BUNSEN-TAGUNG 2025

Physical Chemistry
of the Climate and the Atmosphere

Leipzig University
March 17-19, 2025

BOOK OF ABSTRACTS

LECTURES

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Deutsche Bunsen-Gesellschaft
für physikalische Chemie

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Atmospheric online ion chromatograph

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The atmospheric online ion chromatograph analyzes the soluble components of the air through online collection and liquefaction systems to achieve the function of continuous monitoring of air quality, providing comprehensive and accurate monitoring data for air quality monitoring and pollutant tracing. This equipment adopts a fully plasticized flow system, electrolytic self-regeneration suppression mode, all-weather continuous operation, remote control, remote data transmission, etc., so that the atmospheric online ion chromatograph has perfect and stable testing performance while bringing users an automated and humanized application experience.

Outstanding performance

- It can detect anions in the atmosphere in real time and stably, including but not limited to (F^-、Cl^-、NO_2^-、Br^-、NO_3^-、SO_4^{2-})；
- It can detect cations in the atmosphere in real time and stably, including but not limited to (Li^+、Na^+、NH_4^+、K^+、Mg^{2+}、Ca^{2+})；
- It can detect small molecular acids in the atmosphere in real time and stably, including but not limited to ($HCOO^-$、CH_3COO^-、$C_2O_4^{2-}$)；
- Simultaneously read ⩾10 sets of particle chromatographic data and images, and obtain online detection data.

Atmospheric particulate matter concentration -soluble component analysis system

DIPLÔME

inventions geneva

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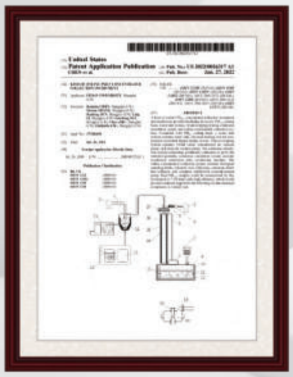
Geneva International Invention Award
Silver Award



US20220026317A1
US Patent

Product Features

- Particle enrichment multiples 3-10 times, small fluctuation, high stability
- Effective particle concentration diameter 30~3000nm
- Input airflow 10-200L/min flexibly adjustable
- Saturation temperature is close to room temperature
- Install a drying tube to eliminate the influence of humidity
- Sampling time can be set as needed
- Dual systems run independently
- Concentrated samples can be tested online and automatically retained at the same time

Product patents and papers

Shang, X., Li, L., Zhang, X., Kang, H., Sui, G., Wang, G., Ye, X., Xiao, H., and Chen, J.*: A semicontinuous study on the ecotoxicity of atmospheric particles using a versatile aerosol concentration enrichment system (VACES): development and field characterization, Atmos. Meas. Tech., 14, 1037–1045, https://doi.org/10.5194/amt-14-1037-2021, 2021.
Shang X, Kang H, Chen Y, Abdumutallip M, Li L, Li X, Fu H, Wang X, Wang L, Wang X, Ouyang H, Tang X, Xiao H, George C, Chen J.
PM1.0-Nitrite Heterogeneous Formation Demonstrated via a Modified Versatile Aerosol Concentration Enrichment System Coupled with Ion Chromatography. Environ Sci Technol. 2021 Jul 20;55(14):9794-9804. doi: 10.1021/acs.est.1c02373

PLENARY LECTURES

SPECIAL SESSIONS

- DBG Awards
- yPC Sessions
- Agnes Pockels Session

The challenge of climate change – Can we still meet the Paris climate targets?

Mojib Latif

Academy of Sciences, Hamburg

In response to the now undeniable climate changes, the international community agreed in 2015 in the Paris Agreement to limit the temperature increase to well below 2 degrees Celsius (°C) above pre-industrial levels and to pursue efforts to limit it to 1.5 °C. Nevertheless, global emissions of so-called greenhouse gases have continued to rise, especially emissions of carbon dioxide (CO_2), the most important gas for global warming. Mankind is facing an unprecedented challenge in tackling the climate problem, which is mainly due to the very long residence time of CO_2 in the atmosphere. Can we still meet the Paris climate targets? And what if we can't?

What drives nighttime chemistry?

A.R. Ravishankara,
Departments of Chemistry and Atmospheric Science, Colorado State University, Fort Collins, CO, USA

Chemistry in the Earth's atmosphere is driven mainly by sunlight. Indeed, this chemistry is termed atmospheric photochemistry. This situation does not mean that chemistry stops at night! I will describe some of the major processes at night and answer the question: "What is the energy source for nighttime chemistry when there are no photons? I will use examples from various laboratory measurements, field studies, and calculations.

Clouds, Chemistry and Climate

Merete Bilde
Department of Chemistry, Aarhus University, Denmark

Aerosol particles in the atmosphere of Earth play an important role in our climate system. They are emitted directly into the atmosphere, for example via oceanic wave breaking or combustion processes. They are also formed in the atmosphere from oxidation of volatile organic compounds followed by cluster formation and condensational growth. Aerosol particles can influence climate by acting as nuclei for the formation of cloud droplets and ice crystals [1]. This talk will have a special focus on the aerosols formed from oceanic wind induced wave breaking. At high wind speeds air is entrained in the upper water column as bubbles. These bubbles rise to the surface where they burst, resulting in release of sea spray aerosol to the atmosphere.

I will give an overview of our laboratory methods and results designed to elucidate the formation, properties and cloud forming ability of atmospheric aerosols [2-4]. In particular, I will present results on sea spray aerosols, the formation of hydrate containing salts and the complex interplay between inorganic and organic components in sea spray aerosol. Results will be discussed in the context of atmospheric chemistry and processes.

Literature:

[1] Masson-Delmotte, V. et al. IPCC, 2021: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. 2021 Cambridge University Press.
[2] Kristensen, K., et al., Environmental Science-Processes & Impacts, 2017. 19(10),1220-1234.
[3] Nielsen, L.S. and M. Bilde, Tellus B: Chemical and Physical Meteorology, 2020. 72(1):1-10.

[4] Christiansen, S., et al., Environmental Science & Technology, 2019. 53(22): 13107-13116.

Bridging Scales in Atmospheric Chemistry

Prof. V. F. McNeill, New York, USA
Departments of Chemical Engineering and Earth and Environmental Engineering,
Columbia University, New York, NY 10027 USA

A fundamental challenge of atmospheric chemistry is bridging the gap between the detailed molecular-level knowledge generated by laboratory experiments and computationally intensive large-scale models. I will discuss our recent progress in automated model reduction, and case studies illustrating my group's approach using process models to: (a) extract kinetic parameters necessary for modeling novel chemistry from laboratory studies (b) evaluate the potential impact of that chemistry under ambient environmental conditions (c) parameterize these processes for large-scale modeling and (d) focus and inform future laboratory studies. I will also discuss recent laboratory work related to the stratospheric heterogeneous chemistry of candidate Stratospheric Aerosol Injection materials and implications for their potential impact on stratospheric ozone.

Experimental modelling of titanium-based (photo-)catalysts for challenges in the energy transition

L. Mohrhusen, Oldenburg, DE, Carl von Ossietzky Universität Oldenburg,
Carl-von-Ossietzky Str. 9-11. 26129 Oldenburg, Germany

To overcome challenges in the energy transition, heterogeneous (photo)catalysis emerges as one of the key technologies. For instance, oxide-based (photo)catalysts allow e.g. for selective oxidations[1] or the utilization of greenhouse gases such as CO_2.[2] Such (photo-)catalysts usually comprise one or more semiconducting oxides supporting (noble) metal nanoparticles. Unfortunately, these metals are expensive and prone to deactivation due to e.g. sintering, coking or CO poisoning. Thus, strategies to replace noble metal in such systems are of critical importance.

Titanium is one of the few elements, that are attractive due to its natural abundancy under economic and ecological aspects. Titanium dioxide (TiO_2) in particular offers a versatile platform: Point defects (e.g. Ti^{3+}) can boost the photocatalytic activity towards oxygen containing molecules.[1] TiO_2 also readily forms hybrid systems with other oxides (e.g. WO_3 clusters)[3] or sulfides (e.g. MoS_2) which could substitute noble metals and mitigate drawbacks such as the relatively wide band gap which limits the ability of pure TiO_2 to absorb most of the solar spectrum. To derive an atomic-level understanding, studies on well-defined model catalysts with surface science tools from *operando* to UHV conditions serve as an essential step to simplify the inherent complexity of industrial catalysts.[4-6] A combination of spectroscopic techniques (esp. XPS and FTIR) with high resolution microscopy (esp. STM) and product analysis techniques (TPD) provides a comprehensive picture. Herein, we present selected results from well-defined (photocatalytic) models en route to the desired Ti-based hybrid materials. Starting from the role of point defects in TiO_2, combinations of TiO_2 with e.g. nanostructured 2D materials such as TiS_2[7] or conducting polymers will be presented.

Literature:

[1] L. Mohrhusen, K. Al-Shamery *Catal. Lett*. **2023**, 153, 2, 321. [2] Moustakas et al., *Chem. Eur. J* **2018**, 24, 12739. [3] L. Mohrhusen et al. *J. Phys. Chem. C* **2020**, 124, 43, 23661. [4] L. Mohrhusen et al. *J. Phys. Chem. C* **2022**, 126, 48, 20332. [5] L. Mohrhusen et al., *Small* **2024**, 2405715. [6] M. Hedevang et al., to be submitted. [7] N. Kruse et al., to be submitted.

Resolving the Anomalous Hydrogen Bond Blueshift – The C≡N Stretching Vibration Reports on Electric Fields and Hydrogen Bond Geometry

J. Kozuch, Berlin/DE, J. M. Kirsh, Stanford/USA
Dr. Jacek Kozuch, Freie Universität Berlin, Fachbereich Physik / Forschungsbau
SupraFAB, Altensteinstr. 23a, 14195 Berlin

Vibrational Stark effect (VSE) spectroscopy has become one of the most important experimental approaches to measure electric fields strengths underlying noncovalent interactions, and quantify their influence on structure and reactivity. However, quantifying electrostatics due to hydrogen bonds (HB), one of the most important noncovalent interactions in molecular design, remains challenging.[1,2] In particular, the nitrile (C≡N) vibrational probe – the most popular VSE reporter used extensively to measure electrostatics in aprotic solvents, at electrode interfaces, and in protein settings – cannot be interpreted via the VSE in H-bonding environments. This is due to the anomalous HB blueshift, an unresolved deviation from the VSE. In this work, we sought to turn this complicating factor into a useful observable.[3] We developed a model for the HB blueshift which is based on HB geometry (i.e., C≡N – HB donor distance and angle) by comparing vibrational shifts predicted via density functional theory to electrostatics from the polarizable AMOEBA force field across different H-bonding environments. We show that our model performs excellently ($R^2 = 0.95$) when compared against experimental IR spectra of nitriles in many settings, such as in solvents, proteins, and within metal-organic frameworks. Furthermore, our work has three major implications. First, this model is general for aliphatic and aromatic nitriles, and a range HB donors. Second, it enables direct quantification of HB geometry for rigid HBs, while dynamic effects must be considered for flexible HBs. Third, we find that the HB geometry dependence arises from multipolar electrostatics and Pauli repulsion contributions, adding to a more nuanced understanding of the origins of the HB blueshift.

Literature:
[1] J. B. Weaver, J. Kozuch, J. M. Kirsh, S. G. Boxer, *JACS*, **2022**, 144, 7562-7567.
[2] J. M. Kirsh, J. B. Weaver, S. G. Boxer, J. Kozuch, *JACS*, **2024**, 146, 6983-6991.
[3] J. M. Kirsh, J. Kozuch, *ChemRxiv*, **2024**, DOI: 10.26434/chemrxiv-2024-rjm5p

In the Land of Marvels: Science, Fabricated Realities, and Industrial Espionage in the Age of the Grand Tour

Prof. Paola Bertucci, Yale University

Jean Antoine Nollet (1700-1770), more famously known as the abbé Nollet, was one of the most popular scientific authors and instrument-makers of the eighteenth century. A leading member of the Paris Academy of Science, the physics tutor to the French Dauphin, and the maker of the *cabinet de physique* of Voltaire and Madame du Chatelet, Nollet was the emblem of public science in the Age of Enlightenment. His best-selling, multi-volume *Leçons de physique expérimentale* was translated into several languages, while his courses of experimental physics in Paris attracted aristocratic ladies along with curious foreigners, entrepreneurs, and numerous young students, including Antoine Lavoisier.

This talk will reveal an aspect of Nollet's career that remained largely hidden during his lifetime: his activity as a secret consultant for the French state. This activity started around 1749 – at the apex of Nollet's celebrity – when he toured Italy for nine months. Officially, his journey was motivated by an international controversy over the therapeutic properties of the newly discovered "electric fire", sparked by Italian experimenters who advanced extraordinary claims about miraculous electric cures. In fact, during his time in Italy Nollet carried out a meticulous operation of technical intelligence gathering on the Italian silk industry. This mission was strategic in the context of the French Bureau of Commerce's reorganization of the French silk industry. I will discuss how Nollet used his public reputation in the experimental sciences as a cover for his secret mission and will illustrate the strategies that he employed to successfully accomplish it.

yPC-Session „How to PhD?”

March, 18, 2025 / Tuesday
09.20-10.20

Panel discussion members: Prof. Dr. Ralf Ludwig, Prof. Dr. Jannika Lauth, yPC Core Team

In the session an early-career and a senior PI will share their perspectives on what makes a successful PhD student, drawing from both their own experiences and their time as supervisors. Following an insightful discussion, audience members will have the opportunity to engage in a Q&A to gain practical advice for navigating their PhD journey.

This session will be held in English.

yPC-Session “Meet the yPC!”

March, 18, 2025 / Tuesday
10.50-11.20

Speakers: yPC Chairs, yPC Core Team

In the session you will have the chance to meet the new speaker team of the young Physical Chemists of the German Bunsen Society. Get to know their ongoing projects, discover opportunities to get involved, and learn how you can shape the future of the young society!

This session will be held in English.

yPC Career Forum + World Café

March, 18, 2025 / Tuesday
13.00-14.30

Invited panelists: Dr. Daniela Fries, Lab Team Lead at BASF; Dr. Ulrike Boehm, R&D Scientist at Carl Zeiss AG

Wondering what career opportunities await you after your PhD? Join us for the yPC Career Forum + World Café, where industry professionals will share their career journeys, insights, and advice on making the transition from academia to industry.

After a short panel discussion, you’ll have the unique opportunity to engage in small, rotating group discussions with our panelists in a World Café format—a dynamic and interactive setting where you can ask questions, gain valuable perspectives, and explore different career paths in a relaxed atmosphere.

Whether you're actively planning your next steps or just curious about your options, this is your chance to connect, learn, and get inspired for your future beyond the PhD!

This session will be held in English.

Deciphering Multistep Photoreactions Involving Radicals and Geminate Ion Pairs

C. Allacher, D.J. Grenda, E. Harrer, A.F. Tiefel, C.H. Nagel, S. Park, Dr. A.K. Dutta, D. Fritsch, Dr. R.J. Kutta, Prof. Dr. J. Rehbein, Prof. Dr. A. Breder, Prof. Dr. P. Nuernberger

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

Elucidating the underlying reaction steps is indispensable for identifying new light-induced reaction pathways and enabling their application. This work investigates the reaction mechanisms and reactivities of organoselenium compounds using time-resolved spectroscopy.

A key focus is the net heterolysis of organic diselenides. After initial homolysis, the fragments, still holding excess energy, undergo electron transfer to form a geminate ion pair. The selenium cations were studied as photo-generated Lewis-acid catalysts. This reaction mechanism, termed *stimulated doublet-doublet electron transfer* (SDET), relies on two distinct stimuli, where the first generates a radical and the second initiates an electron transfer and can also be extended to carbon-selenium bonds [1]. In addition, mechanistic studies of the semi-pinacol rearrangement of selenohydrins were performed, where the phenylselenyl leaving group is activated by a hydrogen bond between the hydroxyl group and selenium atom. Transient absorption recorded in HFIP, show that phenylselenol radical cation is formed instead of a neutral radical, finally linking it to product formation [2]. The results reveal new insights into the photochemistry of organo-selenium compounds with applications from catalysis to medicinal chemistry.

Literature:

[1] A.F. Tiefel, D.J. Grenda, C. Allacher, E. Harrer, C.H. Nagel, R.J. Kutta, D. Hernández-Castillo, P.R. Narasimhamurthy, K. Zeitler, L. González, J. Rehbein, P. Nuernberger, A. Breder, *Nature* **2024**, *632*, 550–556.

[2] S. Park, A.K. Dutta, C. Allacher, A. Abramov, P. Dullinger, K. Kuzmanoska, D. Fritsch, P. Hitzfeld, D. Horinek, J. Rehbein, P. Nuernberger, R.M. Gschwind, A. Breder, *Angew. Chem. Int. Ed.* **2022**, *61*, e202208611

This research is financially supported by Deutsche Forschungsgemeinschaft (DFG) *via* DFG TRR 325 "Assembly Controlled Chemical Photocatalysis" (444632635).

Quantum sensing for free radical generation in living cells and organisms

S. Fan, R. Schirhagl.

Department of Biomaterials & Biomedical Technology (BBT), University Medical Centre Groningen (UMCG), Antonius Deusinglaan 1, 9713 AV, Groningen, The Netherlands.

Free radicals play a crucial role in various biological processes such as cell signaling, aging, and disease progression, but their short-lived and reactive nature makes them challenging to measure. Quantum sensing, utilizing defects in diamond, enables precise detection of magnetic signals that are translated into optical signals, offering nanoscale resolution similar to MRI imaging but at a much smaller scale[1].

In our work, we employed this state-of-the-art technology to investigate free radical generation in diverse biological contexts. These included studies on mitochondrial activity in single heart muscle cells during hypoxia and reoxygenation, free radical dynamics in human keratinocytes subjected to UVB exposure, and oxidative stress in Caenorhabditis elegans models of Huntington's disease[2–4]. By using diamond-based quantum sensors, we were able to observe these processes in real-time, shedding light on the localized generation and behavior of free radicals under various conditions.

This work not only enhances our understanding of the role of free radicals in cellular and organismal physiology but also establishes quantum sensing as a versatile and precise tool for studying these elusive molecules in vivo. The insights gained from this research have broad implications, ranging from better understanding disease mechanisms to developing novel therapeutic strategies for conditions influenced by oxidative stress.

Literature:

(1) Nie, L.; Nusantara, A. C.; Damle, V. G.; Sharmin, R.; Evans, E. P. P.; Hemelaar, S. R.; van der Laan, K. J.; Li, R.; Perona Martinez, F. P.; Vedelaar, T.; Chipaux, M.; Schirhagl, R. Quantum Monitoring of Cellular Metabolic Activities in Single Mitochondria. *Sci Adv* 2021, *7* (21), 573. https://doi.org/10.1126/SCIADV.ABF0573/SUPPL_FILE/ABF0573_SM.PDF.

(2) Fan, S.; Lopez Llorens, L.; Perona Martinez, F. P.; Schirhagl, R. Quantum Sensing of Free Radical Generation in Mitochondria of Human Keratinocytes during UVB Exposure. *ACS Sens* 2024, *9* (5), 2440–2446. https://doi.org/10.1021/ACSSENSORS.4C00118/ASSET/IMAGES/LARGE/SE4C00118_0005.JPEG.

(3) Fan, S.; Nie, L.; Zhang, Y.; Ustyantseva, E.; Woudstra, W.; Kampinga, H. H.; Schirhagl, R. Diamond Quantum Sensing Revealing the Relation between Free Radicals and Huntington’s Disease. 2023. https://doi.org/10.1021/acscentsci.3c00513.

(4) Fan, S.; Gao, H.; Zhang, Y.; Nie, L.; Bártolo, R.; Bron, R.; Santos, H. A.; Schirhagl, R. Quantum Sensing of Free Radical Generation in Mitochondria of Single Heart Muscle Cells during Hypoxia and Reoxygenation. *ACS Nano* 2024, *18* (4), 2982–2991. https://doi.org/10.1021/ACSNANO.3C07959.

Spectroscopy of Fulminic acid, HCNO, using VUV- and soft X-ray radiation

M. Gerlach, Nijmegen/NL, J. Bozek, Gyf-Sur-Yvette/FR, P. Hemberger, Villigen/CH, R. Fink, Tübingen/DE, G.Worth, London/UK I. Fischer, Würzburg/DE
Marius Gerlach, HFML-FELIX, Toernooiveld 7, 6525ED Nijmegen

Fulminic acid, HCNO, is a molecule of interest both for fundamental chemistry and astrochemistry. It possesses a flat potential along the HCN bending mode, with a barrier to linearity of only 11.5 cm^{-1}, making it a "quasilinear" molecule.[1] The degenerate $^2\Pi$ electronic ground state of the HCNO$^+$ cation is subject to Renner-Teller distortion.[2] In the context of astrochemistry, HCNO was first discovered in 2009 in three starless cores and the star-forming region L1527.[3] This motivated us to investigate HCNO in the gas-phase with vacuum ultraviolet (VUV)- and soft X-ray radiation, which is also present in the interstellar medium.

We conducted our experiments at the synchrotron radiation facilities Swiss Light Source (SLS) and SOLEIL. At the VUV beamline of the SLS, we measured the dissociative photoionization of HCNO up to binding energies of 15.3 eV.[4] At the PLÉIADES beamline of SOLEIL, we measured the VUV photoelectron spectra,[4] the Auger electron spectra[5] as well as the fragmentation of HCNO following the Auger-Meitner process.[6] These measurements are supported by high-level calculations analysing the Renner-Teller effect observed in the VUV photoelectron spectrum and the Auger-Meitner process. Additionally, we provided branching ratios on the dissociation of HCNO after interacting with VUV- and soft X-ray photons.

Literature:

[1] P. R. Bunker, B. M. Landsberg, B. P. Winnewisser, *J. Mol. Spectrosc.* **1979**, *74*.
[2] R. Mondal, D. Mukhopadhyay, *Int. J. Quantum Chem* **2020**, *120*.
[3] N. Marcelino, J. Cernicharo, B. Tercero, E. Roueff, *Astrophys. J.* **2009**, *690*, L27.
[4] M. Gerlach, B. Mant, T. Preitschopf, E. Karaev, D. Mayer, H. M. Quitián-Lara, P. Hemberger, J. Bozek, G. Worth, I. Fischer, *J. Chem. Phys.* **2023**, *158*.
[5] M. Gerlach, T. Preitschopf, E. Karaev, H. M. Quitián-Lara, D. Mayer, J. Bozek, I. Fischer, R. F. Fink, *Physical Chemistry Chemical Physics* **2022**, *24*.
[6] M. Gerlach, D. Schaffner, T. Preitschopf, E. Karaev, J. Bozek, F. Holzmeier, I. Fischer, *J. Chem. Phys.* **2023**, *159*, 114306.

Near-Infrared Fluorescent Nanosensors for Pathogen Detection

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Optical sensors are vital for modern research and medicine. They offer a solution for rapid, minimally invasive sensing of analytes with high spatial and temporal resolution. The near-infrared region (NIR, 780–2400 nm) is beneficial because of the reduced background and scattering in this spectral region. In this context, single-walled carbon nanotubes (SWCNTs) have emerged as non-bleaching, near-infrared fluorescent materials that are highly sensitive to their chemical environment. [1] To translate molecular interactions into photophysical changes, the interface of SWCNTs can be decorated with polymers, or recognition units, that provide binding sites for analytes. However, the plethora of interactions (and rate constants) in complex environments limits current sensors by noise from unspecific adsorption, and few generic functionalization strategies exist. Here, we show that DNA anchor structures with capture sequences can be used for the rational assembly of NIR fluorescent sensors *via* a hybridization-based approach. Constraining the flexibility of a connected anchor sequence with so-called guanine quantum defects provided an efficient strategy to reduce unspecific adsorption and tailor the sensor selectivity to complex environments. [2] Separately, we show that the addition of a fluorescent particle, that is sensitive to its chemical environment, can be used to amplify (up to ≈ 120x) and translate optical signals to a different spectral region. [3] This effect, which we called SENSAT, was used to follow enzymatic reactions below their limit of detection in the VIS in the NIR (≈1000 nm). Overall, it presents an alternative strategy for signal transduction with the potential to amplify signals in analytical techniques.

Literature:
[1] J. Ackermann$^+$, J.T. Metternich$^+$, S. Herbertz, S. Kruss, Angew. Chem. Int. Ed. 2022, 61, e202112372. [2] J.T. Metternich, J.A.C. Wartmann, L. Sistemich, R. Nißler, S. Herbertz, S. Kruss, Journal of the American Chemical Society 2023, 145, 14776-14783. [3] J.T. Metternich, B. Hill, J.A.C. Wartmann, C. Ma, R.M. Kruskop, K. Neutsch, S. Herbertz, S. Kruss, Angew. Chem. Int. Ed. Angew. Chem. Int. Ed. 2024, 63, e202316965.

Physical Chemistry of the Climate and the Atmosphere

„Klimaschutz durch grünen Wasserstoff in Verkehr, Energieerzeugung und Prozessindustrie“

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Wasserstoff gewinnt auf dem Weg zu einer klimaneutralen Gesellschaft zunehmend an Bedeutung. Kein anderer energiereicher Stoff ist gleichermaßen vielseitig geeignet, diese Rolle in Mobilität, Wärmeversorgung und als Rohstoff in der industriellen Produktion zu übernehmen. Die offizielle deutsche Politik setzt derzeit auf den Ausbau der regenerativen Stromerzeugung und die batterie-elektrischen Fahrzeuge. Es ist aber seit langem erkennbar, dass mit einer Direktnutzung von erneuerbarem Strom in der Mobilität allein eine CO2-freie post-fossile Gesellschaft nicht möglich sein wird. Es braucht deutlich weitere Anstrengungen. Dies kann nach heutiger Meinung nur durch „grünen“ Wasserstoff erreicht werden. Der so erzeugte Wasserstoff eignet sich als stofflicher Stromspeicher, für den direkten Einsatz als Energieträger in Mobilität und Wärmebereitstellung sowie als Rohstoff in der Prozessindustrie. Gemeinsam mit „grünem“ CO2 sind mit Wasserstoff auch synthetische kohlenstoffhaltige Energieträger einschließlich der E-Fuels möglich. Letztere sind derzeit noch nicht marktfähig, aber perspektivisch in allen Bereichen der Mobilität notwendig, bei denen die direkte Stromnutzung technisch oder wirtschaftlich weder möglich noch sinnvoll ist wie im Schwerlastverkehr, bei Flugzeugen und in der Schifffahrt.

In diesem Beitrag wird der aktuelle Stand der Erzeugung von grünem Wasserstoff sowie dessen Kosten und Anwendungen diskutiert. Es werden auch perspektivisch die voraussichtlichen Mengen besprochen, die national und international in einer künftigen Wasserstoffwirtschaft benötigt werden. Schließlich wird der Blick auch gelenkt auf die Auswirkung einer solchen Wirtschaft auf das Oxidationssystem der Atmosphäre - und damit indirekt auf das Klimasystem - aufgrund unvermeidlicher Emissionen von Wasserstoff in einer breiteren globalen Anwendung.

