BUNSEN-TAGUNG 2024

High-Resolution Structural Methods in Material and Life Sciences

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BOOK OF ABSTRACTS

LECTURES

Deutsche Bunsen-Gesellschaft
für physikalische Chemie

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- DFG
- 25 YEARS DBG & PCCP
- yPC Forum
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Towards predictive protein separations: Imaging protein dynamics at nanoscale interfaces

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Abstract

Recent efforts by our group and others have shown the promise of applying single molecule methods to link mechanistic detail about protein adsorption to macroscale observables. When we study one molecule at a time, we eliminate ensemble averaging, thereby accessing underlying heterogeneity. However, we must develop new methods to increase information content in the resulting low density and low signal-to-noise data and to improve space and time resolution.

I will highlight recent advances in super-localization microscopy for quantifying the physics and chemistry that occur between target proteins and stationary phase supports during chromatographic separations. My discussion will concentrate on the newfound ability of super-protein tracking to inform theoretical parameters by quantification of adsorption-desorption dynamics, protein unfolding, and nano-confined transport. Additionally, I will discuss using phase manipulation to encode temporal and 3D spatial information, and the opportunities and challenges associated with such imaging methods.

Wavefront shaping for single molecule microscopy - why and how to ruin a perfectly good microscope

Yoav Shechtman

The point spread function (PSF) of an imaging system is the system's response to a point source. To encode additional information in microscopy images, we employ PSF engineering – namely, a physical modification of the standard PSF of the microscope by additional optical elements that perform wavefront shaping. In this talk I will describe how this method enables unprecedented capabilities in localization microscopy; specific applications include dense fluorescent molecule fitting for 3D super-resolution microscopy, multicolor imaging from grayscale data, volumetric multi-particle tracking/imaging, dynamic surface profiling, and high-throughput in-flow colocalization in live cells. Recent results on additive-manufacturing of highly precise optics and optical DNA mapping will be discussed as well.

Coherent X-ray imaging as a new tool to probe the 3D structure of complex and biological matter

Tim Salditt, Institut für Röntgenphysik, Universität Göttingen

X-rays can deeply penetrate matter and thus provide information about the functional (interior) architecture of complex samples, from biological tissues and cells to nanoscale composite materials. Until recently, however, this potential of hard x-rays in view of penetration, spatial resolution, contrast, and compatibility with environmental conditions was significantly limited by the lack in suitable in x-ray optics. With the advent of highly brilliant radiation, and the development of lens-less diffractive imaging and coherent focusing, the situation has changed. We now have nano-focused coherent x-ray synchrotron beams at hand to probe nanoscale structures both in scanning and in full field imaging and tomography. We explain how the central challenge of inverting the coherent diffraction pattern can be mastered by different reconstruction algorithms in the optical far and near-field. In particular, we present full field projection imaging at high magnification, recorded by illumination with advanced x-ray waveguide optics, and show how imaging and diffraction can be combined to investigate biomolecular structures within biological cells, also correlatively with super-resolution light microscopy. We present different examples of biophysical and biomedical applications, including 3d virtual histology of human brain tissue.

The DSDC-Algorithm - A Universal Strategy for Simulating Voltammetry of Rough and Porous Electrodes

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Porous electrodes or electrodes with rough surfaces offer a multitude of tailored applications. The theoretical treatment of such structures is, however, challenging since their voltammetric profile is a convolution of the time-dependent current with an inherently random mass-transfer function. Since the latter quantity has no analytical solution, the classical convolutive techniques cannot be applied. Therefore, simulations have been based on severe simplifications of the diffusion space [1,2] or were performed by means of digital simulation. Unfortunately, the latter approach becomes computationally prohibitive when a large and/or highly resolved, three-dimensional diffusion space needs to be considered. To mitigate these problems, we introduce the **d**igital **s**imulation, **d**econvolution, **c**onvolution (DSDC) algorithm, consisting of four successive steps [3]. Firstly, the three-dimensional image of the electrode under investigation is extracted via micro X-ray computed tomography (μ-CT) or atomic-force microscopy (AFM). Subsequently, the purely mass-transfer controlled current of this spatial template is generated by means of digital simulation. In the third and fourth steps, the mass-transfer function is extracted for a set of discrete points in time by numerical deconvolution and finally used for classical convolutive simulations. In this manner, any simplification of the diffusion domain becomes obsolete and the advantages of digital simulation and convolutive modelling are most favourably combined. Finally, this DSDC-algorithm provides an interdisciplinary connection of ex-situ imaging and in-situ electrochemistry which results in excellent agreement of simulated and experimentally acquired data.

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Weakly Bound Materials: Competing Energy Scales, Quantum Effects and Machine Learning

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Weakly bonded interfaces, commonly encountered in hybrid organic-inorganic architectures, give rise to a rich variety of nuclear motion and tunable nuclear structure that is tightly connected to diverse electronic properties in these systems. In this contribution, I will discuss how we push the limits of density-functional theory and different ab initio techniques that capture nuclear motion to unravel the properties of realistic interfaces. I will give an overview of simulation methods that are applicable for large system sizes and that can capture the quantum nature of nuclei in anharmonic potential energy landscapes [1].

I will discuss how they can be connected to first-principles electronic structure and machine-learning approaches [2,3]. Applications where the quantum nature of the nuclei become indispensable to assess structural and electronic properties of 2D materials and interfaces will be shown and discussed [4],

as well as how these can be characterised by the simulation of experimentally observable quantities like tunneling rate constants and advanced vibrational spectroscopy [5,6].

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[3] A. M. Lewis, P. Lazzaroni, and M. Rossi, J. Chem. Phys. 159, 014103 (2023)
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The Deutsche Forschungsgemeinschaft (DFG):
Funding Opportunities for Early Career Researchers at a Glance

Wolfgang Wachter, Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), Bonn/Germany

DFG's funding programmes place particular emphasis on supporting early career researchers. Flexible funding instruments are tailored to meet the specific needs of young scientists and academics, thereby enabling them to pursue their research careers.

For example, the Walter Benjamin Programme enables researchers in the postdoctoral training phase to independently conduct their own research project at a location of their choice in Germany or abroad. The Emmy Noether Programme supports researchers in achieving independence at an early stage of their scientific careers. Postdocs gain the qualifications required for a university research career during a DFG-funded period, in which they lead their own independent junior research group. The Heisenberg Programme provides researchers who have qualified for professorship with the opportunity to prepare for a leading position in science. Other programmes are open to researchers at all career stages, but provide opportunities of special interest to young scientists.

In this contribution, besides briefly presenting some current DFG-related topics, the DFG funding opportunities for early career researchers will be highlighted. There will be also room to discuss some “dos and don’ts” when preparing a funding proposal.

Why do we observe a momentum flow in eNMR measurements?

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Electrophoretic nuclear magnetic resonance (eNMR) is a powerful measurement technique to directly access ion movements in liquid electrolytes. By adding an electric field to the standard NMR setup, directional transport information in the form of drift velocities can be detected. The associated mobilities of the ionic species can be used to calculate important transport parameters like the transference number. The latter is an essential performance indicator for electrolytes used in electrochemical storage devices, e.g. batteries. Especially in highly concentrated electrolytes, like ionic liquids (ILs), the experimental determination of transference numbers is challenging. Here, eNMR together with our transport theory for highly concentrated electrolytes can help resolve recent discussions concerning their reference frame dependence (Fig. 1) [1].

Measurements on pure ILs recently showed a seeming violation of momentum conservation. However, we could show that the momentum is only locally not conserved and, thus, a different constraint governs the transport in these highly concentrated electrolytes: local volume conservation. Considering incompressibility and applying the volume-based description to eNMR measurements yields that the mobilities are better correlated to their partial molar volumes (local volume conservation) than to their molar masses (local momentum conservation) (Fig. 2) [2].

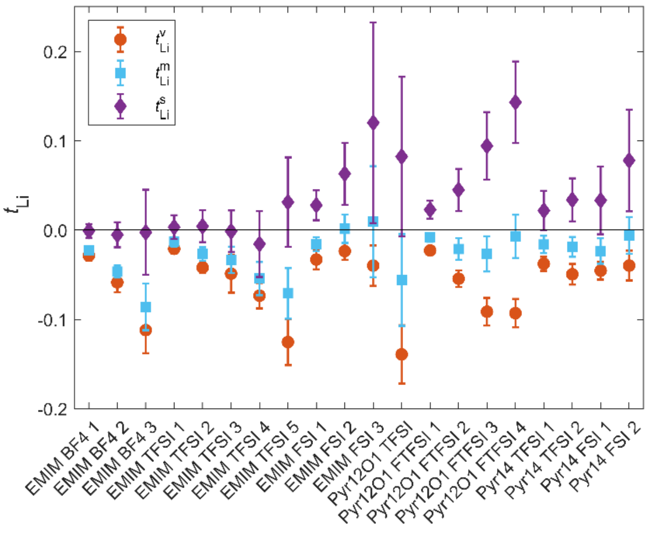

Fig. 1: Li-ion transference numbers in different reference frames derived from eNMR mobilities.

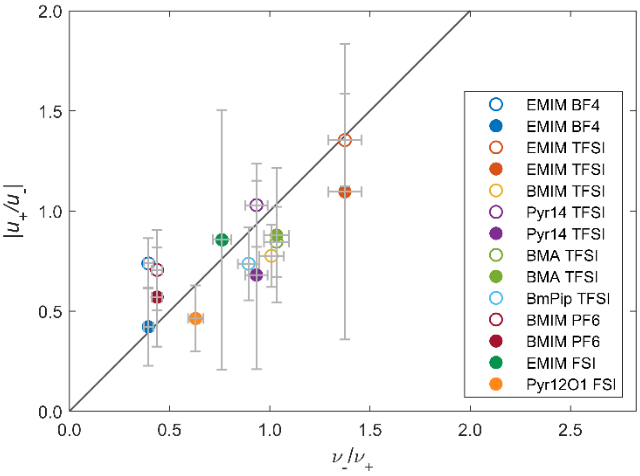

Fig. 2: Ratio of mobilities versus ratio of partial molar volumes of ionic species in pure ionic liquids.

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Revealing structural flexibility with rotational spectroscopy - from individual molecules to chiral complexes

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Flexible molecules can exist in many different structural forms – such as different constitutional isomers, tautomers, conformers, and, if they are chiral, also enantiomers and diastereomers. Structural flexibility of molecules can be inherent to their function, and it can be largely influenced by their environment, for example if they are in a solvent or isolated, or if they are at high temperature or at low temperature. We are interested in investigating structural flexibility of different types of molecular species under the well-controlled conditions of a cold and collision-free supersonic jet in the gas phase. The low velocity distribution of the molecules also allows for efficient complex formation, so that dedicated intermolecular interactions and how they affect structural flexibility can be studied. For our analysis, we use rotational spectroscopy, which is highly structure sensitive.

In this talk, I will introduce the technique and then demonstrate its application to structurally flexible molecules[a], such as alpha-methoxy phenyl acetic acid[b] that is related to mandelic acid. In a next step, the dimers of the chiral molecule 3,3,3-trifluoro-1,2-epoxypropane will be discussed[c]. Even though the individual monomers can be assumed to be rather rigid, complexation results in a variety of structural arrangements. Finally, in the last part of the talk, I will show how complex formation between chiral molecules (chiral tagging) can be exploited for chiral analysis.

References:

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Near-Ambient Pressure Spectroscopy on Co(0001) during Fischer-Tropsch Synthesis

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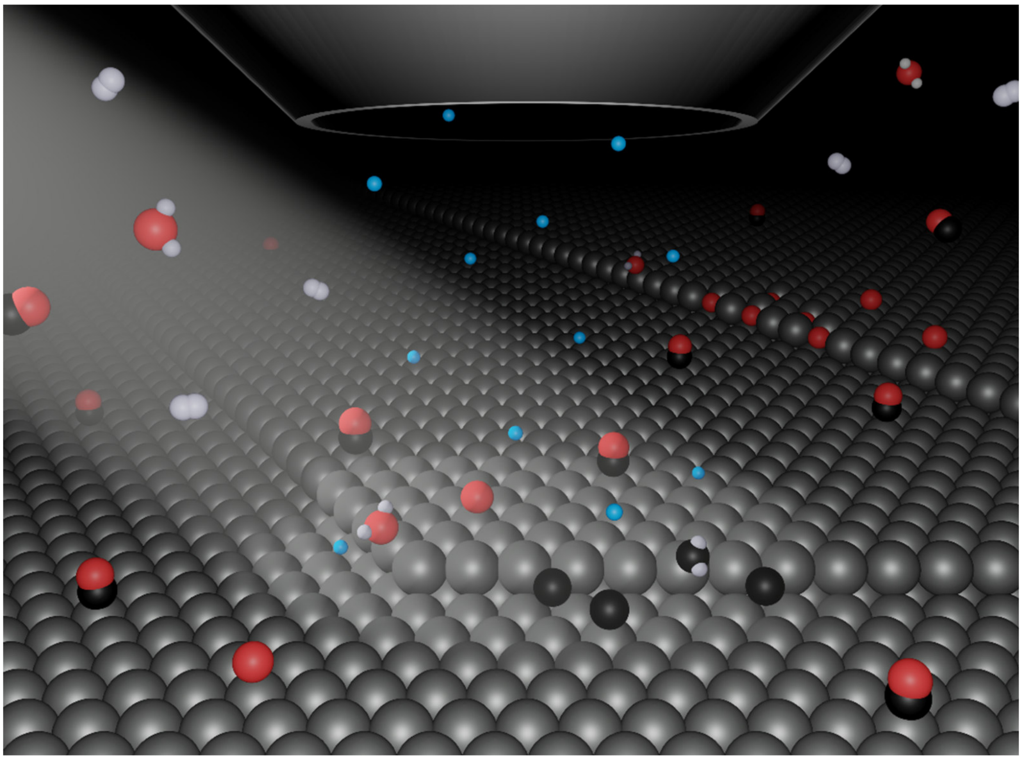
Synthetic fuels are a cleaner, more sustainable alternative to conventional fuels, especially in areas where the use of electric motors is not currently feasible. The production of synthetic fuels is based on Fischer-Tropsch synthesis, the reaction between CO and H_2 to form linear hydrocarbons. Although this is already done industrially over cobalt catalysts, the reaction mechanism is not fully understood and catalysts are prone to a number of deactivation mechanisms such as the oxidation of the active phase and the deposition of carbon and reaction products. As oxidation as well as adsorption behavior can strongly depend on the gas pressure and the structure of the sample, operando studies performed during the reaction are crucial. Here, we present a near-ambient pressure X-ray photoelectron spectroscopy study on Co(0001) model catalysts during exposure to CO, H_2, and mixtures of the two, at 0.25 mbar total pressure. At this pressure, CO seems to be more efficient at keeping the Co(0001) surface metallic than H_2, which is the opposite behavior as reported in the literature for other pressure ranges. We offer an interpretation of these differences based on the preferred adsorption and dissociation sites of CO and H_2 compared to the oxidizing agent water, which is present as an impurity in the gas feed as well as a reaction product. Even on the flat Co(0001) surface, step edges and defects play a significant role for this behavior. Additionally, detailed carbon spectra measured at the HIPPIE beamline of MAX IV allow for the distinction of different adsorbed species: The detected carbon or carbide can be removed by hydrogen and is thus a reaction intermediate, whereas adsorbed hydrocarbons possibly poison the surface.



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Vibro-Polaritonic Chemistry – Shaping Vibrational Spectroscopy and Chemical Reactivity with Confined Infrared Light

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Vibro-polaritonic chemistry is a rapidly growing interdisciplinary research field at the intersection of chemistry and quantum optics, initiated by the experimental realization of light-matter hybrid states named vibrational polaritons.[1] Vibrational polaritons emerge from the strong interaction of infrared (IR) active molecular vibrational modes with resonantly tuned IR radiation spatially confined in Fabry-Pérot cavities. Such light-matter hybrid states have been experimentally observed to alter vibrational spectroscopy[2] and intriguingly shape thermal ground state chemistry in solution[3]. In contrast to traditional photochemistry, which relies on a classical description of radiation, i.e., many photons interact with molecules, vibro-polaritonic chemistry is determined by the quantum nature of the spatially confined electromagnetic field carrying few or even no photons.

In this contribution, I will present theoretical results providing insight into rotational effects on IR spectroscopy of vibro-polaritonic systems and their reactivity. They have been obtained as part of my dissertation at the University of Potsdam under the supervision of Prof. Dr. Peter Saalfrank.[4] I will first discuss non-trivial rotational signatures in IR spectra of vibrational polaritons[5], which can be understood by an analogy to conical intersections and stimulated an experimental realization of gas-phase vibro-polaritonic systems[6]. Secondly, I will illustrate how a generalization of potential energy surfaces to vibro-polaritonic chemistry allows for insight into vibro-polaritonically altered thermal ground state kinetics.[7]

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Kinetic and Spectroscopic Characterization of N_2 and H_2 activation by Tantalum Clusters under Cryo Conditions

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Transition metal compounds find industrial application in numerous catalytic processes, e.g. in the notable Haber-Bosch mediated ammonia production. [1] Small and medium-sized isolated metal clusters can serve as model systems for the so-called active centers to unravel underlying elementary processes. [2]

A customized FT-ICR mass spectrometer serves for studies of size-selected Ta_n^+ clusters under cryogenic conditions with respect to surface adsorbate interactions at the fundamental level, focusing on N_2 and H_2 adsorption and activation. Systematic kinetic, spectroscopic and quantum chemical investigations provide a comprehensive picture of the elementary adsorption steps and mechanisms.

