity compared to other hydrocarbons, presents a unique challenge for the conversion into more valuable compounds. Gas-phase metal oxide clusters serve as excellent model systems to study the active sites of heterogeneous catalysts related to methane conversion.

This study elucidates how the substitution of $Al_3O_4^+$ gas phase clusters with Fe and Co influences their structure and reactivity towards methane. A comprehensive approach combining experimental mass spectrometry (MS) and infrared photodissociation (IRPD) spectroscopy with computational single- and multi-reference methods is used to investigate these systems.

The activation of the C-H bond in methane is typically initiated through homolytic splitting induced by an oxygen radical.[1,2] In contrast to the radical $MAl_2O_4^+$ clusters, the reactivity of the double-substituted $M_2AlO_4^+$ clusters is strongly influenced by the nature of the transition metal. This is due to a rather unusual, non-radical activation mechanism of the C-H bond via heterolytic cleavage.

Literature:

[1] Müller *et al*. J. Am. Chem. Soc. **2020**, *142*, *42*, 18050-18059.

[2] Li *et al*. Angew. Chem. Int. Ed. **2022**, *61*, e202202297.

Ab Initio Studies on the Location and Stability of Brønsted Acid Sites in H–MOR

P. Neuendorf, Berlin/DE, H. Windeck, Berlin/DE, F. Berger, Berlin/DE,
Prof. Dr. J. Sauer, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

Acidic zeolites play a vital role in heterogeneous catalysis. Mordenite in its acidic form (H–MOR) is one of the most widely used catalysts for a variety of reactions. [1] The acidity mainly derives from the presence of Brønsted acid sites (BAS). Knowledge about the location and stability of BAS is of critical importance when designing catalysts and optimising catalytic processes.

This study uses a chemically accurate (± 4kJ/mol) QM:QM embedding scheme (QM = quantum mechanics) to determine the relative stability of all possible BAS in H–MOR. Further, we predict IR and ^{1}H-NMR features for a set of most stable BAS and compare them with experimental spectra. Additionally, we investigate the amount and stability of H-bonded BAS.

We find that the predicted IR and ^{1}H-NMR features fall within the experimental full width at half maximum intervals of 3608 ± 21.4 cm^{-1} [2] and 4.3 ± 0.9 ppm. [3] We also find that, although there are many possibilities, H-bonded BAS in H–MOR are energetically disfavoured compared to BAS that point into empty pore space. This is due to the energy penalty connected with the framework distortions on H-bond formation. This is at variance with other zeolites such as H–MFI for which the most stable BAS also include H-bonded BAS [4], clearly demonstrating characteristic differences between different zeolite frameworks.

Literature:
[1] Vogt, E. T. C., Whiting, G. T., Dutta Chowdhury, A., Weckhuysen, B. M., Adv. Catal., 2015, 58, 143-314. [2] Zholobenko, V. L., Makarova, M. A., Dwyer, J., J. Phys. Chem. 1993, 97, 5962-5964. [3] Huo, H., Peng, L., Gan, Z., Grey, C. P., J. Am. Chem. Soc. 2012, 134, 9708-9720. [4] Windeck, H., Berger, F., Sauer, J., Angew. Chem. Int. Ed. 2023, 62, e202303204.

First-principles study on the electrical conductivity of transition metal oxides

A. Öztürk, Berlin/DE, P. Kraus Berlin/DE,
TU Berlin, Sekr. BA3, Hardenbergstr. 40, 10623 Berlin

Electrical conductivity is an important material's property, affected by the symmetry of the crystalline lattice, chemical bonding, and other phenomena. In this work we present a theoretical investigation of the conductivity of the five transition metal oxides, comparing values obtained using density functional theory to literature experimental values.

Materials	Space Group	Band gap [eV]	Conductivity DC [S/m]
TiO_2-Anatase	$I4_1 / amd$	3.22 [1]	10^{-4} [968 °C] [5]
TiO_2-Rutile	$P4_2 / mnm$	3.00 [2]	10^{-3} [861 °C] [5]
ZnO	$P6_3 / mc$	3.37 [3]	10^{-1} [550 °C] [6]
MoO_2	$P2_1 / c$	0.00 [4]	10^5 [<200 °C] [7]
MoO_3	P / bmn	3.20 [4]	10^{-2} [726 °C] [8]

We selected our materials from the transition metal oxides to investigate the effect of chemical bonding (MoO_2, MoO_3), the symmetry of the crystal lattice(anatase, rutile), and ZnO was used to cover a wide range of electrical conductivity.