Direct observation of the complex S(IV) equilibria at the liquid-vapor interface

T. Buttersack[1], I. Gladich[2], S. Gholami[1], C. Richter[1], R. Dupuy[3], C. Nicolas[4], F. Trinter[1], A. Trunschke[1], D. Delgado[1], P. Corral Arroyo[5], E. A. Parmentier[5], B. Winter[1], L. Iezzi[6], A. Roose[6], A. Boucly[6], L. Artiglia[6], M. Ammann[6], R. Signorell[5], H. Bluhm[1]

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The multi-phase oxidation of S(IV) plays a crucial role in the atmosphere, leading to the formation of haze and severe pollution episodes.[1]

We here contribute to its understanding on a molecular level by utilizing X-Ray photoelectron (XPS) and Raman spectroscopy to report pK_a values of the various S(IV) tautomers and reaction barriers for SO_2 formation pathways.[2] This also includes the first detection of a dissolved gas by XPS. Complementary state-of-the-art molecular dynamics simulations reveal a depletion of bisulfite at low pH at the liquid-vapor interface, resulting in a different tautomer ratio at the interface compared to the bulk.

On a molecular-scale level, we explain this with the formation of a stable contact ion pair between sulfonate and hydronium ions, and with the higher energetic barrier for the dehydration of sulfonic acid at the liquid-vapor interface. Our findings highlight the contrasting physicochemical behavior of interfacial versus bulk environments, where the pH-dependence of the tautomer ratio reported here has a significant impact on both SO_2 uptake kinetics and reactions involving NO_x and H_2O_2 at aqueous aerosol interfaces.

Literature:
[1] T. Liu and J. Abbatt, Nature Chem. 13, 1173-1177 (2021).
[2] T. Buttersack et al., Nature Commun., accepted (2024).

Photo-Redox Chemistry in Atmospheric Aerosols as a Source of Reactive Nitrogen Oxides

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Reactive nitrogen oxides (NO_y) such as nitric oxide, nitrogen dioxide, and nitrous acid propagate radical chemistry in the lower atmosphere that leads to hydroxyl radical formation, which in turn is responsible for generating ozone, aerosols, and controlling the lifetime of greenhouse gases. Sources of NO_y include combustion and microbial activity, while sinks are generally accepted to be through the formation of nitric acid, which was previously assumed to be a terminal sink for NO_y in the atmosphere. Field measurements and atmospheric models, however, suggest that efficient mechanisms exist to recycle NO_y, effectively, converting it from inactive reservoir species such as nitrate and organic nitrate esters, into photoactive forms that can participate in radical chemistry. In this presentation, we will discuss newly discovered mechanisms of NO_y recycling that occur on aerosols and ground-level surfaces and impact the oxidative chemistry of the atmosphere during the daytime. Laboratory kinetics experiments using flow reactors, and a large-volume aerosol chamber coupled to state-of-the-art aerosol and gas analyzers (e.g., aerosol mass spectrometers, chemical ionization mass spectrometers, chemiluminescence analyzers, and long-path optical absorption photometry) were used to study photochemistry that releases NO_y from inactive forms of N present in aerosols through the mediation of redox-active components. The combination of laboratory and chamber experiments both probed the photochemical mechanisms of nitrate reduction in aerosols and enabled us to evaluate the atmospheric relevance of this chemistry. Implications of this chemistry for understanding air pollution in remote and polluted areas will be discussed.

A Chemical Reference Standard for N_2O Isotopomer Ratio

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Nitrous oxide, N_2O, is a tracer of the nitrogen cycle, a potent long-lived greenhouse gas, and a major precursor for stratospheric ozone depletion. The measurement of its isotopomer ratio (i.e., the concentration ratio of $^{14}N^{15}NO$ and $^{15}N^{14}NO$) is a valuable tool for tracking N_2O sources and to elucidate biological N_2O formation mechanisms. In this context, the dimerization of HNO (nitroxyl), both as a direct chemical or enzyme-catalyzed N_2O formation pathway, is of particular interest, but the mechanistic reason for the observed isotopomer preferences is not well understood. Moreover, an easy-to-handle absolute laboratory reference standard is desirable, which would further improve the comparability of environmental isotopomer ratio studies.

This work aims (i) to utilize a spectrally broadband and high-resolution frequency comb-based Fourier transform spectrometer in the mid-infrared [1] to precisely determine N_2O isotopomer ratios and (ii) to use selective reduction of sodium nitrite as a chemical source for N_2O with an isotopomer ratio independent of the isotopic composition of the precursors. Building on previous work [2,3], (iii) a detailed analysis of the kinetic and equilibrium isotope effects in the complex acid-base mechanism for HNO dimerization will be presented, allowing us (iv) to quantitatively determine the pH and temperature dependence of the isotopomer preference. The experiment and theory show excellent agreement for the ^{15}N site preference of N_2O. The isotopomer ratio is strongly pH dependent, but at low pH it is dominated by the equilibration and decomposition of the *cis*-HONNOH reaction intermediate.

[1] I. Sadiek, A. Hjältén, F. Senna Vieira, C. Lu, M. Stuhr, A. Foltynowicz, J. Quant. Spectrosc. Radiat. Transfer 2020, 255, 107263. [2] C. Fehling, G. Friedrichs, J. Am. Chem. Soc. 2011, 133, 17912. [3] K. Zhang, S. T. Thynell, J. Phys. Chem. A 2017, 121,4505.

A Ten-Year Source Apportionment Study of PM_1 at Melpitz Central European Research Station

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Particulate matter (PM) is a key compound of air pollution and a climate-forcing agent which both necessitate long-term measurements to analyze changes in atmospheric aerosol composition. Organic aerosol (OA) constitutes the majority of aerosol mass and includes a variety of compounds [1], complicating detailed chemical analysis. Online measurements from the Aerosol Mass Spectrometer (AMS) and the Aerosol Chemical Speciation Monitor (ACSM), when used with source apportionment models, were successfully used to identify sources of organic aerosol.

Since 2012, an ACSM, in conjunction with a Multi-Angle Absorption Photometer (MAAP), has been operating at the ACTRIS-TROPOS research station in Melpitz, Germany. This measurement has provided valuable data for studying trends in particle composition and OA sources over the past decade, from September 2012 to August 2022. By extending the previous work of a 12-months [2], a rolling PMF approach [3] identified five OA factors, with three linked to primary sources: hydrocarbon-like OA, biomass-burning OA, and coal combustion OA, along with two oxygenated OA types. Trend analysis indicated a significant overall decrease in total PM_1 by -4.59% y^{-1}. However, the difference in PM_1 mass concentration between the Eastern and Western air masses is significantly decreasing by -28 % y^{-1}. This study aims to explore the year-to-year seasonal variability of PM_1 components and contrasts changes between air masses from Eastern and Western Europe.

Literature:
[1] Zhang, Q., et al. (2007) Geophys. Res. Lett., 34(13).
[2] Atabakhsh, S., et al. (2023) Atmospheric Chem. Phys., 842.
[3] Canonaco, F., et al (2020) Atmos. Meas. Tech., 204.

Reactivity of Sea Salt Aerosols with Atmospherically Relevant Acids in the Gas Phase

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As one of the most impactful aerosols in Earth's atmosphere, sea salt aerosols play a significant role in climate processes. Sodium chloride, their main component, is involved in numerous atmospheric processes, including chemical reactions with atmospherically relevant trace gases. These reactions are simulated in our experiments.

We use electrospray ionization (ESI) to produce gas-phase sodium chloride cluster ions. Atmospherically relevant acids, e.g. formic and pyruvic acid, are introduced as reaction gas into the cell of a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) and reaction kinetics are recorded. We observe a sequential acid uptake by both anions and cations, accompanied by HCl release (Figure 1). These results coincide with the observed reactions of sea salt aerosols with sulfuric or nitric acid in both atmospheric conditions [1] and laboratory studies [2]. Reactivity depends on the gas-phase acidity of the neutral reactant. Furthermore, magic cluster sizes identified in prior studies [3] show a reduced reactivity for each acid used in our experiments.

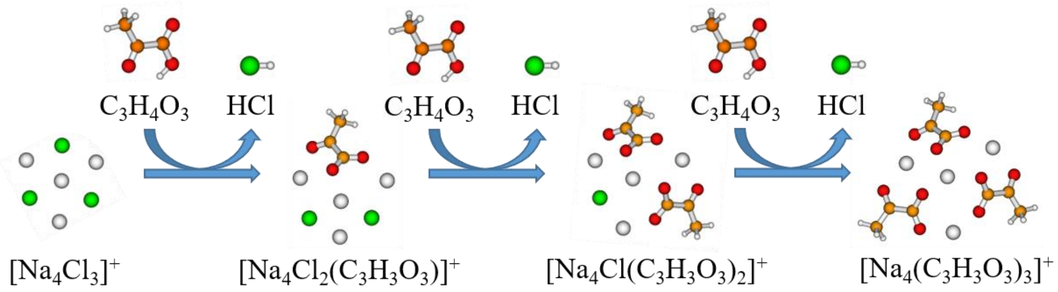

Figure 1: Sequential uptake of pyruvic acid by $[Na_4Cl_3]^+$ with release of HCl.

Literature:
[1] R. von Glasow, Nature Geosci. 2008, 1, 292–293.
[2] M. J. Rossi, Chem. Rev. 2003, 103, 4823–4882.
[3] T. D. Schachel, H. Metwally, V. Popa, L. Konermann, J. Am. Soc. Mass Spectrom. 2016, 27, 1846-1854.

Interfacial chemistry model development and simulation results: CAPRAM-het 2.0

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The air-water interface has been shown in several studies to possess properties different from bulk water, such as lower pH values, higher reaction rates for certain reactions and preference of certain substances over others. [1-3] In atmospheric chemistry, these can result in significant changes, through higher production or consumption of important species at the interface of aqueous aerosols. Although a number of studies have speculated the importance of reactions at the air – aerosol interfaces, the large – scale modeling has remained challenging, due to the lack of data on bulk – interface partitioning, and reaction rate constants. We resolve these challenges by developing a direct relationship between the bulk – interface partitioning and solubility / octanol – water partition coefficients. Implementing such a relationship in the existing CAPRAM reaction mechanism allows us to have a comprehensive model in which all the bulk reactions are also evaluated at the air – water interface. The simulations show significant results, including a 23% increase in HONO and a 358% increase in Cl_2 during the daytime cloud period. Thus, interfacial reactions can affect the tropospheric oxidant budget and can have significant effects in tropospheric chemistry.

Literature:
[1] S. Ghosal, et al. Science 2005, 307 (5709), 563-566. [2] P. Jungwirth, and D. J. Tobias, Chem. Rev. 2006, 106 (4), 1259-1281. [3] V. Buch, et al.; PNAS 2007, 104 (18), 7342-7347.

Photochemistry of carbonyl compounds in the sea-surface microlayer (SML): Insights into a mesocosm study

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The sea-surface microlayer (SML), defined as the boundary interface between the atmosphere and the ocean, is a phenomenon of global relevance, as oceans cover 70% of the Earth’s surface and are mostly expected to carry an SML. [1][2] Being rich in organic material and because of its exposure to strong UV radiation, the SML is expected to be photochemically active. Carbonyl compounds are of special interest, as they are products of photochemical reactions in the surface of the ocean [3] and consequently, they may be involved in abiotic reactions and air-sea exchange. This study examines the photochemical production and degradation of aldehydes and ketones in ambient SML and bulk seawater samples. The seawater samples were collected in a mesocosm field campaign conducted at Sea-sURface Facility (SURF), located at ICBM in Wilhelmshaven. The ambient SML and bulk seawater samples were irradiated for 5 hours in a temperature-controlled aqueous phase photoreactor with a light source that simulates the actinic radiation. Product investigations of the target carbonyl compounds were carried out using a method based on derivatization with a o-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine (PFBHA) reagent, solvent extraction and GC-MS analysis. [4] This study provides a quantitative assessment of the formation and degradation of interfacial products in the sea surface to better understand the differences in chemical conversion turnover and selectivity between the underlying bulk water and SML.

Literature:
[1] O. Wurl, E. Wurl, L. Miller, K. Johnson and S. Vagle, Biogeosciences 2011, 8(1), 121–135.
[2] A. Engel, H. Bange, M. Cunliffe, S. Burrows, G. Friedrichs, L. Galgani. H. Herrmann, N. Hertkorn, M. Johnson, P. Liss, P. Quinn, M. Schartau, A. Soloviev, C. Stolle, R. Upstill-Goddard, M. van Pinxteren, and B. Zäncker, Front. Mar. Sci. 2017, 4.
[3] X. Zhou and K. Mopper, K., Mar. Chem. 1997, 56(3-4), 201–213.
[4] M. Rodigast, A. Munzel, Y. Iiuma, S. Haferkorn and H. Herrmann, Atmos. Meas. Tech. 2015, 8, 2409-2416.

pH Dependent Structure of Model Sea Spray Aerosol Surfaces

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Aerosols have a net cooling effect in our atmosphere, mainly due to their ability to act as cloud condensation nuclei (CCN) and to reflect or scatter incoming solar radiation. The properties of the particle surface are particularly important, as it is the site for many processes which are central to cloud formation, in particular evaporation and condensation. Due to the diversity in origin and in-atmosphere ageing, aerosol surfaces contain a wide variety of chemical compounds. Understanding the resulting surface structure are central in developing a thorough understanding of the role aerosols play in the atmosphere.

In particular, the surface availability of ions and organic compounds is known to affect the hygroscopicity of the particle and thereby its ability to act as a CCN [1]. While the surface propensity of individual compounds has been studied widely, much less is known about more complex systems [2,3]. Here we focus on the impact of bulk pH on the architecture of mixed aqueous interfaces. In atmospheric systems the pH has been shown to range from roughly pH 8 to 2 [4]. Using sum-frequency-generation (SFG) spectroscopy in conjunction with surface tension data we study the surface composition and structure of short and long chain organic acids at different protonation stages, obtained by varying the pH.

Using this approach, we find severe changes in the structuring of the aqueous sub-surface layers depending on the specific composition and pH, and in the Gibbs free energy of adsorption of the studied organics. Based on our results it is feasible that subtle environmental changes may lead to pronounced shifts in surface structure, which is known to play a key role in aerosol hygroscopicity.

Literature:
[1] P. Zieger et al., Nat. Commun. 2017, 8, 15883. [2] M.T. Lee et al., PCCP, 2019, 21, 8418. [3] J. Werner et al., PCCP, 2018, 20, 2328 [4] K.J. Angle, PNAS, 2021, 118, 2, e2018397118

Kinetic analysis of iron complexes with organic acids in the aqueous phase and subsequent impact on iron catalytic cycles

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Iron (Fe) is ubiquitous in the aqueous phase of the atmosphere and is involved in numerous chemical and photochemical processes. [1,2] Additionally, it serves as a micronutrient for microorganisms, which in turn produce strong organic ligands. [3] These ligands influence the solubility, reactivity and iron complex species, which could affect the oxidation capacity in cloud water. Recent experimental observations show that more than 95% of the dissolved iron in clouds is complexed by organic ligands. [4] The complexation of iron impacts the reactivity of iron during the decomposition of hydrogen peroxide (H_2O_2); this process is usually addressed as the 'Fenton-like' reaction.

Here we study the kinetic of the reaction of iron complexes of gluconic (GLU) and succinic acids (SUC) with H_2O_2 in respect to the conversion of Fe (II) at different peroxides and ligands concentrations in the aqueous phase. The investigation was performed using the phenanthroline method and UV-VIS spectrometry. [5]

The second-order rate constant for the classical Fenton reaction in the absence of organic ligands at pH 5 was determined to be $k_{2nd} = 75 \pm 3$ L mol^{-1} s^{-1}, while the rate constant of reaction between H_2O_2 and Fe(II)-GLU complex in the presence of the organic ligand was determined to be $k_{2nd} = (2.2 \pm 0.8) \times 10^3$ L mol^{-1} s^{-1} at pH = 5. The results obtained will contribute to a better understanding of the oxidation capacity by the Fenton-like reaction in clouds.

Literature:

[1] L. Deguillaume, M. Leriche, K. Desboeufs, G. Mailhot, C. George, and N. Chaumerliac, Chem. Rev. 2005, 105, 9, 3388-3431. [2] A. Bianco, M. Passananti, G. Mailhot, A Review. Molecules. 2020, 25, 2, 423-446. [3] A. Butler, Science. 1998, 281, 207-209. [4] A. G. González, A. Bianco, J. Boutorh, M. Cheize, G. Mailhot, A. M. Delort, H. Planquette, N. Chaumerliac, L. Deguillaume, G. Sarthou, Sci. Total Environ. 2022, 829, 154642-15469. [5] APHA. Method 3500-Fe B- Iron Phenanthroline Method. 2003, 3–6.

Multiphase Chemical Kinetics in the Atmospheric, Life, and Materials Sciences

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Multiphase chemical kinetics are involved in many different fields of investigation and application, including the atmospheric, life, and materials sciences. Advanced computer models and algorithms can help to resolve the reaction pathways, kinetic parameters, and uncertainties governing environmental, physiological, and technical multiphase reaction systems. We use a Monte Carlo genetic algorithm (MCGA) for efficient, automated, and unbiased global optimization of model input parameters and determine ensemble solutions to assess and control parametric uncertainty of detailed kinetic multilayer models (KM-SUB, KM-GAP).[1]

With these computational tools, we are able to describe the complex interplay of chemical and mass transport kinetics governing the formation of secondary organic aerosol (SOA), an important subclass of atmospheric particulate matter. We show how the evaporation of SOA is affected by oligomerization and viscous crust formation. Multiphase chemical kinetic models of the human respiratory tract can be used to investigate the health effects of air pollution. We find that the concentrations of reactive oxygen species (ROS) in the epithelial lining fluid (ELF) of the lung are primarily determined by the release of endogenous ROS, while chemical production from inhaled fine particulate matter (PM2.5) accounts only for a minor fraction (~ 1 %) of total ROS. In contrast, the production of highly noxious OH radicals in the ELF is largely (> 90 %) determined by chemical reactions involving PM2.5.[2] We also study the oxidation of carbon nanoparticles, which is relevant for a wide range of technological processes like combustion and synthetic fuel production, as well as environmental issues concerning soot aerosols.[3]

Literature:

[1] Berkemeier, T. et al., ACS Earth and Space Chem. 2021, 5(12), 3313-3323.
[2] Dovrou, E. et al., Env. Sci.: Atmos. 2023, 3, 1066-1074.
[3] Berkemeier, T. and Pöschl, U., Angew. Chem. 2024, Early Online.

Multiphase chemistry modelling for cloud processing and air quality

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For air quality applications and atmospheric chemistry process studies, the MUltiScale-Chemistry-Aerosol-Transport model MUSCAT[1] and the SPectral Aerosol Cloud Chemistry Interaction Model SPACCIM[2] were developed. SPACCIM is a box model designed to consider detailed cloud microphysical processes and multiphase chemistry. MUSCAT has been coupled in an online manner to the numerical weather prediction model ICON. MUSCAT describes the dynamics and multiphase transformation of aerosol particles and relevant trace gases and allows modelled aerosol to interact online with cloud microphysics and radiation. The coupling of MUSCAT to ICON is realised as an additional Eulerian transport scheme using ICON infrastructure, e.g., for tracer definition. The advanced model systems were applied for measurement campaigns (e.g., the Hill Cap Cloud Thuringia 2010 (HCCT-2010)[e.g., 3]) and several air quality intercomparison studies. Both SPACCIM and MUSCAT are able to treat multiphase chemistry process by treating aqueous phase chemistry within cloud droplets and deliquescent aerosol particles in addition to gas phase chemistry. The models make use of detailed and explicit chemical mechanisms such as the Master Chemical Mechanism or the Chemical Aqueous Phase Radical Mechanism (CAPRAM[4]). CAPRAM, developed at TROPOS, is an almost explicit mechanism, which describes relevant chemical aqueous-phase conversions of both inorganic and organic compounds.

Here, we present the near history and current state and exemplary results of this interdisciplinary co-development of sophisticated atmospheric models from an atmospheric chemistry point-of-view.

Literature:
[1] Wolke, R., Schröder, W., Schrödner, R. and Renner, E., Atmos. Environ., 2012, 53, 110–130. [2] Wolke, R., A.M. Sehili, M. Simmel, O. Knoth, A.Tilgner, H. Herrmann, Atmos. Env., 2005, 39, 4375-4388. [3] van Pinxteren, D., K. W. Fomba, S. Mertes, K. Müller, G. Spindler, J. Schneider, T. Lee, J. L. Collett and H. Herrmann, Atmos. Chem. Phys., 2016, 16: 3185–3205. [4] Bräuer, P.; Mouchel-Vallon, C.; Tilgner, A.; Mutzel, A.; Böge, O.; Rodigast, M.; Poulain, L.; van Pinxteren, D.; Wolke, R.; Aumont, B. and Herrmann, H, Atmos. Chem. Phys., 2019, 19, 9209-9239.

Uptake of Molecules by Hydrated Acid Clusters towards Understanding Atmospheric New Particle Formation

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Aerosol particles are one of the most important, yet possibly the least understood, components of our atmosphere. They play a significant role in global warming, influence atmospheric chemistry by participating in heterogeneous reactions, and severely impact human health in polluted areas. Therefore, it is essential to understand aerosol formation and growth in great detail, particularly by uncovering the molecular mechanisms through investigations of collisions between gas-phase molecules and small particles.

In this context, we have introduced a new approach to quantify the uptake process of various molecules by hydrated nitric acid clusters, providing direct information about their sticking efficiency. [1,2] Our molecular beam experiment combines mass spectrometry with cluster velocity measurements. In parallel with the experimental work, we conduct extensive MD simulations to reveal details of the molecule-cluster collisions, allowing us to identify the scattering and uptake processes upon collisions, and subsequently derive uptake cross sections for comparison with experimental values.

Herein, we explore the relationship between uptake and carbon chain length, the position of the O–H group, and alkyl chain branching. Particular attention is also given to the effect of different functional groups on sticking efficiency. The integration of experimental results with MD simulations provides a detailed understanding of the dynamics involved in molecule-cluster collisions. [3]

Literature:
[1] A. Pysanenko, et al., J Chem Phys 2018, 148, 154301.
[2] J. Lengyel, et al., J Phys Chem Lett 2020, 11, 2101.
[3] K. Fárníková, et al., Faraday Discuss 2024, 251, 296.

Spectroscopic VSFG Study of Triton X-100 as a model surfactant for the natural sea-surface nanolayer

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The sea surface microlayer (SML) is the uppermost layer of the water column. It is enriched by surface-active organic matter and is known to modulate exchange processes across the air-water interface. For instance, gas exchange velocity is reduced by wave damping effects. Furthermore, the SML is known to be a major source of volatile organic compounds and secondary organic aerosols in the atmosphere.

Triton X-100 (TX-100) is a commonly used non-ionic model surfactant in marine science to quantify the surfactant state of the sea-surface microlayer, which is often measured by AC voltammetry as surface activity in TX-100 equivalents. The natural composition of the organic matter in the SML can vary depending on environmental conditions, resulting in a variable ratio of soluble (wet) and insoluble (dry) surfactants. A monolayer of dry surfactants (so-called nanolayer) is known to be sufficient to induce significant changes of the viscoelastic properties of the interface. Hence, the question arises if alternative surface-selective measures for surfactant activity (e.g., surface tension or surfactant surface concentration) can be related to the standardized TX-100 method. In this sense, we use Langmuir compression isotherms as well as vibrational sum-frequency generation spectroscopy (VSFG) to derive a surfactant coverage index.

A systematic VSFG and Langmuir trough study on TX-100 solutions (wet surfactant), DPPC (dry phospholipid surfactant) monolayers, and natural SML samples has been performed to get insight into the different perspectives of micro- (AC voltammetry) and nanoscale (VSFG spectroscopy) measurements of the SML. The study aims to establish a VSFG-based definition of the surfactant coverage index as a biogeochemical parameter and to work out a reliable correlation of this index with TX-100 derived surface activity. This will help to better constrain the global impact of the SML based on already existing surface activity datasets.

Comb Spectroscopy of Halogenated Volatile Organic Compounds

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Halogenated volatile organic compounds (HVOCs) significantly influence the photochemistry of the atmosphere, particularly the ozone depletion. While these compounds are naturally produced in the oceans, they are also commonly used in industrial and agricultural applications, where their biological effects may pose a health risks. Spectroscopic detection of HVOCs is valuable for atmospheric monitoring and the monitoring of exposure limits in workplaces. However, this requires accurate spectroscopic models, which in turn depend on high-accuracy laboratory measurements. Optical frequency combs, with their broad spectral coverage and high resolution, are ideal for acquiring these data.

In this work, we use a mid-infrared frequency comb spanning 350 cm^{-1} around 3000 cm^{-1} [1] coupled with a Fourier transform spectrometer with sub-nominal resolution [2] to measure and assign high-resolution spectra of multiple absorption bands of two HVOCs: methyl iodide (CH_3I) [3,4], and dibromomethane (CH_2Br_2) [5]. For CH_3I, we measured and assigned the ν_1 and ν_4 fundamental bands as well as the nearby $\nu_3+\nu_1-\nu_3$ and $\nu_3+\nu_4-\nu_3$ hot bands. The line list in the spectral region of the ν_4 band was incorporated in the HITRAN database. For CH_2Br_2, we also recorded spectra using a comb-based cross-dispersive spectrometer [5]. Both spectra were used to revisit the assignment presented in [6] of the fundamental ν_6 band and the nearby $n\nu_4+\nu_6-n\nu_4$ hot bands, with n = 1–3, of three CH_2Br_2 isotopologues.

[1] G. Soboń, T. Martynkien, P. Mergo, L. Rutkowski, A. Foltynowicz, Opt. Lett. 2017, 42, 1748. [2] Rutkowski, P. Masłowski, A. C. Johansson, A. Khodabakhsh, A. Foltynowicz, J. Quant. Spectrosc. Radiat. Transfer 2018, 204, 63. [3] I. Sadiek, A. Hjältén, F. Senna Vieira, C. Lu, M. Stuhr, A. Foltynowicz, J. Quant. Spectrosc. Radiat. Transfer 2020, 255, 107263. [4] A. Hjältén, A. Foltynowicz, I. Sadiek, J. Quant. Spectroc. Radiat. Transfer. 2023, 306,108646. [5] I. Sadiek, A. Hjältén, F. C. Roberts, J. H. Lehman, A. Foltynowicz, Phys. Chem. Chem. Phys. 2023, 25, 8743. [6] I. Sadiek, G. Friedrichs, Spectrochim. Acta A. 2017, 181,180.

Molecular Insights into Gas-Particle Partitioning, Viscosity and Absorption of Atmospheric Brown Carbon.

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ABSTRACT. Biomass-burning organic aerosol (BBOA), containing numerous brown carbon (BrC) compounds, exerts a notable influence on atmospheric chemistry and the radiative forcing of climate. The influence of evaporation processes on optical properties, volatility, and viscosity of BBOA under different environmental conditions remains poorly understood, leading to uncertainties in predicting the atmospheric and climate effects of BrC. This study presents a molecular characterization of laboratory-generated BBOA proxies analyzed at various stages of evaporation, labeled as PO_x (where x represents the initial to remaining volume ratio after evaporation). The molecular characterization results are then applied for a bottom-up assessment of the volatilities and viscosities of the analyzed mixtures. The individual compound saturation mass concentration values measured using temperature programmed desorption − direct analysis in real time – high resolution mass spectrometry are used to construct volatility basic set (VBS) distributions. These distributions quantify the extent of gas-particle partitioning, revealing more compounds transition from the particle phase to the gas phase with atmospheric dilution. Conversely, atmospheric cooling enhances condensation of the gas-phase compounds into the particle phase, underscoring their sensitivity to both temperature and atmospheric dilution. Furthermore, the VBS-based assessment of gas-particle partitioning is leveraged to estimate the viscosities of BBOA represented by PO_x. These estimates align closely with viscosity values obtained through poke-flow experiments, thus validating the estimation approach. As the degree of evaporation increases, the viscosities of PO_x mixtures exhibit a substantial increase, resulting in a substantial slowdown in particle-phase diffusion. In this study, we also show that the evaporation of the more volatile fractions leads to increased absorption of light in the UV and visible range, further contributing to the radiative forcing of biomass-burning aerosols. This new understanding emphasizes the critical role of evaporation processes and environmental conditions in transforming the volatility and viscosity of BBOA particles. These factors should be adequately integrated into atmospheric transport models for improved accuracy in predicting BBOA aging transformations.