The N_2 and H_2 adsorption processes to Ta_n^+ clusters exhibit dependencies on cluster size n and on adsorbate load. In terms of N_2 adsorption, there is evidence for spontaneous N_2 activation and cleavage by Ta_{2-4}^+, while it appears to be suppressed by Ta_{5-8}^+. [3] The activation and cleavage of N_2 molecules proceeds across surmountable barriers and along much-involved multidimensional reaction paths. Underlying reaction processes and involved intermediates are elucidated. [4,5] Two different processes are characteristic of H_2 adsorption: There are dissociative adsorption processes at low H_2 loadings, followed by molecular H_2 adsorption reactions at high H_2 loadings. The threshold is the completion of the first adsorbate shell.

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Formation, Characterisation and Disassembly of Metallosupramolecular Complexes in vacuo

Niklas Geue[1], Tom S. Bennett[2], Alexandra A. Arama[2], Lennart A. I. Ramakers[1], Grigore A. Timco[2], George F. S. Whitehead[2], Eric J. L. McInnes[2], Peter B. Armentrout[3], Neil A. Burton[2],
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The interest in metallosupramolecular complexes has rapidly grown in the last decades, along with a simultaneous increase in the complexity of the synthesised molecules. Their characterisation can be difficult, as X-Ray crystallography or reliable computations are often not feasible due to the complex size, and solution phase techniques are limited in the information they provide.[1] Ion mobility mass spectrometry (IM-MS), coupled with tandem mass spectrometry and supported by density functional theory calculations and molecular dynamics simulations, are not only uniquely qualified to structurally characterise these complexes, but also to investigate the properties of their fundamental building blocks. I showed that it is possible to a) evaluate and tune their stability by substituting metals, ligands and charge carriers, b) discriminate competing disassembly mechanisms, c) assess the complexes' topology, conformational flexibility, atom density and cavity size, and d) identify novel target molecules for bulk phase synthesis.[2-4]

In the last years I have been studying a range of polymetallic complexes using IM-MS, including a homometallic {$\mathbf{Cr_8}$} ring, open {$\mathbf{Cr_6}$} horseshoe oligomers, a series of heterometallic {$\mathbf{Cr_7M}$} rings (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}) and their related rotaxanes, as well as {$\mathbf{Cr_xCu_2}$} hourglass and {$\mathbf{Cr_{12}Ln_4}$} lanthanide clusters. The common feature of all these complexes is their ability to encapsulate or coordinate secondary ammonium cations $[NH_2RR']^+$ *via* non-covalent interactions, making these supramolecular polymetallic complexes interesting targets for e.g. quantum computing.

Our observations, taken together, provide an empirical framework to follow in for the future design and characterisation of self-assembled polymetallic complexes. We highlight the advantages and opportunities of using IM-MS for synthetic molecules, in combination with computational calculations, yielding a comprehensive overview of how this technique can study various properties of the same compound family.[5]

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High-frequency light-matter interaction in atoms and molecules

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The field of attosecond science is a novel and fast-evolving research area that aims at unravelling the motion of particles in atoms, molecules, and solids. Therein, attochemistry thrives to understand, monitor, and one-day control the movement of electrons in molecules, which will open a new path to steer nuclear dynamics and photochemical reactions. In order to observe the motion of electrons, attosecond resolution and, thus, attosecond light pulses are needed. These attosecond pulses are inherently rooted in the high-frequency regime, ranging from XUV to soft and hard x-ray radiation. Depending on the energy, intensity, and aimed-at observable, different light-matter interactions can be studied. In my thesis, we tackle three different kinds of high-frequency light-matter interaction that originate in three different energy regimes and allow us to gain novel insight into the dynamics of molecules. In the XUV regime, the ionisation dynamics of correlated, multi-particle systems is studied[1,2] together with few-cycle effects[3]. In the soft x-ray regime, attosecond x-ray absorption is introduced as a novel tool to observe coupled electron and nuclear dynamics in a neutral molecule[4]. In the hard x-ray regime, we focus on ultrafast, non-resonant x-ray scattering, which can be transformed into a future technology capable of observing electron dynamics[5]. We are confident that this work will benefit the general understanding of high-frequency light-matter interaction in atoms and molecules, as well as aid and initiate new experiments in the field of attochemistry using XUV ionisation, x-ray absorption, and x-ray scattering.

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High-Resolution Structural Methods in Material and Life Sciences

New insights into the structural dynamics of intrinsically disordered proteins by high-field NMR spectroscopy

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Intrinsically disordered proteins (IDPs) compose about 30% of the human proteome and are highly dynamic entities, making them challenging to study by X-ray crystallography or cryo-EM. However, IDPs are well suited to be examined by NMR spectroscopy. Recent advances in NMR magnet technology allow for increasingly higher magnetic field strengths, up to 28 Tesla (corresponding to 1.2 GHz ^{1}H Larmor frequency). Those high field strengths offer substantially improved resolution, with particular benefits for studying IDPs.

We have derived an improved set of ^{15}N NMR relaxation experiments suited for operation at high-field magnets and applicable to fully protonated systems [1]. Here, we used SNARE proteins as a model system. SNARE proteins play a crucial role during neuronal exocytosis by eliciting the fusion of the synaptic vesicle membrane with the presynaptic plasma membrane. In their pre-fusion state, the membrane-anchored SNARE proteins are disordered [2,3]. To assess the internal dynamics of the SNARE protein SNAP25, we recorded NMR relaxation experiments at different magnetic field strengths, between 600 and 1200 MHz. The field-dependent NMR measurements reveal novel insights into IDP dynamics at the picoseconds to nanoseconds timescale. Our unpublished data will be presented at the conference.

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Introducing complex- and site-selectivity in biomolecular NMR spectroscopy by dynamic nuclear polarization

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Solid-state NMR under magic-angle spinning (MAS) is an important tool in structural biology and materials science. However, NMR's inherently low sensitivity requires long acquisition times or even renders many experiments unfeasible. Dynamic nuclear polarization (DNP) can overcome this limitation by transferring much larger electron spin polarization to neighboring nuclei. Typically, fast spin diffusion within the hyperpolarized ^{1}H bath is taken advantage of, spreading polarization over relatively large distances before transferring the ^{1}H polarization to heteronuclei for detection or further evolution. This results in a fast and uniform enhancement of the whole NMR spectrum.

Interestingly, DNP also features the potential to specifically hyperpolarize nuclei and thus create selectivity in the NMR spectrum. This is particularly useful in biomolecular MAS NMR where spectral crowding becomes a serious problem for large assemblies or complexes. Specific cross-relaxation enhancement by active motions under DNP (SCREAM-DNP) can provide site-specific channels for spontaneous transfer of enhanced ^{1}H magnetization to heteronuclei in a hetNOE-type process. [1,2] A detailed explanation of its mechanism will be given and exemplary applications presented. Effects of uniform or sparse isotope labelling on site-specificity of DNP as well as limitations of the technique will be discussed. In conclusion, SCREAM-DNP has the power to yield selective NMR spectra in complex mixtures, for example, of sought-after biomolecular complex, even in the presence of unbound constituents. [2,3]

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Protein-nucleotide interactions probed by solid-state NMR spectroscopy

N. Schröder, Aachen/D, L. Decamps, Mülheim (Ruhr)/D, K. Sengupta, Mülheim (Ruhr)/D, J. Zehnder, Zürich/CH, P. Wu, Zürich/CH, F. H. -T. Allain, Zürich/CH, S. DeBeer, Mülheim (Ruhr)/D, T. Wiegand, Mülheim (Ruhr)/D
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Interactions between proteins and nucleotides are crucial for many biological processes. This includes DNA replication where numerous proteins are involved in, protein synthesis, which takes place in the ribosome, as well as ATP hydrolysis which is used by various enzymes for catalyzing reactions.

The high-resolution structural investigation of interactions between proteins and nucleotides can be rather difficult. Due to the large structural flexibility of nucleic acids, complexes of those with proteins are notoriously hard to crystallize and in case of large proteins, severe line broadening in solution-state NMR spectra is expected. In solid-state NMR, however, this size limitation does not exist and also crystals are not required, since proteins can be easily sedimented directly in the NMR rotor and are even long-term stable in this state [1]. This makes solid-state NMR an ideal technique for the investigation of those systems, which has for instance recently been shown for a short peptide that forms amyloid fibrils and interacts with RNA [2].

We herein present an experimental approach to investigate nucleotide binding to two different proteins: an archaeal primase and an archaeal ATPase involved in the formation of an iron-sulfur cluster. A particular focus lies on the detection of non-covalent interactions involved in the binding process. The methodological approach is based on three different pillars. (I) Conformational changes in the protein induced by the binding process can be identified by comparing spectra of the nucleotide-bound and the *apo* form. (II) The amino acids involved in the binding process can be identified using ^{31}P-detected spectroscopy by identifying spatial proximities between carbon or nitrogen nuclei of the protein and phosphorus nuclei of the nucleotide. (III) Non-covalent interactions involved in the binding process can be identified by ^{1}H-detected experiments at fast magic-angle spinning (MAS) at 100 kHz MAS frequency.

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Photophysics and Photochemistry of Individual Plasmonic Nanostructures

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A surface plasmon in a metal nanoparticle is the coherent oscillation of the conduction band electrons leading to both absorption and scattering as well as strong local electromagnetic fields. These fundamental properties have been exploited in many different ways, including surface enhanced spectroscopy and sensing, photocatalysis, photothermal cancer therapy, and color display generation. Chemical synthesis and assembly of nanostructures are able to tailor plasmonic properties that are, however, typically broadened by ensemble averaging. Single particle spectroscopy together with correlated imaging is capable of removing heterogeneity in size, shape, and assembly geometry and furthermore allows one to separate absorption and scattering contributions. In this talk I will discuss our recent work on distinguishing the different contributions that cause plasmon decay as probed by the homogeneous single-particle linewidth.[1-4] In particular, I will focus on plasmon damping due to energy and charge transfer from the metal to its environment with the goal to mechanistically understand how energy conversion from an incident photon to a plasmon and then a localized excitation can be maximized while circumventing fast metal-intrinsic internal conversion that simply leads to heat generation.

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Infrared Scanning Near-Field Spectroscopic Studies of Self-Assembled Nanostructures Based on Photo-Crosslinkable Block Copolymers

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Block copolymers, i.e., chemically distinct polymer blocks which are covalently bond, are known for their ability to self-assemble into a variety of morphologies on the nanometer scale [1]. The self-assembly of block copolymers has been extensively investigated for 2D films, however, less attention has been paid to 3D bulk morphologies [2,3]. To achieve long-range ordered samples in the thermodynamic equilibrium, in this work, 3D bulk morphologies were prepared via solvent annealing.

Infrared scanning near-field optical microscopy (IR-SNOM) offers the unique possibility of infrared chemical imaging and spectroscopy with a spatial resolution down to around 20 nm [4]. When irradiating a well-defined diblock copolymer consisting of polystyrene and a methacrylate-based copolymer decorated with photo-crosslinkable units at an independently addressable absorption band of a polymer block, chemical imaging of the blocks' nano-ordered spatial arrangement is possible.

Here, the internal nanostructure of self-assembled 3D bulk morphologies with lamellar and cylindrical nanostructures is studied by means of IR-SNOM. When selectively exciting each polymer block, a switch of the relative optical phase, related to the local absorption, is observed, revealing a strong phase segregation via spectroscopic contrast.

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Integrated FRET Messengers for Spatially Resolving Material Properties and Processes

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Spatially resolving material properties, such as contact forces, stresses, and/or damage, is highly desirable towards developing next generation *smart materials*.[1] Towards this goal, we develop ways of integrating Förster resonance energy transfer (FRET) chemistry, which is a chemical measure of nano-distances, into polymer material architectures, such that FRET output reflects material conformations both with and without applied pressures.

Our methods are three-fold, and include (i) integrating FRET pairs into polymer brush layers to reflect polymer conformation [2] and (ii) for probing molecular transport through polymer brushes [3]. In this talk, we will go into detail on how these systems can be generalised towards (iii) integrated FRET messengers in other polymer materials, such as electrospun fibers (Figure 1, left).[4] We show that the FRET messengers can be integrated at very low concentrations, in such a way that they do not affect any fiber material property. The technology allows for confocal laser scanning microscopy (CLSM) read-out of FRET messenger material conformations in the as-spun fibers, which revealed spine-like nanostructures within the fibers (Figure 1, right). Further to this, the read-out could rapidly identify material irregularities, and when the fibers were physically damaged, the damage could be quantified based on the FRET. Our systems provide a non-invasive optical measure of changing material properties, which holds great promise for identifying material properties in real-time.

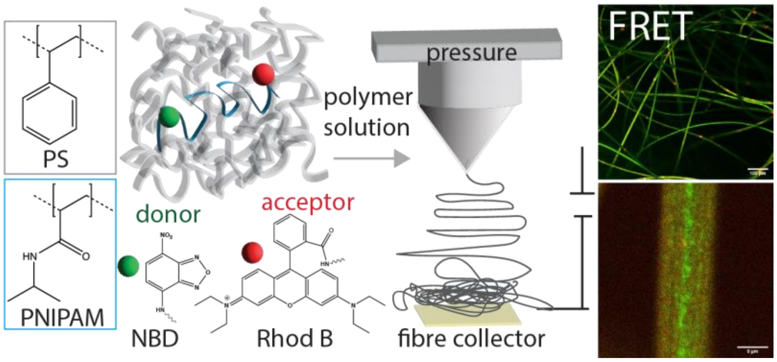

Figure 1. Schematic describing the integration of FRET messenger polymers into electrospun polystyrene (PS) fibers, along with CLSM analysis of FRET. [4]

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Constructing and characterizing organic nanostructures via low temperature scanning probe microscopy

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Constructing low-dimensional covalent assemblies with tailored size and connectivity is the key for applications in molecular electronics where optical and electronic properties of the quantum materials are highly structure dependent. We present a versatile approach for building such structures molecule by molecule on bilayer sodium chloride (NaCl) films with the tip of an atomic force microscope (AFM), while tracking the structural changes with single-bond resolution. [1] Covalent homo-dimers in *cis* and *trans* configurations and homo-/hetero-trimers were selectively synthesized by a sequence of dehalogenation, translational manipulation and intermolecular coupling of halogenated precursors (see Figure). This work shows ways for synthesizing elusive organic nanoarchitectures, studying structural modifications and revealing pathways of intermolecular reactions. Moreover, possibilities for tweaking the AFM bond imaging technique using torsional and flexural higher eigenmodes of qPlus sensors will be illustrated. [2] Torsional eigenmodes can be utilized to perform lateral force microscopy with single bond resolution.

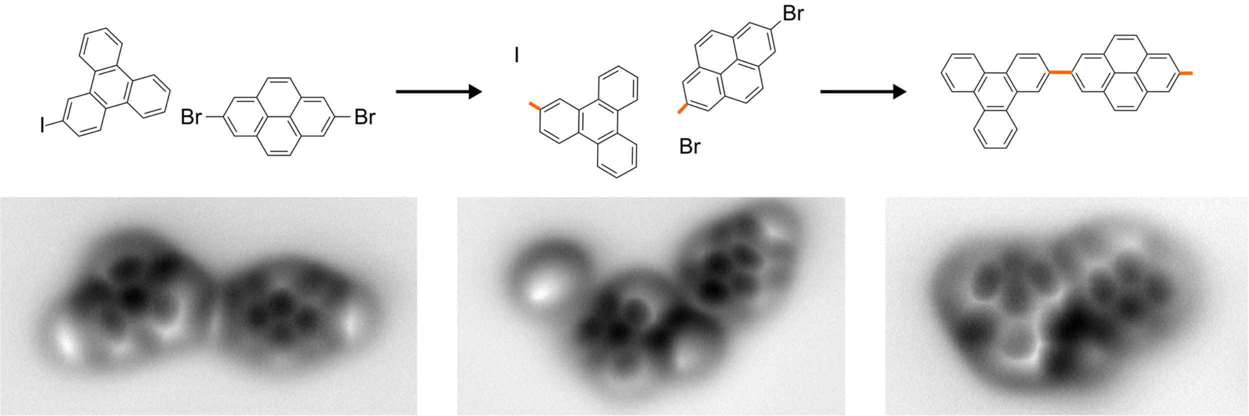

Figure: Tip-induced cross-coupling reaction between triphenylene and pyrene precursors. Each reaction step was triggered via voltage pulses. Structural changes are visualized via high-resolution AFM images.