We report the effect of different pseudopotentials (NC [9] and SSSP [10]) on the calculated electronic conductivities and related properties, such as band gaps, static dielectric constants, bulk polarizabilities, phonon modes.

Literature:
[1] Z. Ma, et al., Optik (Stuttg.) 2021, 241, 167107. [2] S. Mo, et al., Ching. Phys. Rev. B. 1995, 51, 19. [3] P. Yangn, et al., Ceram. Int. 2015, 41.2, 2446-2452.
[4] P. Eleonora, et al., NMS 2023, 13.8, 1319. [5] E. Marshall, et al., Phys. Rev. B. 1942, 61.1-2, 56. [6] P. Miller, et al., Phys. Rev. B. 1941, 60.12, 890.
[7] J. Li, et al., Mater. Lett. 2016, 174, 188-191. [8] A. Pandit, et al., Solid State Commun. 1991, 80.2, 125-127. [9] D. Hamann, et al., Phys. Rev. B. 2013, 88.8, 085117. [10] G. Prandini, et al., Npj Comput. Mater. 2018, 4, 72.

Software Development Tools For Reproducible Research

N. O. B. Lüttschwager, Göttingen/DE

Georg-August-Universität Göttingen, Institut für Physikalische Chemie

Tammannstraße 6, D-37077 Göttingen

In recent years, there has been a tendency to publish not only one's research findings but also the data and source code that was used to process that data—it has become more important to publish not only *what* a study found, but also *how* these findings *exactly* came about. And for good reasons: additionally to a higher level of transparency and confidence in the results, researchers can then build not only on the knowledge of their peers and predecessors, but they can build on and / or learn from the published research code, much like it is now done routinely in the open source software community. Thanks to this community, the necessary tools to manage, publish, and collaborate on research code are now mature and readily available.

A possible source of friction in the endeavor to share one's source code and, importantly, *make it runable* by other people, is that the latter requires documenting the used software environment very precisely and in a standardized way to make the documentation useful. In this contribution, I will present ways to document and reproduce data evaluation workflows which are more robust than a mere Python "requirements.txt" file, ranging from different package managers to "containers" [1], a form of light-weight virtual machines that contain all dependencies of a software project. A particularly helpful and increasingly popular tool to perform data evaluation with scripting languages is Jupyter Notebook and JupyterLab [2], which are browser-based editors that allow to blend source code, formatted text and (graphical) output in a single document. I will present tips and address good practice for writing notebooks and show how to convert them into publishable formats that can serve directly as supplementary material for a paper. Lastly, when handling a non-trivial amount of source code, it becomes very difficult to track changes and manage backups, which is where source control software should be employed. I will show how to use the software Git to perform version control, view changes, and backup source code into a software repository.

[1] D. Nüst *et al.*, *PLOS Computational Biology*, **11** (2020), e1008316. DOI:10.1371/journal.pcbi.1008316. [2] B. E. Granger and F. Pérez, *Computing in Science & Engineering*, **23** (2021), 7–14. DOI:10.1109/MCSE.2021.3059263.

A Case Study on the Photochemistry of Monosubstituted N-Donor Triarlymethyl Radicals

Lars Roß,[1] Mona E. Arnold,[2] Francisca de Almeida Neno Bartley,[1] Julia Zolg,[2] Ludwig A. Kibler,[3] Alexander J.C. Kuehne[2], and Christoph Bannwarth[1]

[1]Institute of Physical Chemistry, RWTH Aachen University, Melatener Str. 20, 52074 Aachen, Germany.
[2]Institute of Organic and Macromolecular Chemistry, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany.
[3]Institute of Electrochemistry, Ulm University, Albert-Einstein-Allee 47, 89081 Ulm, Germany.

Light-emitting triarylmethyl radicals can be functionalized with donor moieties to significantly increase their photoluminescence quantum yield ϕ. Radicals can – in contrast to closed-shell systems – overcome the problem of spin statistics. In this collaborative study, we describe a dependence of the quantum yield on the donor strength of the substituted donor moiety. In this work, the mechanisms behind the photophysics of the substituted triarylmethyl radicals will be investigated by means of quantum chemical methods to rationalize the experimentally observed trend. To explain this trend, this work will concentrate on three characteristic donor moieties: a weak donor, a medium donor, and a strong donor. The medium donor, *N*-carbazole, has an experimental quantum yield ϕ of 91% [1] and is the current state of the art in this field. Even though high quantum yields can already be achieved, basic understanding of the photophysical mechanism to rationalize the effect of donor strengths on the photoluminescence quantum yield (PLQY) is missing.