The Photochemistry of Nitrate in $K_n(NO_3)_{n+1}^-$ and $Na_n(NO_3)_{n+1}^-$ anionic salt clusters

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In the atmosphere, as well as the hydrosphere, the nitrate anion is one of the most important trace species. Its photolysis in the actinic region >290 nm produces NO_2^- as well as O^-, which immediately reacts with water to from a hydroxyl radical $OH^{\cdot}$ and OH^- [1]. Several studies showed that the nitrate photolysis in artic ices also plays a major role for the composition of the ambient air[2]. The quantum yield for the production of these fragments is small. This is attributed to the cage effect, which means that the products are prevented from separation due to the influence of the solvent. For the systems investigated in this work, the nitrate anion predominantly sits on the surface lowering the cage effect, allowing for a more direct study of the nitrate photochemistry. Previous experiments on copper nitrate clusters also showed a small quantum efficiency for the n-π* transition in the UV region, which leads to the photolysis. These clusters mainly fragment through the loss of neutral copper nitrate[3].

In this study the photochemistry of anionic salt clusters $K_n(NO3)_{n+1}^-$ and $Na_n(NO3)_{n+1}^-$, n = 1 - 5 is examined. The experiments were conducted on an Apex 9.4 T FTICR mass spectrometer. The clusters were produced using electrospray ionization. Photodissociation spectra for the wavelength region of 220 – 350 nm were recorded. In total three main absorption features were found, one towards 220 nm and two in the actinic region centered around 298 nm and 318 nm. Just as for the previous study of copper nitrate clusters, also here the loss of neutral potassium and sodium nitrate units dominates. However, for both systems also fragments containing O^- and NO_2^- were detected. The partial photodissociation cross section for these fragments lies in the range of 10^{-21} cm^2.

[1] J. Phys. Chem. Lett. 2014, 5, 11, 1958–1962
[2] Geophys. Res. Lett. 1999, 26, 6, 595 – 698
[3] Phys. Chem. Chem. Phys. 2021, 23, 16, 9911 - 9920

Surface Structure and Water Adsorption on K-Feldspar Microcline (001)

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Feldspar minerals are a group of abundant silicate minerals, which have a profound impact on our environment and climate. In the lithosphere, silicate weathering is an important part of the geological carbonate-silicate cycle, which regulates atmospheric carbon dioxide levels on geological timescales. In the atmosphere, airborne feldspar mineral dust particles are efficient ice nucleating particles catalysing the glaciation of mixed-phase clouds. Since both silicate weathering and ice nucleation take place at the feldspar-water interface, fundamental insights into feldspar-water interactions are central to their understanding. However, most existing experimental studies focus on macroscopic properties of the feldspar-water interface, while molecular-level insights into the interaction between feldspar and water are sparse.

Here, we present atomic force microscopy (AFM) and temperature programmed desorption (TPD) experiments on the most stable K-feldspar surface, microcline (001). Atomic-resolution imaging reveals features consistent with pairs of surface hydroxyl groups, suggesting that as-cleaved microcline (001) forms a hydroxyl-terminated surface with residual water even *in vacuo* [1]. TPD curves of water desorbing from microcline (001) show a single peak, which gradually shifts from 235 K to 180 K until the first water layer is saturated [2]. For higher coverages, the peak intensity still increases, but the peak temperature stays fixed at 180 K [2]. This finding confirms theoretical predictions that the binding energy of water on K-feldspar decreases with coverage until the first water layer is filled [3]. Our results provide important experimental insights into the atomic-scale surface structure and water adsorption on K-feldspar minerals.

Literature:

[1] T. Dickbreder and F. Sabath et al., Nanoscale 2024, 16, 3462. [2] T. Dickbreder et al., in preparation. [3] Pedevilla et al., J. Phys. Chem. C 2016, 120, 6704.

The role of nitrogenated hydrocarbons in extraterrestrial atmospheres

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The atmosphere of Titan, Saturns largest moon, consists of 95% nitrogen and 5% methane and no oxygen, resulting in a rich hydrocarbon chemistry. UV irradiation drives the formation of (ionic) polycyclic aromatic nitrogen heterocycles (PANHs) in its mesosphere, creating its characteristic opaque haze.[1] A similar chemistry likely occurred in earth's atmosphere before the buildup of oxygen more than 2 billion years ago, which is why Titan is considered to be a prehistoric earth from an atmospheric chemistry perspective.[2] UV photons and energetic particles can also destroy atmospheric PANHs and the dissociation products are fed back to the chemical inventory, where they can initiate new reactions. However, little is known about the life cycle of nitrogenated hydrocarbons under these conditions. [2]

We study the dissociation of cationic triazacoronene ($C_{21}H_9N_3$) a large model PANH, by a combination of laser dissociation and vibrational spectroscopy to identify the isomeric structure of key intermediates. For this we use the instrument for photodissociation of PA(N)Hs (i-PoP) and infrared multi photon dissociation by the free electron laser FELIX.[3]

We find that the nitrogen atom can be retained in the cationic photoproducts and is not eliminated in the form of HCN as would be expected. We furthermore observe that hydrogen loss products of large PANHs are extremely reactive, highlighted by the formation of heavier mass fragments in the dissociation experiments.[3] These intermediates could play a key role in the bottom-up formation of larger PANHs.

Literature:
[1] C. Nixon, ACS Earth and Space Chem. 2024, 8, 406-456 [2] A. Pavlov, M. T. Hurtgen, J. F. Kasting, M. A. Arthur, Geology, 2003, 31, 87-90. [3] D. Schleier, J. Kamer, A. Jiao, G. F. Schneider, H. Linnartz, J. Bouwman, PCCP, 2024, 26, 15547

Biophysical Chemistry and Biophotonics

UV-Induced Selection of Early Life Codons

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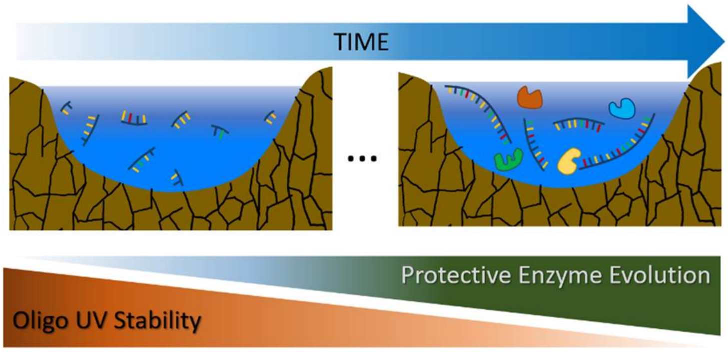
Ultraviolet (UV) light poses a threat to the integrity of the genetic code. Despite detailed studies on the photostability of DNA mononucleotides, the UV susceptibility of DNA oligonucleotides is not thoroughly understood. We recently studied UV induced self-repair, a protective mechanism and found a strong sequence selectivity of short DNA oligonucleotides under UV exposure. [1-3] Here, we investigate the UV induced sequence selectivity of short DNA oligonucleotides in a broad sequence pool which closes a missing gap between top-down and bottom-up approaches towards understanding the emergence of life prior to the last universal common ancestor (LUCA). Using a Monte Carlo method combined with experimental next-generation sequencing data, we were able to quantify the UV susceptibility of proto-genomes as they likely could have emerged on early Earth. Our results show surprising compatibility with evolution models of the genetic code, suggesting that UV light may have been a critical selection pressure in the development of early life.



Literature:
[1] Crucilla, S. J.; Ding, D.; Lozano, G. G.; Szostak, J. W.; Sasselov, D. D.; Kufner, C. L., Chem. Commun. 2023, 59 (91), 13603-13606. [2] Kufner, C. L.; Crucilla, S. J.; Ding, D.; Stadlbauer, P.; Sponer, J.; Szostak, J.; Sasselov, D. D. D.; Szabla, R., Chem. Sci. 2024, 15, 2158-2166. [3] Bucher, D. B.; Kufner, C. L.; Schlueter, A.; Carell, T.; Zinth, W., J. Am. Chem. Soc. 2016, 138 (1), 186–190.

Understanding the oligomeric plasticity of the bacterial B_{12}-dependent photoreceptor CarH from *Bacillus megaterium* on the molecular level

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The bacterial coenzyme B_{12} (AdoCbl) dependent photoreceptor CarH is a transcriptional regulator that in response to high light intensities enables the biosynthesis of carotenoids, thus, protecting the cells against photooxidative damage caused by singlet oxygen and other reactive oxygen species. In the dark, binding of AdoCbl leads to CarH tetramerization and subsequent binding to the operator DNA inhibiting transcription. Upon absorption of light the tetramer disassembles due to protein conformational changes caused by 4',5'-anhydroadenosine dissociation, thus, releasing the DNA and allowing gene transcription. Due to the requirement of green light and the modular structure, CarH is of great interest in biomedical and optogenetic applications. Hence, understanding the underlying mode of action in detail at the molecular level will help to broaden the optogenetic toolbox.

So far detailed structural and photophysical investigations were only performed on CarH from the thermophilic bacterium *Thermus thermophilus* (*Tt*).[1,2] Most recently a biochemical study on CarH from *Bacillus megaterium* (*Bm*) revealed a high plasticity in oligomerization, operator architecture, and DNA binding.[3] However, the molecular basis of the oligomeric plasticity as well as its influence on the protein structure and mode of action remain unclear. By using state-of-the-art spectroscopic and biochemical techniques the detailed reaction mechanism of *Bm*CarH will be presented and compared to *Tt*CarH wildtype. The basis of the oligomeric plasticity is assessed by detailed investigations on site-directed mutant proteins.

[1] R.J. Kutta et al., Nat. Com. 2015, 6, 7907.
[2] M. Jost et al., Nature 2015, 526, 536.
[3] J. Fernández-Zapata et al., J. Biol. Chem. 2018, 293 (46), 17888.

Stability, conformation and interactions of proteins and polyelectrolytes: spectroscopic approach

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In the cellular and extracellular environment, proteins can undergo conformational changes and alter their functionalities by modifying the functional groups of specific amino acids in response to external conditions. These changes are also influenced by interactions with abundant macromolecular species in natural fluids. The combined use of various spectroscopic techniques can provide insight into these protein behaviours.

In this study, we examine the stability and aggregation behaviour of high mobility group box 1 (HMGB1) protein, focusing on how the redox state of thiol groups affects its properties. Using nano differential scanning fluorimetry (nanoDSF), we identified significant differences in melting temperatures, enthalpies of unfolding, and refolding capacities across different domains and the full-length protein. These findings highlight the thermodynamic distinctions between protein variants with different cellular and extracellular functions. We further investigated HMGB1 dynamics at the molecular level by site-directed spin labelling electron paramagnetic resonance (SDSL EPR) to explore interactions with natural and synthetic polyelectrolytes, which are clinically relevant for modulating HMGB1 to control inflammation.

Additionally, we studied pepsin's conformation, stability, and activity in water saturated with CO_2 at high pressure using circular dichroism and nanoDSF. This media provides a biocompatible acidic environment (pH ~3) at 30 MPa, where pressure enhances enzymatic reaction kinetics. These studies open new prospectsa for examining protein function and adaptation under extreme conditions.

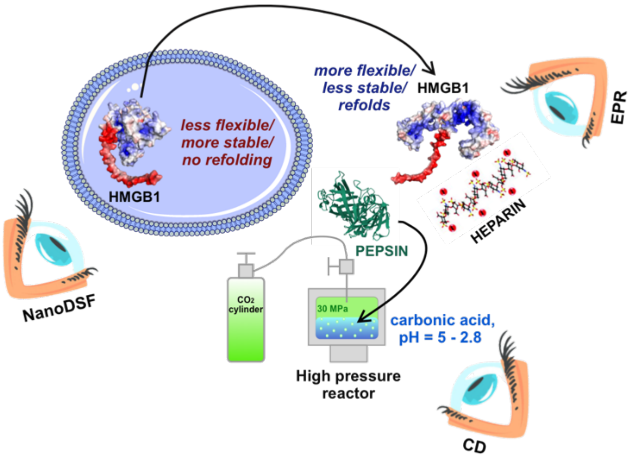

Fig.1 Overview of the biochemical research problems and the spectroscopic techniques used.

Expanding the toolbox of *in cellulo* transient absorption spectroscopy

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Biologically relevant chromophores are ubiquitously employed in sensing, imaging, and therapy. Certain organic fluorophores as well as metal coordinated compounds exhibit photobiological activity due to their tunable excited state and electron or energy transfer processes.[1]

While the target site of application for these 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 dyes and relevant functional molecules in 2D cell layers as well 3D models. Previous works in the group address these concerns for fluorophores, and for photosensitisers in live human cancer cells.[2]

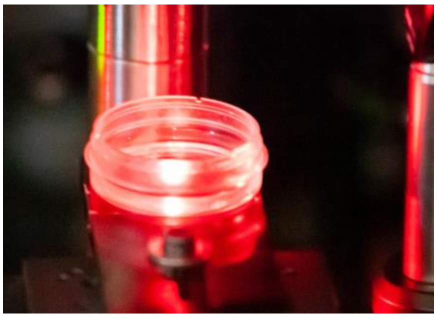
Figure 1 in cellulo Transient Absorption Setup

In this work, two classes of molecules are explored – (i) photoacid polymers as light switchable amphiphiles, which are designed for targeted release of drugs. These molecules,[3] are measured in cellulo using transient absorption spectroscopy to elucidate their excited state proton transfer. And (ii) “dark” but “loud” photoacoustic agents[4] were measured *in cellulo*, thus obtaining temporal environment specific information for non-emissive molecules. The outlook is to use transient absorption microscopy to probe the spatial information about the localisation of these molecules, which will complement the kinetic data.

[1] S. Jaswal, J. Kumar, *Materials Today: Proceedings* **2020**, *26*, 566.
[2] a) A. Chettri, T. Yang, H. D. Cole, G. Shi, C. G. Cameron, S. A. McFarland, B. Dietzek-Ivanšić, *Angewandte Chemie International Edition in English* **2023**, *62*, e202301452; b) T. Yang, A. Valavalkar, A. Romero-Arenas, A. Dasgupta, P. Then, A. Chettri, C. Eggeling, A. Ros, U. Pischel, B. Dietzek-Ivansic, *Chemistry (Weinheim an der Bergstrasse, Germany)* **2022**.
[3] A. Chettri, L. I. Kaberov, N. Klosterhalfen, S. Perera, M. Jamshied, F. H. Schacher, B. Dietzek-Ivanšić, *Chemistry - A European Journal* **2024**, *30*, e202401047.
[4] M. Müller, N. Liu, V. Gujrati, A. Valavalkar, S. Hartmann, P. Anzenhofer, U. Klemm, A. Telek, B. Dietzek-Ivanšić, A. Hartschuh et al., *Angewandte Chemie International Edition in English* **2024**, *63*, e202405636.

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Plant flowering is a light-dependent process requiring activation of the photoreceptor cryptochrome (CRY) by excitation of a bound flavin adenine dinucleotide (FAD). The biophysical principles of CRY photoactivation from the photochemical signal to the protein response of reversible oligomerization is unclear. This oligomerization is commonly utilized for artificial optogenetic control of cellular processes. Recently, several point mutations were identified leading to light-independent, constitutive activity. We employed time-resolved UV-vis and FTIR difference spectroscopy to study these mutants of the aspartic acid D393 responsible for the microsecond proton transfer to the $FAD^{\bullet -}$ [1] and of a nearby methionine M378 in plant cryptochrome (pCRY).

All mutations led to enhanced self-association of the photoreceptor already in dark according to size exclusion chromatography, indicating the importance of the amino acids D393 and L378 for maintaining the dark state structure of pCRY. However, differences between the D393 and L378 mutants are observed in the degree of self-association, light response and active site conformation. UV-vis and FTIR difference spectroscopy demonstrate that the L378R mutant fully mimics the light-activated state of pCRY as D393 is deprotonated already in the dark. Therefore, the introduced arginine lowers the pK_a of D393. In contrast to L378R, all mutants of D393 still show light-dependent oligomerization upon blue light-induced $FAD^{\bullet -}$ formation with a systematic trend in lifetimes from microseconds to seconds. These findings indicate that the negative charge within the active flavin binding site is the activation signal of plant cryptochromes as a unifying mechanism of cryptochrome signaling [2].

[1] Thöing, C., Oldemeyer, S. and Kottke, T., *J Am Chem Soc* **137,** 5990 (2015).

[2] Kottke, T., Xie, A., Larsen, D.S. and Hoff, W.D., *Annu Rev Biophys* **47**, 291 (2018).

Redox sensitive near Infrared Fluorescent Nanosensors

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Molecular sensing based on the near infrared (NIR) photon emission of single-walled carbon nanotubes (SWCNTs) is used in a broad range of applications.[1] The NIR overlays with the tissue transparency window (> 1000 nm) and SWCNTs can be chemically tailored to interact specifically with important (bio)molecules. A property that has been less exploited is the redox potential of analytes. Here we show that SWCNTs can be used to monitor chemical reactions and electrical (voltage) changes in the NIR. For this purpose, we modify (6,5)-SWCNTs with different redox-active sp^3 quantum defects that can be switched between two redox states. These quantum defects create an additional fluorescence emission feature at 1130 nm, which responds to oxidizing or reducing molecules. We show reversible chemical reactions of the quantum defects. Additionally, sensors fluorescence responds to a changing electric potential as shown in correlative cyclic voltammetry and NIR-spectroscopy experiments. In summary, we show the redox sensitive quantum defects in SWCNTs, which could have great potential for (bio)sensing or monitoring electrochemical processes.

Literature:

1. Ackermann, J., Metternich, J. T., Herbertz, S. & Kruss, S. Biosensing with Fluorescent Carbon Nanotubes. *Angewandte Chemie (International ed. in English)* 61, e202112372; 10.1002/anie.202112372 (2022).

2D-IR Spectroscopy Shows the Influence of Sequence Specificity on the Macrostructure of Single-Repeat GLFG Hydrogels.

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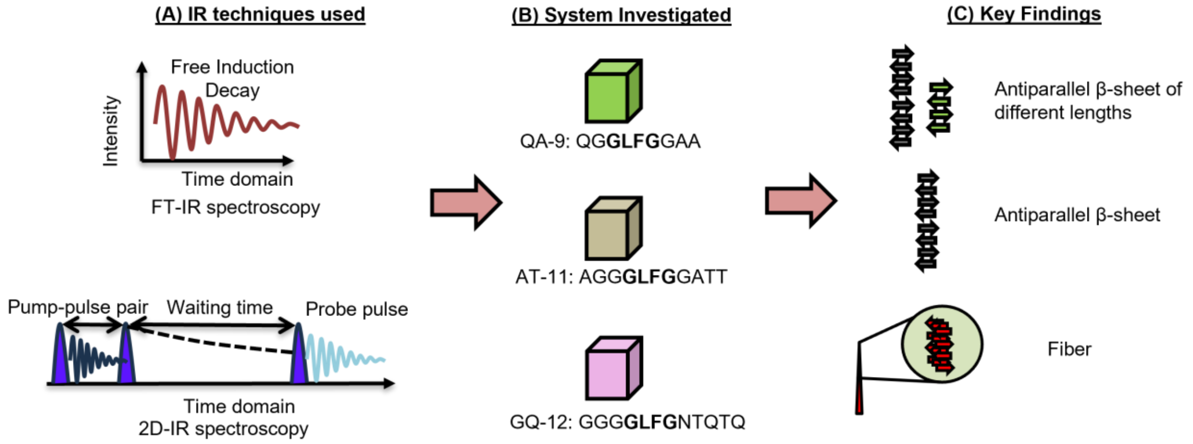
The nucleocytoplasmic transport allows regulated exchange of material from the nucleus to the cytoplasm and vice versa thereby playing a key role in maintaining cellular metabolism. In this regard, the role of Nuclear Pore Complex (NPC) is central, a complex molecular machinery which allows unregulated entry of materials of sizes < 5 nm but serves as a macromolecular sieve for cargos whose sizes exceeds the desired limit [1,2]. The material property of this machinery is imparted primarily by the presence of the repeat sequence, GLFG / FG / GxFG (G: Glycine, L: Leucine, F: Phenylalanine, x: any other amino acid residue), which upon a hydrophobic collapse forms a mesh-like network imparting NPC with its cargo-regulating functionality. While concerted effort has been directed towards the understanding of NPC functionality, the secondary structure(s) of the protein which composes the non-globular macrostructure of the NPC is yet to be fully understood. In this regard, infrared spectroscopy serves as a viable spectroscopic tool, since the amide-I vibration is sensitive to the secondary structure adopted by proteins [3]. The sensitivity is due to differences in H-bonding, therefore amide-I vibration directly reports on the environment in which the oscillator resides which is directed by the folding of the protein. For such investigation, handier than the traditional Fourier-transform one-dimensional infrared (FT-IR) spectroscopy is femtosecond (fs) two-dimensional infrared (2D-IR) spectroscopy, an ultrafast technique which reports not only on the secondary structure of proteins by providing a high-resolution FT-IR spectrum, but also informs on the relative orientation of the oscillators and ensemble heterogeneity through cross-peaks formation and inhomogeneous broadening respectively, in the 2D-IR spectrum [4]. In addition, dynamic information is imparted using sub-100 fs pulses which permits observation of ultrafast processes which governs local fluctuations in proteins. As a first step towards the understanding of NPC macrostructure, this contribution explores the role of a single GLFG repeat in three short chain amino-acid sequences differing in N- and C- terminal sequences (see TOC figure, *vide infra*). The 2D-IR spectra reveal the formation of fiber containing β-sheets in one of the GLFG sequence whereas non-fibrous β-sheets primarily constitute the other two sequences with unstructured regions composed of random coils and turns sharing commonality in all three sequences. Our overall findings show that amino-acid sequences which are not integral to the GLFG sequence may also play a vital role in determining the overall macrostructure of the NPC.



The TOC figure shows (A) Spectroscopic techniques utilized for investigating the structure of model single-repeat GLFG hydrogel systems with differing N- and C-terminal sequences (B) The amino-acid sequence for the three hydrogel systems investigated and (C) The predominant secondary structures which contribute to the hydrogel macrostructure.

References:

[1] Petri et al. *Biomacromolecules*, 2012, 13, 6, 1882–1889. [2] Schmidt et al. *Trends in Biochemical Sciences*, 2016, 41, 1, 46 – 61. [3] Moran et al. *J. Phys. Chem. Lett.*, 2014, 5, 11, 1984–1993. [4] Hamm & Zanni, 2011, *Concepts and methods of 2D infrared spectroscopy*, Cambridge University Press.

Monitoring structural motifs of nucleic acid complexes using UV resonance Raman spectroscopy

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Nucleic acids (NAs) rely on non-covalent interactions to form the secondary and tertiary structures essential for their biological functions. Among these interactions, hydrogen bonding between base pairs and base stacking are the most dominant forces, shaping the structural dynamics and functionality of both DNA and RNA. Techniques capable of providing detailed chemical insights under near-physiological conditions are crucial for dissecting these structural motifs and tracking their conformational changes. In this study, we use UV resonance Raman (RR) spectroscopy to monitor the vibrational signatures of NAs, focusing on marker bands that reveal the presence of hydrogen bonding between base pairs. While RR spectroscopy has been widely used to characterize protein fingerprints, its application in studying DNA and RNA complexes remains limited. Here, we examine various NA complexes, ranging from simple nucleotide mixtures to short double-stranded DNA helices and G-quadruplexes, which serve as model systems for Watson-Crick and Hoogsteen base pairs, respectively. To validate the fingerprints of these secondary structural elements, we compare the experimental spectra with theoretically predicted Raman spectra generated using advanced density functional theory (DFT) calculations. Our findings underscore the potential of using UV RR spectroscopy as a tool to monitor NA interactions.

Catalysis

Elucidating active sites in selective oxidation reactions as a basis for rational catalyst design

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Selective oxidation reactions are among the most important chemical processes but a scientific understanding of their mode of operation is still missing. [1] Recent combined operando/transient spectroscopic analysis of supported vanadia catalysts has provided fundamentally new insight into the active vanadium and oxygen sites, [2,3] which were not defined so far. We discuss the implications of these findings for current and future developments within the field.

Focusing on the selective oxidation of propane to propylene, over ceria-supported vanadia (VO_x/CeO_2) [2] hydrogen transfer from propane to V=O is identified spectroscopically as the first (rate-determining) step, which is followed by hydrogen spill-over to ceria OH acting as lattice oxygen site. The nature of this V/O-hetero active site is shown to be crucial for the mechanistic behavior (CeO_2 *vs* TiO_2). [3] Based on these new findings, rational catalyst design was successfully applied to $VO_x/TiO_2/CeO_2$ catalysts, by moderating the ceria oxygen reactivity with titania. [5]

Moving from supported catalysts to commercial bulk oxide systems with their increased complexity, we apply the developed methodology (IR, multi-λ Raman, UV-Vis, impedance) to identify active Mo=O sites and oxygen ion transport within $Fe_2(MoO_4)_3$ catalysts as essential characteristics of catalyst functioning. [4]

Summarizing, we demonstrate the potential of recent transient spectroscopic developments [6] for active site identification as a scientific basis for describing the characteristics of selective oxidation catalysts and for rational catalyst design.

Literature:

[1] Nanostructured Catalysts: Selective Oxidation (Eds.: C. Hess, R. Schlögl), RSC, 2011. [2] L. Schumacher, J. Weyel, C. Hess, J. Am. Chem. Soc. 2022, 144, 14874. [3] L. Schumacher et al., ACS Catal. 2023, 13, 8139. [4] L. Schumacher, M. Radtke, J. Welzenbach, C. Hess, Chem. Commun. 2023, 6, 1. [5] L. Schumacher, J. Shen, K. Hofmann, C. Hess, Catal. Today 2023, 426, 114387. [6] J. Weyel, L. Schumacher, M. Ziemba, M. Pfeiffer, C. Hess, Acc. Chem. Res. 2024, 57, 2643.

Single Atom Alloy Catalysis for Selective Non-Oxidative Butanol Dehydrogenation: From Pd/Cu(111) Single Crystals to Pd/Cu Nanoparticles Supported on Al2O3

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Single atom alloy (SAA) catalysts were conceived through in silico studies, validated by surface science research and demonstrated industrial relevance in chemical reactor experiments.[1] However, the structure-reactivity relationships and reaction mechanisms in SAA-based catalysis remain incompletely understood, particularly for real powdered catalysts compared to single-crystalline models. In this study, we present an atomistic-level investigation of Pd single atoms alloyed into supported Cu nanoparticles. Using IRAS CO titration, we reveal that temperature-dependent de-aggregation behaviour is similar between Pd/Cu(111) and Pd/Cu-NP/Al2O3, with optimal Pd de-aggregation occurring at 550 K. Both de-aggregated catalysts exhibit prior selectivity in non-oxidative butanol dehydrogenation, achieving 100% selectivity on the supported SAA, while Pd/Cu(111) still shows some decomposition to CO. A Pd coverage-dependent analysis of aldehyde selectivity indicates that cluster formation diminishes selectivity, which can be restored via de-aggregation through 550 K annealing. Additionally, in situ isothermal IRAS reveals the progression from alkoxy adsorption to aldehyde formation and ultimately CO adsorption on Pd clusters on supported Cu-NP.