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Scanning Probe Microscopy for Atomic-Scale Imaging, Spectroscopy, and Manipulation: New Frontiers in Materials Analysis, Design, and Prototyping

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Atomic-scale properties of surfaces, including their geometric structure, chemical reactivity, and electronic and magnetic properties, play critical roles in multiple fields of science and technology. Real-space microscopic techniques for the atomic-scale analysis and modification of physicochemical surface properties are therefore of great relevance. Over the past decade, new developments in the field of (low-temperature) scanning probe microscopy (LT-SPM) have opened new vistas for the application of SPM techniques in chemistry and materials science. Bond-resolving spatial resolution achieved by functionalization of the tip apex with suitable molecules allows for the clarification of structures of molecules or two-dimensional materials [1]. Manipulation of molecules and nanostructures with the SPM tip provides access to prototypes of new chemical compounds, which are not yet accessible by conventional chemical synthesis. In this contribution, the focus is on the on-surface synthesis of new carbon nanomaterials and the characterization of the structural, electronic and magnetic properties by scanning probe techniques, including bond-resolving scanning tunneling microscopy/spectroscopy (BR-STM/STS) and non-contact atomic force microscopy (nc-AFM) (Figure 1).

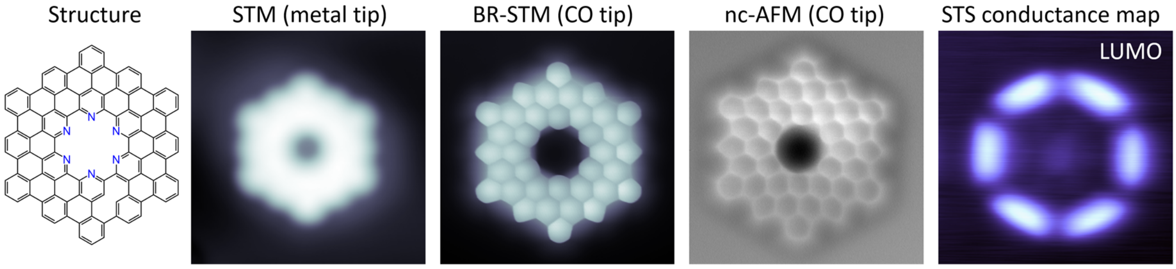

Figure 1. High-resolution SPM imaging and spectroscopy of N-doped cycloarene.

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Investigating doubly-hydrogen bonded cationic dimers in carboxyl-functionalized ionic liquids: Spectroscopic evidence in liquid and gas phase

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We report the formation of hydrogen-bonded structural motifs in carboxyl-functionalized ionic liquids by means of temperature-dependent linear infrared spectroscopy. The analysis of the CO and OH stretching bands reveal doubly hydrogen bonded cationic dimers (c=c), resembling the archetype H-bond motif known for formic acid. With increasing temperature, this (c=c) binding motif opens and is replaced by (c−c−a) cluster species, with a remaining single cationic hydrogen bond and an additional hydrogen bond between cation and anion.[1] To clarify this bulk spectroscopic evidence, we explored the structural motifs of these H-bonded configurations at the molecular level by analyzing the cryogenic ion vibrational predissociation spectroscopy of cold (~35 K) gas phase cluster ions with quantum chemical methods.[2] The (2,1) clusters ions show doubly hydrogen-bonded cations solely, despite removing one anion and thus enhancing like-charge repulsion. Obviously, cooperative H-bond attraction is not only able to compensate for the repulsive Coulomb forces but also to ignore the H-bond accepting capabilities of the counter anion completely. The similarity of the CO and OH vibrational features in the bulk liquid and the gas-phase ion spectra challenges the general wisdom that small clusters adopt different structures than the dominant arrangements found in the condensed phase. Herein, we provide evidence that strong and directional hydrogen bonding motifs are common to both density regimes.

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Super-resolved fluorescence microscopy combined with AFM to investigate the inner structure of core-shell microgels

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Super-resolved fluorescence microscopy (SRFM) is an excellent toolbox to investigate microgels at the lower end of their size spectrum. [1,2] The sub-µm objects with high solvent content are predestined for investigations with techniques such as point accumulation for imaging in nanoscale topography (PAINT), direct stochastic optical reconstruction microscopy (dSTORM) and DNA PAINT, to name only few. [1,3,4]

In our research, we investigate the polymeric substructure and functionalisation of core-shell architecture microgels. Functionalisation of the core polymer to perform dSTORM or DNA PAINT allows to observe this part of the microgel independently of the shell, while PAINT is applied to represent the whole polymer structure. In contrast to the often-assumed clear separation of core and shell polymer, we are able to visualise that the core polymer tends to continuously grow during shell polymerisation. In combination with atomic force microscopy (AFM) it is revealed, that the core polymer expands to nearly the same size as the overall polymer network. Those results indicate polymer growth of the shell polymer from within the core-network, instead of growth just from the fringes, which is in accordance with light scattering data reported in literature. [5]

Funded by the German Research Foundation (DFG) grant SFB 985 (project A6).

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Strategies to Obtain Highly-Ordered Deuterated Water Ices Based on Calorimetry, X-Ray and High-Resolution Powder Neutron Diffraction

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Water ices crystallizing from the liquid phase show long-range order of their oxygen atoms, but disorder of their hydrogen atoms. At low temperatures, hydrogen ordering is thermodynamically favored but often geometrically frustrated. Whether an ice phase is hydrogen-ordered or disordered drastically impacts electrical and mechanical properties, *e.g.*, vacuum permittivity, brittleness and flow plasticity [1]. Studying hydrogen ordering is therefore important for understanding the inner structure of icy objects in space as well as glacier creep [2]. Neutron diffraction is considered as the “gold standard” technique for structure determination of water ices but demands deuterated ices. Since ordering of the heavier deuterium atoms is often hampered, strategies for overcoming the kinetic barriers are of key importance.

Based on the ice XII-XIV system [3,4] we here present powerful strategies unlocking the full degree of order in deuterated ice, *i.e.*, introduction of ionic, Bjerrum and isotope defects, isothermal annealing under pressure and long-time storage. Explored by calorimetry, powder X-ray diffraction and high-resolution powder neutron diffraction the new protocol allows for tripling of the degree of order relative to the yet known weakly ordered ice XIV, potentially related to structural distinctiveness between weakly and highly ordered ice XIV. These strategies can be employed for other ice phases and hold the potential for future discoveries of new forms of ice with distinct material properties.

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Characterization of biohybrid superlattices with single crystal diffraction and single-crystal small-angle X-ray scattering

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Self-assembly is a key tool for the formation of biomolecular structures, but also for the construction of functional nanomaterials. We have recently established a novel method for the self-organization of biomolecular building blocks and nanoparticles. Here, protein cages, engineered with opposite surface charge, are used as an atomically precise ligand shell for the assembly of inorganic nanoparticles. [1] The assembly of these protein-nanoparticle composites yields highly ordered nanoparticle superlattices with unprecedented precision. These biohybrid materials show interesting optical properties, such as the anomalous refraction of light. [2,3]

Our current work describes the formation of hetero protein structures composed of two different types of protein cages. These two cages have different outer diameters and form well-shaped protein crystals. We characterized these structures with single-crystal protein crystallography and single-crystal small-angle X-ray scattering. Moreover, we investigated the assembly requirements for two-component protein materials. To this end, several variants of ferritin nanocages were designed to determine the surface characteristics necessary for the formation of large-scale binary three-dimensional assemblies. These nanocage variants were employed in protein crystallization experiments and macromolecular crystallography analyses, complemented by computational methods. We identified several essential features for successful assembly. [4]

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Investigating cathode dynamics in realistic desalination reactors using *operando* high-energy synchrotron X-ray microscopy

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Four billion people suffer from lack of clean water at least one month of the year.[1] This critical water shortage applies not only to the supply of potable water, but also to water for use in industrial, agricultural, and energy applications. While water resources like seawater are abundant, hardly any water resource is clean enough for direct use. Desalination provides a methodology to render unusable waters from such water resources fit for use. An innovative and particularly energy-efficient electrochemistry-based approach is the Desalination Battery (DB), which stores the energy input during desalination in chemical bonds between ions and faradaic electrode, allowing for its recovery during the salination process. DBs are at the forefront of the water-energy nexus[2]. While they are promising for seawater desalination (e.g., for seawater to brackish water conversion), practical implementation and their full potential still need to be unlocked. To this end, foundational understanding of the atomic- to electrode-scale physics/chemistry underlying functionality and degradation must be unraveled.

Towards this end, we utilized our unique flow-by reactor setup to combine electrochemistry, conductivity, and temperature measurements with high-energy (75 keV) operando synchrotron X-ray diffraction (HEXRD) microscopy. Our investigation encompasses both the atomic and electrode levels, using a 3-electrodes setup with $LiMn_2O_4$ and $Na_{0.44}MnO_2$ as electrode active materials. As such, we were able to simulate a realistic electrode environment for operando measurements, as well as observe spatially resolved structural changes by scanning the beam across the electrodes surface. These phenomena are manifested through changes in unit cell parameters and the emergence of new phases during desalination cycles. Specifically, we tracked the changes in XRD patterns over the course of several desalination cycles in LiCl and NaCl solutions, as well as synthetic seawater and mixed solutions of $LiCl/MgCl_2$. We were able to observe high selectivity of $LiMn_2O_4$ towards Li^+, even in the highly concentrated synthetic seawater solutions, and could not observe the emergence of a new Mg^+ rich phase down to potentials of 0 V vs. AgCl. $Na_{0.44}MnO_2$ exhibited good cycling behavior in synthetic seawater akin to pure NaCl solutions, and apart from the Na^+ rich phase showed no signs of additional new phases, suggesting a highly selective nature towards Na^+. Furthermore, we compared constant current and constant potential protocols and observed distinct differences in peak shift behavior. Ongoing analysis of the unit cell parameters and atomic positions allows us to allocate specific intercalation sites to specific potentials, providing foundational insight into the chemistry and physics underlying the selectivity of these materials.

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Nanospectroscopy and nanochemical imaging using photothermal AFM-IR on biomolecular sensors and hydrated self-assembled-monolayers.

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Nanostructured self-assembled-monolayers (SAMs) on solids are common platforms for functionalizing and controlling chemical and physical properties of surfaces with applications in diverse fields such as corrosion, catalysis and bio-sensors. Here AFM-IR is used to obtain nanoscale topographic information and spectroscopic, i.e. chemical information on such systems [1], in order to better understand the interplay between nanostructure and function.

First, results on aptamer SAMs on gold used as SARS-CoV-2 biosensors will be presented. AFM-IR was employed to characterize the surface after each fabrication step and after analyte binding to the receptor layer to provide insight to molecular conformational and structural variation as well as chemical composition of this system. Binding of single molecule proteins was detected (Figure 1). Second, biomolecule-repellent oligoethylene glycol (OEG)-based SAMs on gold were studied. In such systems the molecular conformation of OEG and the structure of interfacial water are thought to strongly influence the repellent character [3]. AFM-IR investigation of water films adsorbed on nano-domains of OEG SAMs were performed under elevated relative humidity and provided structural details of the OEG moieties and adsorbed H_2O.

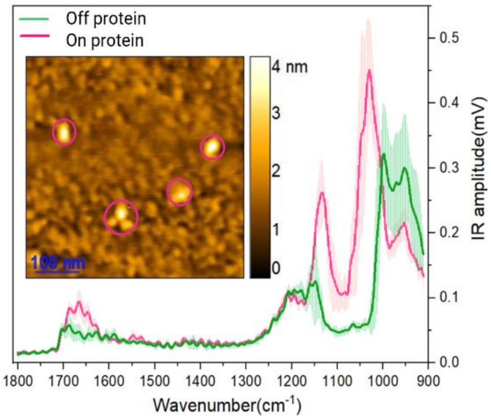

Figure 1: AFM- IR spectra of bound protein (circled in the height image) in pink and of the receptor layer in green.

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Solid-state molecular-recognition events in organic mechanochemistry probed by NMR Spectroscopy

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Molecular-recognition events are pivotal in biology and chemistry, for instance life would not been possible without them. I herein focus on studying solid-state recognition processes in the highly emerging field of organic mechanochemistry. In recent years it was shown that mechanochemical strategies can be beneficial in directed conversions of organic compounds. Finding new reactions proved difficult, and due to the lack of mechanistic understanding of mechanochemical reaction events, respective efforts have mostly remained empirical. Spectroscopic techniques are crucial in shedding light on these questions. In this contribution, I discuss the opportunities and challenges of solid-state nuclear magnetic resonance (NMR) spectroscopy in deciphering the molecular principles behind mechanochemically-facilitated solid-state molecular recognition events.

Ex-situ solid-state NMR is the method-of-choice for structural characterization of reaction mixtures taken from the milling jar requiring no further post-processing. Using the example of an aromatic bromination reaction of a cyclic sulfoximine, I highlight the importance of mixing on mechanochemical reactions, which needs to be disentangled from the effect of pressure during the milling process. *In-situ* solid-state NMR approaches using the centrifugal pressure induced during magic-angle spinning (MAS) obviously lack such efficient mixing processes, but still allow for (small) amounts of product formation.

I will also present our results on the mechanochemical formation of racemic crystals upon reacting the enantiopure entities. The effects of ball milling in a vibrational milling device as well as resonant-acoustic mixing (RAM) on the formation of racemic aggregates is probed. Our data reveal the importance of an increased particle surface caused by decreasing particle sizes upon milling leading to a highly efficient and fast formation of racemic crystals upon mechanochemical energy input. Extensions of such investigations to amino acids will be discussed as well.

Molecular-level operando electron microscopy

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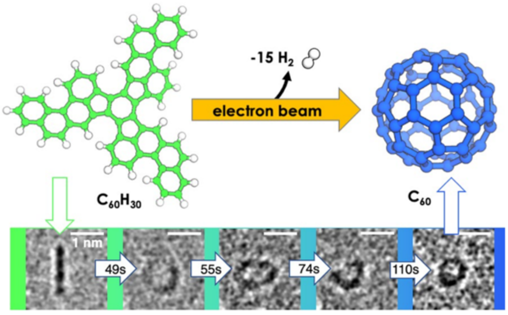
Utilizing cutting-edge single-molecule atomic resolution time-resolved electron microscopy (SMART-EM) techniques, we observe visually dynamic molecular events and interpret them with chemical rationale.

From a macroscopic perspective, the radiolytic processes are reasonably well understood and mainly regarded as unwanted destructive side-effects during the imaging process. However, these “side-effects” can also be regarded as a synthetic tool if the molecular-level radiation chemistry is adequately understood. With this, we are particularly interested how the microscopic information can be correlated to the accumulated knowledge from classical chemistry and how it can be applied to become a valuable tool for the chemist.

The talk will focus on visually verified recent discoveries of reaction mechanisms that proceed under the influence of the electron beam to form precise nanostructures and how these structures are identified [1,2,3,4]. Finally, using this *operando* electron microscopy approach, we will delve into unpublished results which show how we use the electron beam as an imaging tool and as a synthetic tool to construct novel nanostructures. Lastly, we'll examine the role of accelerated electrons, their interaction with molecules, and compare their effects to conventional energy sources like heat or light.



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Locally resolved quantification of polymer load at anisotropic nanoparticles via energy-filtered transmission electron microscopy

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The polymer grafting density on nanoparticle surfaces is a key parameter that controls the behavior of these particle/brush nanosystems. For example, the matrix compatibilization of polymer-grafted nanoparticles[1] and surface-pattern formation in brush-grafted nanoparticles[2] can be strongly influenced by this parameter. Moreover, it is an established conception that fluctuations of polymer grafting densities among distinct sites of anisotropic nanoparticles also affect structure formation, like e.g. in the site-selective self-assembly of brush-grafted nanorods.[3]
By comparison with thermogravimetric analysis, we demonstrated the capability of energy-filtered transmission electron microscopy to quantify polymer load at (gold) nanoparticles at the single particle level.[4] This method also allowed us – for the first time – to locally quantify polymer load at anisotropic nanoparticles at high spatial resolution.[4] Based on this approach, we discovered that also gold nanorods uniformly engulfed with a polymer layer can undergo site-specific (tip-to-tip) assembly and revealed the mechanistic origin for this.[5]

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Tracking Morphology and Chemical State of Working Electrocatalysts using Correlated *Operando* Microscopy and Spectroscopy

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The ability to elucidate the working state of a catalyst under working conditions is crucial for the rational design of optimized catalysts for chemical conversion reactions. While there have been rapid advances in the development of *operando* techniques that allow us to investigate electrocatalysts within a liquid electrolyte and under applied potential, we cannot obtain complete information about the catalyst under reaction conditions with only a single technique. For example, *operando* X-ray absorption spectroscopy (XAS) allows us to track chemical changes in an electrocatalyst under reaction conditions, but it provides limited information about its nanoscale morphology. On the other hand, we can visualize the morphology of working catalysts with liquid phase transmission electron microscopy (LP-TEM) experiments, but the image sequences provide limited chemical state information. Here, I will discuss how we can bridge the gap between LP-TEM and XAS with *operando* LP-transmission X-ray microscopy (TXM) and obtain both morphology and chemical state of catalysts under the same conditions. Particularly, I will focus on our studies of well-controlled model Cu_2O cubes under electrochemical nitrate reduction reaction conditions and discuss how our findings regarding their redox kinetics impact our understanding of the active phase for ammonia selectivity.