Intersystem crossing is less likely to happen in radical systems due to the higher energy of the excited high spin state. Hence, the non-radiative pathway primarily investigated is internal conversion from the excited state D_1 into the D_0 ground state. We make use of non-adiabatic transition state theory to calculate the internal conversion rate constant. For this purpose, the conical intersection geometries are identified and used to determine the internal conversion rates. [2] The radiative decay via fluorescence is calculated from the Einstein coefficients. [3] The oscillator strengths are determined as vertical deexcitations along molecular dynamics trajectories to obtain nonzero oscillator strengths also for electric dipole forbidden transitions. With these two approaches, we are able to determine computationally derived PLQYs that allow rationalization of the experimentally observed trend in the PLQYs.

Literature:
[1] Nakamura, K.; Matsuda, K.; Rui, X.; Furukori, M.; Miyata, S.; Hosokai, T.; Anraku, K.; Nakao, K.; Albrecht, K., *Faraday Discuss* **2023**, Advance Article.
[2] J. H. Harvey, *Phys. Chem. Chem. Phys.* **2007**, *9*, 331.
[3] R. C. Hilborn, Am. J. Phys. **1982**, *50*, 982.

An Automated Reaction Discovery Approach via New Atomic Frontier Orbital Features

Y.Chen, Aachen/52074
Prof. Dr. Christoph Bannwarth, RWTH Aachen University, Melatener Str. 20, 52074 Aachen

Exploring a complete reaction network based on known mechanisms or experimental results requires enormous manual work. Various algorithms have been developed to facilitate the effort and predict reaction paths [1]. Herein, we use atomistic features from semiempirical electronic structure theory [2]. In addition, a predictive algorithm is proposed for searching reactive reaction path. The construction of the corresponding reaction coordinate incorporates considerations of steric hindrance and buried volume. Subsequently, newly generated structures are screened to identify those that are thermodynamically accessible and then undergo a new elementary reaction search. To maintain low computational costs, both reaction site prediction and reaction simulations are conducted at the semiempirical tight-binding level [3], with structural and energetic corrections applied using low-cost density functional theory (DFT) methods. The performance of this algorithm is demonstrated for different model reactions, some of which are difficult to describe using, e.g., well-established Fukui functions.

Literature:
[1] J. Unsleber, Journal of Chemical Theory and Computation,2022, 18 (9), 5393-5409. [2] P. Steinbach, M.Sc. thesis, RWTH Aachen, 2021. [3] C. Bannwarth, Wiley Interdisciplinary Reviews: Computational Molecular Science, 2021, 11, e1493.

Magnetic coupling analyses of *μ*-oxo-bridged dinuclear first row transition metal complexes

Justin Krampe, Prof. Dr. Vera Krewald, TU Darmstadt, Fachbereich Chemie, Quantenchemie, Peter-Grünberg-Str. 4, 64287 Darmstadt

Magnetic coupling in transition metal complexes results from the interaction of electron spins, which are mostly localized on the magnetic centers. These interactions give rise to different spin states, the energetic splitting of which is usually parameterized with the Heisenberg-Dirac-van Vleck-Hamiltonian. The origin of the resulting ferromagnetic and antiferromagnsetic coupling and the strength of the coupling can be interpreted with the concepts of Goodenough, Kanamori and Anderson.[1]

Quantum chemistry can predict the electronic structures of magnetically coupled complexes. Different levels of theory like Density Functional Theory (DFT) or Complete Active Space (CAS) methods with subsequent perturbation theory can be utilized to calculate the magnetic coupling constants between two centers. However, the computed coupling strength can differ by up to an order of magnitude depending on how electron correlation is treated. Comparison with experimental data reveals which level of theory performs well, allowing more detailed analyses of coupling paths.[2] This is particularly relevant for iron dimers, where multiple contributors, e.g. spin-orbit-coupling or double exchange effects, are known to influence the magnetic coupling strength.[3]

Building on analyses introduced by B. Hoffman[4] and J.-P. Malrieu[5], we present a joint analysis of CASSCF and broken-symmetry DFT calculations for magnetic interactions in μ-oxo-bridged transition metal complexes, specifically a systematic series of complexes from a (μ-O)-Mn$^{II}_2$ case to a (μ-O)-Cu$^{II}_2$ case.