Literature:
[1] R. T. Hannagan, Chem. Rev. 2020,120, 21,12044-12088

Two are Better than One: Exploring Single and Dual Active Sites in the Novel Material Class of Highly Dispersed Ternary Alloys

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Heterogeneous catalysis is essential for meeting the rising demand for energy, fuels, and chemicals. A key challenge in catalysis is the activation of stable feedstocks such as carbon dioxide or water. Activation of such unreactive molecules requires highly active catalysts, which typically comes at the cost of reduced selectivity. Single-atom alloy (SAA) catalysts offer a promising way to overcome this activity-selectivity tradeoff. Binary alloys, with a single dopant type embedded in a host surface, form individual dopant sites or larger clusters, while ternary alloys – containing two different dopant elements – can additionally create hetero dopant pairs (dual atom alloys, DAAs). Ternary alloys thus promise to exceed the capabilities of binary alloys, for example, in consecutive reactions with elementary steps that require different active sites or in the activation of hetero bonds.

However, even a basic understanding of fundamental properties such as aggregation and segregation energies in ternary alloys is lacking. These properties are critical, as they determine the accessibility of active sites and whether SAAs or homo/hetero DAAs form. To address this, we provide segregation and aggregation energies for all combinations of 3d, 4d, and 5d transition metals (TMs) on Cu(100), Cu(111), and Ag(111) surfaces, using the optB86b-vdW functional. We identify general trends for active site formation across the periodic table: early and late TM dopants form SAAs rather than homodimers, while central 4d and 5d TMs tend to form dimers or larger clusters.

These insights lay the foundation for future catalysis research and, for the first time, enable experimentalists and theoreticians to make a rational choice of dopants for a particular reaction of interest based on a data set that comprises all transition metals.

Literature:

[1] R. T. Hannagan, G. Giannakakis, M. Flytzani-Stephanopoulos, E. C. H. Sykes, Chem. Rev. 2020, 120, 12044.

TunNOx: Development and Testing of a Photocatalytic Reactor for Efficient NO_x-Abatement of Road-Tunnel Exhaust

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During the last decades, heterogeneous photocatalysis has attracted significant attention for remediation of harmful pollutants (VOCs, NO_x) in the urban atmosphere. Typically, TiO_2 surfaces are used on which radicals (HO_2, O_2^-, OH) are formed during irradiation by UV-light, which oxidize adsorbed trace gases (VOCs => CO_2; NO_x => nitrate). During former pilot studies controversial results have been obtained for the remediation of NO_x in street canyons or in road tunnels. Low NO_x conversion was explained by low surface to volume ratio applied and by transport limitation.

Based on these former results, in the present TunNOx project a highly efficient photocatalytic reactor was developed, which can be integrated into transverse ventilation systems of road tunnels. First, an active photocatalytic coating was developed and tested in the laboratory at variable reactant concentrations, humidity, temperature and irradiance levels. Superior abatement of nitrogen oxides (NO_x) and nitrous acid (HONO) was observed even at high NO_x levels, low temperature and high humidity, which are typically not beneficial in photocatalysis. Second, by using a porous photocatalytically coated mesh, a prototype reactor was developed, which was adapted to the conditions typically prevailing in tunnel ventilation systems and which could be used as one segment of a larger reactor. Based on experimental results of the abatement of NO, NO_2 and diesel exhaust in the prototype reactor a simple model was developed by which NO_x abatement of 45-80 % is calculated for typical road tunnel conditions.

Nitrate Reduction Electrocatalysis to Ammonia – A Comparative Study of the Catalytic Performance of Ni and Cu 2D c-MOFs

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The electrochemical nitrate reduction reaction (NO_3RR) is an approach for the sustainable synthesis of the high-value chemical ammonia. As such, the NO_3RR not only presents a green alternative for the energy and emission-intensive Haber Bosch process, but it simultaneously eliminates NO_3^- pollution of the water. Two-dimensional conjugated metal-organic frameworks (2D c-MOFs) are a class of promising electrocatalysts due to their high conductivity, large surface area and easily accessible catalytic centres. In this work, two HHTP-based 2D c-MOFs with copper or nickel as catalytic centres were analysed and compared with respect to their catalytic activity towards NO_3RR. An initial comparison was made using cyclovoltammetric measurements in the absence and presence of nitrate. Furthermore, product analyses were carried out using UV/VIS spectroscopy after chronoamperometric measurements. Contrary to expectations, the results showed that $Ni_3(HHTP)_2$ has a better faraday efficiency for the production of ammonia than $Cu_3(HHTP)_2$. For a more profound understanding of the reaction mechanisms taking place, spectro-electrochemical measurements were carried out. The potential-dependent *in-situ* Raman measurements offer insights into the differences of the catalytic behaviour and the molecular interactions of $Ni_3(HHTP)_2$ and $Cu_3(HHTP)_2$with nitrate and the intermediates. Understanding the processes of electrocatalytic nitrate reduction advances the rational design of catalysts. This is an important step towards superseding the Haber-Bosch process and thus paving the way to a more sustainable future.

Synthesis of metal-alloy tipped CdS nanorod heterostructures

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CdS nanorods 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 CdS nanorods 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 CdS nanorods that are tipped with Ni-Ir material. Starting point is the synthesis of well-known CdS seeds followed by the growth of the elongated CdS shell. Then Ni domains are synthesized at the tips of the rod-shaped nanostructures before Ni-Ir alloys are formed. The synthesis is also applicable for nanorods with an CdSe core. The (CdSe/)CdS/Ni-Ir nanostructures were investigated by TEM and optical methods such as UV/Vis. Due to the different surface energies, the tips of the 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. The synthesis of Pt on the sides of the CdS/Ni-Ir nanorods was also reported, theoretically further favoring charge separation. In future we plan on investigating the charge separation of these synthesized nanostructures.

Electrochemistry

Simultaneous Topography and Spectroscopy Analysis of Nanoscale-Printed Polymer Arrays

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Scanning electrochemical cell microscopy (SECCM) has become a pivotal tool for printing and patterning polymers at the micro- and nanoscale. [1] Analyzing nanoscale features of SECCM deposits remains challenging, as standard polymer characterization methods are often limited to resolutions above 1 micron. Here, we present a combined approach using scattering-type scanning near-field optical microscopy (s-SNOM) with nano-FTIR to achieve simultaneous topographical/chemical nanoscale characterization of SECCM-printed polymers. [2] This integrated technique enables in-depth analysis of polymer growth mechanisms under various electropolymerization conditions/parameters and reveals the impact of electrolyte selection on deposit morphology, including unwanted crystal formation. By integrating s-SNOM and nano-FTIR, we streamline the multi-step spectroscopy and microscopy workflows typically required, enhancing throughput, improving the characterization resolution, and minimizing sample transfer damage. Applying this method to SECCM-deposited polyaniline (PANI) and polypyrrole (PPy) arrays, we observe high resolution crystal growth in PANI deposits using KNO_3 electrolyte, and achieve successful IR characterization of printed PPy deposits with a 200 nm diameter. Our findings show the potential of integrated/hyphenated nanoscale techniques to deepen the understanding of local polymerization processes, enabling more rapid and precise improvements of SECCM fabrication and advancing the field of polymer-based nanoscale sensor array development.

Literature:
[1] E. E. Oseland, Z. J. Ayres, A. Basile, D. M. Haddleton, P. Wilson and P. R. Unwin, Chem. Commun. 2016, 52, 9929-9932.
[2] A. M. Charrier, A. C. Normand, A. Passian, P. Schaefer and A. L. Lereu, Comm. Mater. 2021, 2, 59.

Spectroelectrochemical insights into electrochemical CO_2 capture using anthraquinone derivatives

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With regard to global climate politics of atmospheric carbon dioxide (CO_2), the strategy of Carbon Capture and Utilization (CCU) is a topic of high scientific interest. As the first step in CCU process is CO_2 capture, capturing processes of CO_2 on catalytic surfaces with low energy demand are of great importance, with electrochemical CO_2 capture as a promising technology.[1] In literature mainly aromatic carbonyl molecules were reported for electrochemical interactions with CO_2 in solution.[1] For evaluation of the electrochemical performance of quinones for CO_2 capture, we have investigated evaporated thin-films of the industrially used pigment anthraquinone (AQ) in aqueous solution. Besides demonstration of morphological changes upon reversible CO_2 capture and release, also an uptake capacity of 5.9 $\mathrm{mmol}_{\mathrm{CO2}}\ \mathrm{g}_{\mathrm{AQ}}^{-1}$ was quantified by Fourier-transform infrared (FTIR) spectroscopy. UV-Vis spectroelectrochemistry (SEC) revealed a colour change from pale yellow to orange under inert conditions by formation of hydroxy-AQ. However, in presence of CO_2 an intense yellow colour from the AQ-carbonate species was observed, which was also supported by in-situ FTIR SEC.[2]

In recent years, effort within the scientific community was made to characterize the influence of alkyl and alkoxy substituents on the electrochemistry and SEC of quinones by introducing terms of "*weak*" and "*strong*" binding to CO_2.[3] However, in nature and catalysis hydrogen bonds play a critical role in forming the actual active centres while up to now most of the electrochemical CO_2 capture studies focussed on halogen or alkyl substituted quinones. In order to move a step forward and investigate the influence of hydrogen bond-forming substituents on anthraquinones, we have selected six hydroxy (-OH) and amino (-NH_2) substituted AQ derivatives and thoroughly studied their electrochemical behaviour and performance in UV-Vis SEC in acetonitrile solutions.[4] Our results show that the formation of radical and di-anionic species upon electrochemical reduction can be clearly tracked via SEC and that a strong influence of CO_2 is observed. Furthermore, binding constants for all six derivates were determined and we show that the existing terms of "*strong*" and "*weak*" binding can be extended by a unique behaviour of di-hydroxy-AQ. In this collaborative work, in-depth density functional tight binding (DFTB) calculations well supported these experimental findings via their calculated energies, UV-Vis spectra and molecular geometries.[4]

[1] G. Choi et al., *Nano Energy*, 2023, **112**, 108512. [2] D. Wielend et al., *J. Mater. Chem. A*, 2018, **6**, 15095–15101. [3] F. Simeon et al., *J. Phys. Chem. C*, 2022, **126**, 1389–1399. [4] C. Schimanofsky et al., *J. Phys. Chem. C*, 2022, **126**, 14138–14154.

Electrochemically Triggered Energy Release in Norbonadiene-based Molecular Solar Thermal Systems: How the Push-Pull System Affects Selectivity and Onset Potentials

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Molecular solar thermal (MOST) systems combine the conversion, storage, and release of solar energy using switchable photoisomers.[1] For the release of the stored energy, electrochemical triggers are an intriguing concept that allow to control the energy release by the applied potential.[2,3] So far, cyclabilities of up to 99.8% have been achieved.[4] However, cyclability is strongly dependent on the molecular design.[5] In this work, we systematically investigated the influence of push-pull substituents on the electrochemically triggered energy release of norbornadiene-based MOST systems. We combined in-situ photoelectrochemical infrared reflection absorption spectroscopy (PEC-IRRAS) with density functional theory (DFT). We observe a substituent-dependent variation of the onset potential of up to 0.7 V. This variation is mainly determined by the electron donating group, on which the HOMO is localized and, thus, determines the ionization potential. The push-pull functionalities further affect the selectivity, which was highest for the NBD derivative 1-cyano-2-p-methoxyphenyl-norbornadiene/quadricyclane with a p-methoxyphenyl functionality. Changing the position of the methoxy group in this functionality from para to meta reduces the selectivity from 99% to 48%.

1. Wang, Z. et al., Joule 2021, 5 (12), 3116-3136.
2. Brummel, O. et al., ChemSusChem 2016, 9 (12), 1424-1432.
3. Franz, E. et al., ChemSusChem 2022, 15 (18), e202200958.
4. Waidhas, F. et al., J. Mater. Chem. A 2020, 8 (31), 15658–15664.
5. Franz, E. et al., ChemSusChem 2022, 15 (24), e202201483.

Electrochemical production of cement precursor for sustainable cement production

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Cement production is the single largest industrial source of CO_2 emissions globally constituting approximately 9% of all anthropomorphic CO_2, and its manufacture is only expected to rise.[1] Conventionally, cement is generated through intensive heating of calcium carbonate ($CaCO_3$) via the burning of fossil fuels. Cement clinker precursor, ($Ca(OH)_2$) a material involved in the production of cement can be effectively generated electrochemically from the identical starting material without the need for intense heating. This process is mediated via the two half reactions constituting water electrolysis, namely the oxidation of water to generate protons and the reduction of water to generate hydroxide ions. This electrochemical approach to cement production operates at high current efficiency and circumvents the need for fossil fuel ignition, lowering the overall energy consumption while simultaneously attenuating the release of CO_2. The electrochemical method can be extended to magnesium containing carbonate minerals for the production of magnesium-based cements. Siliceous minerals have also been subject to investigation and suggest the underlying process follows a similar pathway, allowing for the application of cement manufacturing using ubiquitous silicate minerals.

1. Barbhuiya, S.; Kanavaris, F.; Das, B. B.; Idrees, M., Decarbonising cement and concrete production: Strategies, challenges and pathways for sustainable development. *Journal of Building Engineering* **2024,** *86*, 108861.

Tracing overdischarge-induced degradation in lithium-ion cells using cyclic voltammetry and differential voltage analysis

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Differential voltage analysis (DVA) and cyclic voltammetry (CV) are powerful electroanalytical techniques. While CV can be used to study the kinetics of electron transfer reactions [1], DVA can visualise phase transitions by correlating the open-circuit voltage and exchanged charge [2]. Recently, DVA receives an increasing attention in the battery community for characterising full-cell setups. In contrast, CV is less prominent for batteries, yet the prevalently used technique for ex-situ characterisations of novel electrode materials in half-cell configuration.

In this study, we have investigated the overdischarge process of $LiFePO_4$ pouch cells – which is usually presumed to result in a decomposition of the solid electrolyte interphase (SEI) and a corrosion of the copper current collector – in a complementary electrochemical analysis which uses both, CV and DVA in full-cell mode. For this purpose, CV consisting of three low sweep-rate scans and DVA of three low current rate cycles was performed. Degradation was traced by successive CV/DVA sequences during, pre- and post-overdischarge which allowed to pinpoint the features, the limitations, and similarities of both techniques.

In this manner, we demonstrate that CV can successfully identify the dynamics of degradation processes, indicating that an irreversible side reaction starts at cell voltages below 0.55 V. For this reason, this study underlines that CV can be effectively used for spotting dynamic degradation mechanisms which are hardy seen in DVA. This may pave the way for further analysis which can be used for fingerprinting characteristic degradation.

[1] Kim, T., et al. (2020). Journal of Electrochemical Science and Technology 11.
[2] Lewerenz, M., et al. (2017). Journal of Power Sources 368.

Analytical solutions for the impedance of symmetrically distributed relaxation processes

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Distribution of relaxation times (DRT) analysis of impedance data is a powerful tool for unravelling entangled relaxation processes. However, reconstructing the DRT function from experimental data is an ill-posed inversion problem which suffers from noisy input and, hence, assigns a pseudo-signal to any kind of noise. To circumvent the resulting overfitting, different methods have been proposed, which are usually based on regularization.

Alternatively, carefully selected distributed basis functions (e.g. Gauss-type, Cauchy-type, Matern-type) can be included in the algorithm of DRT reconstruction. This concept originates from the work of Cuicci and coworkers and has been implemented in their great software package DRT-tools [1]. While this works exceptionally well for minimizing the demand on regularization, it must be kept in mind that the impedance of real-world relaxation processes of the constant phase element type [2] is not represented by any of the resulting DRT functions.

Bridging this gap was therefore the motivation for the present study. We derived analytical solutions for the impedance of several different types of distribution functions. The resulting impedances are compared with classical relaxation models and special features are pinpointed. The choice of an optimized basis function for reconstructing the DRT from experimentally acquired impedance data will improve electrochemical analysis in future work. Additionally, analytical solutions may be used for assigning a physical origin to the distributed behaviour in the impedance of certain types of electrodes.

[1] T. H. Wan, M. Saccoccio, C. Chen, F. Ciucci, Electrochimica Acta, 2015, 184, 483-499, [2] K. S. Cole, R. H. Cole, Journal of Chemical Physics, 1941, 9, 341-351

Reaction Kinetics and Dynamics

Excited-state wavepacket dynamics of the photoredox catalyst $Ti^{IV}(Cp)_2(NCS)_2$

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Titanium-based complexes are a highly intriguing single electron transfer catalysts in organic radical chemistry due to their low toxicity and high natural abundance of their metal center.[1] The redox couple Ti^{IV}/Ti^{III} offers access to radical intermediates via electron transfer to a bound substrate.[2] This ability has been used in several catalytic cycles with stoichiometric metal reductants and, more recently, in photoredox catalysis.[2,3]

Recently, we reported the observation of the entry events of $Ti(Cp)_2(NCS)_2$ into the photo-catalytic cycle in real-time.[4] Using time-resolved mid-infrared spectroscopy, we identified the intermediate states involved and tracked the reductive quenching reaction of the active catalyst with a sacrificial amine electron donor over broad timescales, spanning from picoseconds to hundreds of microseconds.

Here we report on the very early dynamics of the electronic relaxation of the locally excited singlet state, S_3. To this end, we employed ultra-fast near-UV-pump/white-light-probe spectroscopy with a time resolution of a few tens of femtoseconds. We could observe a prompt, structureless transient absorption ranging from 600 to 900 nm. On timescales below two picoseconds, the absorption exhibits coherent oscillations with a frequency of 140 cm^{-1}. An analysis of probe-wavelength dependence of their phase and amplitude provides evidence that they are due to vibrational wavepacket dynamics in the energetically lowest singlet excited state, S_1, of the complex. TDDFT suggests that the initial S_3-to-S_1 internal conversion creates a coherent superposition in the Cp-Ti-Cp bending vibration of S_1.

We are currently in the process of conducting complementary experiments on the fully methylated complex $Ti(Cp^{*})_2(NCS)_2$ to verify this assignment.

Literature:

[1] M. Castro Rodríguez et al., *Org. Process Res. Dev.* **2017**, *21*, 911-923.
[2] A. Gansäuer, H. Bluhm, *Chem. Rev.* **2000**, *100*, 2771-2788.
[3] Z. H. Zhang et al., *Angew. Chem. Int. Ed.* **2020**, *59*, 9355-9359.
[4] J. Schmidt et al., *Angew. Chem. Int. Ed.* **2023**, *62*, e202307178.

Controlled Growth of Two-Dimensional SnSe/SnS Core/Crown Heterostructures

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Tin sulfide (SnS) and tin selenide (SnSe) are promising 2D metal chalcogenides known for their low toxicity, natural abundance, and optoelectronic properties. Orthorhombic α-SnS and SnSe are particularly suitable for solar light absorption due to their availability, high absorption coefficients and bandgap, which is positioned within the Shockley-Queisser limit for optimal solar cell efficiency. The control of size, shape, and composition of SnS- and SnSe-nanostructures is therefore important for both basic science and potential applications.

Here we demonstrate that 2D SnSe- and SnS-nanosheets, and SnSe/SnS core/crown heterostructured nanosheets (HNSs) can be synthesized by colloidal wet chemistry methods. We demonstrate that especially the reactivity of anionic S- and Se-precursors plays a crucial in the formation of 2D HNSs. The addition of a highly reactive S-oleylamine precursor during the growth of SnSe nanosheets leads to intermediate formation of a SnS-crown inside a SnSe nanosheet and the formation of HNSs. Furthermore, we show that also multiple crown HNSs can be produced through subsequent additions of S-Oleylamine.

The SnSe/SnS HNSs were investigated via TEM, and UV–Vis-NIR spectroscopy. STEM, HRTEM, EDX and XRD measurements were utilized to determine the elemental composition and the crystal structure of the nanosheets.

Literature: Schulz, J.; Schindelhauer, L.; Ruhmlieb, C.; Wehrmeister, M.; Tsangas, T.; Mews, A. Controlled Growth of Two-Dimensional SnSe/SnS Core/Crown Heterostructures. *Nano Lett* **2024**. https://doi.org/10.1021/acs.nanolett.4c03393.

Accurate determination of hydrogen and oxygen isotope effects on liquid water structure and dynamics

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The structure and dynamics of water at the molecular level have been subject of intense study for many years. Experimental studies of water have often relied on isotopic substitution of hydrogen or oxygen atoms. Different isotopes of the same element, while chemically equivalent, are subject to different nuclear quantum effects, and isotopic substitution can affect both dynamical and structural properties. Therefore, to an extent, these techniques have confounded the picture that we have of the molecular details of water. To settle outstanding questions regarding the properties of liquid water, and draw conclusions on isotopic substitution effects, we have used Coupled Cluster Molecular Dynamics (CCMD) in extensive path integral molecular dynamics simulations of liquid H_2O, D_2O, and $H_2{}^{18}O$, thus describing the electronic structure with "gold standard" CCSD(T) accuracy while taking into account nuclear quantum effects. We quantify substantial isotope substitution effects on orientational relaxation and H-bond dynamics, key to H_2O as a solvent. Our accurate simulations and excellent statistical convergence even allow us to evaluate small structural $^{16}O/^{18}O$ isotope substitution effects. Thus, with CCMD, we are able to quantify fundamental structural and dynamical properties of water and offer a deeper understanding of isotopic substitution and nuclear quantum effects.

Ultrafast Excited State Dynamics of the Nitrene Formation in Bis-Carbene-Ni/Pd/Pt-Azides

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Nitrenes are highly reactive subvalent nitrogen species that are often used as intermediates in many organic and pharmaceutical syntheses. There they are usually utilized in C−H functionalization and aziridination and can be accessed photochemically with ease from both organic and metalorganic azide precursors.[1, 2]

Here, we investigated the UV-induced photochemistry of three square-planar metal-azides coordinated by a tridentate ligand possessing two carbene and one amido donor (Metal=Ni, Pd, Pt). Utilizing femtosecond UV-pump-mIR-probe and UV-pump-Vis-probe spectroscopy, we were able to record the primary photochemical processes following the UV-excitation, which differ significantly depending on the metal center. Furthermore, we succeeded in identifying the key intermediates preceding nitrene formation using quantum chemical calculations.

The nickel-based complex undergoes almost exclusively ground-state recovery (GSR) and seems to remain on the singlet surface, while both the palladium, as well as the platinum species exhibit complex, but distinct intersystem crossing dynamics. Additionally, the quantum yield increases significantly with the mass of the metal center.

Literature:

[1] P. F. Kuijpers, J. I. van der Vlugt, S. Schneider, B. de Bruin, *Chem. Eur. J.* **2017**, 23, 13819.
[2] T. Schmidt-Räntsch, H. Verplancke, J. N. Lienert, S. Demeshko, M. Otte, G. P. Van Trieste, K. A. Reid, J. H. Reibenspies, D. C. Powers, M. C. Holthausen, S. Schneider, *Angew. Chem. Int. Ed.* **2022**, 61, e202115626.

Femtosecond laser ionization mass spectrometry for *in-situ* analysis of vapor-liquid-equilibria of isomeric mixtures

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The analysis of isomers with similar fragmentation patterns in classical electron impact mass spectrometry remains an analytical challenge, where chromatographic separation is not trivial or costly.

Chirped femtosecond laser ionization mass spectrometry (fs-LIMS) provides a tool for the distinction of isomers [1] and quantification of the corresponding mixtures [2]. The approach is based on the systematic variation of the spectral phase of the fs-laser pulse, which affects the fragmentation pattern specific for each isomer. The spectral phase is systematically modulated by a 4*f*-shaper with a focus on linear and quadratic chirp. Ultimately, the method is capable of *in-situ* quantification of mixtures of isomers without chromatographic separation with an accuracy below five molar percent in composition [2].

The manipulation of the spectral phase provides an elegant way of introducing isomer-specific light-matter interaction. However, there are challenges in chemical analytics, where the goal of quantification of compositions can be reached *in-situ* even without varying the spectral phase. Here, fs-LIMS experiments are carried out in a home built linear time-of-flight mass spectrometer. Samples are introduced by an effusive gas inlet. Characteristic dissociation reactions are investigated through ion yield ratios of fragment ions relative to either the precursor ion or another fragment ion.

In this work we present the *in-situ* quantification of ternary mixtures including 2-ethyltoluene, 3-ethyltoluene and 4-ethyltoluene. In the case of largely differing vapor pressures non-ideal vapor-liquid-equilibria are involved. These non-ideal vapor-liquid-equilibria are relevant for separation by distillation, life time cycle of pollutants and breath gas analysis. In addition, two examples for non-ideal vapor-liquid-equilibria are presented, i.e., mesitylene // *n*-propyl benzene and 1-propanol // 2-propanol mixtures. The experiments provide access to a quantification of the thermodynamic equilibrium between gas and liquid phase.

Current efforts of this project aim at the investigation of azeotropic mixtures.

Literature

[1] N. Reusch, V. Krein, N. Wollscheid, K.-M. Weitzel, *Z. Phys. Chem.*, **2018**, *232(5-6)*, 689-703.

[2] V. Schäfer, K.-M. Weitzel, *Anal. Chem.*, **2020**, *92*, 5492-5499.

Taking acid-base chemistry to the next (electronic) level: Anion effects on the excited-state proton transfer of photobasic quinolines

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Acid-base reactions are at the heart of many chemical and biological processes. The ability to spatially and temporally control them by the use of photoacids or photobases, *i.e.* molecules which have a decreased or increased excited state pKa (pKa*), has opened up a variety of new research areas. One of them are physiological applications, where photoacids are used, for example, for cancer treatment or targeted drug release.[1] The fact that human blood can be (partially) replaced by "physiological salt" with a NaCl concentration of 0.14 M underlines the necessity to study the effect of the medium on these reactions in more detail.

In our work, we explore the relationship between the pKa* of a photobase and the effect electrolytes in solution have on the involved excited-state proton transfer (ESPT) step. More specifically, we focus on the role of the anion in the series NaF, NaCl and NaI. While these *salt effects* are fairly well understood for photoacids,[2] systematic studies on their photobasic counterparts are still quite scarce. Our approach consists of a series of nine quinoline derivatives which are characterized by pKa* values close to that of water. Their excited state equilibria are therefore neither completely on the protonated nor on the unprotonated side. By means of steady-state experiments, we find that the addition of salts leads to a shift in this equilibrium that is proportional to the coordination number of the used anion. Further, we use time-resolved techniques, namely transient absorption (TA) spectroscopy, to investigate the involved reaction rates as well as their dependence on pKa*, salt concentration and temperature.

[1] T. Sun, L. Kang, H. Zhao, Y. Zhao, Y. Gu, *Advanced Science* **2024**, *11*, 2302875.
[2] N. Agmon, *J. Phys. Chem. A* **2005**, *109*, 13–35.

Acknowledgements:

We would like to thank the Deutsche Forschungsgemeinschaft (SPP 2102 "Light-controlled reactivity of metal complexes", grant 404382951) for supporting this work.