Exploring different coatings of NCM-based cathode materials by electrochemical strain microscopy

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The coating of NCM cathode materials has been proven to be advantageous for a better mechanical stability as well as enhancing the ionic and electronic conductivity. [1, 2] Various types of coatings, including materials like $LiNbO_3$, alumina oxide, and borides, are employed, with a typical thickness of the coating between 40 nm and less than 10 nm. Atomic Force microscopy (AFM) is an excellent method to investigate properties at this range due to the high spatial resolution. Electrochemical strain microscopy (ESM) is an advanced AFM technique for investigating battery materials. [3, 4] In this method, an AC field is applied between the tip and sample, which stimulates ions to oscillate. Due to the direct contact between the tip and the sample surface, the movement of the ions is directly transferred to the tip and is measured. Thereby, the amplitude of the cantilever, which contains information about the mobility of the ions, as well as the phase and frequency shift, which provide material contrasts and information about mechanical properties, is recorded.

Within this contribution the influence of different coatings on signals such as phase and amplitude and thus, on local ion mobility and mechanical properties, is critically discussed. A thorough introduction to ESM, its working principle, and the theory behind it, will be provided. The analytical results reveal the impact of calcination temperature on the structure of the $LiNbO_3$ coating on the typical cathode material NCM622 ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) and Ni82 ($LiNi_{0.82}Mn_{0.07}Co_{0.11}O_2$). Furthermore, insights into local ion mobility, mechanical properties, and coating uniformity are presented. Significant differences in the ESM amplitudes between different coatings are found. Related measurements, like by TEM, show that at about 400°C a crystallization process of the coating's material occurs. This might also explain a very strong ESM amplitude signal observed for coatings calcined at high temperatures, based on a change of the excitation mechanism in ESM. Thus, different signal origins in ESM are introduced and discussed with respect to characterize the properties of NCM coatings.

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Biophysical Chemistry and Biophotonics

Near-Infrared Fluorescent Biosensors Based on DNA Quantum Defects

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Semiconducting single-walled carbon nanotubes (SWCNTs) are versatile near-infrared (NIR) fluorophores. [1] In most cases, they are noncovalently modified to create sensors that change their fluorescence when interacting with biomolecules. However, this noncovalent chemistry has several limitations and prevents a consistent way to molecular recognition and reliable signal transduction. Here, we introduce a widely applicable covalent approach to create molecular sensors without impairing the fluorescence in the NIR (> 1000 nm). [2] For this purpose, we attach single-stranded DNA (ssDNA) via guanine quantum defects as anchors to the SWCNT surface. A connected sequence without guanines acts as flexible capture probe allowing hybridization with complementary nucleic acids. Hybridization modulates the SWCNT fluorescence and the stability increases with the length of the capture sequence ($20 > 10 \gg 6$ bases). The incorporation of additional recognition units *via* this sequence enables a generic route to NIR fluorescent biosensors with improved stability. To demonstrate the potential, we design sensors for bacterial siderophores and the SARS CoV-2 spike protein. In summary, we introduce covalent guanine quantum defect chemistry as rational design concept for rapidly adaptable biosensors. [2]

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Large-scale opening of the Influenza A virus M2 proton channel: Combining surface-enhanced infrared absorption and computational spectroscopy

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Viroporins are small ion/proton channel-forming proteins in membranes of enveloped viruses that play important roles at multiple stages of the viral life cycle, and thus present promising targets for antiviral therapy. In particular, the M2 proton channel from Influenza A virus (IAV) has garnered much attention for this family of proteins, when it was shown that its pH-activated proton conductance can be inhibited, thereby, stopping flu infection – an inhibition strategy currently affected by antiviral resistances. Although the chemical steps involved in pH-activation are well understood, the intricate large-scale reorganization of the protein necessary for channel opening remains elusive. To address this gap of knowledge, we employ surface-enhanced infrared absorption (SEIRA) spectroscopy,[1] which enables us to monitor the function of membrane proteins within a single, planar solid-supported bilayer lipid membrane (ssBLM) via their distinctive vibrational fingerprint. By in-situ monitoring of the structural changes upon pH-activation within the ssBLM, we noticed signals characteristic of a reorientation of transmembrane α-helices associated with IAV M2's channel opening.[2] To validate this interpretation, we calculated computational IR spectra based on a structural model from nuclear magnetic resonance and obtained an excellent match with the experimental picture. Through the integration of experimental and computational spectra, we quantified the mechanical opening of the transmembrane helices, refining the picture of how IAV M2 opens during infection. Interestingly, this very mechanical motion is blocked by M2 inhibitors. In the future, we aim to utilize this approach to enable a combined structural and functional analysis of viroporins of current relevance and contribute to the discovery of new antiviral drugging strategies.

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Exploring heme-enzyme tunability with resonance and surface-enhanced resonance Raman spectro-electrochemistry

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The development of artificial metalloproteins designed to catalyze new types of transformations presents a promising avenue in biocatalysis holding a significant potential for technological or medical applications. For that, enzymes utilizing heme as an active site are particularly attractive due to the inherent structural and redox versatility of metalloporphyrins. Such versatility allows for a broad spectrum of small molecule activation and coupled redox reactions. The advancement of the field necessitates the use of spectroscopic tools capable of correlating the structural or molecular information of the system of interest with its function or performance. A combination of electrochemistry with surface-enhanced resonance Raman (SERR) spectroscopy stands out as a method of detecting chromophore-selective vibrational spectrum under the control of applied potential. In the example of the heme-containing enzyme studied here, resonance Raman provides an elegant way of decongesting Raman spectra through selective and amplified detection of the vibrational fingerprint of the Fe-porphyrin, thereby enabling identification of the oxidation, spin, and coordination state of the metal ion. The nanostructured metal surface serves as surface-enhanced Raman active support on which the biomolecule of interest is interfaced, and electrochemistry provides a means to inject or remove an electron from a molecule to drive a redox reaction. Here, the application of SERR spectro-electrochemistry and its benefits are presented on the example of a rationally engineered, redox-active multimeric heme-containing protein (HTHP). Various HTHP variants have been tailored to accommodate diverse coordination patterns of hemes, influencing their oxidation, spin, and redox properties. These modifications lay the foundation for expanded redox chemistry of heme in protein scaffold.

Labeled carbohydrates for the investigation of protein-ligand interactions with 2D-IR spectroscopy

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This research aims to establish thiocyanate- and azide-labeled carbohydrates for the characterization of carbohydrate-protein interactions with IR-spectroscopy. Recently we overcame the spectral congestion of IR spectra of carbohydrates by incorporating thiocyanate and azide into monosaccharides [Gasse 1, Gasse 2]. Focusing on glucose and galactose, this study compares different labeling sites, and their potential to explore the metabolic pathways, e.g. the phosphorylation of glucose with ATP in hexokinase.
Additionally, the investigation extends to carbohydrates with more specific biological contexts. The characterization of azide-lactose may be used to scrutinize its distinct interactions with lactase. Furthermore, the examination of azide-N-acetylglucosamine can provide insights into the link between proteins and glycans, with importance e.g. in cellular signaling processes.

The experimental analysis employs FTIR and 2D-IR spectroscopy techniques, enabling a detailed exploration of the structural dynamics of the labeled samples on an ultrafast time scale.

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Molecular Thermodynamics Behind the Liquid-Liquid Phase Separation of Proteins

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Recent research highlights the functional role of biomolecular condensates, which can form membraneless organelles inside biological cells by a process known as liquid-liquid phase separation (LLPS). Despite its importance, a detailed molecular-level understanding of the thermodynamic driving forces that are at play in the process is largely lacking. Using atomistic molecular dynamics (MD) simulations on the intrinsically disordered domain of human fused in sarcoma (FUS) RNA-binding protein, we investigate the individual contributions of protein and water molecules towards the free energy changes that govern LLPS [1]. Our results show that thermodynamic contributions from both protein and water are equally important for driving the process. Among the various factors considered, solvation entropy and protein interaction energy are identified as the most substantial contributions [1]. Similar solvation entropy profiles are also observed for a globular protein (γD-crystallin) and the MD simulation results are in excellent agreement with the entropy changes obtained from terahertz calorimetry experiments [2]. These findings open the way for a universal view on the thermodynamics of association processes in biological systems, with a focus on the role of water in modulating protein-protein interactions and shaping the formation of membraneless organelles.

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Ratiometric near infrared imaging of the neurotransmitter dopamine

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Microscopy has seen tremendous progress in the past few years. Fluorescent sensors, which detect and measure light emitted by fluorescent molecules, are powerful tools to study dynamic chemical changes in complex biological systems. Often fluorescence intensity is used as readout but such signals are affected by laser fluctuations or movements of the sample. Here, we present for the first time ratiometric imaging of the neurotransmitter dopamine using a fluorescent nanosensor in combination with a reference nanomaterial.

We combine calcium copper silicate (Egyptian Blue) nanosheets (EB-NS) and single-walled carbon nanotubes (SWCNTs) for advanced analyte detection. Both materials fluoresce in the beneficial near infrared (NIR) tissue transparency window. While EB-NS fluorescence (920 nm) remains unchanged in response to the neurotransmitter dopamine, DNA modified SWCNTs increase their NIR signal (980 nm). The ratio between these two signals is therefore a robust measure for the local dopamine concentration. We implement a NIR wide field fluorescence imaging setup that images both signals at the same time, which enables us to image dopamine release patterns from neuronal cells. Therefore, this ratiometric approach enables robust non-invasive NIR monitoring of cellular responses to external stimuli.

Coulomb repulsion mediated via Trp4$^{\circ+}$ formation triggers conformational changes in Drosophila melanogaster Cryptochrome

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Cryptochromes (CRY) are light-(in)dependent regulatory proteins. In the fruitfly Drosophila melanogaster (Dm), CRY is the primary blue-light receptor mediating circadian photo-entrainment. Light absorption by protein-bound flavin adenine dinucleotide (FAD) leads to its reduction via consecutive electron transfer along a conserved tryptophan tetrad, resulting in the C-terminal tail (CTT) release mediating signal transduction accompanied by tryptophan decomposition and FAD dissociation. By spectroscopic, biochemical, and computational investigations on DmCRY wildtype and single and one double variants we demonstrate that a positive charge at the protein surface in form of the terminal surface exposed tryptophanyl radical cation is the essential trigger for the CTT release due to Coulombic repulsion with nearby cationic amino acids within the C-terminus even under reductive in vivo conditions. This is confirmed by constitutively active variants with positively charged amino acid on the terminal tryptophan position. Our results may provide a general molecular mechanism of CRY activation.

Development of microfluidic 3D bioprinting platform for cell manipulation at a single entity level – a proof-of-concept

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Additive manufacturing, also known as 3D printing, enables a broad field of precise fabrication and manipulation applications. Bioprinting takes a special place among other additive manufacturing techniques as it involves a layer-by-layer deposition of live cells along with biomaterials and active biomolecules – so called bioinks, to produce 3D cell cultures, prosthetics and artificial tissues. [1]

Here, we developed a proof-of-concept approach to bioprinting aimed to precisely dispense live cells with a single cell precision and microscale resolution. This type of bioprinting is designed to precisely position various cell types in a tissue, which is particularly important to replicate highly organized biological environments as close as possible. In contrast to other state-of-the-art approaches, based on bioink deposition by extrusion, droplet, or laser-based deposition that lack flexibility in the choice of bioinks featuring sufficient viscosity, composition, and durability during printing, along with compromised spatial resolution. [2-4]

Here, we developed a microfluidics-based platform for countable and accurate cell-imitating micromer® particle translocation between a bead donor reservoir and the culture media. The microfluidic approach on a forged glass capillary nozzle enabled an automated bioprinting setup that is able to move the nozzle with microscale precision in all three dimensions to ensure precise cell deposition. Cell translocation through the nozzle creates a distinct current trace (in a similar way to Coulter counter [5]), which was utilized in a two-detector referenced current setup combined with inverted optical microscopy to develop this printing method. Currently, an individual cell counting during translocation, three-dimensional displacement in a cell media located in a custom incubator setup, and high performing data handling are achieved. The current development is only one of the initial steps for the future systematic analysis, manipulation, and creation of artificial cellular networks across a multitude of biomedical applications, from drug testing to artificial organs and prosthetics. [6]

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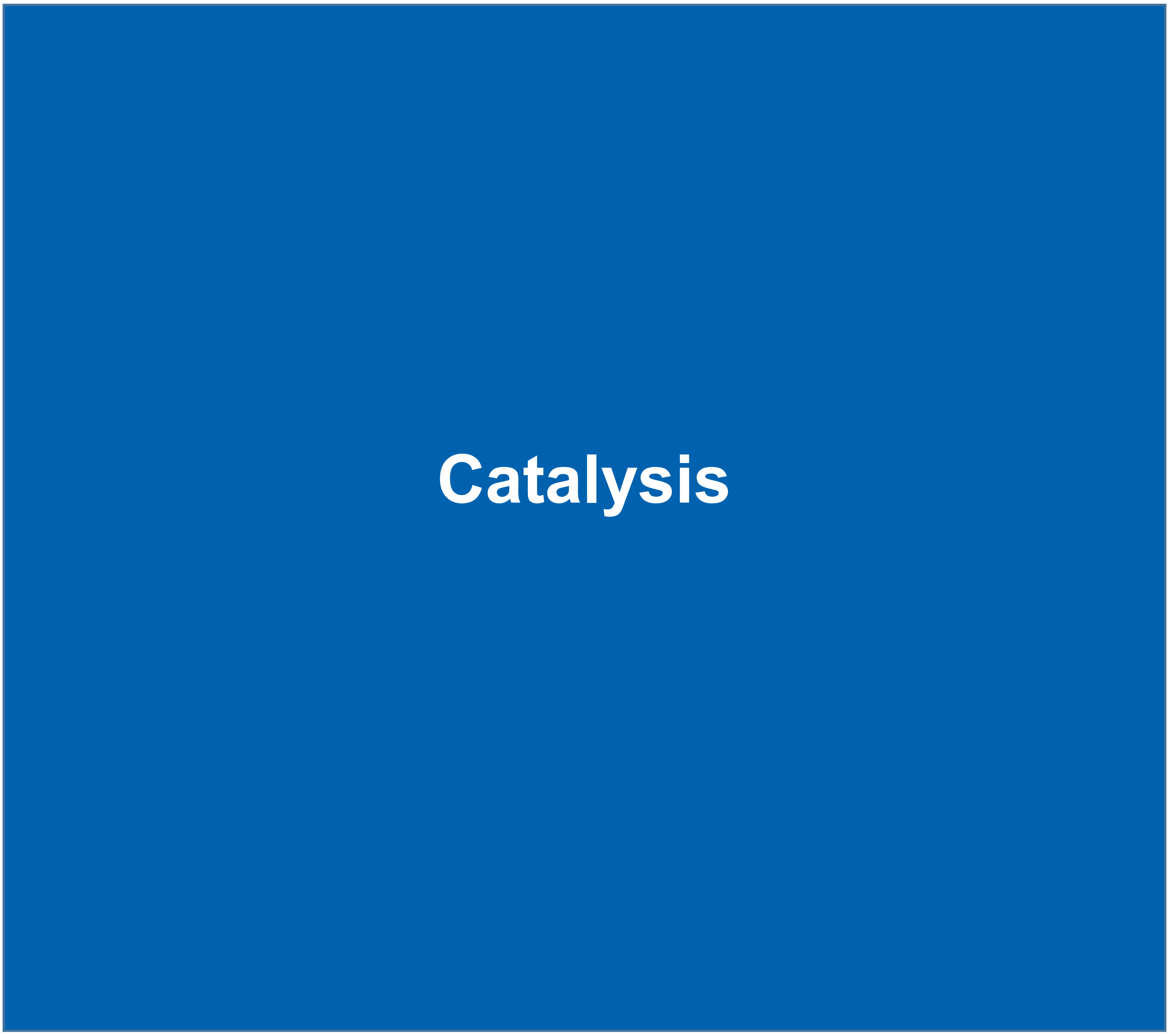

Catalysis

Shining Light on Sustainability: Melem Nanorods Unleash the Power of Visible Light for CO_2 Photoreduction Coupled with Alcohol Oxidation

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Abstract:

The primary aim of this present study was to meticulously engineer diverse materials derived from melem, with the intention of exploring their synergistic photocatalytic efficacy in the context of CO_2 valorization concomitant with organic synthesis. The present study reports the successful synthesis of melem 2D nanosheets (MNS) through a controlled low-temperature melamine pyrolysis process. Subsequently, an innovative room temperature, template-free strategy was employed to fabricate melem nanorods (MNRs) via a concurrent etching and defect engineering of MNSs facilitated by H_2SO_4. The incorporation of acid ions within the MNSs structure resulted in the formation of a remarkable 1D morphology, characterized by an abundance of carbon vacancies, which concurrently induced numerous additional $–NH_2$ groups into the material. MNRs, as an exemplary proof-of-concept prototype, have demonstrated remarkable success as a dual-functional reaction system facilitating proficient visible light-driven CO_2 photoreduction to CH_3OH while simultaneously effecting the transformation of benzyl alcohols into valuable benzaldehydes via a green cooperative photoredox mechanism. This enhanced reactivity can be attributed to several critical factors: i) the abundant presence of basic $–NH_2$ groups, which serve as active sites to capture and activate CO_2 molecules; ii) the simultaneous involvement of $–NH_2$ groups in activating the aromatic alcohol entities through intramolecular hydrogen bonding; and iii) the modification of defects, tailoring the band structure of MNRs and significantly augmenting their visible-light-harvesting capabilities. This modification, in turn, leads to prolonged photocharge carrier lifetimes and superior surface redox reaction kinetics, as unveiled through comprehensive analysis and experimentation. This remarkable observation underscores the compelling synergy stemming from the prolonged lifetimes of both electrons and holes, in conjunction with the potent $-NH_2$ sites present within the MNR structure. This study introduces an innovative approach for fabricating morphology and defect-engineered molecular-based photocatalysts, dedicated to artificial photosynthesis which exhibit remarkable charge separation and transfer with isolated redox catalytic sites.