Literature:
[1] a) J. Kanamori, *J. Phys. Chem. Solids* **1959**, 10, 87-98. b) P. W. Anderson, *Solid State Phys.* **1963**, 14, 99-214.
[2] a) M. Roemelt, V. Krewald, D. A. Pantazis, *J. Chem. Theory Comput.* **2018**,14.1, 166-179. b) C. J. Stein, D. A. Pantazis, V. Krewald, *J. Phys. Chem. Lett.* **2019**, 10, 6762-6770.
[3] A. Mihail, N. Spiller, F. Neese, *Phys. Chem. Chem. Phys.* **2022**, 24, 20760-20775.
[4] H. P. Jeffrey, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.* **1975**, 97, 4884-4899.
[5] C. J. Calzado, J. Cabrero, J. P. Malrieu, R. Caballol, *J. Chem. Phys.* **2002,** 116, 2728-2747.

Computational Design of New Anthracene-based Imine Ligands and Cu(I) Complexes

L. Zitta, Braunschweig/DE, O. Lange, Braunschweig/DE,
S. Tschierlei*, Braunschweig/DE
TU Braunschweig, Institute of Physical and Theoretical Chemistry, Department of
Energy Conversion
Rebenring 31, 38106 Braunschweig

Cu(I) photosensitizers are known to have a broad range of applications in modern photochemistry. An extensive body of data exists on different Cu(I) complexes with 1,10-phenanthroline as a starting ligand. However, such complexes have limited absorption in the visible light region particularly above 450 nm despite excessive numbers of derivatisations. [1, 2, 3]

Therefore another strategy must be proposed in which switching the parent-compound of the starting ligand may be an option. This study focuses on anthracene-based imine ligands and their Cu(I) photosensitisers. Anthracene itself is a well-known organic dye with characteristic visible absorption and has already been applied photochemically as a singlet oxygen sensor. [4] Derivatives thereof with nitrogen donor atoms e.g. 9-azaanthracene and those bound to copper(I) are investigated computationally with (time-dependent) density functional theory on their structural and absorptive properties and are compared to established compounds with 1,10-phenanthrolines.
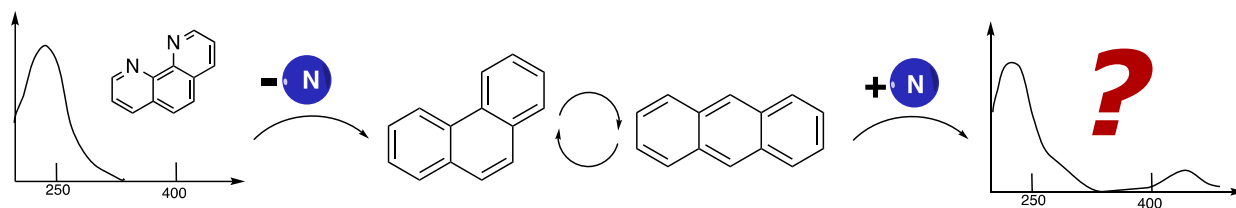
Literature:

[1] J. Beaudelot, S. Oger, S. Peruško, T.-A. Phan, T. Teunens, C. Moucheron, G. Evano, *Chem. Rev.*, **2022**, *122(22)*, 16365-16609.
[2] Y. Yang, F. Doettinger, C. Kleeberg, W. Frey, M. Karnahl, S. Tschierlei, *Front. Chem.*, **2022**, *10:936863*.
[3] F. Doettinger, Y. Yang, M. Karnahl, S. Tschierlei, *Inorg. Chem.*, **2023**, *62*, 8166-8178.
[4] A. Kastrati, F. Oswald, A. Scalabre, K. M. Fromm, *Photochem,* **2023**, *3(2),* 227-273

Exploring Efficient Density Matrix Methods for Potentially Linear Scaling in Extended Tight-Binding Density Functional Theory Calculations

T. K. Schramm, Aachen/GER, C.-M. Röper, Aachen/GER
Prof. C. Bannwarth, RWTH Aachen University, Melatener Str. 20, 52074 Aachen