Multiphoton Processes and Light-Induced Multi-Electron Charge-Transfer in Covalent Polyoxometalate Dyads and Triads

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Artificial systems for solar energy conversion often underly multi-electron and charge separation processes due to formation of multiple reduced or oxidized intermediates to promote the desired transformation. Polyoxometallate (POM)-based systems are particularly promising for generating green fuels, as they offer structural variability and are characterized by unique electron storage and transfer properties. By covalently functionalizing POMs with light-absorbing, noble-metal-free bodipy-quinone dyads and metal complexes such as ferrocene, as well as proton/electron donors, a diverse array of dyads and triads with tunable (photo)redox properties can be created. This allows for independent optimization of both light absorption and charge transfer characteristics to the POM. This research primarily focuses on investigating this novel class of compounds concerning light-induced multi-electron and multi-proton processes, as well as iterative structural optimization. To characterize these systems, we employ spectroscopic techniques like time-resolved spectroscopy and spectroelectrochemistry to examine the light-induced formation and properties of charge-separated states during multiple electron transfers from the peripheral groups to the POM. The observed spectral changes upon reduction of the POM prove delocalization of several charges across multiple metal centres.

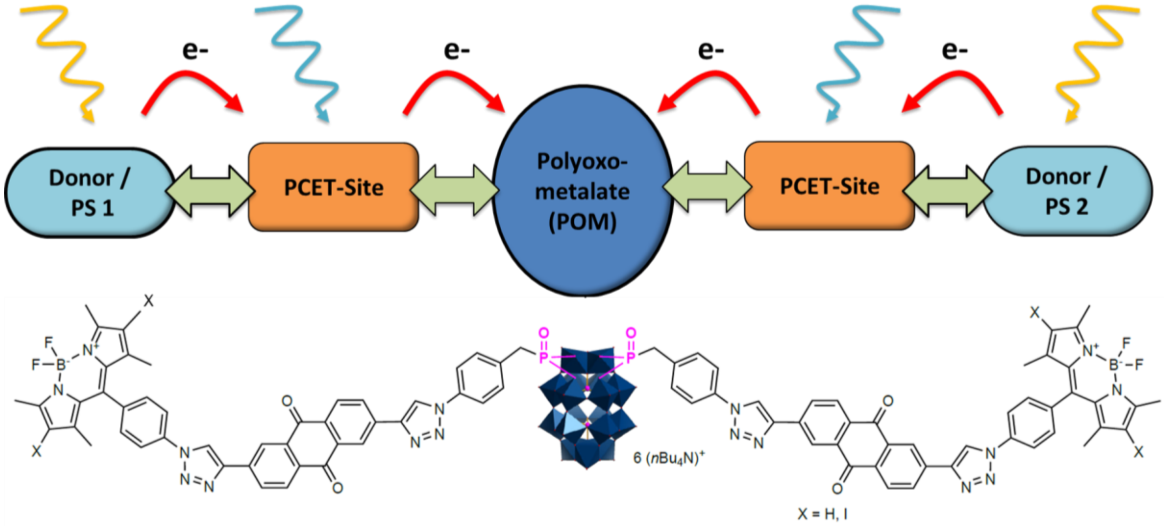

Figure 1. Schematic and molecular structure of bodipy-quinone POM triads. The charge transfer as well as the proton or cation coupled transfer steps will be addressed by using a set of spectroscopic tools covering all relevant time scales of the reaction processes.

Laser-Based Investigation of Self-Decay Rate Constants of Organic Peroxyl Radicals in the Atmospheric Aqueous Phase

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Volatile organic compounds (VOCs) are essential components in atmospheric chemistry, the oxidation of which mainly proceeds through free radicals. Radical-driven oxidation processes of VOCs contribute significantly to the formation of secondary pollutants, influencing atmospheric composition and air quality. [1] Free radical species such as hydroxyl radicals (OH) lead in the presence of oxygen to the formation of organic peroxyl radicals (RO_2) in the gas and aqueous phase. However, the behavior in the aqueous phase (cloud droplets, fog, rain or hygroscopic particles) can be different due to solvent effects. [2] RO_2 are important intermediates in atmospheric oxidation processes and can be involved in the formation of secondary organic aerosol (SOA) in the atmosphere. [3]

This study illustrates a detailed investigation of the recombination and self-decay rate constants of RO_2 in the aqueous phase. To characterize and identify the radical species, the laser flash photolysis-long path absorption (LFP-LPA) setup is applied to measure the absorption time profiles of RO_2. [4] In this method, OH or SO_4^- are formed by photolysis of hydrogen peroxide (H_2O_2) or peroxydisulfate ($S_2O_8^{2-}$) at $\lambda = 248$ nm and are used as the precursor to oxidize the organic compound: methanol, ethanol, 2-propanol, 2-butanol, methyl vinyl ketone, and methacrolein to form RO_2. The absorption time profiles of self-decay of peroxyl radicals, including unimolecular decay and recombination reactions, were measured and the rate constants were determined using a model mechanism. This approach provides valuable insights and fate of these radical species in the atmosphere.

Literature:
[1] J.J. Orlando et al., Chem. Soc. Rev. 2012, 41, 6294-6317. [2] H, Herrmann et al., Phys. Chem. Chem. Phys, 2010, 11, 3796-3822. [3] T. Chen et al., npj clim. atmos. sci. 2022, 5(1), 95. [4] T. Schaefer et al., Environ. Sci. Technol. 2015, 49, 343-350.

Impact of Sulfur-Containing Groups on Aqueous-Phase OH Radical Oxidation – Atmospheric Implications for Small Organosulfur Compounds

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Organosulfur compounds are important components of atmospheric aerosols and cloud droplets, impacting human health, environment, and climate. To date, while their formation mechanisms have become better understood, the transformation pathways, particularly concerning aqueous-phase OH radical oxidation, have remained largely unexplored. In this study, we used laser flash photolysis-long path absorption setup and competition kinetics methods to investigate reaction rate constants and temperature effects on aqueous-phase OH radical oxidation of five small organosulfur compounds. Moreover, we examined the importance of sulfur-containing groups (sulfate and sulfite groups) on kinetics by extending the structure-activity relationship (SAR) model to organosulfur compounds.

Our results indicated the rate constants ranging from 10^6 to 10^8 L mol^{-1} s^{-1}, showing a positive temperature dependence across temperature range of 278 to 318 K. Our findings also revealed a strong deactivating effect of two sulfur-containing groups on oxidation kinetics. Specifically, sulfate group had an α-neighboring effect (F value) of 0.22, while sulfite group had a F value of 0.05. Furthermore, the β-neighboring effect (G value) for sulfate group was 0.44 and for sulfite group was 0.32. These values suggest that the presence of two sulfur-containing groups reduces hydrogen abstraction rates upon OH radical oxidation due to their strong electron-withdrawing natures. They were also integrated into the SAR model, expanding its predictive capabilities for other atmospherically important organosulfur compounds. Overall, the experimentally determined oxidation kinetics address a crucial gap in model development, improving our understanding and prediction regarding the lifetimes of organosulfur compounds in the atmosphere.

Radical Yields and Fe Conversion Kinetics in Fenton Reactions: The Critical Role of Salts in Particle-Phase Chemistry

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The particle phase of the atmosphere is a complex compartment in which the high concentration of salts and organic compounds create non-ideal conditions where chemical reactions take place. [1] Amongst these processes, reactions between Fe and H_2O_2, known as Fenton reactions, play important roles in oxidation cycles. The electrolytes present in this environment can act as inert or non-inert towards Fe. [2] When Fe complexes are formed, the reactivity of Fenton reactions is modified. [3] We have investigated such effects in the presence of high concentrations (I_m = 3 – 4.5) of anions typically present in aerosol samples, namely sulfate, nitrate, chloride, and bromide.

Rate constants measured in the presence of different salts at 293 K and pH 3 using the *ortho*-phenanthroline method for monitoring Fe (II) conversion were contrasted with the reaction in diluted conditions ($k_{reference} = 44 \pm 8$ M^{-1} s^{-1}). The observed rate constants decreased as follows: SO_4^{2-} > Br^- > reference ≥ NO_3^- > Cl^-. The reactivity in Fenton reactions agreed with the stability constants estimated for the Fe(II) complexes. The rate constants for the reactions between $FeSO_4$ and $FeBr^+$ with H_2O_2 were derived as 254 ± 10 and 83.2 ± 8 M^{-1} s^{-1}, respectively. The presence of Cl^- decreased the observed rate for the Fenton reaction due to its lower interaction with Fe ($\log K_{FeCl+} = -0.2$), which decreased the reactivity with H_2O_2. The rate of OH and HO_2 radical formation monitored in spin-trapping experiments agreed with the observed in the Fe(II) conversion experiments.

Literature:
[1] A. J. Rusumdar et al., Atmos. Chem. Phys. 2020, 20, 10351–10377. [2] S. Scheinhardt, et al., Atmos. Environ. 2013, 74, 102–109.[3] D.L. Sedlak and J. Hoigné, Atmos. Environ. 1993, 27, 2173–2185

Luminescent Fe(III) complex sensitizes aerobic photon upconversion and initiates polymerization with green light

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Recent years, remarkable progresses have been made in developing photoactive first-row transition metal complexes, such as chromium, manganese, iron, cobalt, providing important fundamental understandings in respects of the molecular design and applications of photoactive 3d metal complexes.[1] These new types of photoactive meal complexes are seen as more sustainable alternatives to the noble metal complexes due to their competitive photophysical and photochemical properties. Photosensitizers based on iron could be highly attractive for energy conversion based applications, such as photon upconversion and photocatalysis, due to the high natural abundance, low cost, and low-energy visible light absorption. However, this still remains a significant challenge due to the inherently extremely short excited state lifetimes.[2]

This contribution will provide some fundamental insights and catalytic strategies of employing luminescent $3d^5$ iron(III) complex for sensitizing photon upconversion and photoredox catalysis. Specifically, we use a Fe(III) complex for sensitizing aerobic triplet-triplet annihilation upconversion with a few anthracene-based annihilators, which is supported by pre-association between the Fe(III) complex and the anthracenes in their ground states. Introduction of an anthracene-based mediator leads to 6-fold enhanced upconversion quantum yield up to ~ 0.2% in aerobic solution. Driven by a Fe(III)-sensitized upconversion pair, photocatalytic radical polymerizations of acrylate monomers are efficiently initiated under aerobic conditions with green light. Our study makes a fundamentally important step toward efficient photochemical reactions using low-cost iron.

Reference:

[1] a) N. Sinha, O. S. Wenger, *J. Am. Chem. Soc.* **2023**, *145*, 4903–4920; b) W. R. Kitzmann, J. Moll, K. Heinze, *Photochem. Photobiol. Sci.* **2022**, *21*, 1309–1331; c) Amy Y. Chan, Atanu Ghosh, Jonathan T. Yarranton, Jack Twilton, Jian Jin, Daniela M. Arias-Rotondo, Holt A. Sakai, James K. McCusker, D. W. C. MacMillan, *Science* **2023**, *382*, 191–197; d) D. Kim, V. Q. Dang, T. S. Teets, *Chem. Sci.* **2023**, *15*, 77-94.

[2] a) P. Dierks, Y. Vukadinovic, M. Bauer, *Inorg. Chem. Front.* **2022**, *9*, 206-220; b) L. H. M. de Groot, A. Ilic, J. Schwarz, K. Wärnmark, *J. Am. Chem. Soc.* **2023**, *145*, 9369-9388.

Spin-correlation in photocatalytic flavin based reactions – examples on (bio)chemical systems

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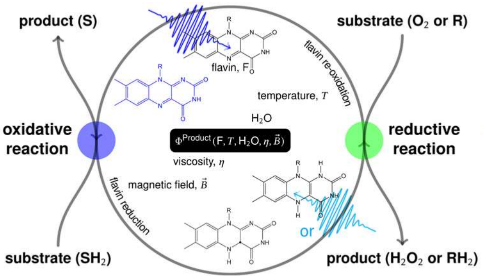
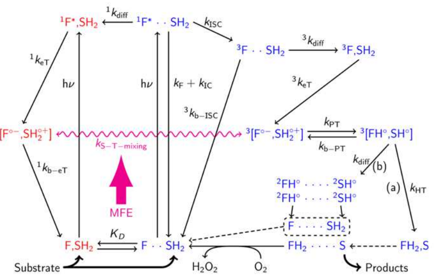
Flavins (7,8-Dimethyl-10-alkylisoalloxazine, F) are found in nature as cofactor in enzymes and photoreceptor proteins and are employed in many biochemical thermally activated as well as light driven reactions. While most redox-active coenzymes catalyse either only one or two electron transfer processes, flavin based coenzymes are involved in both types of electron transfer processes.[1] Accordingly, due to their photoredox characteristics they have also been employed in chemical photocatalytic application.[2,3] In light induced reaction, the lowest triplet state of flavin (^{3}F) acts as a photocatalyst by electron abstraction from a substrate molecule, while electron abstraction by the excited singlet flavin (^{1}F) is immediately followed by electron back transfer and, thus, is unproductive. The total spin state of flavin radical anion and substrate radical cation is decisive for product formation, *i.e.*, reaction proceeds from spin correlated radical pairs (SCRP).





Accordingly, external and internal parameters such as solvent, temperature, viscosity, magnetic field, and substitution by heavy atoms (Br, I) allow to optimize/tune the product quantum yield of photocatalytic reactions. This is demonstrated on a few examples from chemistry and biology by diverse steady-state and time-resolved spectroscopies accompanied by computational simulations.

Literature:

[1] Donat-P. Hader et al., Photochemistry and Photobiology in Flavins Photochemistry and Photobiology, 2006, 328. [2] U. Megerle et al., PCCP, 13(19), 8869–8880, 2011. [3] T. Hartman et al., ChemPlusChem, 86(3), 373–386, 2021.

Accurate determination of hydrogen and oxygen isotope effects on liquid water structure and dynamics

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The structure and dynamics of water at the molecular level have been subject of intense study for many years. Experimental studies of water have often relied on isotopic substitution of hydrogen or oxygen atoms. Different isotopes of the same element, while chemically equivalent, are subject to different nuclear quantum effects, and isotopic substitution can affect both dynamical and structural properties. Therefore, to an extent, these techniques have confounded the picture that we have of the molecular details of water. To settle outstanding questions regarding the properties of liquid water, and draw conclusions on isotopic substitution effects, we have used Coupled Cluster Molecular Dynamics (CCMD) in extensive path integral molecular dynamics simulations of liquid H_2O, D_2O, and $H_2{}^{18}O$, thus describing the electronic structure with "gold standard" CCSD(T) accuracy while taking into account nuclear quantum effects. We quantify substantial isotope substitution effects on orientational relaxation and H-bond dynamics, key to H_2O as a solvent. Our accurate simulations and excellent statistical convergence even allow us to evaluate small structural $^{16}O/^{18}O$ isotope substitution effects. Thus, with CCMD, we are able to quantify fundamental structural and dynamical properties of water and offer a deeper understanding of isotopic substitution and nuclear quantum effects.

The Transition State in Chemistry and Physics

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In this work, we derive from the time dependent Schrödinger equation [1] a linear first order wave equation for resonant transition frequency eigenvalues. In the derivation, we model the transition state under the constraints given by Eyring´s transition state theory [2]. In the derived equation, the energies and angular frequencies are explicitly expressed in terms of d´Broglie wavelength and velocity such that the stationary starting state and the transition are closely coupled. This allows applying the equation on stationary states, too. Its antisymmetry features we express by spin component functions from which we get the electron (and positron) wave function through a linear combination. These wave functions simultaneously solve the Schrödinger and the Dirac equation [3]. However, the solutions, corresponding to the negative and positive energy solutions of the Dirac equation, feature now positive and negative frequencies but the same, positive kinetic energy when we evaluate the Schrödinger equation. In this formalism, the severe interpretation problems of the Dirac equation are significantly softened.

Further, we show that the derived equation takes the form of a Lagrangian as the natural dynamic variable is velocity *v* instead of momentum *p* in the Schrödinger equation. We discuss the substitution rules that allow to transform the equations into each other and their relation to the Legendre transform between the Hamilton and the Lagrange function.

Literature:
[1] E. Schrödinger, Quantisierung als Eigenwertproblem, Ann. Phys.,1926, 79, 489-527.
[2] H. Eyring, The Activated Complex in Chemical Reactions, J. Chem. Phys., 1935, 3, 107-115.
[3] P. A. M. Dirac. The Quantum Theory of the Electron, Proc. R. Soc. Lon., Ser. A. 1928, 117, 610-624.

Spectroscopy

Discerning the mechanism behind red emission of carbon dots: Is it aromatic domains, molecular fluorophores, or surface trap states?

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Carbon dots (CDs) are fluorescent carbon-based nanomaterials which have emerged as a promising material for applications such as sensing, bioimaging, photovoltaics, and photocatalysis. They are widely studied in these contexts due to their photostability, biocompatibility, water solubility, tunable emission, sensitivity to the surrounding environment, and ease of synthesis. However, their emission appears in the blue spectral region, which limits their application. In recent years researchers have been trying to design carbon-based quantum dots with emission properties extended to the red spectral region.

In this contribution, we report on carbon dots generated following a solvothermal synthesis route which shows a dual emission: the classical blue emission and an additional redshifted emission band. The emission mechanism of CDs, and especially the mechanism behind such red emission from CDs is not well understood. In general, several types of excited states could be responsible for emission in CDs: aromatic domains, molecular fluorophores, or surface trap states. We explore the nature of the emission bands and the mechanism behind this dual emission. For this purpose, we employ absorption, steady-state, and time-resolved emission spectroscopy. Temperature-dependent studies enable us to gain insight into the population dynamics of the distinct emitting states and their interactions. Further, we explore the impact of pH to unwind how CD emission is affected by specific interactions with the surrounding environment, e.g., via hydrogen bonds, and identify the nature of the emitting state.

Direct Determination of Giant Magnetic Anisotropies in Heavy Triplet Pnictinidenes

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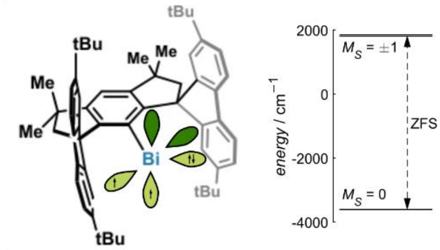
Pnictinidenes (R─Pn) are molecules containing a monosubstituted pnictogen atom (Pn = P, As, Sb, Bi) in the formal oxidation state +1. They are generally highly reactive transient species and frequently show triplet ground states with very large magnetic anisotropies (zero-field splitting, ZFS) [1-3], which are sharply increasing with the atomic number. Their magnetic properties render triplet pnictinidenes prime building blocks for future molecular nano magnets [4]. Further steps in this direction require robust magneto-structural correlations. However, determination of ZFS in the range of hundreds up to thousands of wavenumbers poses severe experimental challenges.



Electronic strucutre and spin energy levels of the investigated bismuthinidene.

Herein, we employ frequency-domain Fourier transform THz electron paramagnetic resonance (FD-FT THz-EPR) spectroscopy in the range from 3 to 6000 cm^{-1} to characterize the magnetic and electronic properties of different types of heavy triplet pnictinidenes. First, a study on in-situ photo-generated metalloarsinidenes (Pd-As and Pt-As), shows a high localization of the spin density at the pnictogen atom, in line with quantum chemical calculations [5]. Second, we determine a positive axial ZFS of 5422 cm^{-1} in an even heavier organobismuthinidene (R─Bi, see Figure) [6], which is to the best of our knowledge, the largest magnetic anisotropy experimentally determined for a molecule up to now. Our studies establish FD-FT THz-EPR as a unique method to probe ZFS up to thousands of wavenumbers and helps establishing magneto-structural correlations in the fascinating class of isolable and in-situ generated triplet pnictinidenes.

Literature:

[1] Schmidt-Räntsch, T. et al., Angew. Chem. Int. Ed. 2022, 61, e202115626. [2] Moon and Cornella, ACS Catal. 2022, 12, 1382. [3] Pang et al., Science. 2023, 380, 1048. [4] Chapyshev et al., Chem. Eur. J. 2021, 27, 1258. [5] Neben et al., submitted. [6] Al Said et al., submitted.

Probing the electronic structure of benzene derivates at the air−water interface of aqueous aerosol droplets

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A large part of atmospheric chemistry occurs in aqueous environments or at aqueous interfaces, where (photo-)chemical reactions can be accelerated by up to several orders of magnitude. [1] The key to understanding the chemistry and photoresponse of molecules in and 'on' water lies in their valence electronic structure for which UV photoelectron spectroscopy (PES) is a suitable and direct measurement method. [2] Recently, we published a proof-of-principle study showing schematically for the phenol−water system that UV PES is feasible with aqueous aerosol droplets, that the method is surface-sensitive due to the limited escape depth of the generated low-kinetic-energy photoelectrons, [2] and that our droplet photoelectron imaging ("droplet-PEI") technique complements and expands upon conventional methods. [4] In this work, we successfully expanded UV droplet-PEI to a whole range of atmospherically relevant benzene derivatives in aqueous solution. We used 1 + 1 photoionization with femtosecond and nanosecond laser pulses and demonstrate the effect that chemical substitution, photoexcitation, solute concentration, surface occupancies, and pH have on the probed electronic structure and relaxation dynamics. Our findings underscore the importance of solute–solute interactions at droplet surfaces and their role in modifying the photoresponse of the organic solutes. The study contributes to a broader understanding of molecular behavior at aqueous interfaces, which is key in fields like atmospheric chemistry and biochemistry, where water interfaces play a critical role in reaction dynamics.

Literature:
[1] K. Wilson, A. M. Prophet, Annu. Rev. Phys. Chem. 2024, *75*, 185–208.
[2] D. Luckhaus et al., Sci. Adv. 2017, *3*, e1603224. [3] L. Ban, B. L. Yoder, R. Signorell, Annu. Rev. Phys. Chem. 2020, 71, 315. [4] J. Heitland et al., J. Phys. Chem. A 2024, 128, 35, 7396–7406.

A single nanoparticle setup for action spectroscopy

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The unique combination of an ion trap for mass spectrometry with a cold head allows adsorption of messenger species on the surface of a single nanoparticle (NP) which opens new paths for single NP techniques in the gas phase. The isolation of unsupported individual particles is important to investigate their intrinsic properties in the absence of inhomogeneous broadening in an ensemble — which is for example essential to distinguish the damping factors of a localized surface plasmon resonance [1] — and interactions with a supporting surface. Our main goal is to advance and establish the method of single NP action spectroscopy, that indirectly records absorption spectra by monitoring the heat-driven desorption of a messenger species, as key component of a new tool box to characterize single nanoparticles in the gas phase.

Our group has proven the quantitative validity of single NP action spectroscopy by comparison to solution spectra [2] and applied it to measure the quenching of the localized surface plasmon resonance of 50 nm Au NPs [3]. Recent investigations on the fluorescence emission from CdSe/CdS quantum dots and charging of silica particles have paved the way to temperature determination *in situ* [4] and full control of the cationic charge state. Here, we present our progress on performing single NP action spectroscopy with improved control over the tagging species. Furthermore, we characterized adsorption and desorption dynamics in the ion trap, which is relevant for the quantitative determination of absorption spectra. A deeper understanding of sorption behavior is a prerequisite to control NP temperature and to use temperature programmed desorption schemes to characterize NP surfaces in the future.

Literature:
[1] S. A. Lee, S. Link, *Acc. Chem. Res.* 2021, 54, 1950. [2] B. Hoffmann, T. K. Esser, B. Abel, K. R. Asmis, *J. Phys. Chem. Lett.* 2020, 11, 6051.
[3] B. Hoffmann, S. C. Leippe, K. R. Asmis, *Molecular Physics* 2024, 122, e2210454. [4] S. C. Leippe, F. Johst, B. Hoffmann, S. Krohn, K. Papagrigoriou, K. R. Asmis, A. Mews, B. Bastian (submitted).

Investigating the *ortho*-halogenation of benzyl alcohol

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Benzyl alcohol is a molecule with notable conformational flexibility and intriguing chirality aspects. [1][2] The *para*-halogenation of benzyl has been shown to have an almost negligible effect on the conformational landscape. [3] The present study investigates the impact of introducing an *ortho* halogen (chloro-, bromo-, iodo-) to benzyl alcohol by employing supersonic jet FTIR spectroscopy paired with quantum chemical calculations. DFT calculations indicated the existence of three distinct monomer structures. Further transition state and DLPNO-CCSD(T) single point calculations reduced the number of main conformers, one chiral with an OH-X contact and one planar. These results are supported by the FTIR spectra, which revealed the existence of two main, stable monomer conformers in the expansion. Additionally, the data indicated that the OH stretching wavenumber of the chiral conformer is dependent on the halogen, while that of the planar conformer remains unaffected. Furthermore, by adding a small fraction of a heavier carrier gas the relaxation of the energetically higher planar into the most stable chiral conformer was enabled, thereby providing an additional confirmation for the signal assignment. The investigation of the *ortho*-halogenated benzyl alcohol dimers showed that a homochiral pairing is preferred in theory with a slightly rising possibility for heterochiral pairing with heavier halogens. Experimentally this was confirmed although the signals assigned to the heterochiral complex are relatively weak. [4]

Literature:

[1] R. Glaser, G. R. Nichols, *J. Org. Chem.* **2000**, 65, 755.
[2] K. A. Utzat, R. K. Bohn, J. A. Montgomery, H. H. Michels and W. Caminati, *J. Phys. Chem. A* **2010**, 114, 6913.
[3] M. Lange, E. Sennert, M. A. Suhm, *Synlett* **2022**, 33, 2004.
[4] E. Sennert, M. A. Suhm, *Phys. Chem. Chem. Phys.* **2024**, 26, 26976.

Investigation of the gas-phase thermodynamical equilibrium between citraconic and itaconic anhydride using microwave spectroscopy

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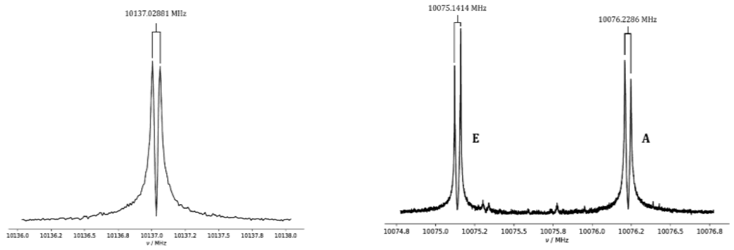
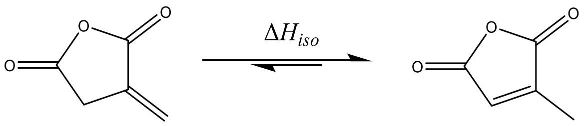
Microwave spectra of citraconic anhydride and itaconic anhydride are reported in a frequency range of 6-18 GHz. For both molecules, isotopic measurements of ^{13}C mono-substituted isotopologues yielded a molecular substitution structure (r_S) which - for citraconic anhydride - was complemented with data on ^{18}O isotopologues. These spectra strongly indicate that a previous study [1] on itaconic anhydride assigned the spectrum to the one of citraconic anhydride instead. In addition to the microwave spectra, a gas-phase study of isomerization between the tautomers was carried out, which was assisted by theoretical calculations. These were also used to benchmark the experimentally determined substitution structure.





Itaconic anhydride

Citraconic anhydride

Literature:

[1] T. J. McMahon, *J. Mol. Spec.* **2018**, *347*, 35-40.