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Photocatalysis sensitized by photoactive chromium complexes

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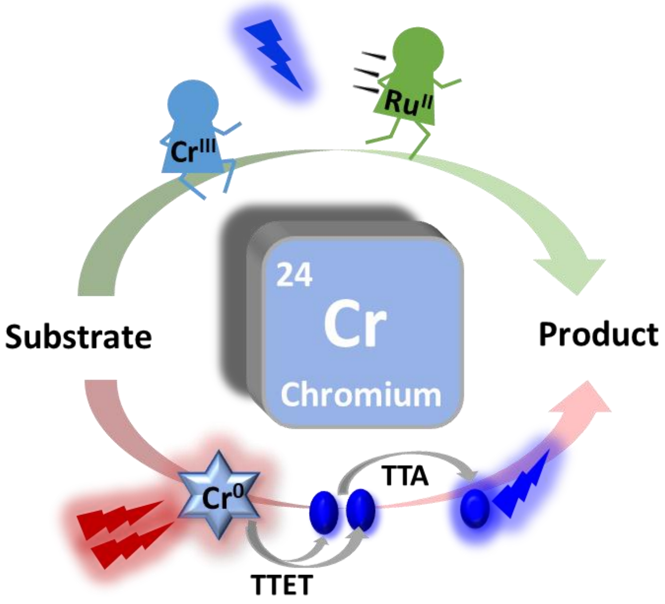
Recently, remarkable progresses have been made in exploiting photoactive first-row transition metal complexes, such as chromium, manganese, iron, cobalt, providing important fundamental understandings in respects of the molecular design and applications of photoactive 3d metal complexes.[1] These new types of photoactive meal complexes are seen as more sustainable alternatives to the noble metal complexes due to their competitive photophysical and photochemical properties.

Photoactive chromium complexes in different oxidation states are drawing particular attention in photocatalysis due to their high excited state reactivity in electron- and energy-transfer processes.[2] This contribution will provide some fundamental understanding of the photoredox catalytic activities of photoactive Cr^{III} polypyridine catalysts and a strategy of using low energy light input with a photoactive Cr^{0} complex for energy transfer photocatalysis. Throughout a comparative study of the photocatalytic behaviours of a photoactive $3d^3$ Cr^{III} polypyridine complex and a $4d^6$ Ru^{II} photocatalyst, we find that the photoredox catalytic activity of the Cr^{III} complex is substantially lower than that of the Ru^{II} catalyst, and no evidence is found that the driving forces for forward- and reverse-electron transfer could account for this observation. These different catalytic activities can be attributed to the fundamental difference in the valence electron configurations of the photoexcited Ru^{II} and Cr^{III} complexes and their reduced forms. Photoactive $3d^6$ Cr^{0} isocyanide complexes exhibit metal-to-ligand charge transfer (^{3}MLCT) excited state with long luminescence lifetimes sufficient for diffusion-controlled energy transfer process.[2a] Sensitized by a photoactive $3d^6$ Cr^{0} isocyanide complex, strong red-to-blue photon upconversion can be obtained, which enables blue light-dependent polymerization with red light.[3]



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Switchable Hybrid Catalyst for a Molecular Solar Thermal System

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Molecular solar thermal (MOST) systems combine solar energy conversion, storage, and release using switchable photoisomers (photoswitches). One challenge is, however, to control the energy release in an efficient and selective manner.[1] In our study, we combine the advantages of heterogeneous catalysts with electrochemical controllability and high selectivity known from homogeneous catalysts. In particular, we investigated the energy release from the norbornadiene/quadricyclane (NBD/QC) based MOST system p-methoxyphenyl-ethyl ester-NBD/QC (mPENBD/mPEQC) by a Co(II)porphyrin complex, [5-(p-carboxyphenyl)-10,15,20-tri(p-tert-butylphenyl)porphyrinato] cobalt(II), anchored to an atomically defined $Co_3O_4(111)$ surface. We demonstrate that this hybrid catalyst exhibits high activity in catalyzing the energy release from mPEQC to mPENBD. By applying a potential of $< -1.4\ V_{fc}$, we are able to reduce the catalytically active Co^{II} center to Co^{I}, resulting in deactivation of the catalyst. The original activity is recovered when the Co center is reoxidized. Thus, we can implement a catalyst, which can be switched on and off by the applied potential. To test the stability of the system, we performed 100 conversion cycles. Within the accuracy of our experiment, we do not observe the formation of side products.

Literature:

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MoS_2-based model catalysts for hydrotreatment of biooils: Combined insights from STM & XPS from UHV to *operando* conditions

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Hydrotreatments of (fossil) oils using promoted MoS_2-based catalysts are well-established industrial processes, primarily for the removal of heteroatoms (S, N, O, …).[1-3] The process is currently becoming more relevant in the energy transition, e.g. for upgrading of biooils from sustainable feedstocks such as sewage sludge or biomass pyrolysis. However, such biooils appear as complex feedstocks that are more rich in impurities and heteroelements (O, N) and thus remain challenging due to stability problems and catalyst deactivation.[4]

In contrast to the established use in (oxygen free) hydrodesulphurization (HDS), where in-situ formed S vacancies act as active sites, the sulphide catalyst will be exposed to nitrogenates and oxygenates in the desired hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) processes. Thus, S atoms may be partially exchanged by N or O, triggering an active site blocking and strong catalyst degradation on the long term. [5,6]

As a well-defined model system, this work investigates 2D MoS_2 nanoparticles on Au (111) surfaces (fig. 1) being exposed to H_2 and N or O containing molecules at relevant temperatures to mimic hydrotreatment conditions. Herein, we present combined insights from scanning tunnelling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) from UHV to near-ambient pressure (NAP) conditions to elucidate the underlying processes at an atomistic level. Our results show that the MoS_2 nanoparticles are generally surprisingly robust but respond to elevated H_2O levels by a small uptake of oxygen starting from the particle corners and edges, leading to an ongoing restructuring of the catalyst. The rate of the oxidation can be steered by the presence of hydrogen in the feed.

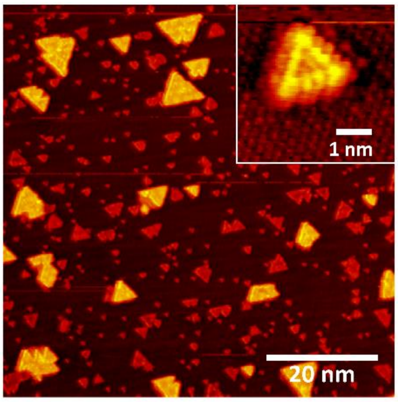

Figure 1: Scanning tunneling micrograph of 2D MoS_2 nanoparticles on a Au(111) support. The inset shows an atomically resolved individual particle.

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Time-Resolved Spectroscopic Studies on the Net Heterolysis of Homopolar Selenium-Carbon Bonds

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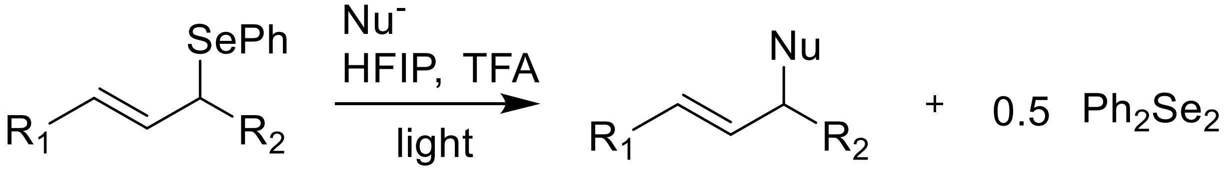
When thinking about chemical bonds, one considers polarity as the major factor determining if a bond cleavage occurs homolytically or heterolytically, as bonds with a negligible dipole moment exclusively undergo homolysis, whereas heterolysis requires a sufficiently high dipole moment (i.e. an electronegative leaving group) or some kind of external bond activation [1]. For selenium-carbon bonds, such activations are usually performed using strong electrophiles (e.g. Me^+) [2], which allow substitution of selanes with nucleophiles. However, as such harsh conditions are often detrimental, softer alternatives are desirable. We demonstrate that by combining the selectivity of photochemistry [3] with the unique radical chemistry of organoselenium compounds [4] and the exceptional properties of the solvent hexafluoroisopropanol [4, 5], net heterolysis of the homopolar selenium-carbon bond can be achieved and utilized in a subsequent S_n1-type substitution.



The mechanism of this reaction is disclosed using transient absorption spectroscopy with streak-camera detection [6] and other advanced spectroscopic techniques, as well as theoretical and synthetic investigations.

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Synthesis of Hollow Nickel-Platinum Tips on Dot-in-a-Rod Nanostructures

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Semiconductor-metal hybrid nanostructures are promising candidates for a green photocatalytic hydrogen evolution. The underlying processes for hydrogen evolution in these structures are the absorption of photons in the semiconductor and the subsequent charge-carrier separation across the semiconductor-metal interface. The electrons, residing in the metal tip after the separation process, reduce protons to hydrogen. Unfortunately, the production of effective, long-time stable and cost-efficient photocatalysts is still challenging.

Here, we present the preparation of a novel hybrid nanostructure composed of a CdSe/CdS dot-in-a-rod nanoparticle with a hollow tip, which consists of a Pt/Ni alloy. The formation of hollow tips is nearly unexplored in the field of metal-tipped CdSe/CdS dot-in-a-rod structures and holds a great potential for cost-efficient hydrogen production cocatalysts. For an application-oriented design of the metal tips, a deep understanding of the present formation mechanism of the hollow tips is mandatory. The preparation is a two-step synthesis. Firstly, nickel tips are grown onto CdSe/CdS dot-in-a-rod structures. Secondly, platinum cations are reduced on the nickel tips. To this point, we assume a combination of a galvanic exchange process together with a reduction of the platinum cations through reducing agents. We also see an influence of the oxide layer of the firstly grown nickel tips. We take a detailed view in the growth of these particles and give an outlook for their potential applications.

Electrochemistry

Isopropanol electro-oxidation on well-defined model Pt-Ru alloys: activity and composition

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The growing field of renewable energy drives innovations in hydrogen-based energy storage and conversion technologies. “Rechargeable electrofuels” are substances that are charged by hydrogenation and discharged by dehydrogenation in a closed-loop electrochemical system, with the isopropanol/acetone couple being a top candidate. [1, 2, 3] Pt-Ru alloys are the state-of-the-art electrocatalysts for isopropanol-to-acetone conversion in fuel cells. [3, 4] Commercially available Pt-Ru/C catalysts have demonstrated high activity for fuel cell operation, with current peaks around 0.75 V_{RHE} and a minor peak at around 0.15 V_{RHE}. [3, 4] The latter, known as the pre-peak, is of great importance in fuel cell applications. It is highly desirable to selectively increase the activity of the catalyst in the low-potential region. We investigated the stability and chemical composition of the well-defined Pt-Ru alloy catalyst as a function of applied potential by means of synchrotron radiation photoelectron spectroscopy coupled with an *ex situ* immersion electrochemical cell. Immersion of the Pt-Ru alloy catalyst at potentials above 1.2 V_{RHE} results in surface oxidation and dealloying. Upon returning to 0.0 V_{RHE}, we observed the formation of ultra-small Pt aggregates. The activity of the Pt-Ru alloy model catalysts was studied by cyclic voltammetry before and after oxidative treatment. Our studies suggest that the low-potential activity of the Pt-Ru alloy catalysts is associated with the presence of ultra-small Pt aggregates.

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Spectroelectrochemical methods for the elucidation of photoredox processes

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

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

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

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Cyclic voltammetry for batteries:
Differences between liquid-state and solid-state

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Potential sweep methods involve measuring the current response while the applied potential is swept. In the most common technique, named cyclic voltammetry (CV), the sweep rate is kept constant up to a point where it is then reversed. These techniques are well established for probing redox reactions in liquid electrochemistry. More recently, potential sweep methods have also been widely utilized for studying redox reactions in both solid electrolytes and solid electrodes.

For an insertion reaction, however, the classic analysis must be modified to account for fundamental differences between solid-state and liquid-state storage. After a review of the decisive differences between typical liquid-state and solid-state, first, necessary modifications to the classical analysis are discussed. Numerical simulations are presented to illustrate how in intercalation systems the current response depends on the sweep rate and insertion thermodynamics. Second, CV measurements under wide range of sweep rates using TiO_2 and Nb_2O_5 thin films (different thicknesses) are presented which allow for testing the proposed novel analysis. It is shown how reliably solid-state kinetic parameters (e.g., Li diffusivity in TiO_2 thin films) can be obtained. [1]

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Electronic Structure, Li-ion Mobility and Mechanical Properties in Individual NCM Particles – a Correlative Study

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The behavior of NCM cathode materials under electrochemical load have been intensively investigated by spectroscopic and microscopic methods. A strong gradient in the lithium concentration within individual NCM particles has been revealed. [1-4] This effect is directly related to the (dis)charging behavior of the material and a more detailed understanding is crucial for improving the kinetic performance and long-term cycling stability of NCM cathode material.

In this contribution correlative results from near edge X-ray absorption fine structure (NEXAFS) and atomic force microscopy (AFM) on individual NCM622 particles embedded in typical binder matrix are presented. While by NEXAFS the electronic structure is investigated, AFM provides information about the Li-ion mobility. Interestingly, both techniques reveal a direct link to the Ni2+/Ni3+ ratio in the particles. Furthermore, the microscopic data indicates a direct dependency between the mechanical behavior, the local Li ion mobility, and the electronic structure of the NCM material. Therefore, the spectroscopic and microscopic investigations are extended by nanoindentation experiments of the identical system and as a function of the SOC. A significant gradient in hardness and reduced modulus is found by indentation mapping.

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Electrochemical 3D Printing of Sn Microstructures as Future Anodes for High-Power Lithium Ion Batteries

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Lithium-ion batteries (LIBs) are energy storage devices suitable for applications spanning multiple scales, from portable electronics to electric vehicles. Despite the booming success of LIBs, they still fall short in providing simultaneously high capacity and high charging rates, causing the current enormous efforts to improve the performance of LIBs active materials. Instead, however, an unconventional approach is to develop a three-dimensional (3D) battery [1] with high aspect ratio cathode and anode features, capable to overcome the limitation of the planar design even with already existing materials. To achieve significant advantages, however, the proximity between the cathode and anode as well as their critical dimensions should approach micrometer and nanometer scales.

In order to satisfy this requirement, we are developing various electrochemical additive manufacturing (AM) techniques [2] capable to fabricate nanostructured Sn anodes. Our advanced 3D printing approach is based on the confinement of electrodeposition using localized delivery of precursor species in liquid, where metal ions are injected with a nanopipette and driven by a pressure flow. The advantage of this approach is the automated feedback mechanism, based on the variation of ionic current through the nanopipette, so that the nanopipette is precisely positioned and maintained at a constant distance from the printed object. The feedback allows for the precise control of the print process and guarantees close monitoring of the growth of the metallic features, which is key for the fabrication of high-aspect ratio structures. By utilising nozzles with dimensions of 150-250 nm, sub-microscale critical dimension of the produced structures can be achieved, whereas the layer-by-layer (and voxel-by-voxel) assembly opens the almost unlimited design freedom. These advances in 3D microprinting are the key to successful realization of the 3D batteries with improved performance characteristics.