The widespread success of conventional density functional theory (DFT) methods for molecular modeling of chemical systems has motivated the development of more efficient approaches suited for increasingly larger systems. Currently, such semiempirical calculations are limited to around 1000 atoms by the $O(N^3)$ scaling of the diagonalization of the Fock matrix (**F**) in the self-consistent field (SCF) procedure, rendering the study of intricate biological systems with several thousand atoms impractical. [1] However, McWeeny [2] recognized that solving for an idempotent ($\mathbf{D}^2 = \mathbf{D}$) density matrix (DM) directly would effectively circumvent this limiting diagonalization step, paving the way for truly linearly scaling SCF calculations for application to large molecules.

DM methods can be broadly categorized into density matrix minimization (DMM) and purification (DMP) techniques: DMM methods follow the strategy of minimizing an energy density functional, where the initially correct idempotency of a guess matrix is retained by implicit purification of an auxiliary DM at each optimization step. DMP schemes, however, exploit the common eigenbasis of **D** and **F** by using an initial guess with correct eigenfunctions but incorrect idempotency that needs to be recovered before final convergence of the purification. [3] This study seeks to compare efficient implementations of DMM and DMP methods for extended tight-binding calculations using GFN*n*-xTB [4], specifically targeting systems with up to 10000 basis functions.

Literature:
[1] J. Kussmann, M. Beer, C. Ochsenfeld, WIREs Comput Mol Sci 2013, 3, 614.
[2] R. McWeeny, Proc. R. Soc. London, Ser. A 1956, 235, 496.
[3] D. R. Bowler, T. Miyazaki, Rep. Prog. Phys. 2012, 75, 036503.
[4] C. Bannwarth, *et. al.*, WIREs Comput Mol Sci 2020, 11, e1493.

Transport and Storage

Alkali deuteron substitution in a S53P4 bioglass

Kevin Rein, Karl-Michael Weitzel

Department of Chemistry, Philipps-Universität Marburg, 35032 Marburg

The electric field assisted ion exchange (EFAIE) is an experimental technique which allows to manipulate the physical properties of solid electrolytes, especially near the sample surface [1]. In EFAIE native alkali cations are exchanged by foreign cations of same valence state through sputtered or molten electrodes [1, 2]. The ion exchange can lead to, among other things, chemical toughening, introducing of antimicrobial properties or the formation of waveguides structures [2, 3, 4].

The alkali deuteron substitution (ADS) is a special form of the EFAIE, where D^+ ions are formed from molecular D_2 at the interface between the sample and a sputtered platinum electrode. These D^+ ions replace the native (and mobile) alkali ions. This technique is an adaptation of the alkali proton substitution technique first introduced by Omata and coworkers [5].

In this contribution, we present results of an ADS experiment on a S53P4 bioglass. Bioactivity implies, in general, the exchange of ions, which triggers the questions for the mobility of ions in the bioglass [6]. In the S53P4 bioglass the nature of the relevant charge carrier has not yet been identified beyond doubt. Here, the ADS experiment allows to identify the Na^+ as the native charge carrier. It further provides access to the specific conductivity and the activation energy of the cationic transport in the S53P4 glass system.

Evidence for this conclusion originates from the quantification of concentration depth profiles in the ADS treated sample by means of ToF-SIMS, exhibiting a characteristic replacement of the native Na^+ ions by the external D^+ ions. The concentration depth profile has been simulated within the framework of the Nernst-Planck-Poisson (NPP) transport theory. The theoretical analysis shows a pronounced concentration dependent diffusion coefficient for the native Na^+ ions and a constant diffusion coefficient for the D^+ ions.

[1] N. Takamure, A. Kondyurin and D. R. McKenzie, J. Appl. Phys. 125, 175104 (2019).

[2] M. E. Nordberg, E. L. Mochel, H. M. Garfinkel and J. S. Olcott, J. Am. Ceram. Soc. 47, 215-219 (1964).

[3] D. Guldiren, S. Aydin, Mater. Sci. Technol. C 78, 826-832 (2017).

[4] M. J. Li, S. Honkanen, W. J. Wang, R. Leonelli, J. Albert and S. I. Najafi, Appl. Phys. Lett. 58, 2607 (1991).

[5] T. Ishiyama, S. Suzuki, J. Nishii, T. Yamashita, H. Kawazoe and T. Omata, Solid State Ionics 262, 856-859 (2014).