Optimizing $CsPbBr_3$ Nanocrystals for LEDs: Spectroelectrochemical Study of DDABr Ligand Effects

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Lead halide perovskites (LHP) have gained the interest of many researchers due to their potential application in solar energy generation or as nanocrystals (NCs) in light emitting devices (LEDs). The advantages are their defect tolerance, their easy wavelength tunability and their high photoluminescence quantum yield which can be useful in such devices. However, the use in LEDs is until now still hindered because of the low conductivity due to the organic ligand shell surrounding the NCs and the lack of easy band position tunability, which can favor the charge transport from the electron or hole transport layer.

A very promising ligand for $CsPbBr_3$ NCs in LEDs is didodecyl dimethylammmonium bromide (DDABr). Manna *et al.* have shown further external quantum efficiency improvement by ligand stripping.[1] Here, we show that the LED is not only improved by the loss of ligands. Based on UPS measurements and spectroelectrochemistry (SEC), we attribute the improvement of DDABr NCs to a better alignment to the hole transport layer. This result is extended to a SEC comparison of different ligand amounts on native (OA/OAm) NCs and DDABr-covered NCs. This approach gives us insight into the hole injection into the NC depending on the nature of the ligand and also on the number of ligands. We can learn from this comparison, supported by theoretical calculations, that hole injection becomes more difficult with less ligand surface coverage and that hole injection is facilitated in DDABr NCs. Looking at the shifts, it is even possible to obtain a good comparison between SEC and UHV techniques like UPS.

[1] Dai J., *et al.* ACS Applied Materials & Interfaces **2024** *16* (9), 11627-11636.

Spectroscopy of the Phthalocyanine Cation and its Metallic Derivatives

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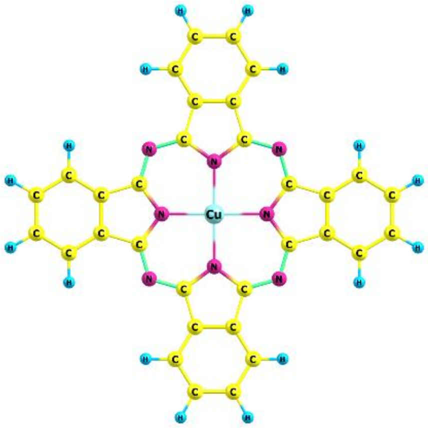

Phthalocyanine and its metallic derivatives have been studied extensively in the last years due to their electronic, optical, and magnetic properties. They are already used in applications like optical data storage, gas sensors, and dyes in infrared laser systems. Potential future applications include nonlinear optical materials, photovoltaic cells, and enzyme-like catalysts.

Here we investigate the spectroscopy of the phthalocyanine molecular cation, both in its pristine form [1], and doped with a magnesium, copper, zinc or iron atom, respectively. Experimentally, the molecule under investigation was tagged with three helium atoms, resulting either in $H_2PcHe_3^+$ or in $MPcHe_3^+$, where M is either Mg, Cu, Zn or Fe, and Pc^{2-} is the conjugate base of phthalocyanine. Then, messenger-type UV-vis spectroscopy has been performed between 300 and 900 nm wavelength.

Quantum chemical calculations, mainly TDDFT, are performed to rationalize the experimental findings and determine the character of the electronic excitations. Here, symmetry breaking and consequent state splitting play a crucial role as they can explain certain spectroscopic features. The excitations can be divided into three categories: charge transfer, metal–to–metal and ligand–to–ligand. All three types of excitations are influenced by the environment, e.g. ligand–to-ligand excitations are significantly shifted in energy, depending on the present transition metal.

Literature:

[1] S. Bergmeister, L. Ganner, M. Ončák, E. Gruber, Adv. Sci. 2024, 11, 12.

Linear and Two-Dimensional IR Spectroscopy of an Isotopically Labeled Multifunctional Vibrational Probe

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Vibrational spectroscopy studies of biomacromolecules often rely on the site-specific introduction of infrared probes. Preferably, these are small non-native moieties, whose stretching vibration is highly sensitive to the local environment.[1] Here, we report on the prospective IR probe, 3-(4-azidophenyl)propiolonitrile, which contains several IR-active functional groups. There are multiple viable approaches for incorporating it into a biomolecule, such as copper-catalyzed click chemistry involving the azide group[2] or 1,4-conjugate addition to the C≡C-triple bond of the propiolonitrile group[3].

The linear FTIR spectrum of (4-azidophenyl)propiolonitrile is highly perturbed in the spectral region of the asymmetric azide stretching fundamental due to the presence of Fermi resonances. We managed to assign the fundamental transition via isotope labeling at the β-N of the azide group. In combination with DFT calculations, this allowed us to construct a two-tiered Fermi resonance Hamiltonian to identify the combination tones that are anharmonically coupled to the azide stretching fundamental.

Additionally, we performed ultrafast vibrational spectroscopy on the isotopically deperturbed IR probe with a time-resolution of around two hundred femtoseconds. 2D-IR spectra feature a delayed appearance of cross-peaks between the azide asymmetric and the in-phase propiolonitrile stretching modes. Along with narrowband IR-pump/IR-probe spectroscopy, these results reveal an irreversible intramolecular vibrational energy redistribution (IVR) that involves different subsets of low-frequency modes coupled to either the azide or the propiolonitrile oscillator. Our data shows a time constant of 2.3 ps for the IVR, whereas energy dissipation to the solvent occurs on a time scale of 18 ps.

Literature:

[1] H. Kim and M. Cho, *Chem. Rev.* **2013**, *113*, 5817–5847.
[2] B. Stump, *ChemBioChem* **2022**, *23*, e202200016.
[3] J. C. Worch et al., *Chem. Rev.* **2021**, *121*, 6744–6776.

Raman and UV-Vis modulation excitation spectroscopy: A powerful approach to identify active species in copper-ceria catalysts

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Modulation excitation spectroscopy (MES) is a transient spectroscopic method which enables new insight into active sites and reaction mechanisms in heterogeneous catalysis. In MES, the concentration of at least one reactant is periodically changed (modulation) leading to the periodic response of actively participating species (excitation), while spectator species do not respond periodically to the external perturbation. The total response of the system is measured as a set of time-resolved spectra, which are converted into phase-resolved spectra, only containing features of active sites and species.[1]

In this work, we combined Raman and UV-Vis spectroscopy with the MES approach to unravel active oxygen and copper species in low-loaded copper-ceria catalysts (0.43 wt%) for CO oxidation. Raman-MES shows the exclusive role of the ceria support, providing direct evidence for the participation of surface lattice oxygen thus supporting a Mars-van Krevelen mechanism. In addition, UV-Vis-MES provides high sensitivity towards the low copper loading highlighting major Cu^{2+}/Cu^{+} redox activity compared to Ce^{4+}/Ce^{3+} during CO oxidation. Based on the combined Raman and UV-Vis MES results, we propose a reaction mechanism starting with CO adsorption on Cu^{2+}. For CO oxidation, oxygen is provided from ceria at the copper-ceria interface, releasing electrons that are consumed in the reduction of, mainly, Cu^{2+} to Cu^{+}. Finally, the vacancies are replenished by fast dissociating molecular oxygen.[2]

Summarizing, the applied novel methodology is demonstrated to provide new mechanistic insight that is not accessible by conventional steady-state spectroscopies. Thus, this approach is of potential interest for the investigation of supported catalysts for more complex reactions, such as CO_2 activation.[2]

[1] Weyel, J.; Schumacher, L.; Ziemba, M.; Pfeiffer, M.; Hess, C. *Acc. Chem. Res.* **2024**, *57* (18), 2643–2652.
[2] Hoyer, H.; Hess, C. *J. Phys. Chem. C* **2024**, DOI: 10.1021/acs.jpcc.4c05826.

Vibrational Spectroscopy of $AlFe_2O_4^+$ and $AlCo_2O_4^+$: Unexpected Structural Isomers upon Transition Metal Substitution

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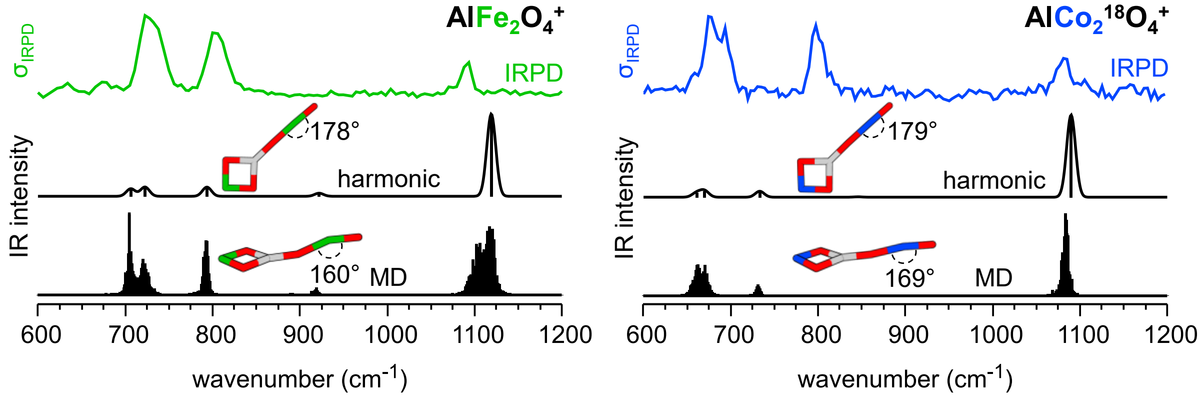

This study presents experimental and computational evidence for a new structural motif of the doubly transition metal (TM) substituted $Al_3O_4^+$ gas phase clusters $AlFe_2O_4^+$ and $AlCo_2O_4^+$. In contrast to the monosubstituted analogs $Al_2FeO_4^+$ and $Al_2CoO_4^+$, which have a planar bicyclic structure with a terminal $Al–O^{\bullet -I}$ radical,[1] the doubly substituted clusters exhibit a "key-like" structure with a planar four-membered ring connected to a terminal $O–TM^{+III}–O^{-II}$ unit.

Identifying the structure of $AlFe_2O_4^+$ and $AlCo_2O_4^+$ requires going beyond the commonly used harmonic approach, in which infrared (IR) spectra are calculated with density functional theory (DFT) for a single local minimum structure.[2-4] To achieve convincing agreement between spectroscopic experiments and theory, we use molecular dynamics (MD) simulations, which provide fully anharmonic IR spectra that include finite temperature effects. Obtaining converged IR spectra based on MD simulations with hybrid DFT functionals is a computationally very demanding task. Therefore, we use machine learning interatomic potentials (MLIPs) based on the MACE architecture to model the potential energy surface and for the dipole surface. This approach captures the large amplitude motions of the $O–TM^{+III}–O^{-II}$ moiety and improves on the harmonic approximation for IR intensity predictions.

Literature:

[1] Müller *et al*. J. Am. Chem. Soc. **2020**, *142*, 18050-18059. [2] Asmis; Sauer, *Mass Spectrom. Rev.* **2007**, *26*, 542-562. [3] Santambrogio *et al*., *J. Am. Chem. Soc.* **2008,** *130*, 15143-15149. [4] Li *et al.*, *Angew. Chem., Int. Ed.* **2022,** *61*, e202202297.

Measurement of the Single Photon Photoelectron Elliptical Dichroism of Electrosprayed Anions

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Investigations aiming at the determination of molecular chirality by chiroptical techniques continue to attract a significant amount of interest in chemistry, physics biology and pharmacology. Some focus has been put on the measurement and analysis of the photo ion circular dichroism (PICD) – a total ion yield effect – and the Photoelectron Circular Dichroism (PECD) – a molecular frame angular distribution effect. Most efforts have put immense work into establishing “perfect” circular polarization.

In recent years it has been demonstrated, that Photoelectron Elliptical Dichroism (PEELD) – which considers a systematic variation of the elliptical polarization of light – is also a powerful approach for studying chirality. Basically, PEELD is the extension of PECD to a variation of elliptical polarization. So far, PEELD has been reported for a number of neutral analytes using multi photon ionization, demonstrating advantages over plain PECD experiments.[1,2,3] PEELD measurements with single photon ionization have not been reported yet, due to the comparably high ionization energy of neutral analytes.

In this work we demonstrate the measurement of PEELD in single photon photodetachment of electrons from electro-sprayed anions. Photodetachment of electrons from anions has recently been developed as a new technique for chirality analysis.[4,5,6,7] When combined with electro-spraying the anions of interest, the technique, ESI-PECD, allows the study of proteins containing many amino acids.[5]

As analytes we chose, amino acids, for which the PECD has already been studied by ESI-PECD in our group, i.e. phenylalanine and tryptophan.[7] Preliminary results indicate that the PEELD of the phenylalanine-anion scales linearly with the STOKES parameter S_3. We note, that there are literature reports indicating non-linear variation of the PEELD with S_3, however, in the case of multi photon ionization.[1,2,3]

The study of PEELD in photodetachment is expected to shed new light on the fundamental question of asymmetry in the photoelectron angular distribution comparing multiphoton and single photon processes. It is argued that a well-defined elliptic polarization has to be preferred over an ill-defined circular polarization.

[1] A. Comby, D. Descamps, S. Petit, E. Valzer, M. Wloch, L. Pouységu, S. Quideau, J. Bocková, C. Meinert, V. Blanchet, B. Fabre, Y. Mairesse, Phys. Chem. Chem. Phys. **2023**, *25*, 16246 – 16263.
[2] A. Comby, E. Bloch, C. M. M. Bond, D. Descamps, J. Miles, S. Petit, S. Rozen, J. B. Greenwood, V. Blanchet, B. Fabre, Y. Mairesse, Nat. Commun. **2018**, *9*, 5212.
[3] J. B. Greenwood, I. D. Williams, Phys. Chem. Chem. Phys. **2023**, *25*, 16238 – 16245.
[4] P. Krüger, K.-M. Weitzel, Angew. Chem. Int. Ed., **2021**, *60*, 17861 – 17865.
[5] P. Krüger, J. H. Both, U. Linne, F. Chirot, K.-M. Weitzel, J. Phys. Chem. Lett., **2022**, *13*, 6110 – 6116.
[6] J. Triptow, A. Fielicke, G. Meijer, M. Green, Angew. Chem. Int. Ed., **2022**, *62*, e202212020.
[7] J. H. Both, A. Beliakouskaya, K.-M. Weitzel, to be submitted (Nov. 2024).

Towards an understanding of the binding of H_2 with aromatic rings: The complex of benzonitrile with H_2 and its isotopologues

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Benzonitrile is among the few benzene derivatives that have been observed in the interstellar medium[1]. Since H_2 is commonly found in the interstellar medium the complex of benzonitrile with H_2 is of special interest in an astrochemical context. The resulting dimer could serve as precursor for the hydrogenation reaction of benzonitrile, possibly mediated by grain surface interactions in space. In this way, benzylamine or even toluene could be formed in the interstellar medium[2,3]. We study the complex formation under laboratory conditions using cavity microwave jet-spectroscopy. These measurements are further complicated by the presence of *ortho* and *para*-hydrogen where the lowest rotational state of the respective species is retained in the complex. Previous microwave studies consistently observed a higher binding propensity of *ortho*-hydrogen (beyond what is statistically expected), for example OCS + H_2. Even more extreme is the case of HCN + H_2 where completely different binding sites have been suggested for *ortho*-H_2 and *para*-H_2[5]. We systematically investigated the binding propensities of ortho/para H2, HD and ortho/para D2 with benzonitrile with isotopes in natural abundance and ^{15}N labelled benzonitrile. From these measurements we are also able to draw conclusions about the molecular structure of the complexes.

Literature:
[1] B.A. McGuire, A.M. Burkhardt, S. Kalenskii *et al.*, *Science* **359**, *6372* (2018). [2] M.I. McAllister, C. Boulho, L.F. Gilpin *et al.*, *\Org. Process Res. Dev.* **23**, *5* (2019). [3] P. Theulé, F. Borget, F. Mispelaer *et al.* , *Astron. Astrophys.* **534**, *A64* (2011). [4] Z. Yu, K.J. Higgins, W. Klemperer *et al.*, *J. Chem. Phys.***127**, 054305 (2007) [5] Masazumi Ishiguro, Kensuke Harada, Keiichi Tanaka *et al.*, Chem. Phys. Lett. **554** 33 (2012).

Boosting HIGHrISC Emitters for OLEDs

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In organic light emitting diodes (OLEDs), electronic excitations are generated by electron-hole recombinations. For reasons of spin-statistics ¼ of these excitations adopt singlet spin multiplicity and ¾ triplet multiplicity [1]. Unless special precautions are taken, the latter fraction is lost for light emission. Various approaches have been introduced to harvest the triplet excitations, such as phosphorescence [2] and thermally activated delayed fluorescence (TADF) [3] emission. In the HIGHrISC [4] or hot exciton [5] ansatz, molecular triplet excitations are converted into singlet ones *via* reverse intersystem crossing (rISC) from a higher triplet state $T_{n\geq2}$. With HIGHrISC, the emission may occur from a singlet state with a large oscillator strength and a small bandwidth – advantages compared to the other approaches. Challenges with HIGHrISC are the preferential population of the $T_{n\geq2}$ state and the competing internal conversion $T_{n\geq2} \rightarrow T_1$.

Our group has shown by direct and sensitized excitation, that acridones are HIGHrISC active [4]. The behavior can be ascribed to a $T_{n\geq2}$ state of $^3n\pi^*$ character. According to El-Sayed's rule, such a state can undergo fast rISC to the emissive S_1 state of $^1\pi\pi^*$ character. Indeed, femtosecond spectroscopy gives evidence for rISC on the picosecond time scale. Fluorescence quantum yields and HIGHrISC behavior of acridones are strongly affected by the energy gap between the $^3n\pi^*$ and $^1\pi\pi^*$ state. As will be shown in this contribution, this gap and their emission parameters can be tuned by suitable substituents and/or inter- and intramolecular hydrogen bond donors.

Literature:
[1] G. Hong et al., Adv. Mater. 2021, 33, 2005630. [2] B. Minaev et al., Phys. Chem. Chem. Phys. 2014, 16, 1719. [3] Y.C. Liu et al., Nat. Rev. Mater. 2018, 3, 20. [4] K.A. Thom et al., J. Phys. Chem. Lett. 2021, 12, 5703. [5] Y. Xu et al., Chem. Soc. Rev. 2021, 50, 1030.

Vibrational spectroscopy of Cu^{2+} paddle-wheel complexes with hydrogen isotope adducts

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Porous materials like metal-organic frameworks (MOFS) and zeolites containing under-coordinated Cu centres play an important role in dihydrogen adsorption as well as the efficient isotope separation of H_2/D_2. To understand the adsorption behaviour of such materials better and design tailor-made materials with improved properties like selectivity, gas-phase clusters can serve as model systems for studying the binding interactions between hydrogen isotopes and transition metal ions. In the present gas-phase study, our focus lies on the spectroscopic characterization of ionic clusters mimicking secondary building units (SBU) of MOFs.

The vibrational spectra of $[Cu_2(OAc)_3\text{- }2(H_2/D_2)]^{+1}$ and $[Cu_2(OAc)_4OH\text{- }1(H_2/D_2)]^{-1}$ complexes, generated in a cryogenic ring-electrode ion trap, are measured for both fingerprint (1000-1900 cm^{-1}) and mid-IR regions (2400-4400 cm^{-1}) using infrared photodissociation (IRPD) spectroscopy. On comparison with calculated harmonic spectra (B3LYP-D3/def2TZVPP), the cation with two Cu^{2+} centres is found to have a highly symmetric paddle-wheel (PW) motif, whereas the anion with four OAc^{-1} linkers and an OH group assumes a distorted PW structure.

The $\nu_{\mathrm{HH}}(\nu_{\mathrm{DD}})$ stretching vibrations, appearing at 4020 cm^{-1}(2889 cm^{-1}) for $[Cu_2(OAc)_3]^{+1}\text{-}2H_2(2D_2)$ and 4111 cm^{-1}(2957 cm^{-1}) for $[Cu_2(OAc)_4OH]^{-1}\text{-}1H_2(1D_2)$, indicate a slight red shift when compared to free $\nu_{\mathrm{HH}}(\nu_{\mathrm{DD}})$ stretching frequency. The binding position of the isotopes also differ in the two gaseous subunits that have been investigated. Furthermore, ion-yield measurements of the H_2/D_2 adducts, performed in the temperature-controlled ion trap give a direct insight into the adsorption behaviour, indicating the stability of the paddle-wheel complexes and preferential binding nature.

High resolution infrared spectroscopy of $PFCl_2$ and isotopic chirality

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The concept of isotopic chirality is of fundamental interest, introducing a completely new isotope effect arising from the parity violating weak nuclear force [1−4]. Because of the different weak nuclear charge of the isotopes with different numbers of neutrons, the enantiomers of molecules which become chiral by isotopic substitution, like $PF^{35}Cl^{37}ClF$, are predicted to have different ground state energies separated by a parity violating energy difference $\Delta_{pv}E$ in the aeV range, depending on the molecule. This has been calculated to be about 3.5 aeV for $PF^{35}Cl^{37}ClF$ [4], whereas it is exactly 0 by symmetry for the symmetrical isotopomers. In principle, $\Delta_{pv}E$ can be measured by special experiments [5]: for ongoing efforts, see [2,6]. The analysis of rovibrationally resolved infrared spectra provides a first step towards such experiments on parity violation in chiral molecules. We present here the analysis of the high resolution infrared spectra of $PFCl_2$, measured both with our Bruker (ZP 2001) IFS 125 HR Zürich Prototype Fourier Transform spectrometer ($T=295$ K, 650−1000 cm^{-1}, resolution: 0.0015 cm^{-1}) and in a supersonic jet expansion ($T=15-20$ K) with our diode laser spectrometer between 830−834 cm^{-1} and 838−841 cm^{-1}. We analyzed the ν_1 ($\nu_0=836.6$ cm^{-1}) and ν_5 fundamentals ($\nu_0=517.8$ cm^{-1}) of $PF^{35}Cl_2$, as well as the ν_1 fundamental of $PF^{35}Cl^{37}Cl$ ($\nu_0=835.5$ cm^{-1}), the latter analysis made possible because the diode laser spectra at low T simplified the spectra. The ν_1 fundamentals are strongly perturbed by a Coriolis-type resonance with the $\nu_3 + \nu_5$ level. We present also the first ground state rotational parameters for $PFCl_2$, obtained using combination differences. The results will be discussed in relation to our *ab initio* calculations and as they pertain to isotopic chirality, molecular parity violation, biomolecular homochirality, and the fundamental symmetries of physics and chemistry.

[1] M. Quack, Angew. Chem. Int. Ed., 1989, 101, 588. [2] M. Quack, G. Seyfang, G. Wichmann, Chem. Science, 2022, 13, 10598. [3] M. Hippler, E. Miloglyadov, M. Quack, 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. [4] R. Berger, G. Laubender, M. Quack, A. Sieben, J. Stohner, M. Willeke, Angew. Chem. Intl. Ed. (Engl.), 2005, 44, 3623. [5] M. Quack, Chem. Phys. Lett., 1986, 132, 147−153. [6] M. Quack, J. Stohner, M. Willeke, *Annu. Rev. Phys. Chem.*, 2008, 59, 741.

Linear and Nonlinear Optical Properties of Colloidal WS_2

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Colloidal synthesis has emerged as a powerful method to produce high-quality transition metal dichalcogenides (TMDCs) in solution, providing a scalable approach to size-[1,2], phase-[1,3] and composition[4]-controlled nanosheets (NSs) of these widely researched optoelectronic materials. Among TMDCs, WS_2 is known for high nonlinear susceptibility due to its broken inversion symmetry at monolayer (ML) thickness. [5]

Here, we present a detailed characterization of colloidal WS_2 NSs using TEM, UV/Vis, Raman, and photoluminescence spectroscopy, confirming the synthesis of phase-pure, semiconducting, ML-dominated 2H-WS_2 on both microscopic and ensemble level. We used a custom femtosecond-laser confocal microscope for spectral and spatial mapping of drop-casted WS_2 NSs to correlate structural motifs, such as NS orientation and aggregation, with spectral information. This approach revealed low structural order among drop-casted WS_2 NSs, enabling, in combination with the high ML content, isotropic and efficient second harmonic generation. The nonlinear susceptibility was calculated at 4.28 to 7.55 nm/V, matching or exceeding those of commercially available WS_2 ML samples. Additionally, shifting photoluminescence contributions from neutral excitons and negative trions under one- and two-photon absorption were observed.

This work highlights the suitability of colloidally synthesized TMDCs for the purpose of optical studies, while high nonlinear susceptibility expands the portfolio of potential applications for colloidal TMDCs as functional 2D semiconductors.

[1] Niebur, A.; Söll, A. et al. Nanoscale, 2023,15, 5679-5688.

[2] Frauendorf, A.P.; Niebur, A. et al. J. Phys. Chem. C. 2021, 125, (34), 18841-18848.

[3] Kapuria, N. et al. J. Mater. Chem. A, 2023, 11, 11341-11353.

[4] Fröhlich, M. et al. Phys. Chem. Chem. Phys., 2024,26, 13271-13278.

[5] Wang, Y. et al. Opt. Mater. Express 2019, 9,1136-1149.

HFIP-Driven Microhydration of the Hexafluorophosphate Anion Probed by Gas-Phase Vibrational Spectroscopy: Solute-Solvent vs. Solvent-Solvent Interactions

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1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) has gained prominence as an organic solvent, primarily for its catalytic behavior through its hydrogen-bonding capabilities, particularly in aqueous environments. However, understanding its role in hydrogen-bond networks at a molecular-level remains poorly characterized. Useful insights can be gained from studying isolated, microsolvated ions in the gas phase. [1,2]

In this study, we focus on examining HFIP's role on the microhydration of the hexafluorophosphate anion ($\mathrm{PF_6^-}$), in particular, evaluating the formation of solute-solvent vs. solvent-solvent interactions. The anion complexes $[\mathrm{PF_6^-}(\mathrm{HFIP})_x(\mathrm{H_2O})_y]$ are systematically investigated by IR photodissociation spectroscopy of the corresponding, cryogenically cooled D_2 adducts, in the spectral region between 2200 – 4000 cm^{-1} and assigned using electronic structure calculations. Information on the nature and strength of the formed hydrogen bonds can be extracted from the observed redshift of the O-H stretching transition of the solvent molecules upon microsolvation.

In single-solvent complexes, we observe O-H stretching frequency redshifts of the solvent molecules of less than 200 cm^{-1}, indicating the formation of rather weak ionic hydrogen bonds. In the mixed-solvent complex (x,y = 1) the observed red-shift of one of the O-H stretching bands is twice as large ($\Delta\nu$ = 464 cm^{-1}), suggesting a cooperative solvation effect between HFIP and water. Global minimum-energy structure searches using density functional theory calculations identify the lowest energy isomer of $[\mathrm{PF_6^-}(\mathrm{HFIP})(\mathrm{H_2O})]$ to reflect a structure in which HFIP rather engages in a hydrogen bond with water, a neutral solvent molecule, than interacting with the solute ($\mathrm{PF_6^-}$). It not only leads to a strengthening of the directly involved intermolecular hydrogen bond but also cooperatively affects the more remote anion-water interaction.

Literature:
[1] I. Colomer, A. E. R. Chamberlain, M. B. Haughey, T. J. Donohoe, Nat. Rev. Chem. 2017, 1, 1-12. [2] O. Hollóczki, A. Berkessel, J. Mars, M. Mezger, A. Wiebe, S. R. Waldvogel, B. Kirchner, ACS Catal. 2017, 7, 1846–1852.