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Novel electrochemical methodology for the removal of HF from carbonate-based $LiPF_6$-containing Li-ion battery electrolytes

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Baseline Li-ion battery (LIB) electrolytes comprise $LiPF_6$ salt dissolved in carbonate solvents. Traces of HF are always present in these electrolytes due to trace amounts of water and the hydrolysis of $LiPF_6$ in carbonate solvents. [1] Interfacial and interphasial chemistry on cathodes and anodes of LIBs are impacted by HF. On the cathode, HF has negative effects, including transition metal dissolution and capacity fading. [2] On the anode, HF is involved in the formation and evolution of the solid electrolyte interphase (SEI). [3] The SEI originates in the thermodynamic instability of electrolyte moieties (salt, solvent, impurities) on the anode surface. This results in the reduction of electrolyte moieties, which may react with Li^+ to form solid insoluble products on the anode surface, thereby kinetically stabilizing the interface by limiting electron and solvent transport, while allowing Li^+ transport. [4]

The objective of this work is to remove ppm-levels of HF from carbonate-based $LiPF_6$-containing electrolytes to mitigate cathodic degradation and to enable foundational studies of SEI nucleation (e.g., direct PF_6^- anionic direction) without interfering HF effects. We propose an electrochemical purification approach, which is complementary to conventional approaches using scavenging molecules. [5] We made use of the knowledge that HF is the only electrolyte moiety in baseline carbonate $LiPF_6$-containing LIB electrolyte that electrochemically (more specifically electrocatalytically) reacts on metal electrodes at relatively high potentials (significantly > 1.5 V vs. Li/Li^+) at which all other electrolyte moieties remain intact. Our basic hypothesis therefore is that the application of a suitable potential to a high-surface area catalytically active electrode will result in the electrocatalytic reduction of all HF in the electrolyte, while all other moieties remain effectively unchanged. For this purpose, we used a porous Cu-foam working electrode, which is integrated into a Teflon cone-type cell which contains a second Pt working electrode that allows to electrochemically test the HF concentration in the electrolyte via cyclic voltammetry (CV). We report on the successful removal of HF to levels below a few ppm. Additionally, we observe CV features which we tentatively assign to of direct anion reduction. Investigations are underway to gain deeper insight the specifics of this reactions. We anticipate that the developed electrochemical method could lead to new opportunities for HF removal and basic research on the SEI reaction in electrolytes containing $LiPF_6$.

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Reaction Kinetics and Dynamics

The formation mechanism of pyrrole under interstellar conditions

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The pyrrole moiety is found in many essential biomolecules including the heme complex, vitamins, as well as chlorophyll, making it a fundamental building block of life. It is assumed to be formed in early stages of star formation, but potential reaction pathways have not yet been described. Conditions in these environments are harsh with temperatures around 10 K and average collision times ranging from hours to years. For chemistry to occur efficiently within cold molecular clouds, a reaction must be barrierless and proceed via an addition-elimination type mechanism to release the excess energy contained in the final products.

In this study we demonstrate that pyrrole can be created in cold molecular clouds through the reaction of aminocarbene (H-C-NH_2) with propargyl radicals (C_3H_3). The latter have been recently detected in the interstellar medium,[1] while the former is produced in the reaction of methylidyne (CH) with ammonia.[2]

We generated aminocarbene from cyclopropylamine and propargyl radicals from propargyl iodide simultaneously in a pyrolysis microreactor. The reaction mixture was isomer-selectively analysed using mass-selected threshold photoelectron spectra recorded on a photoelectron photoion coincidence (PEPICO) setup. To shed light on the reaction mechanism we employed quantum chemical calculations in combination with KinBot.[3] The latter automatically explores the potential energy surface and identifies transition states and intermediates. Our experimental and theoretical data show that pyrrole forms barrierlessly and that it is the lowest energy pathway in the reaction between aminocarbene and propargyl radicals.

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

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As one of the most important aerosols in the Earth's atmosphere, sea salt aerosols significantly affect the climate on earth. Sodium chloride, their main component, is involved in numerous atmospheric processes such as chemical reactions with atmospheric trace gases.

In our experiment, we use gas-phase sodium chloride cluster ions to model chemical reactions in sea salt aerosols. Singly and multiply charged anions as well as cations are generated by electrospray ionization (ESI) and reaction kinetics are recorded via a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). Atmospherically relevant acids, such as formic and pyruvic acid, are used as reaction gas. A sequential uptake of the acid by anions as well as cations with release of HCl is observed (Figure 1), similar to previously observed reactions of sea salt particles with sulfuric or nitric acid in the atmosphere [1] and in laboratories [2]. Furthermore, the sodium chloride cluster ions show a higher reactivity towards pyruvic than towards formic acid, which might result from the lower proton affinity of pyruvate. Magic cluster sizes - identified in previous studies [3] - show reduced reactivity.

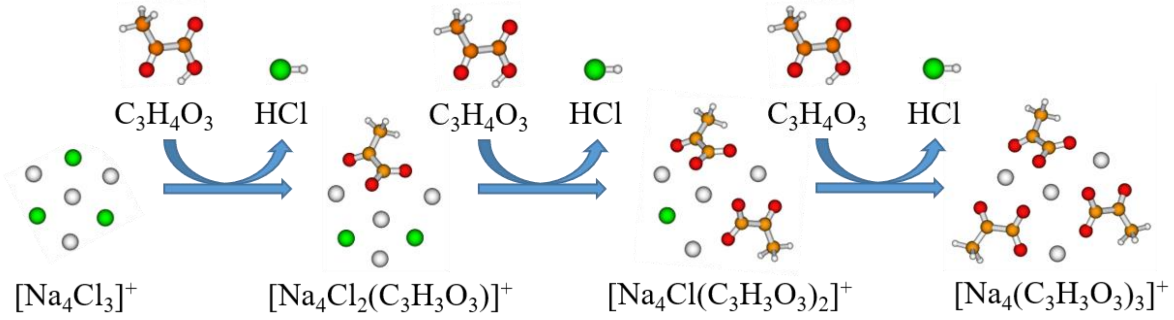

Figure 1: Observed reaction of $[Na_4Cl_3]^+$ with pyruvic acid.

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Spectroscopic Investigation of Organic Peroxyl Radicals in the Atmospheric Aqueous Phase

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Volatile organic compounds (VOCs) play a key role in atmospheric chemistry, especially their oxidation processes have a significant impact on the formation of secondary organic aerosols (SOA) in both gas and aqueous phase. [1] Free radicals, as important oxidant in the atmosphere, can be involved in the reaction of SOA to form different products. The transformation and degradation products in the gas phase can be different compared to the aqueous phase (cloud droplets, fog, rain or hygroscopic particles). [2] Organic peroxyl radicals are important reactive intermediates in oxidation process in the atmospheric aqueous phase, which can further participate in a series of complex reactions to form a variety of products. [3]

This study presents a comprehensive spectroscopic investigation of hydroxy peroxyl radicals in the aqueous phase. In order to characterize and identify the optical properties of peroxyl radicals, a laser flash photolysis-long path absorption (LFP-LPA) coupled with a ICCD camera is applied to measure the UV spectrum of peroxyl radicals. [4] In this method, OH radicals are formed by photolysis of hydrogen peroxide (H_2O_2) at $\lambda = 248$ nm and are used to oxidize the organic precursors: methanol and ethanol to form peroxyl radicals. The formation, unimolecular decay, and recombination reactions of peroxyl radicals were studied to better understand the fate of these radical species in the atmosphere.

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Excited-state proton transfer reactions in Ru- and Fe- complexes with pyrazine moietys

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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, meaning molecules which have a decreased or increased pKa in the excited state, opens up a variety of possibilities in polymer sciences[1], electrochemistry[2], or photolithography[3]. While organic photoacids and photobases are extensively studied, their metal coupled counterparts are still not well understood and only a few reports exist [4,5].

In our work, we introduce a novel version of the well-known Ru(dqp)$_2$ (dqp=di(quinolin-8-yl)pyridine) complex where pyridine is exchanged for pyrazine, yielding not only a further increased lifetime but also a complex with photobasic properties. This is due to the accumulation of electron density on the external nitrogen upon excitation. We are interested in understanding, and quantifying, the involved proton transfer process as well as the excitation wavelength dependent relaxation pathways in different solvents. Further, we examine the effects of substituting the central metal atom by its earth-abundant analogue iron. This affects both the photophysical dynamics of the complex as well as its photobasic behavior. For these investigations we use both steady-state as well as time-resolved electronic and vibrational techniques.

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Excited-state dynamics of carbazole-based blue-emitting materials in organic solvents and as thin films

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We present our recent studies of carbazole-based deep-blue emitting materials using time-resolved emission and transient absorption spectroscopy from sub-picoseconds up to few hundreds microseconds. They are often used as donor-acceptor-type thermally activated delayed fluorescence (TADF) materials or as host materials such as in 1,3-bis(*N*-carbazolyl)benzene (mCP) for organic light emitting diode (OLED) applications. Transient absorption experiments of mCP in THF detect the formation of the T_1 triplet state from S_1 with a quantum yield of about 20%, a band maximum at 450 nm, and a lifetime on the microsecond time scale. Strong spectral overlap of S_1 stimulated emission and S_1 excited state absorption suggests that S_1–S_1 singlet-singlet annihilation (SSA) based on a bimolecular diffusive mechanism should be feasible at high mCP concentrations in thin films. Other relaxation processes (see Fig. 1) will be discussed in detail. Furthermore, we will compare the excited-state dynamics of a donor-acceptor type TADF material, 3,6-di-*tert*-butyl-9-(2,12-di-*tert*-butyl-5.9-dioxa-13*b*-boronaphtho[3,2,1-*de*]anthracene-7-yl)-9H-carbazole (TB-tCz), with donor and moieties, independently, in solvents and also as thin films.

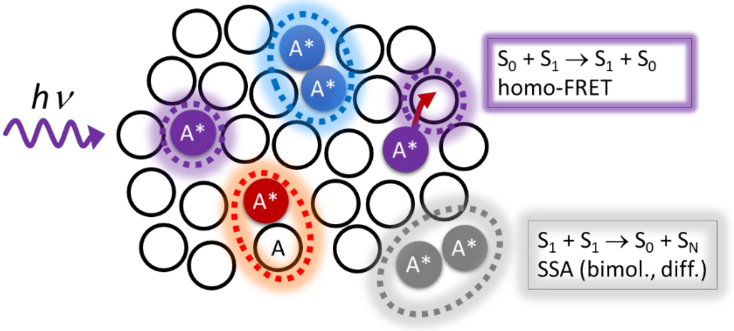

Fig 1. Overview of the different relaxation pathways of mCP in the excited state. [1]

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Rate constants of carbon nanotube-based biosensors measured in single molecule fluorescence experiments

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Functionalized single walled carbon nanotubes (SWCNTs) are powerful biosensors for small molecules. Analyte binding alters their near infrared (NIR) fluorescence emission reversibly. Dissociations constants (K_d) of such sensors can be derived from ensemble fluorescence spectra at different concentrations. However, the rate constants are too fast to measure them in solution. The challenge of measuring very fast on- or off-rates can be addressed by single nanosensor experiments in the single molecule regime (< 1 nM) to avoid convolution by flow as with stopped flow or microfluidic methods. Here, we measure and report for the first time the rate constant of DNA modified SWCNT-based sensors for the important neurotransmitter dopamine using single nanosensor / single molecule measurements.

For this purpose we image monochiral (6,5)-SWCNTs nanosensors immobilized on glass surfaces and excite them at 561 nm to detect their NIR fluorescence emission at 980 nm. Single molecule traces show association and dissociation events of the analyte (dopamine), which enables measuring of rate constants (k_{off}) by analyzing the dwell times and identifying on (τ_{off}) and off (τ_{off}). Together with the equilibrium, K_d values k_{on} rates can be derived. We compare the rate constants for different DNA modifications of the SWCNT and find differences that can be exploited for selective sensing and bioimaging. Additionally, we show how differences in rate constants can be used to increase the ‘kinetic selectivity’ beyond ensemble properties.

In summary, we demonstrate single nanosensor single molecule measurements and report for the first time their rate constants.

Ultrafast Formation of Metallo-Nitrenes

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Nitrenes have shown great potential as nitrogen-transfer reagents, owing to their high reactivity. For the same reason they are often found only as transient species and have to be prepared in-situ. [1] Therefore, to utilize their synthetic potential to the fullest, a firm understanding of the primary processes leading up to their formation is crucial.

Recently, the reaction pathway of nitrene-formation, starting from metal azide complexes via N_2-cleavage, has been elucidated in our lab for a pincer-type platinum azide complex using ultrafast transient spectroscopy. [2] This revealed a curious bent azide diradical, preceding the expulsion of dinitrogen.

Herein, a set of square-planar diazide complexes[3], $[M(N_3)_2(dppe)]$ (dppe=1,2-Bis(diphenylphosphino)ethan, M=Ni, Pd, Pt) was studied using ultrafast UV-pump-mIR-probe and time-resolved FTIR-spectroscopy.

For all complexes nitrene formation is observed, with an increase of the quantum yield dependent on the mass of the metal. Additionally an intermediate triplet state preceding the nitrene formation could be identified.

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Insights into spectral and dynamical properties of multiexcitons and the role of surface traps in semiconductor nanorods

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Absorption of multiple photons by a single semiconductor nanocrystal moiety leads to the formation of multiexcitons. The multiexcitons are not merely an exotic property of these materials but is of practical relevance for applications such as in nanocrystals-based lasers and light-emitting diodes at high brightness or are very attractive for light-harvesting applications with potential to increase solar conversion efficiencies in solar cells or light-driven catalytic applications. However, multiexcitons are short-lived due to fast Auger recombination, which is detrimental for their potential usages. To gain control over the fast relaxation dynamics, it is crucial to understand Auger recombination in nanocrystalline systems and the impact of structural parameters as size, shape or surface functionalization.

Transient absorption (TA) spectroscopy allows to follow Auger process in nanocrystals. In the established approaches changes in decay dynamics of bleach signatures of the excitonic transitions with increasing pump fluence are evaluated to extract information on Auger recombination of high-order excitons. However, this evaluation does not allow to discriminate the order of the excitonic state and additionally is complicated in case of trapping and formation of surface excitons in nanocrystals, which can result in similar short-time scale decay contributions. In this contribution we describe an approach to discriminate higher-order multiple excitons and explore the role of surface excitons in the process of multiexciton decay. We developed a strategy to extract characteristic spectral signatures for mutliexcitons of different order and to follow their decay pathways by applying the Markov Chain Monte Carlo methods on fluence dependent TA of CdSe@CdS nanocrystals with varying surface functionalization. We observe that biexciton decay forms a mono-exciton state different than the mono-exciton formed directly by photon absorption, which can be assigned to the formation of surface localized exciton state.

Acknowledgement: This work is supported by Walter Benjamin fellowship from German Research Foundation (DFG)—project number 2117104.

Temperature-dependent OH Radical Reaction Kinetics with Amino Acids in the Aqueous Phase

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Amino acids from diverse natural sources are known to be produced in the upper layer of the ocean, the sea-surface microlayer. [1][2] In the aqueous phase, amino acids can react with the hydroxyl radical (OH), one of the most reactive radicals in the atmosphere. Therefore, the study of the kinetics of amino acid oxidation is relevant for gaining deeper insights into their degradation mechanisms and assessing their environmental impact, particularly in relation to marine biological activity. Temperature-dependent studies of the reactivity of OH with alanine, glycine, serine, asparagine, valine, iso-leucine, and threonine have been performed with a laser flash photolysis - long path laser absorption (LFP - LPLA) setup to investigate second order rate constants and the parameters of activation using the competition kinetics method. The measurements have been carried out at 278 K, 288 K, 298 K, 308 K, and 318 K taking into account the average temperatures of water in the surface of the ocean. The determined rate constants at 298 K are $(2.5 \pm 0.1) \times 10^8$ M^{-1} s^{-1}, $(3.5 \pm 0.2) \times 10^8$ M^{-1} s^{-1}, $(8.7 \pm 0.4) \times 10^8$ M^{-1} s^{-1}, $(9.7 \pm 0.3) \times 10^8$ M^{-1} s^{-1}, $(1.3 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, $(1.4 \pm 0.1) \times 10^9$ M^{-1} s^{-1} and $(1.5 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, respectively. They have been investigated at pH = 9, which represents the basic marine environment. These measurements aim to provide a set of kinetic data to describe the aqueous oxidation processes of organic matter in the surface of the sea.

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Photocatalysis at the surface the TiO_2 on its real time

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An acute understanding of photocatalytic reaction dynamics on metal oxides is crucial for the efficient development of technology used for self-cleaning surfaces and for air and water purification. By utilizing femtosecond X-ray laser pulses synchronized with an optical laser (1.6 eV) at FLASH in Hamburg we were able to directly follow the reaction dynamics during photocatalysis at the surface of anatase $TiO_2(101)$ for different prototypical systems; $CO/O_2/TiO_2$ and H_2O/TiO_2. This technique allowed us to monitor the dynamics of reaction product formation with high chemical sensitivity and in real ultrafast time scale. The femtosecond resolution soft X-ray photoemission spectroscopy results are combined with theoretical calculations to provide crucial insight concerning reaction mechanisms and dynamics. Furthermore, the observation of subtle transient core level shifts provides information on interfacial charge transfer during the initial steps of the reaction immediately following the formation of the photogenerated charge carriers [1,2].