[6] F. Baino, S. Hamzehlou, S. Kargozar, J. Funct. Biomater. 9, 25 (2018).

Lithium Diffusion in Doped Crystalline Silicon

Timo Kassubek, Karl-Michael Weitzel

Department of Chemistry, Philipps-Universität Marburg

Silicon is a potential anode material for lithium ion batteries (LIB), due to its high theoretical capacity [1]. Despite the enormous technical and fundamental interest in Silicon and Silicon-derived anode materials, the data base for Lithium diffusion in Silicon is sparse. Neither the diffusion coefficients of Li nor its activation energy are established beyond doubt.

Here we report on a systematic study of lithium diffusion in crystalline silicon wafers as a function of the degree of n- and p- doping. The transport is induced by depositing Li metal under inert gas atmosphere onto a Si wafer and tempering the sample at elevated temperature for a specific time. Subsequently, remaining Li metal is removed and the sample is subjected to concentration depth profiling by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS).

The concentration depth profiles unambiguously demonstrate that two different transport pathways are operative. The diffusion coefficient of one component appears to be independent of the dopant concentration, the second diffusion coefficient increases exponentially with increasing dopant concentration, i.e. decreasing resistance. The first mechanism is assigned to interstitial transport, the second mechanism is assigned to defect transport.

[1] B. A. Boukamp, G.C. Lesh, R. A. Huggin, J. Electrochem. Soc., 128, 725, (1981)

A molecular dynamics study of oxygen diffusion in brownmillerite $Sr_2Fe_2O_5$

S. Ambaum, Aachen/DE, N. L. Allan, Bristol/UK, R. Dittmann, Jülich/DE, R. A. De Souza, Aachen/DE

Sonja Ambaum, RWTH Aachen University, Landoltweg 2, 52074 Aachen

The topotactic phase transition of some perovskites, from perovskite $ABO_{3-\delta}$ to brownmillerite $A_2B_2O_5$, has recently attracted attention because of its potential for application in redox-induced resistance random access memories (ReRAM). The perovskite phase with its disordered vacancy distribution shows high oxide-ion mobility in contrast to the brownmillerite phase with its one-dimensionally ordered oxygen vacancies. The key process for the phase transition is the diffusion of oxygen point-defects, but oxygen diffusion coefficients have been obtained neither experimentally nor computationally. Furthermore, insights into the mechanisms of oxygen diffusion from atomistic simulations have been limited to static calculations.

In our study, we employed molecular dynamics (MD) simulations with empirical pair potentials (i) to obtain oxygen diffusion coefficients for both the brownmillerite $Sr_2Fe_2O_5$ phase and the perovskite $SrFeO_{2.5}$ phase; and (ii) to elucidate the paths and mechanisms of oxygen diffusion used by the systems. In particular, we investigated non-stoichiometric systems with oxygen excess or oxygen deficiency in order to study diffusion processes by means of oxygen interstitials or oxygen vacancies independently from each other. The investigation of the stoichiometric system allowed us to achieve a deep and detailed description of the system.

Reading between the grain of oxide-ion conductors: the thermal history of space-charge layers

Adrian L. Usler [a], Fabian Ketter [a], Roger A. De Souza [a]

[a] RWTH Aachen University, Aachen, Germany

The excess resistivity of grain boundaries in oxide-ion conducting polycrystals is generally attributed to the presence of space-charge layers in which oxygen vacancies are depleted. A simplified description of the grain-boundary impedance with closed-form expressions can be provided if the acceptor cations take a uniform concentration profile throughout the sample (Mott–Schottky case). Analysing impedance data with the Mott–Schottky model, however, is problematic in two aspects: first, this dilute-solution model is often applied to heavily substituted electrolyte materials, the conductivities of which are known to be largely determined by point-defect interactions. Second, ceramic samples are usually prepared by sintering at high temperatures, thus permitting the acceptor cations to attain electrochemical equilibrium before their movement is frozen upon cooling.

In this work, we present impedance spectra calculated from continuum-level simulations of space-charge layers at a grain boundary. Simulations are carried out in the scope of the restricted-equilibrium and the Poisson–Cahn space-charge models, to account for thermal history and for point-defect interactions, respectively. We discuss the errors that arise from an analysis of these more complex cases with the simplified Mott–Schottky model and propose a consistency check to reveal cases that are not adequately described by the Mott–Schottky model.