The UV/Vis photodissociation spectra of diatomic FeH$^+$: A potential carrier of diffuse interstellar bands?

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Aromatic hydrocarbons are thought to be carriers of Diffuse Interstellar Bands (DIBs), but only the fullerene cation C_{60}^+ has been identified as a carrier of four bands up to date. Iron is one of the most abundant transition metals in the interstellar medium and iron compounds can be potential carriers of DIBs. We report the photodissociation spectra of diatomic FeH$^+$ in the 250–600 nm region (16667–40000 cm^{-1}). A broad absorption band is centred around 310 nm that origins from transitions into the repulsive section of a set of quintet state potential curves. Bands with a width in the range of 100 cm^{-1}, which origin from transitions to bound vibrational levels of excited quintet states, are also observed. Multireference calculations reveal an exceedingly complex electronic structure, with a dense manifold of triplet, quintet and septet states, which are all accessible in the Franck-Condon region of the electronic ground state. The observed photodissociation spectrum does not match the DIB at 4428 Å. Nevertheless, the observed absorption features are close to known DIBs and have similar band width and shape, indicating that diatomic molecules can act as DIB carriers. In the case of FeH$^+$, the broadening of the peaks is most likely caused by predissociation.

Gas-phase excited state reactivity and spectroscopic characterization of redox active $[M(dgpy)_2]^{n+}$ (M=Mn, Co) complexes

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The interest towards (earth-abundant) chelated 3d-transition metal based photocatalysts/photosensitizers has given rise to many developments, by chemical variation of the ligands and oxidation states of the metals, in the field of photocatalysis.[1] We report on progress of gas-phase reactivity investigations on the homoleptic $[M(dgpy)_2]^{n+}$ (M = Mn, Co; dgpy=2,6-diguanidylpyridine) class of complexes, which have shown novel behavior regarding conservation of geometry between different oxidation states and high photocatalytic activity in the solvent phase.[2-3] Using a gas-phase approach to observe the spectroscopic and reactive properties of these complexes is instrumental to understanding the intrinsic properties of these complex-ion species without solvent interactions, as well as allowing for more accurate description using quantum-chemical calculations. Previously, the ground state of the $[Mn(dgpy)_2]^{m+}$ (m= 1-4) complex species was investigated.[4]

We present here gas-phase reactivity experiments which were conducted by adding neutral molecules with low ionization potential and high vapor pressure to the helium buffer gas of the ion trap. Spectroscopic UV and IR photodissociation (PD) measurements were carried out using a modified 3D Paul trap mass spectrometer (amazon ETD, Bruker Daltonics; IR-Experiments at FELIX [5]). Excited state ion-molecule redox reactivity following UV irradiation of the trapped ions was observed between the $[Co(dgpy)_2]^{3+}$ species and triethylamine, yielding a triethylamine cation and the corresponding $[Co(dgpy)_2]^{2+}$. The influence of storage time and laser pulse energy on the reaction process are discussed. Further avenues of excited state analysis using ion trap femtosecond pump-probe spectroscopy are outlined.

Literature:
[1] Chem. Sci., 2024,15, 77-94. [2] Angew. Chem. Int. Ed. 2018, 57, 8027. [3] Inorg. Chem. 2022 61 (37), 14616-14625. [4] J. Am. Soc. Mass Spectrom. 2024, Adv. article (DOI: 10.1021/jasms.4c00113). [5] FELIX-Nijmegen NL, Radboud University

High Resolution GHz and THz (FTIR) Spectroscopy and Quantum Dynamics of Tunneling in Aniline

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Inversion at the nitrogen atom in aromatic amines is of particular interest because of the widespread occurrence of the -NH_2 substituent in aromatic biomolecular compounds, in particular nucleic acids. Aniline ($C_6H_5NH_2$) is the prototype for their quantum tunneling dynamics with an early spectroscopic determination for the inversion barrier (about 450 +/- 80 cm^{-1}) [1,2], much lower than for ammonia NH_3 (about 2000 cm^{-1} [3]). Aniline has about 20 vibrational-tunneling levels importantly populated at room temperature and the rotational transitions within these levels are all overlapping in the same frequency range (< 500 GHz). Here, we report highest resolution results from our GHz measurement from 75 GHz to 500 GHz and from the THz (FIR) range measured with our 2009 ETH-Bruker prototype spectrometer at the SLS (Swiss Light Source). We observed the rotationally resolved spectrum and analysed vibrational-tunneling structures (I_0, $10b_1$, T_1, I_1, $10b_1I_1$, T_1I_1) among others (notably also the hot band $I_{3\leftarrow 1}$ at 700 cm^{-1}) providing accurate rotational parameters. We firmly assigned the spectra, including also the nuclear spin statistics seen by the intensity patterns in the GHz range and in part also resolved the hyperfine structure. The results are also discussed in relation to transient chirality in aniline –NHD and ammonia NHDT [3] and in relation to our ongoing efforts on precision experiments concerning the electroweak force of the standard model of particle physics (SMPP) by measuring the parity violating energy difference between the two enantiomers of chiral molecules [4-6]. We discuss in particular the closely related spectroscopic challenges in the vibrational tunneling dynamics for 1,2-Dithiine ($C_4H_4S_2$) as a prototype for measuring parity violation needing the analysis of parity states in the mid-IR range in very dense spectra with multiple overlapping rotation-vibration-tunneling structures (see reviews [5,6]).

[1] Quack, M., Stockburger, M., *J. Mol. Spectrosc.*, **1972**, 43, 17-111
[2] Fehrensen, B., Luckhaus, D., Quack, M., *Z. Physik. Chem.*, **1999**, 209, 1-19
[3] Fabri, C.,Marquardt, R., Csaszar, A.G., Quack, M., *J. Chem. Phys.*, **2019**, 150, 014102
[4] Quack, M., *Chem. Phys. Lett.*, **1986**, 132, 147-153
[5] Quack, M., Seyfang, G., Wichmann, G., *Proc. Nobel Symposium* 167 on Chiral Matter, Stockholm **2021,** 207-266 (World Scientific, Singapore 2023)
[6] Quack, M., Seyfang, G., Wichmann, G., *Chemical Science*, **2022**, 13, 10598-10643

Internal Hydrogen Bonds in Zeolites

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Knowledge about type and position of active sites in zeolites is a prerequisite for the rational design of catalysts and catalytical processes. In non-defective zeolites, the active sites are Al–O(H)–Si Brønsted acid sites (BAS). Using our chemically accurate QM:QM embedding methodology (QM = quantum mechanics), we provide evidence that some of these sites form internal hydrogen bonds to Si–O–Si acceptor sites in the zeolites H-MFI and H-FER.[1]

For the zeolite H-MFI, nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy indicate multiple structurally different proton sites.[2,3] The ^{1}H-NMR signal at 4.2 ppm and IR signal at 3614 cm^{-1} are commonly attributed to unperturbed BAS.[2] The assignment of further signals at 7.0 ppm in ^{1}H-NMR and at 3250 cm^{-1} in IR has been debated.[3,4]

For the unperturbed BAS, we predict signals from 3.9 to 4.5 ppm for ^{1}H-NMR and from 3614 to 3628 cm^{-1} for IR. This is in good agreement with the experimental signals[2] at 4.2 ppm and 3614 cm^{-1}, respectively, validating the accuracy of our predictions. The predicted signals for the hydrogen bonded BAS range from 4.7 to 10.3 ppm for ^{1}H-NMR and from 3016 to 3585 cm^{-1} for IR, agreeing well with the broad experimental peaks[2] centred at 7.0 ppm and 3250 cm^{-1}, respectively. The length of internal H-bonds varies substantially with their framework position which reflects in a wide spread of predicted ^{1}H-NMR and IR signals.

Literature:

[1] H. Windeck, F. Berger, J. Sauer, Angew. Chem. Int. Ed. 2023, 62, e202303204. [2] E. Brunner, K. Beck, M. Koch, L. Heeribout, H. G. Karge, Microporous Mater. 1995, 3, 395-399. [3] C. Schroeder, V. Siozios, C. Mück–Lichtenfeld, M. Hunger, M. R. Hansen, and H. Koller, Chem. Mater. 2020, 32, 1564-1574. [4] M. Abdolrahmani, K. Chen, and J. L. White, J. Phys. Chem. C 2018, 122, 15520-15528.

Surfaces and Interfaces

Nitrile Groups as Build-in Molecular Sensors for Interfacial Effects at Electrocatalytically Active Carbon Materials

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Within an electrocatalytic cycle, short-ranged electric fields at electrode surfaces play an important role in the reaction mechanism. These field effects can be characterized using the vibrational Stark effect, which arises from the interaction between a local electric field and a vibrational mode of surface-bound molecular groups and can be measured by spectroelectrochemical methods such as *in-situ* electrochemical Raman spectroscopy.

Expanding the range of catalytically active systems suitable for electrochemical Stark spectroscopy, we herein investigate a carbon-based porous material of C_2N stoichiometry that shows electrocatalytic activity for the hydrogen evolution reaction (HER). [1,2] Through *in-situ* Raman spectroscopy, it is demonstrated that nitrile groups with defect character act as vibrational sensor groups. Specifically, the $\nu(C\equiv N)$ vibrational mode at ~2235 cm^{-1} exhibits a linear shift in response to the applied electric voltage, according to the vibrational Stark effect under non-catalytic conditions in a KCl electrolyte. Under HER conditions in HCl electrolyte, deviations from the linear shift indicate rearrangement processes within the electrochemical double layer and suggest a semi-permanent conditioning of the electrode's surface due to the hydrogen evolution process.

[1] W. Zhang et al., Small 2022, 18, 2204116. [2] R. Walczak et al., Angew. Chem. Int. Ed. 2018, 57, 10765.

Cross-Linked Metal Nanoparticle Networks for Physiological Monitoring and Chromatographic Gas Sensing

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Digitalization and the emerging use of artificial intelligence for addressing today’s challenges in environmental monitoring and protection, medical diagnosis and food quality assessment require distributed, inexpensive, low-power and small footprint physical and chemical sensors.[1] Due to their highly perturbation-sensitive, interparticle tunnelling-based charge transport, networks from molecularly cross-linked nanoparticles are promising materials for resistive strain[2,3] and gas sensors.[4,5] We report the investigation of the percolation-induced anisotropic strain sensitivity of dithiol cross-linked gold nanoparticle networks and demonstrate their integration into skin-conformal physiological sensing elements for pulse wave monitoring and gesture sensing (Figure 1a).[3] Further, we investigate the selective sorption/transport dynamics of analyte molecules in such nanoparticle networks and demonstrate how dynamic features of their chemiresistive responses upon exposure to volatile organic compounds (VOCs), caused by these chromatographic effects, boost machine learning assisted analyte recognition (Figure 2).[5]

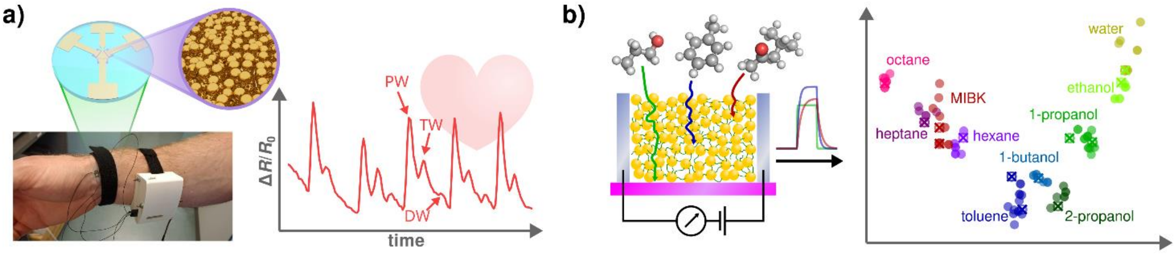

Figure 1: a) Pulse wave recorded by a wearable sensor consisting of a molecularly cross-linked gold nanoparticle network.[3] b) Sorption dynamics of a nanoparticle network-based VOC sensor and their use for machine-learning based analyte recognition.[5]

Literature: [1] H. Schlicke, R. Maletz, C. Dornack, A. Fery, *Small* **2024**, 10.1002/smll.202403502. [2] H. Schlicke, S. Kunze, M. Rebber, N. Schulz, S. Riekeberg, H. K. Trieu, T. Vossmeyer, *Adv. Funct. Mater.* **2020**, *30*, 2003381. [3] B. Ketelsen, H. Schlicke, V. R. Schulze, S. C. Bittinger, S. Wu, S. Hsu, T. Vossmeyer, *Adv. Funct. Mater.* **2023**, *33*, 2210065. [4] H. Schlicke, S. C. Bittinger, T. Vossmeyer, *ACS Appl. Electron. Mater.* **2020**, *2*, 3741. [5] H. Schlicke, S. C. Bittinger, H. Noei, T. Vossmeyer, *ACS Appl. Nano Mater.* **2021**, *4*, 10399.

Influence of long-range attraction on desorption kinetics

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Desorption of molecules from surfaces is an omnipresent process both in nature and technology. Despite its conceptual simplicity, fundamental details can be surprisingly complex and are often poorly understood. In many cases, first-order kinetics is assumed, which implies the absence of adsorbate-adsorbate interactions and desorption being the rate-limiting step. While this might be a good approximation in some cases, it is far from reality in the case of adsorbates forming an ordered structure.

Here, we study the desorption of a submonolayer film of 3-nitrophenol from the natural cleavage plane of calcite kept in ultrahigh vacuum. Interestingly, two distinctly different desorption regimes are observed during isothermal desorption monitored by dynamic atomic force microscopy. Initially, at high coverages, the coverage decreases almost linearly in time, indicating a constant desorption rate. Beyond this linear regime, at low coverages, a drastic increase in desorption rate is observed until the surface is completely empty. The transition between these two regimes is associated with a critical island width. The increase in desorption rate when falling below a critical island width indicates that a long-range attractive interaction between the molecules is present. The herein observed phenomenon of two different desorption regimes is expected to be of general significance when interactions beyond next-neighbor attraction are present.

Investigation of Model Hydrogels of Increasing Complexity that Approach the Structural Features of Mucins

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Mucus, which is a complex biological hydrogel and consists of Mucus glycoproteins (mucins), lipids, ions, proteins, cells, cellular debris, and water as components [1], surrounds the surfaces of the human body. It fulfills important functions, such as acting as a protective barrier against foreign bodies or minimizing friction between organs [2,3]. It is well known that this kind of slime forms a three-dimensional viscoelastic network structure which is stabilized by diverse molecular interactions for instance hydrogen bonding, hydrophobic and electrostatic interactions [4]. Our goal is to comprehend how the dynamic properties of native mucus are related to its mesoscopic structure. This project is related to the collaborative research centre (CRC) 1449 which is financed by the German Research Foundation and tends to investigate the protective functions of hydrogels at biological interfaces. For this purpose we try to mimic the viscoelastic properties of this biological hydrogel by synthesizing a non-toxic one which consists of poly(ethylene oxide) (PEO) as well as hydrophobically modified poly(methacrylic acid) (HM-PMAA). Due to the inauguration of C_{12} or C_{16} – side chains to PMAA we also obtain hydrophobic interactions besides the already existing hydrogen bonds between PMAA and PEO, which forms a hydrogel after blending both polymers in a certain ratio and a certain pH-range. After the establishment of this model-system a non-ionic surfactant, here Brij O 10, was additionally added so as to strengthen the hydrophobic interactions and to understand the self-assemblance of the side chains acting as crosslinking points in the hydrogel network. In all performed experiments Macro- and microrheology are the key methods for hydrogel characterization.

Literature:

[1] W. J. Weigand, A. Messmore, J. Tu, A. Morales-Sanz, D. L. Blair, D. D. Deheyn, J. S. Urbach, R. M. Robertson-Anderson, PLos ONE, **2018**, 13(8), 1-19
[2] J. Witten, T. Samad, K. Ribbeck, Curr. Opin. Biotechnol. **2018**, 52, 124–133
[3] S. K. Lai, Y. Y. Wang, D. Wirtz, J. Hanes, Adv. Drug. Deliv. Rev. **2009**, 61, 86–100
[4] R. Bej and R. Haag, JACS, **2022**, 144(44), 20137-20152

Refining the CO sensing mechanism of Au doped SnO_2 gas sensors using modulation excitation IR spectroscopy

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Sensitive and selective gas sensors are essential for identifying and monitoring greenhouse gases and pollutants such as CH_4, NO_x and CO. [1] To enable a rational design of sensor materials for this purpose, a deep understanding of the underlying sensor mechanism is of great importance, which can often be obtained using established *operando* spectroscopic techniques. [2] To clearly identify the active surface species, which are involved in the primary sensor response, transient spectroscopic methods like modulation-excitation (ME) DRIFT spectroscopy can be used, which can lead to new mechanistic insights. [3] Here, we present a detailed ME-DRIFTS study of the mechanism of gold-loaded tin oxide (Au/SnO_2) during CO gas sensing, in combination with resistance and further spectroscopic (UV-Vis, XPS, IR) measurements. Applying *in situ* ME DRIFTS combined with phase sensitive detection (PSD), we could show that surface lattice oxygen atoms are the active oxygen surface species reacting with CO to CO_2 by a redox mechanism, leading to the fast, initial sensor response to CO exposure before inert surface adsorbate accumulation. Carbonates are not directly involved in the initial sensor response but are mainly formed after the sensor reaction by readsorption of CO_2, hindering the regeneration of the sensor material, similar to the behaviour observed during ethanol gas sensing [4]. Summarizing, our results demonstrate the great potential of transient spectroscopy to gain new insight into gas-sensing mechanisms by selectively identifying the active surface species, as illustrated by Au/SnO_2 used for CO and ethanol gas sensing.

[1] S. Dhall, B.R. Mehta, A.K. Tyagi, K. Sood, Sens. Int. 2021, 2, 100116. [2] A.-K. Elger, C. Hess, Angew. Chem. Int. Ed. 2019, 58, 15057. [3] J. Weyel, L. Schumacher, M. Ziemba, M. Pfeiffer, C. Hess, Acc. Chem. Res. 2024, 57, 18, 2643.[4] M. Pfeiffer, C. Hess, J. Phys. Chem. C 2022, 126, 8, 3980.

Unraveling the Structural Complexity of Two-Dimensional Metallic Aerogels Using Graph Theory

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The production of aerogels in two dimensions (2D) is an attractive but challenging task that can be achieved by phase-boundary gelation at the liquid-liquid interface. Understanding the direct influence of experimental parameters on the formation, geometry and properties of these structures provides the opportunity to uncover fundamental features that influence the gelation process. The flat structure of 2D aerogels allows for easy geometric analysis and determination of fractal features without overlapping components complicating the analysis. The aim is therefore to investigate in detail the parameters that influence the gelation mechanism and to determine the direct effect of the structural change on the mechanical and electrical properties of the 2D meshes. The detailed investigation is carried out by applying graph theory and node-based multifractal analysis to 2D gold meshes, which quantify the morphology of the composite network to provide multiple descriptors for numerical comparison of the effects of different synthesis conditions. With this information, the underlying aggregation mechanisms can be investigated in more detail. Furthermore, the identified structure-property relationships provide the necessary insight to precisely control the mechanical and electrical properties of the 2D metal aerogels required for specific applications.

Investigations on the Behavior of Amphiphilic Block Copolymers and Surfactants in Deep Eutectic Solvents (NADES)

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Natural deep eutectic solvents (NADES) are a novel class of polar solvents that has the potential to become a non-toxic and cheap alternative to conventional organic solvents and ionic liquids. Amphiphilic self-assembly is very a well-established phenomenon for solutions of surfactants or amphiphilic polymers in water, allowing to functionalize them.[1] Structure formation by surfactants in DES has been studied to some extent [2], but the solubility of polymers and in particular self-assembly of amphiphilic polymers is a topic that has been addressed to a very limited extent.[3]

In this study, we designed custom block copolymers guided by extensive solubility assessments of various homopolymers. Notably, polyacrylamide-b-poly(N-isopropylacrylamide) (PAm-PNiPAm), with PAm as the soluble segment, demonstrates excellent solubility in our NADES reline. The resulting copolymer exhibits enhanced viscosity and shear-thinning in reline, which can be tuned by adjusting block lengths, offering a means to control NADES properties. The systems were studied comprehensively by rheology and with respect to the their mesoscopic structure by small angle neutron scattering (SANS). Furthermore, substituting the insoluble block with poly(dimethylacrylamide) (PDMAm) imparts thermoresponsive behavior, broadening potential applications, particularly for drug delivery systems. Furthermore, we are also working with some self-tailored cationic surfactants which can affect the physicochemical properties of our DES.

Literature:
[1] H. Vanda, Y. Dai, E.G. Wilson, R. Verpoorte, Y.H. Choi, Compt. Rend. Chim. 21, 628 (2018)
[2] A. Sanchez-Fernandez, G.L. Moody, L.C. Murfin, T. Arnold, A.J. Jackson, S.M. King, S.E. Lewis, K.J. Edler, Soft Matter 14, 5525 (2018)
[3] P. Patidar, B. Kanoje, A. Bahadur, K. Kuperkar, D. Ray, V.K. Aswal, M. Wang, L.J. Chen, P. Bahadur, Colloid Polym. Sci. 299 (2021) 117–128

Spiralling Hierarchal Structures in Chiral Lipid Monolayers Mapped with SFG Microscopy

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The importance of phospholipids cannot be overstated. Their amphiphilic nature promotes self-assembly into two-dimensional membranes in which the hydrophobic tails tightly pack and point away from the membrane interface. Beyond this well-defined out-of-plane structure, the specific in-plane molecular arrangement also has profound implications in a vast range of physiological processes. Studies of model systems have shown condensed lipid islands (rafts) to form with a wide range of sizes and morphologies. Whilst there has been some suggestion that these domains possess in-plane molecular anisotropy and mesoscopic structural chirality, the details of their in-plane molecular orientations nevertheless remain largely unknown.

Here, we employ a newly developed Sum-Frequency-Generation (SFG) microscope with a novel imaging system to investigate the condensed lipid domains within monolayers with mixed chirality. We find that the domains possess curved in-plane molecular directionality within a spiralling mesoscopic hierarchal packing structure. By comparing different enantiomeric mixtures, both the molecular and spiral turning directions are shown to depend on the chirality, but with a clear deviation from mirror symmetry in the formed structures. This demonstrates strong enantioselectivity in the domain growth process, with potential connections to the evolution of homochirality in all living organisms.

Literature:

Fellows, A.P., John, B., Wolf, M.; Thämer, M. Spiral packing and chiral selectivity in model membranes probed by phase-resolved sum-frequency generation microscopy. *Nat Commun* **2024**, *15*, 3161.

A hidden film assembly mechanism: reconstruction-by-reconstruction cycle growth of HKUST-1 MOF layers

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Thin films of metal-organic frameworks (MOFs) grown in a layer-by-layer manner have been the subject of growing interest. Especially for optical applications, they could have a large impact if the optical quality of them is high.[1] Here, we investigate one of the most popular MOFs, the HKUST-1 lattice. We have selected a synthesis procedure from known components resulting in a quick but perfect growth regarding the optical scattering and film cracks. This enables the fabrication of films of excellent optical quality within some few ours. Furthermore, we address the known, but up-to-now not understood observation that the expected growth rate of one monolayer per cycle is strongly exceeded, in our case by a factor of 4, which is a strange inconsistency in the literature. We offer a growth model using an interplay between surface oversaturation and a reconstruction process in every cycle. This leads to a reconstruction-by-reconstruction (RbR) cycle growth with a 4-times higher growth rate compared with the layer-by-layer mechanism. This represents a new film assembly mechanism of possible interest also for other MOF film syntheses.[2]

[1] T. Koehler, I. Strauss, A. Mundstock, J. Caro, and F. Marlow: Reversible Photoalignment of Azobenzene in the SURMOF HKUST-1. J. Phys. Chem. Lett. 12 (2021) 8903–8908
[2] T. Koehler, J. Schmeink, M. Schleberger, F. Marlow: A hidden chemical assembly mechanism: reconstruction-by-reconstruction cycle growth in HKUST-1 MOF layer synthesis (subm.) http://arxiv.org/abs/2409.18666

Depth-Resolved Vibrational Spectroscopy of Organo-Aqueous Interfaces

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Surfactant covered aqueous interfaces belong to the most abundant interfaces on our planet, with their unique properties being at the heart of numerous physico-chemical processes in nature. Examples span from biological activity to environmental chemistry such as oceanic gas uptake or atmospheric reactions. The sheer presence of the interface induces structural changes to water, manifesting as alterations to the distribution of molecular orientations, diffusion dynamics, and the strength and interconnectivity of the H-bond network. However, despite decades of research, some of the most fundamental aspects of interfacial water remain unknown, controversial, or experimentally unverified, particularly the thickness of the structural anisotropy and a depth-dependent view of the H-bond connectivity.

In this work, we directly address these points by employing our recently developed depth-resolved vibrational spectroscopy based on the simultaneous measurement of both sum- and difference-frequency generation (SFG and DFG) responses. With their combined analysis, the observed spectral features can be precisely depth-profiled on the sub-nm scale. Here, we present the findings from analyzing both the O-H stretch and H-O-H bend vibrations at the pure air-water interface as well as those with charged surfactants, decomposing the spectra into their constituent sources and comparing them to *ab initio* molecular dynamics simulations. This allows a direct measure of the anisotropic thickness to be extracted as well as the elucidation of the structural variations induced by the interface in each system.

Literature:

1) Balos, V.; Garling, T.; Duque, A. D.; John, B.; Wolf, M.; Thämer, M., Phase-Sensitive Vibrational Sum and Difference Frequency-Generation Spectroscopy Enabling Nanometer-Depth Profiling at Interfaces. *J. Phys. Chem. C* **2022**, *126*, 10818-10832.

2) Fellows, A.P.; Díaz Duque, A.; Balos, V.; Lehmann, L.; Netz, R.R.; Wolf, M.; Thämer, M. How Thick is the Air–Water Interface? - A Direct Experimental Measurement of the Decay Length of the Interfacial Structural Anisotropy. *Langmuir* **2024**, 40, 35, 18760-18772.

Femtosecond Laser Ablation (fs-LA) – A New Approach to XPS Depth Profiling

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XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers by using argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. A prototype XPS depth profiling instrument has been constructed that employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (several 10s microns) and is much faster than traditional ion beam sputter depth profiling. fs-LA XPS depth profile results will be shown for selected thin films, coatings, multilayers and oxidised surfaces and the outlook for this new technique discussed.