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Exploring the photophysics and chemistry of triarylamine with regard to the applicability in photocatalysis

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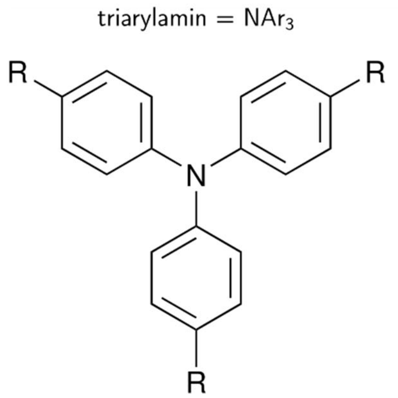
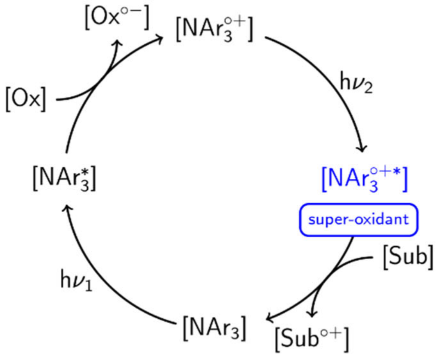
Triarylamines Ar_3N generally can undergo a reversible one-electron oxidation, allowing the formation of the stable radical cation ($Ar_3N^{\circ+}$). This makes them particularly attractive for photocatalytic oxidations of substrates with extremely high oxidation potentials *via* oxidative consecutive photoinduced electron transfer (con-PET) accumulating two photons of light.[1]





Since electrochemically formed $Ph_3N^{\circ+}$ undergoes dimerization,[2] we characterize the photophysics and photochemistry of Ph_3N in the presence and absence of molecular oxygen *via* transient absorption from fs to ms in the UV-visible spectral range exploring the potential *in situ* formation of $Ph_3N^{\circ+}$ by a diffusion-controlled reaction with molecular oxygen. Following excitation of Ph_3N and formation of the excited singlet state efficient intersystem crossing leads to the biradical triplet state, which turns out to undergo a ring closure reaction either mediated by molecular oxygen or by bimolecular reaction of two intermediates. In the latter case, two different ring closure products are formed, one of which undergoes a further H-atom rearrangement.

Approaches to overcome the photoinstability of Ph_3N by concrete structural modifications for applications of photocatalytic con-PET type will be discussed.

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Simulated Annealing for exploring minimum energy structure and dynamics: CO on NaCl surface

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The interaction of CO with an NaCl (100) surface has been a subject of intrigue for over a century. The potential energy surface (PES) of CO/NaCl has been extensively explored for decades. Experimental techniques like polarization IR spectroscopy and helium atom scattering have provided insights into the structure of a monolayer of CO on NaCl (100) surface. However, the scenario becomes more complex and less understood when this monolayer is buried under 100 layers of α-CO. We recently observed that isomerization occurs through resonance enhanced tunneling in this buried CO monolayer system [1].

Simulated Annealing (SA) is a probabilistic technique for approximating the global optimum of a system [2]. We used SA to explore the PES of CO/NaCl and to determine the minimum energy structure for both a bare monolayer and a buried monolayer, as well as the minimum energy path for isomerization.

Our findings reveal that the imposition of the α-CO overlayer on the monolayer acts as a template, compelling the monolayer to alter its prior structure. Our work corroborates the hypothesis that the α-CO overlayer increases the barrier height for isomerization, aligning with assumptions made previously.

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Blackbody Infrared Radiative Dissociation and Master Equation Modelling of Hydrated Anions

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Ambient blackbody radiation leads to dissociation of molecular clusters being stored under ultra-high vacuum conditions via vibrational excitation. The underlying process is known as blackbody infrared radiative dissociation (BIRD). BIRD rates can be measured in a temperature-controlled Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS). Master Equation Modelling is used to simulate the BIRD process and predict temperature dependent dissociation rates for given dissociation energies. Comparison of MEM theory and experimental results allows to determine ligand binding energies of molecular clusters.

Water clusters often have several low-lying isomers. Relatively weak hydrogen bonds frequently break and form new in different structures already at moderate internal energies. Therefore, water clusters are difficult to be described by a classical MEM approach using only the lowest energy isomer. We modified the standard master equation modeling to account for multiple isomers in the simulation.

The multi-well approach can improve the accuracy of determined binding energies by fitting the model to the experimental data. The method was introduced looking at $CO_3^{\bullet-}(H_2O)_{1,2}$ clusters.[1] Recently, the BIRD-MEM approach was used to determine binding energies of $CO_4^{\bullet-}(H_2O)_{1,2}$ and $O_2^{\bullet-}(H_2O)_{1\text{-}7}$.

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Oleic Acid Derivatives at the Air/Water Interface: Isomer-Specific Reactivity Trends in Monolayer Ozonolysis

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The air/water interface plays a crucial role in the context of atmospheric chemistry and climate regulation. The sea surface microlayer (SML), the uppermost thin layer of the ocean water column, serves as a dynamic interface where exchange of energy and matter between the atmosphere and the underlying seawater takes place. Moreover, the SML is characterized by accumulation of organic matter, leading to intensified chemical transformations. Although it is generally assumed that the formation and emission of volatile organic compounds (VOC) to the atmosphere is dominated by biotic processes, it has been shown more recently that abiotic photochemistry and ozonolysis may in fact contribute to the VOC pool to a comparable extent.

As a model system for organic monolayer reactivity, this study investigates the ozonolysis of mono-unsaturated *trans*-fatty acids, specifically oleic acid derivatives with altered double bond positions (6, 9, 11) in the alkyl chain. Building upon previous research on their *cis*-isomer counterparts, we employ Langmuir through measurements coupled with time-resolved vibrational sum frequency generation spectroscopy to monitor the surface concentration changes of fatty acids throughout the reaction. Additionally, molecular dynamic simulations were conducted to get further insight into the molecular structures and local ozone availability that determine the experimentally measured trends of the surface rate constants.

Using the same initial surface concentrations, our findings reveal a notable increase in reactivity with an increasing distance between the double bond and the carboxylic acid group (corresponding to a reduced distance to the gas phase). Additionally, our results indicate a higher reactivity of the *cis*-isomer compared to the *trans*-isomer. This intriguing observation suggests potential structural order effects within the distinct monolayers.

Spectroscopy

Advancements in Ultra-Short Pulsed Atomic Beams for Surface Science Experiments

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In surface science, the utilization of pulsed molecular or atomic beams is a commonly used practice, particularly in their role as pump pulses within pump–probe experiments However, the pulse duration of molecular beams is constrained to 10 - 100 µs due to the mechanical response of pulsed valves and chopper wheels. Even the photolysis of precursor molecules yields atomic beams with a pulse duration of only a few hundred ns, limited by factors such as photolysis pulse duration and volume, laser bandwidth, and experimental geometry. To address this limitation of conventional photolysis, the method of bunch compression photolysis has been introduced.[1] By employing spatially chirped femtosecond UV laser pulses for hydrogen iodide photolysis, an ensemble of H atom photoproducts is created, rebunching into a short pulse at a fixed point in space and resulting in atomic pulses shorter than 1 ns.

In a recent report [2], it was highlighted that a pulsed H atom beam with a duration of 700 ps can be generated. Additionally, due to the sufficient intensity of the H atom pulses, angle- and velocity-resolved H atom scattering experiments were conducted on epitaxial graphene grown on Ir(111). The findings revealed a surprisingly narrow angular distribution when H atoms were incident normal to the surface. The experiments observed a strongly inelastic scattering channel at high incidence energy, with quasi-elastic scattering dominating at low incidence energies.

This marks a successful implementation of ultra-short H atom pulses in surface scattering experiments.

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Gas phase investigations on the redox-active complex $[Mn(dgpy)_2]^{n+}$

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Transition metal complexes can often be stabilized in different oxidation states. Therefore, they can fulfill various roles in applications, like oxidative or reductive agent in chemical reactions, model complex for an enzyme or as catalyst.[1-3] Usually, changes in oxidation state are accompanied by geometrical reorganization of the ligand sphere. A class of complexes that does preserve its geometry during redox processes is synthesized in the group of Katja Heinze and of the type $[M(dgpy)_2]^{n+}$ (M = transition metal; n = 1-4, dgpy = 2,6-diguanidylpyridine). The ability to preserve the complexes geometry is achieved by using this specific push-pull ligand (dgpy). These complexes also show interesting optical properties like panchromatic absorption or an increase of its oxidative potential after electronic excitation.[4-7]

In this work, we present our results on gas phase investigations on the complex of the type $[Mn(dgpy)_2]^{n+}$ (n = 1-4). The measurements were carried out with modified 3D Paul trap instruments (amazon Speed and amaZon ETD, Bruker Daltonics). Ions were transferred into the gas phase by Electrospray Ionization (ESI). The mass spectrometer was extended by a self-built gas mixing device to introduce neutral molecules into the ion trap, inspired by the work of K. Koszinowski et al.[8] and J. Oomens et al.[9]. All experiments were carried out under multi-collision conditions regarding the He used as buffer gas for operation of the ion trap. With this experimental setup we were able to investigate relative gas phase stabilities, absorption spectra and reactivity of the complex species observed after ESI process or after reduction via electron transfer.

Six complex species could be obtained and analyzed with our set of methods. UVPD and gas phase reactivity are of special interest, due to the already described optical properties and oxidative potential of the complexes in condensed phase.

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Spectroscopic Investigation of Charge Carrier Dynamics in Water Soluble Poly (heptazine imide) Photocatalysts

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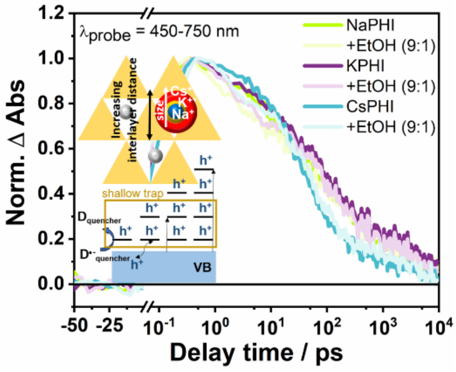
Polymeric carbon nitrides (PCNs) have attracted worldwide attention in the field of catalysis **[1-2]**. Recently, a novel family of PCNs termed as “ionic carbon nitride” has emerged out which comprises stacks of 2D negatively charged poly (heptazine imide) (PHI)-based networks and positively charged alkali metal cations and exhibit superior photocatalytic performances **[3]**. In this work, an in-depth study of photophysical processes of a series of PHI materials prepared by alkali hydroxide-assisted co-thermal condensation with melamine have been presented **[4]**. The decay kinetics suggests geminate recombination of electrons and holes within ~100 ps, followed by trap-assisted recombination. Presence of ethanol as a sacrificial electron donor accelerated the decay of the transient absorption (TA) signal only within ~100 ps in case of NaPHI and KPHI, which can be ascribed to the faster charge recombination in the presence of the radical anions generated after hole extraction. This suggests that photo-driven electron storage in the PHIs is enabled by localized trap states. However, the effect of accelerated decay in presence of ethanol is negligible for CsPHI, probably due to absence of shallow traps to be quenched. TA anisotropy (TAA) kinetics study suggests fast geminate electron-hole recombination in the sub-100 ps, while the considerable loss of TAA on a sub-ns timescale is due to trap-assisted recombination corresponding to interlayer charge hopping of PHIs **[5]**. Thereby, the work highlights the importance of effective electron donor for long-lived photogenerated CN radicals and provides insights into fast charge transfer processes in PHIs.



Acknowledgement

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Solvation Shell Water around Citrate-stabilised Gold Nanoparticle

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The factors affecting gold nanoparticles (Au NPs) mediated reactions have been extensively studied in aqueous and other media. However, it's worth remembering that the solvent and the reactant molecules do play a role in dictating the outcome of a reaction. We turn our attention to the water molecules in close proximity to citrate-stabilised Au NPs.

We use Raman and infrared spectroscopies and obtain the solvation shell water response for three different sizes of Au NPs by employing vibrational solvation shell spectroscopy. [1] The Raman solvation shell spectra were recovered from data collected using two different excitation sources. The ones retrieved from the spectra measured with 514.5 nm laser excitation display signs of weaker H-bonding in solvation shell than in bulk water, in stark contrast with the Raman solvation shell spectra under 632.8 nm laser excitation and the infrared solvation shell spectra, both of which show signs of stronger H-bonding in solvation shell than in bulk water. We hypothesise this difference to be caused by differing depths of surrounding water being probed by the different methods. Nanoscale optical finite element simulations were employed to test this hypothesis. The probing depth difference would corroborate that the water molecules that are closest to the citrate-capped Au NPs, experience a depletion in the extent of H-bonding whereas the water layers slightly away (but still in the solvation sphere of each individual NP) experience a strengthening of H-bonding network, compared to the H-bonding in bulk water.

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Hydrogen bonding in ionic liquids probed by ^{1}H and ^{19}F fast-field-cycling NMR relaxometry

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Due to its central role in influencing the thermodynamical, structural and dynamical properties in ionic liquids, there is a strong scientific interest in a detailed description of hydrogen bonding in this substance class.[1] We studied two different ionic liquids: Firstly, triethylammonum bis(trifluoromethylsulfonyl)imide ($[N_{222H}][NTf_2]$), which is known for the formation of strong hydrogen bonds between cations and anions and secondly the phosphonium analogue triethylphosphonium bis(trifluoromethylsulfonyl)imide ($[P_{222H}][NTf_2]$), forming comparatively weaker hydrogen bonds. Structurally these two ionic liquids differ only slightly in the central atom of the cation. However, the dynamical properties are strongly affected by the different hydrogen bond strength. In this work we measured frequency- and temperature-dependent ^{1}H and ^{19}F relaxation rates by using fast-field-cycling NMR relaxometry (FFC NMR), which provides access to translational and rotational correlation times as well as self-diffusion coefficients. Since the protons are only located on the cations and the fluorine nuclei only on the anion we obtain these properties ion-specific. Molecular dynamics (MD) simulations are used to validate our results. Both approaches, FFC NMR and MD simulations, show higher rotational correlation times and lower self-diffusion coefficients for $[N_{222H}][NTf_2]$ indicating a stronger hydrogen bond.

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Modifying the Electronic Structure of $CsPbBr_3$ Nanocrystals by Ligand Exchange with Cinnamic Acid Derivatives

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Lead halide perovskites (LHP) show unique properties such as an easy modification by anion exchange or the lack of trap states within the band gap. Therefore, they exhibit great prospects for application in LED and photovoltaics. For these applications, it is essential to know the absolute band edge positions, in particular for building efficient devices. A method to study the electronic structure is a combination of photoluminescence spectroscopy and electrochemical techniques which is also referred to as spectroelectrochemistry (SEC).[1,2]

In our work, we aim to tune the electronic structure of $CsPbBr_3$ nanocrystals by altering their surface chemistry. Cinnamic acid has been used as a model molecule for introducing different dipole moments to PbS nanocrystals.[3] Here, we adapt the strategy toward LHPs, and establish ligand exchange protocols to remove the native ligands after hot-injection synthesis by derivatives of cinnamic acid. We proceed with studying the band edge positions by SEC of such newly functionalized LHPs to assess their suitability for application in LEDs.

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Strong Confinement in Colloidal Flat PbSe Quantum Dots: New Optical and Electronic Properties

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The direct wet-chemical synthesis of two-dimensional (2D) lead chalcogenide semiconductors yields photoluminescent materials with strong excitonic contribution at room temperature. [1,2,3] In the spirit of the recent Nobel prize for the discovery and synthesis of quantum dots (QDs) we report herein on our studies of strongly confined wet-chemically synthesized flat lead selenide (PbSe) QDs. These 2D nanocrystals possess dimensions of e.g. 6 x 5 x 0.8 nm^3 and exhibit PL in the near-infrared region between 860 – 1510 nm with a PL quantum yield of up to 60 %, which is mainly determined by their lateral dimensions. [1,2] Their highly efficient photoluminescence (PL) at fiber-optics-relevant telecommunication wavelengths renders colloidal lead chalcogenide 2D semiconductors intriguing materials for future solution-processable optics.

Scanning tunnelling spectroscopy of single PbSe NCs reveals a conduction and valence band density of states that is typical for QDs rather than a steplike function linked to 2D nanoplatelets and substantiates the strong confinement in the flat PbSe QDs.

Our results paint a comprehensive picture of the optical and electronic properties of near-infrared active 2D PbSe QDs.

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Space- and Time-Resolved Mapping of the Exciton Diffusion in Nanostructured Organic-Inorganic Perovskites

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Metal halide perovskites are promising light-harvesting components for future optoelectronic applications such as solar cells, light-emitting diodes, and photodetectors.[1,2] The applicability of such devices is subject to the bound electron-hole pair (exciton) properties. In addition to the exciton generation and decay, one should also understand their transport and diffusion behaviour.

The examined nanostructured organic-inorganic perovskites are provided by colloidal synthesis, leading to a high defect tolerance and tuneable optical properties. Additionally, it enables a shape and size control of the structures, allowing the growth of nanostripes, nanosheets and nanoplatelets.[3] This reduced dimensionality and changed crystal structure influences the exciton dynamics and needs to be understood in terms of their applicability as optoelectronic devices.