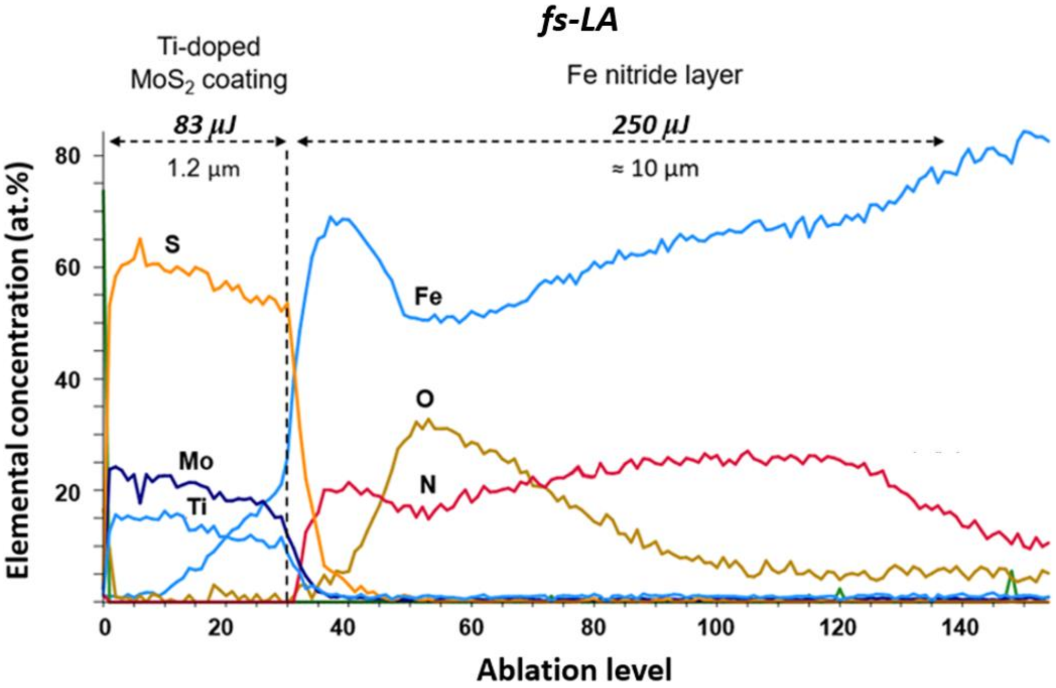

***Figure 1**: fs-LA XPS depth profile of a EN31CrMoV9 steel subjected to a duplex gas nitriding surface treatment followed by PVD deposition of a titanium-doped molybdenum disulfide (MoS_2:Ti) coating*

Keywords: XPS, depth profiling, femtosecond laser ablation, thin film, coating

Influence of surfactants on the surface propensity of ions at the ocean-air interface

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Aqueous solution-vapor interfaces play a major role in atmospheric processes, for example in the interaction of the oceans or of aqueous aerosols with trace gases [1]. The largest contiguous aqueous solution-vapor interface is that of the oceans with air, covering more than 70% of the Earth's surface [2]. Studies have shown that the ocean-air interface is covered by a thin film of amphiphilic compounds, including surfactants [3]. This so-called sea surface microlayer significantly influences many processes with importance to the global ecosystem, such as the exchange of trace gases (e.g., CO_2) and heat, and the generation of aerosol particles [4,5].

The goal of our investigations is to elucidate the impacts of surfactants on the surface propensity of ions in seawater. We use X-ray photoelectron spectroscopy (XPS) coupled with a liquid microjet [6,7], which is able to quantitatively describe the presence of surfactants and ions at the liquid-vapor interface at the molecular level. The results of our investigations show that the presence of positively and negatively charged surfactants can strongly change the propensity of ions for the seawater-air interface, which has consequences for the availability of ions in heterogeneous reactions involving, e.g., trace gases.

Literature:

[1] Carpenter, L.J. et al. Chem. Rev. 115, 4015-4034 (2015). [2] George, C. et al. Chem. Rev. 115, 4218–4258 (2015). [3] Brüggemann, M. et al. Nat. Commun. 9, 2101 (2018). [4] Wurl, O. et al. Elem. Sci. Anth. 5, 31 (2017). [5] Engel, A. et al. Front. Mar. Sci. 4, 262783 (2017). [6] Winter, B. and Faubel, M. Chem. Rev. 106, 1176–1211 (2006). [7] Dupuy, R. et al. J. Chem. Phys. 154, 060901-30 (2021).

Co_3O_4 and 2-propanol: Liquid-solid or better gas-solid catalysis?

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Heterogeneous catalysis is pivotal to produce chemicals on an industrial scale. To make these processes more efficient, selective or energetically favourable substantial efforts are put into the development of better catalysts. As such metal oxide catalysts, such as the spinel oxide Co_3O_4, have gained attention for their versatility, tunability and natural abundance. Co_3O_4 was found to have exceptional properties when it comes to alcohol oxidation reactions, such as the reaction of 2-propanol to acetone [1]. This reaction proceeds with liquid as well as with gaseous 2-propanol, however it is yet to be fully understood if and how changes in the interfacial adsorption occur when changing from liquid to gas phase catalysis. We apply sum frequency generation spectroscopy to study the surface structure of 2-propanol on Co_3O_4 under these two conditions. The most striking difference observed is that the frequency of the different CH_3 stretch vibrations is roughly 10-30 cm^{-1} lower in the liquid phase than in the gas phase. This suggests that liquid 2-propanol is adsorbed in its deprotonated state at the Co_3O_4 surface, which is in contrast to the gas phase where 2-propanol seems to be partly molecularly adsorbed. Besides, experiments with added water indicate that the ratio between protonated and deprotonated 2-propanol at the Co_3O_4 surface can shift depending on the amount of water added.

Literature:
[1] S. Anke *et al.*, “Selective 2-Propanol Oxidation over Unsupported Co3O4 Spinel Nanoparticles: Mechanistic Insights into Aerobic Oxidation of Alcohols,” *ACS Catal.*, vol. 9, no. 7, pp. 5974–5985, May 2019

Controlled Two-Dimensional Assembly of Gold Hedgehog Nanoparticles

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The arrangement of nanoparticles into large ordered structures has attracted great attention in the nanoscience due to their special electronic and photonic properties. Modifying the surface of the particles with different ligands opens a wide range of possibilities for linking nanoparticles and exploring their orientation and cross-links. In this work, we utilise our recently developed two-dimensional gelation of hedgehog-like gold particles, which exhibit pronounced stochastic branching and intense optical activity. We show that the two-dimensional Au hedgehog (HH) aerogels can be prospectively used in electrocatalysis and as substrates for surface-enhanced Raman spectroscopy (SERS).

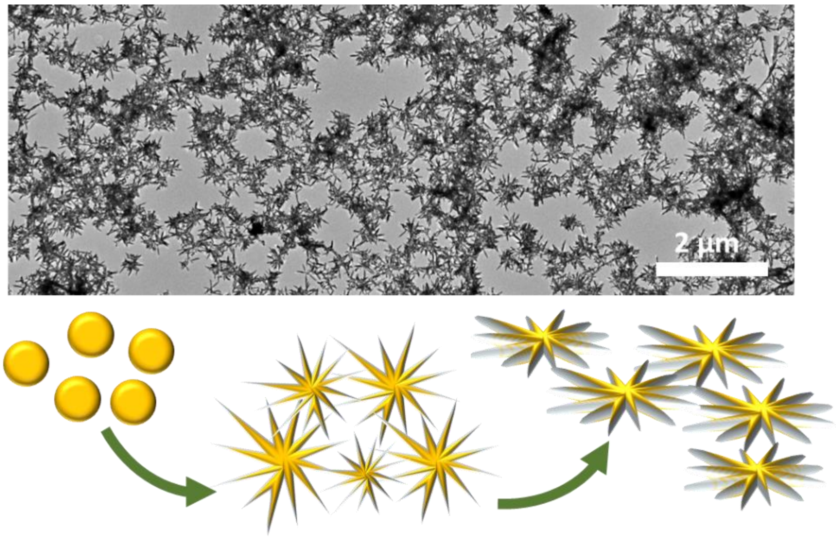

Figure 1 TEM image of the two-dimensional Au hedgehog aerogels and scheme of the work

Theory and Data Science

Why alloying with noble metals does not decrease the oxidation of platinum

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Despite its well-known nobility, even platinum is subject to corrosion under the harsh conditions that many technical applications require. In case of ammonia oxidation, the well-known “cauliflower” reconstruction is most likely caused by a transport reaction mediated by volatile PtO_2 [1,2] and is accompanied by a loss of much of the platinum.

In our investigation [3] we examine how to enhance the stability of platinum in the solid phase under harsh oxidative conditions through the formation of alloys and intermetallic compounds. We model the formation of gaseous PtO_2 using Density Functional Theory coupled with thermodynamic calculations to extrapolate to typical reaction conditions. The results are carefully assessed based on experimental data.

We observe that the stability of platinum within alloys correlates with expected reactivity trends of the alloying metals. Combining it with very noble metals like gold thus facilitates its oxidation. Conversely, strongly stabilizing elements like tungsten oxidize themselves, since the platinum- and oxygen affinity of the secondary metal are related to each other. Despite their similarity, these two properties are however not identical, which leaves some room for optimization. Based on our results we suggest copper as a superior replacement for the widely used rhodium, which has a considerably stronger effect on platinum, while at the same time being less prone to oxidation especially at lower temperatures. Provided oxidation is not a problem for the catalyst performance, more reactive metals like tungsten might be viable as well. Our results demonstrate that alloying has been unjustly overlooked as a strategy, yet it offers a relatively straightforward way to enhance catalyst durability.

References:
[1] O. Nilsen et al., *Appl. Catal.* A, 207, 43. [2] L. Hannevold et al., *Appl. Catal.* A, 284, 163. [3] A. Kafka, F. Hess, *Phys. Chem. Chem. Phys.*, 26, 24631.

Analysing ferromagnetic & antiferromagnetic contributions in μ-oxo bridged first row transition metal complexes

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Molecular magnets in small $[M_2O]^{2+}$ binuclear active sites in transition metal complexes represent interesting candidates as qubits in modern quantum computers.[1] However, their complex electronic structures requiring multiconfiguational approaches represent a challenge for state-of-the-art quantum chemical methods, especially their resulting magnetic properties essential for their application in quantum computers are not completely understood.[2] Magnetic interactions arise from multiple exchange pathways, characterized by the metal-metal distances, bridging anions, and the spatial orientation of the respective ligand fields on the metal centers.[3]

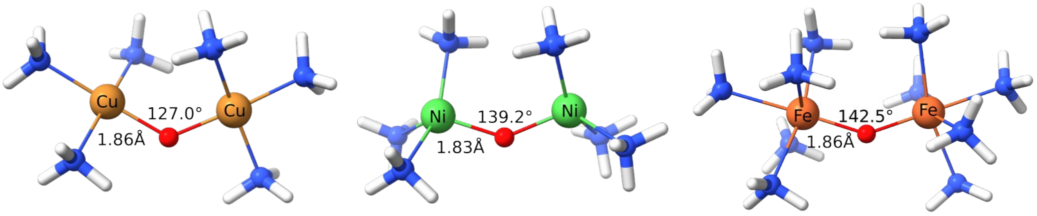

Figure 1: Dinuclear, μ-oxo bridged Cu^{+II}, Ni^{+II} and Fe^{+II} complexes studied here.

We analyze the magnetic interactions in three dinuclear model complexes by combining a classical Hartree-Fock framework with broken-symmetry density functional theory (BS-DFT) and complete active space self-consistent field (CASSCF) methods. This approach will be demonstrated by varying the M–O–M angles and M–O–M–N dihedral angles in μ-oxo-bridged copper(II), nickel(II), and iron(II) model complexes, providing new insights in the electronic structure and allowing us to decouple the ferromagnetic and antiferromagnetic contributions to the magnetic interactions.

Literature:

[1] a) A. A. Starikova, V. I. Minkin, *New Journal of Chemistry,* **2017**, 41.14, 6497-6503. b) R. Rabelo, *et al.*, *Magnetochemistry,* **2020***,* 6.4, 69.

[2] a) C. J. Stein, D. A. Pantazis, V. Krewald, J. *Phys. Chem. Lett.* **2019**, 10, 6762-6770. b) C. J. Calzado, J. Cabrero, J. P. Malrieu, R. Caballol, *The Journal of chemical physics* **2002,** 116, 2728-2747.

[3] a) O. Kahn, «Molecular magnetism», *Courier Dover Publications*, **2021**. b) Van H. Crawford, *et al.*, *Inorganic Chemistry*, **1976**, 9, 2107-2110.

Modelling Electron Attachment and Fragmentation Channels in Acetyl Chloride Clusters with a Genetic Algorithm

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Electron attachment to acetyl chloride (AC, CH_3COCl) in the atmosphere can trigger the release of chlorine radicals and other reactive organic species, significantly affecting climate-relevant atmospheric processes such as ozone depletion, nitrogen transport, and secondary pollutant formation.

Our experimental results show that dissociative electron attachment (DEA) to acetyl chloride predominantly yields Cl^- ions at approximately 2 eV, with minor fragment peaks such as CH_3COO^- possibly originating from dimers or larger clusters. Cl^- remains the major product both in isolated molecules and clusters when acetyl chloride is co-expanded with helium or argon. Cluster mass spectra reveal prominent $(AC)_nCl^-$ ions and a minor $(AC)_nHCl_2^-$ ion series, aligning with isotopic patterns.

To determine the observed structures and the reaction energetics, we use our in-house genetic algorithm [1], previously successful in modelling the potential energy surface of C_{120}^+ and $Ag^+(H_2O)_{4-6}$ [2–3]. We combine the semi-empirical GFN2-xTB method with our graph-based clustering approach to increase genetic diversity [4] and identify the fittest groups based on their energy. Finally, we show that our approach accelerates the search for “original ideas” within the genetic algorithm, actively hindering the algorithm to become stuck in a single basin.

Literature:
[1] G. Schöpfer, M. Gatt, M. Ončák, https://git.uibk.ac.at/c7441332/genetic-algorithms. [2] M. Kappe, A. Schiller, E. Gruber, D. Jank, M. Gatt, G. Schöpfer, M. Ončák, A. M. Ellis, P. Scheier, J. Chem. Phys. 159, 204302 (2023). [3] M. Hütter, G. Schöpfer, M. Salzburger, M. K. Beyer, M. Ončák, RSC Adv. 14, 22185 (2024). [4] M. Gatt, G. Schöpfer, M. Ončák, https://github.com/photophys/structure_clustering.

Linear-scaling PNO-MP2 for periodic systems

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There is a growing demand for *ab initio* quantum chemical methods in material sciences,[1] e.g. to aid in designing new energy materials or elucidate catalytic reaction mechanisms through the study chemical reactions on surfaces. Canonical correlated wavefunction methods usually suffer from a steep polynomial scaling which is exacerbated in periodic boundary conditions[2] due to the long-range nature of the Coulomb interaction. The advent of (DL)PNO methods has paved the way for applying high-level *ab initio* quantum chemistry to chemically relevant molecular sizes.[3] At the moment, the condensed phase *ab initio* toolset is mostly limited to DFT which lacks systematic improvability and is known to have difficulties with noncovalent interactions such as dispersion.

We present a novel linear-scaling periodic PNO-MP2 implementation in TURBOMOLE, characterised by its state-of-the-art local density fitting, efficient PAO-OSV-PNO generation and use of the Laplace transformation to reduce the steep polynomial scaling.[4] This development further provides access to double hybrid functionals which are amongst the most accurate density functionals. In contrast to the majority of periodic plain wave MP2 implementations, we work in the LCAO framework with Gaussian basis sets.[5,6] This ansatz is particularly advantageous for studying dynamics on 2D surfaces where the efficient PNO scaling facilitates low adsorbate coverages necessary to avoid spurious interactions of the adsorbate with its periodic images.

References:
[1] Booth, Grüneis, Kresse and Alavi, *Nature* **2013**, *493*, 365.
[2] Schäfer, Ramberger and Kresse, *J. Chem. Phys.* **2017**, *146*, 104101.
[3] Neese, Wennmohs and Hansen, *J. Chem. Phys.* **2009**, *130*, 114108.
[4] Schmitz, Helmich and Hättig, *Mol. Phys.* **2013**, *111*, 2463.
[5] Pisani *et al.*, *J. Comp. Chem.* **2008**, *29*, 2113.
[6] Irmler, Burow and Pauly, *J. Chem. Theory Comput.* **2018**, *14*, 4567.

Molecular Dynamics and Computational Spectroscopy for Systems in Soft Condensed Phase

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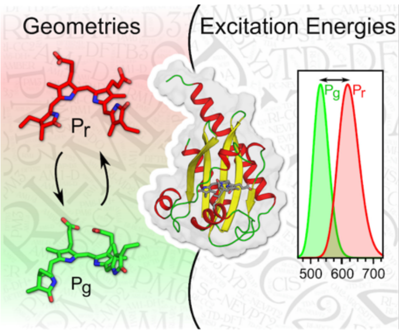
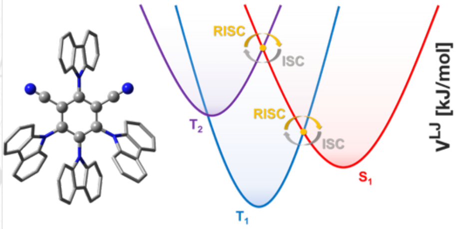
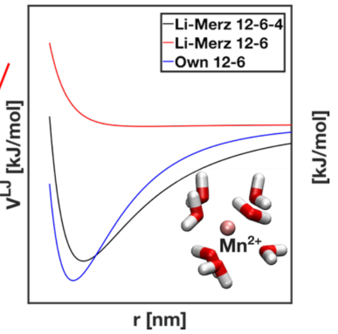
Molecular dynamics is a wide-spread simulation technique, which (i) we have employed to elucidate photophysical processes based on potentials from electronic structure calculations [1] and (ii) can be used to obtain structural insights into biological macromolecules like proteins and DNA using classical force fields [2]. Complementary to this, computational molecular spectroscopy allows to establish structure-property relationships. For example, our calculations helped to assign chemical shifts and hyperfine couplings to atoms of chromophores [3]. We have also combined both in the framework of quantum mechanics/molecular mechanics (QM/MM) simulations to understand the molecular origin of the difference in optical absorption between the photoproduct (P_g) and dark state (P_r) of the photoreceptor protein Slr1393 [4]. Furthermore, our QM/MM-optimized structures provided further details of structural rearrangements in the binding pocket [5]. Currently, we are working on unravelling the mechanisms leading to thermally activated delayed fluorescence in donor-acceptor cyanoarenes [6] and on the parameterization of metal ions, which is a prerequisite for classical MD simulations.







Literature:
[1] C. Wiebeler et al., *J. Phys. Chem. Lett.* **2017**, 8, 1086–1092.
[2] S. Dürauer et al., *Mol. Cell* (submitted).
[3] P. Kurle-Tucholski et al., *J. Magn. Reson.* **2023**, 353, 107497.
[4] C. Wiebeler et al., *Angew. Chemie Int. Ed.* **2019**, 58, 1934–1938.
[5] L. Köhler et al. *Chem. Sci.* **2023**, 14, 6295–6308.
[6] M. Streiter et al., *J. Phys. Chem. C* **2020**, 124, 15007–15014.

Active Learning of Permutation-Invariant-Polynomial Neural Network Potentials for Multi-State PIMC Simulation

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Path Integral Monte Carlo (PIMC) simulations allow for efficient sampling of static finite temperature properties by giving numerically exact results with respect to quantum Boltzmann statistics within the canonical ensemble. In this context, we recently proposed an approach to Path Integral Simulations based on the previous work of Schmidt and Tully [1] to consider multiple electronic states in molecular systems, including non-adiabatic effects, as relevant for many systems e.g. transition metal complexes.

However, due to the large number of required steps to achive convergence in such PIMC simulations, computing these potentials on the fly is unfeasible and a global representation needs to be computed beforehand. Deep learning based on Neural Networks (NN) provides the perfect basis to find such a global representation while keeping the computational effort minimal.

Here, we propose a scheme based on active learning to automatically train Permutation-Invariant-Polynomial (PIP) NN that can accurately predict potential energy surfaces of multiple electronic states. Additionally, the scheme allows for explicit control over large and small value asymptotic behaviors if known, thus reducing the needed training set size and minimizing unphysical behavior in the PIMC simulation due to large step sizes.

Literature:
[1] J.R. Schmidt, J.C. Tully, J. Chem. Phys. 2007, 127, 09.

A defect chemical perspective on grain-boundary corrosion in $UO_{2+\delta}$: A case study of the $\Sigma5(310)[001]$ grain boundary

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Nuclear power is a well-established, reliable and low-emission alternative to fossil fuels. The major concern, beyond safe reactor operation, is the need to store spent nuclear fuel (SNF) for the ~10^5 years for which it will remain radioactive. The current global consensus on how to address this problem is to store SNF in deep geological repositories; however, despite the best possible efforts to encapsulate the SNF, allowances must be made for ground water to come into direct contact with it, and the resulting release of toxic and radioactive elements into the local environment due to corrosion of the SNF [1, 2].

I will describe a study of the defect chemistry of a model grain boundary in $UO_{2+\delta}$, which is the main constituent material of SNF, which is motivated by three observations: (i) grain boundaries in this material are particularly susceptible to corrosion, (ii) corrosion is linked to the degree of oxygen excess of the material δ, (iii) corrosion involves the oxidation of U^{4+} ions to U^{5+}. Using atomistic methods, we calculate the segregation energies of oxygen interstitials, uranium vacancies, and U^{5+} ions across the $\Sigma5(310)[001]$ grain boundary. These data are used as input in a continuum model of point-defect concentrations in the grain boundary region. Our results indicate that the $\Sigma5(310)[001]$ grain boundary in $UO_{2+\delta}$ is negatively charged, with positively charged adjacent space-charge layers in which the U^{5+} concentration is enhanced. We propose that the enhanced U^{5+} concentration in the grain boundary regions renders them more susceptible to corrosion, an effect which could be counteracted by acceptor doping.

Literature:

[1] D. W. Shoesmith, J. Nucl. Mater., 2000, 282, 1–31. [2] R. C. Ewing, Nat. Mater., 2015, 14, 252–257.

Transport and Storage

Structural Transformations within the [Li/Triglyme][NTf_2] Solvate Ionic Liquid as a Function of Triglyme Content and Implications on the Transport Properties

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Glyme-based electrolyte solutions provide new concepts for developing suitable lithium-ion batteries by forming so-called solvate ionic liquids (SILs). These promising electrolytes are most efficient in an equimolar mixture of [Li][NTf_2] and glyme, wherein each $[Li]^+$ cation is supposedly fully solvated by a single glyme molecule [1].

We studied the competition between triglyme molecules and the salt anions for the coordination to the lithium cations in various mixtures of triglyme ($H\text{-}(CH_2\text{-}O\text{-}CH_2)_4\text{-}H$) and the lithium salt by means of molecular dynamics (MD) simulations at temperatures between 300 K and 480 K. The findings from our MD study are supported by mid-infrared and far-infrared spectra [2].

We could show that the structural motifs in the lithium coordination sphere depend almost exclusively on the mixing ratio of triglyme and salt. At low salt concentrations, the $[Li]^+$ cations are solvated by two triglyme molecules leading to solvent-separated ion pairs only. With increasing salt concentration, $[Li]^+$ is predominantly solvated by a single triglyme molecule as $[Li(glyme)_1]^+$. Up to the equimolar mixture, the cations are spatially separated from their counterions and the mixture indeed acts as a SIL. At the highest investigated salt concentration, the $[Li]^+$ cation is solely surrounded by anions resulting in contact ion pairs.

The structural changes affect the transport properties of the system significantly. While self-diffusion coefficients of all components increase, the viscosity decreases. Besides, the change in the number of charge carriers also impacts the mixture's conductivity.

Literature:

[1] K. Ueno, K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, J. Phys. Chem. B 2012, 116, 11323–11331. [2] J. K. Philipp, K. Fumino, A. Appelhagen, D. Paschek, R. Ludwig, 2024, submitted.

Gigantic increase of electrical conductivity in $SrTiO_3$ under the influence of protons

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Strontium titanate ($SrTiO_3$, STO) is a potential anode material for solid oxide fuel cells (SOFC). The electrical conductivity is in general discussed in terms of anionic conductivity (O^{2-}) and electronic conductivity. The latter can be manipulated by doping. The overall electrical conductivity is low at room temperature and becomes technically interesting at temperature well above 500°C. [1-3].

In the case, where hydrogen is used as a fuel, the hydrogen molecules must be converted to protons at the anode of the SOFC. This immediately triggers the question of proton conductivity in this material. According to Norby and coworkers, the hydrogen ion conductivity (H^+ and H^-) is supposed to be negligible at room temperature and is relevant only above 500°C in doped STO. [5]

The conversion of hydrogen to protons at a catalytic interface and the subsequent quantification of proton conductivity has recently been demonstrated by Rein et al. [6] Here we report on a study in which we convert hydrogen molecules to protons at a catalytic interface in contact with an STO sample. Experiments have been conducted at 180°C. Initially, the electrical conductivity of the sample is on the order of nS/cm as expected from literature information. However, with increasing time the electrical conductivity of STO increases exponentially by 5 orders of magnitude reaching a value of 0.1 mS/cm. This appears to be the largest value of electrical conductivity reported for an undoped sample of STO so far.

Upon removing hydrogen from the gas phase in contact with the sample, the conductivity collapses instantaneously by a factor of 100. Adding hydrogen to the gas phase again leads to an increase of the conductivity to the previous level.

The question clearly is, what are the charge carriers in this experiment? The classical point of view would point to electronic conductivity induced by the protons. However, change in the optical property of the material (blackening) is not observed. On the other hand, the concentration of protons in the material is smaller than the current detection limit of our analysis (< 1%). The findings reported above are absolutely reproducible. Current efforts go to replacing the hydrogen by deuterium. The detection level for deuterons in secondary ion mass spectrometry is superior to protons Additional efforts in identifying the charge carrier of this gigantic conductivity will be reported in this contribution.

[1] Alberto Varone, Michele Ferrari, Renewable and Sustainable Energy Reviews, Volume 45, 207-2018, (2015)
[2] Tatsumi Ishihara, Perovskite Oxide for Solid Oxide Fuel Cells, Springer US, Boston, MA, (2009)
[3] Runping Li, Cheng Zhang, Jianhua Liu, Junwen Zhou, Lei Xu, Mater. Res. Express 6, 102006, (2019)
[4] M. Siebenhofer, A. Viernstein, M. Morgenbesser, J. Fleig, M. Kubicek, *Mater. Adv.*, 2, 7583, (2021)
[5] S. Steinsvik, Y. Larring, T. Norby, Solid State Ionics 143, 103–116, (2001)
[6] K. Rein and K.-M. Weitzel, J. Mat. Chem. A, **12**, 14117-14128, (2024)

Electric Field Effects on brownmillerite $Sr_2Fe_2O_5$ and perovskite $SrFeO_x$: Haven ratio, non-linear enhancement of oxide-ion mobilities, and phase transition thermodynamics

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The brownmillerite material $Sr_2Fe_2O_5$ undergoes a topotactic phase transition between the insulating brownmillerite (BM) phase and a conducting perovskite (PV) phase. This transition can be induced by applying an external electric field, thus $Sr_2Fe_2O_5$ is attracting attention for resistive-switching random access memory (ReRAM) devices. A key process of this phase transition—and therefore of the switching kinetics—is the diffusion of oxygen point defects. Recent molecular dynamics (MD) simulations [1] provide insight into mechanisms of oxygen diffusion (interstitial/interstitialcy and vacancy), along diffusion coefficients for both phases. However, effects of an electric field on these diffusion processes have yet to be investigated.

In this study, we use molecular dynamics (MD) simulations to complement investigations of the oxide-ion migration in $Sr_2Fe_2O_5$ by applying an electric field in different cell directions. The responses of the two diffusion mechanisms to the applied field are analysed and interpreted by existing theoretical models [2]. The considerations allow the calculation of Haven ratios for each mechanism and for both phases. Additionally, we examine the phase transition itself, which is strongly influenced by the electric field.

Literature:

[1] S. Ambaum, N. L. Allan, R. Dittmann, R. A. De Souza, *Chem. Mater.* **2024**, *36*, 2039. [2] A. R. Genreith-Schriever, R. A. De Souza, *Phys. Rev. B* **2016**, *94*, 224304-1.