An expanded confocal fluorescence-lifetime imaging microscope (FLIM) visualizes exciton migration under ambient conditions. The separation of excitation and detection path enables a time- and space-resolved mapping of the excitons. This technique gives an insight into the exciton dynamics like the type of diffusion, the diffusion path, and the diffusion length.

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Transient broadband circular dichroism and circularly polarized luminescence of copolymer films with supramolecular chirality

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Over the last few years we have developed an experimental approach to record simultaneously the transient absorption (TA) and transient circular dichroism (TrCD) response of photoexcited systems over the ultraviolet–visible spectral range (260–700 nm) with a time resolution of 100 fs (Fig. 1). [1,2,3] In particular, giant CD signals from chiral polyfluorene copolymer thin films with intrinsic [1,3] and induced [2] supramolecular chirality made it easy to detect the generally very weak TrCD responses and allowed us to further optimize the TrCD spectroscopy techniques. In this presentation we would also like to show our recent steady-state and transient circular polarized luminescence spectroscopy (CPL) studies on these systems and in particular the experimental parameters that influence the CPL response.

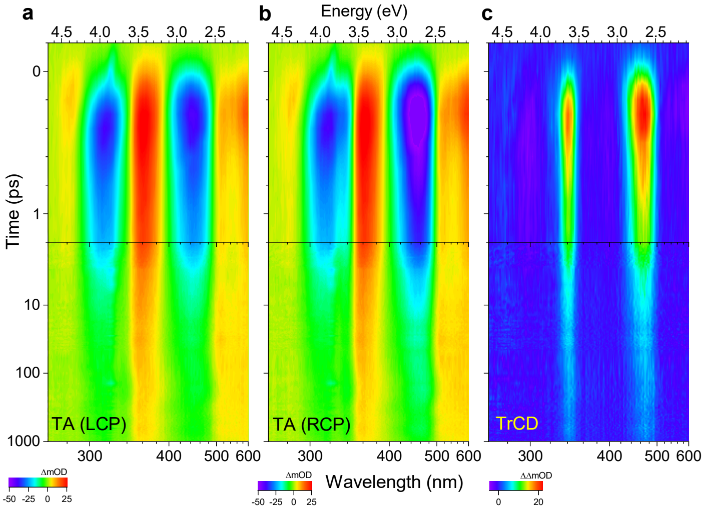

Fig 1. Contour diagrams of ultrafast TA and TrCD spectra of a thin *c*-PFBT film after excitation at 320 nm. (a) TA for probing with left-circularly polarized light. (b) TA for probing with right-circularly polarized light. (c) TrCD (difference of the contour diagrams shown in panels a and b). [1]

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Ultra-fast laser absorption spectroscopy for dynamic measurements

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Laser absorption spectroscopy (LAS) can provide high-bandwidth, species-specific, *in situ* measurements of thermodynamic conditions and a wide range of molecular species. It has been well-established and developed for air pollution monitoring, agricultural, industrial, and automotive emissions detection, and thermochemistry diagnostics. For some specific conditions with time scales less than milliseconds, *e.g.*, reaction kinetic studies, and planetary entry conditions, ultra-fast measurement systems are required to capture the parameters during the dynamic processes.

In this study, dynamic processes with time scales of a few hundred microseconds to several milliseconds were generated by a shock tube. Coupled with this facility, two ultra-fast LAS spectrometers were developed based on a continuous wave (CW) QCL at 9.2 µm and an intrapulse QCL laser at 5.2 µm, covering the frequency from 140 Hz to 900 kHz. The CW-QCL based spectrometer was tested in three different running modes (140 Hz, 10 kHz and 40 kHz) according to PTB optical gas standard to provide traceable results of NH_3 line parameters and absolute NH_3 mole fraction during dynamic processes. The intrapulse QCL laser-based spectrometer ran at an ultra-fast repetition rate of 900 kHz with a pulse width of 200 ns, was used for simultaneously measuring gas phase NO, H_2O mole fraction, and the dynamic temperature. Overall, we validated different ultra-fast LAS techniques for dynamic parameter measurements such as species mole fraction and temperature, which can be used in different application scenarios as mentioned above.

High-Resolution Photoelectron Spectroscopy of NO_3^- Excited via the ν_3 Fundamental and $2\nu_3$ Overtone

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The nitrate radical (NO_3) was one of the first radicals to be spectroscopically detected and plays an important role in the night-time chemistry of the atmosphere [1,2]. Despite the small size, the spectroscopy of ground state NO_3 is complicated by vibronic coupling with the $\tilde{B}\ ^2E'$ excited electronic state. As a result of this coupling, it was proposed that the antisymmetric N-O stretching vibration (ν_3) has a vanishingly small infrared intensity that is significantly lower than one of its combination bands ($\nu_3 + \nu_4$) [2]. This idea has caused a long-lasting debate about whether the ν_3 fundamental frequency is located near 1050 cm^{-1}, as predicted by the vibronic coupling models, or close to 1490 cm^{-1}, where a strong infrared transition was initially observed in 1985 [3]. While recent findings provide increasing support for a ν_3 frequency near 1050 cm^{-1} [4], this assignment is still not universally accepted.

Here, we employ high-resolution photoelectron spectroscopy of vibrationally excited anions to provide direct experimental evidence that the ν_3 fundamental frequency is located at 1051±3 cm^{-1}. Using this recently developed technique, termed IR-cryo-SEVI [5,6], cryogenically cooled NO_3^- anions are vibrationally excited via the infrared-active ν_3 fundamental or $2\nu_3$ overtone with an infrared laser before photodetachment. This selective vibrational pre-excitation allows us to observe strong photodetachment transitions into vibrational levels of neutral NO_3 that involve ν_3 excitation, most importantly the fundamental ν_3 level. The findings are further supported by spectral simulations using the vibronic coupling model mentioned above.

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Probing electronic structure of aqueous organic solutes with UV droplet photoelectron spectroscopy

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A large part of chemistry, particularly atmospheric and biochemistry, occurs in aqueous environments. To understand the chemistry and photoresponse of aqueous organic solutes, insight into their electronic structure and photodynamics is vital, and the most direct way to probe it is UV photoelectron spectroscopy (PES). [1] Conventional aqueous-phase PES is performed using liquid microjets (LJs) coupled to magnetic-bottle spectrometers. However, LJ-PES has uncertainties in the LJ streaming potential, vacuum level offsets, and the instrument function for low kinetic energies. [2] Here, we demonstrate that UV photoelectron velocity-map imaging (VMI) of aqueous submicrometre droplets is a potent complementary means for probing the aqueous-phase electronic structure of organic molecules. [3] VMI provides the photoelectron angular distribution, allowing for better insight into the scattering behaviour of low kinetic energy (< 5 eV) electrons in water. Phenol, a common moiety in photoactive protein chromophores and previously measured in LJs, is investigated as a proxy organic solute. We used Monte Carlo simulations of electron-transport scattering to retrieve the original photoelectron band shape without distortions from inelastic scattering. [4] In agreement with the value from X-ray LJ-PES, we report a vertical binding energy of phenol in aqueous droplets of 7.8 ± 0.1 eV. [5] Additionally, we discuss how light confinement, probing depth, and the timescale of phenol's relaxation dynamics following photoexcitation to its $S_1/1\pi\pi^*$ state differ in droplets compared to LJs.

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Determination of the Molar Fraction and Enantiomeric Excess Using Photoelectron Circular Dichroism of Electrosprayed Anions

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We present a new method for the determination of the molar fraction and the enantiomeric excess in mixtures of chiral molecules, which is applicable to large molecules of biochemical interest. The approach is based on the methodology of photoelectron circular dichroism (PECD) measured in the photodetachment from electrosprayed anions reported earlier.[1] The examination of the circular dichroism of anions has received a lot of attention in the last few years stimulated by the investigation of the PECD and the photoion circular dichroism (PICD) of anions. [1,2,3,4]

The electrospray setup employed opens the possibility to investigate analytes that are usually not easy to ionize or have a low vapor pressure, preventing the investigation of the PECD through photoionization of neutrals. Furthermore the PECD in the photodetachment of anions has the advantage of being a one-photon process, therefore not requiring intense laser fields.

In a first step of the experiment we have demonstrated the possibility to distinguish D- and L-tryptophan by photodetachment from the corresponding anions. The PECD values were on the order of ±5% at 234 nm for the dimeric-monoanion of tryptophan.

In a second step the quantification of the molar fraction and enantiomeric excess (e.e.) was accomplished using that PECD analysis. The measured PECD value scaled linearly with the molar fraction of the enantiomers and the molar fraction of a measured test sample lies within the margin of error of our analysis. The fact that the e.e. analysis can successfully be performed on the dimer anion suggests that either LL and DD interactions dominate and/or the PECD of a LD dimer is zero. The possibility to investigate the PECD of mass selected anions represents an advantage compared to absorption circular dichroism spectroscopy, which measures the circular dichroism of all species present in a mixture or needs an additional chromatographical separation step.[5,6]

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2,9-Dimethyl-1,10-phenanthroline Ligands and Cu(I) Complexes with Polycyclic Aromatic Hydrocarbons: The Point of no Return for the Excited State

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2,9-Dimethyl-1,10-phenanthroline (**dmp**) is a common starting ligand in photocatalytic applications *e.g.* proton reduction.[1] Many studies focus on tuning of the **dmp** system *e.g.* with additional chromophores like pyrene to enhance various photophysical properties such as visible attenuation coefficients $\varepsilon(\lambda_{\mathrm{abs}})$ or excited-state lifetimes τ_{em}.[2,3] This study focuses on the photophysical impact of attaching well-known polycyclic aromatic hydrocarbons in the 4,7-positions of **dmp**. The introduced hydrocarbons are phenanthrene (**P**), 9,9-dimethyl-9*H*-fluorene (**F**) and anthracene (**A**). The phenyl-substituted variant **bcp** is also included. Photophysical properties of the ligands and Cu(I) complexes are significantly improved by the substitution. However, the anthracene species strongly deviates from other systems as it is suspected that the excited state migrates from **dmp** to anthracene. This finding is explained through a hybrid approach of TDDFT computations and a comprehensive comparison of steady-state and time-resolved spectroscopy.

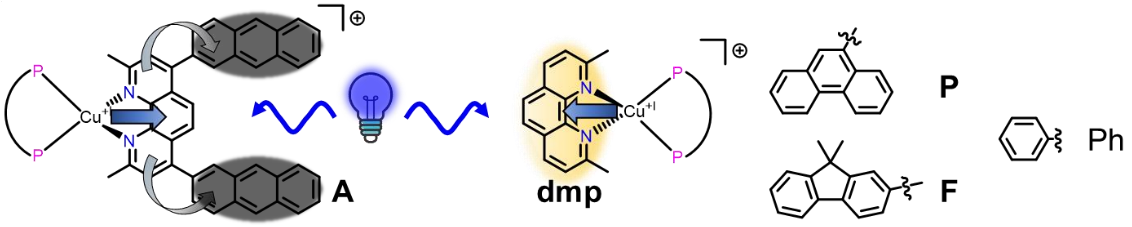

Figure 1: Excitation of Cu(I) complexes with different excited-state decay pathways.

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Unraveling the photochemistry of $Ti^{IV}Cp_2(NCS)_2$

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Titanium-based complexes are a highly intriguing building block for catalytic transformations due to their facile electron transfer capabilities, Ti being one of the most abundant elements, and being non-toxic.[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[2] or with photoredox co-catalysts[3]. The catalysis was lately improved by exclusively using the Ti^{IV}/Ti^{III} couple as an ideal green photoredox catalyst[4].

Recently, we reported the observation of the entry event of $Ti^{IV}Cp_2(NCS)_2$ into a photocatalytic cycle in real-time.[5] In this study we were able to show the thermally activated delayed fluorescence of $Ti^{IV}Cp_2(NCS)_2$ after excitation with 450 nm light. Furthermore, we were able to observe the reductive quenching of the reactive triplet state with NPh_3 as an electron donor using time-resolved spectroscopy.

In a further step, we now want to investigate the following steps in the catalytic cycle. Therefore, we employ a substrate that acts as the amine electron donor to reduce the titanocene as well as the epoxide for radical arylation. To achieve this goal, we will utilize the long pump-probe delays of up to 300 μs of our synchronized double Ti:Sapphire regenerative amplifier setup for fs-UV/Vis-pump/mIR-probe spectroscopy. To aid the analysis of the spectroscopic findings, we will employ density functional theory as well as cooperate with synthetic chemists. From these experiments, we hope to gain further insight into the later mechanism of the photocatalytic cycle as it is still unclear if one or two equivalents of the substrate are involved.

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Photoactive Electrospun Nanofibers as Materials for Light-driven Catalysis

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Abstract

Our significant reliance on fossil fuels as a main energy source can be reduced by using hydrogen, a clean and sustainable fuel. Artificial photosynthetic systems that are capable of recycling the catalyst in addition to producing clean hydrogen are needed for this progress [1–3]. Here, we demonstrate the integration of molecular photosensitizers (PS)($[Ru(bpy)_3]^{2+}$) and hydrogen evolution reaction catalyst (CAT) (polyoxometalate ($(nBu_4N)_7K_3[P_2W_{18}O_{62}]$)) during electrospinning into polymeric nanofibers (polyacrylonitrile (PAN)) to create photoactive fibers.

To investigate the impact of immobilization on the charge transfer rate between PS and CAT, transient (fs/ns) absorption and emission studies were done. The decay dynamics of the excited carrier at different catalyst concentrations is also presented. When compared to the solution, the fiber sample exhibits a blue shift in emission and a red shift in steady-state absorption. The fsTA data revealed long-lived excited carriers with a tri-exponential decay profile. The transient emission showed a quenching of emission intensity for samples with a higher concentration of POM which is due to electron transfer to the catalyst. The recombination time from the radiative ^{3}MLCT state was found to be around 1.4 µs. This research will contribute to the understanding of charge transport in heterogeneous systems based on nanofibers.

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Periodic calculations of vibrational circular dichroism: How are they supposed to work?

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Chiroptical spectroscopy provides an increasingly important, cost-effective alternative for the study of chiral substances in the solid state. In recent years, vibrational circular dichroism (VCD) – the chiral form of IR absorption spectroscopy – has come into focus as a very sensitive probe of molecular conformation and environment. VCD differs from electronic circular dichroism in that it relates directly to vibrational transitions in the supramolecular chiral framework, such as functional groups connected by covalent or non-covalent interactions. Solid-state VCD thus proves to be highly susceptible to the enantiomorphism of molecular crystals and can also be deployed to study polymorphic forms. [1]

The interpretation of VCD spectra requires accurate calculations that yield the magnetic response of the electronic structure bound to nuclear motion (i.e., the vibrations). For solids, this has long been considered infeasible due to the periodic boundaries imposed by the crystal structure. [2]

We show that it is possible to formulate VCD with an explicit account for periodicity. Separating the molecular from the supramolecular chirality, we identify unique non-local patterns that can be attributed to chiral crystal packing and space group symmetry. [1-4]

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Unravelling the OH stretch spectrum of formic acid

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Recent combined multi-experimental and theoretical vibrational spectroscopic efforts have tremendously contributed to and extended our understanding of the internal dynamics of formic acid (HCOOH), the smallest carboxylic acid [1]. One important result is that the well-known v_5-$2v_9$ OH bend-torsion Fermi resonance plays a far more important role than previously believed [2]. The OH stretch has long been known to be strongly perturbed by several resonances, leading to a significant intensity redistribution. However, the analysis of its rotationally-resolved spectrum was achieved only as recently as 2023 [3], almost two decades after its first measurement [4]. Using high-level full-dimensional perturbative (Canonical Van Vleck) and variational (GENIUSH-Smolyak) vibrational models in combination with full-dimensional potential energy and property surfaces, it is found that the perturbers belong to a large network of coupled vibrational states that build on the well-known v_5-$2v_9$ Fermi resonance. Many of the observed OH stretch perturbers are highly-excited multi-quantum vibrational states ($n \geq 3$) so that normal mode labels become inadequate to properly label the bands. The question arises of how – if at all – the interaction can be understood in chemical bonding terms which is addressed in light of the underlying OH bend-torsion v_5-$2v_9$ Fermi resonance.

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Of highs and lows: Combining high resolution microwave spectroscopy with low resolution Raman spectroscopy and what we can learn about hydrogen bonding

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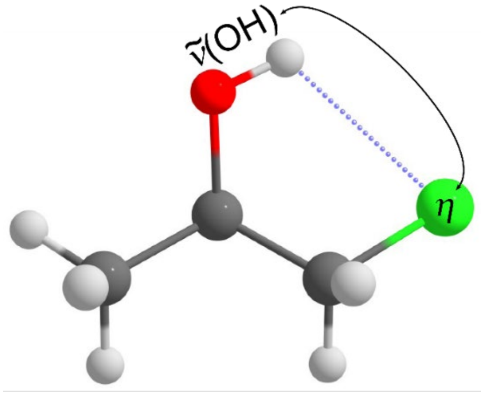
Hydrogen bonding is ubiquitous in nature as it is fundamental in protein folding and DNA helices among others. However, what should be classified as a hydrogen bond is not necessarily clear. One way to commonly judge hydrogen bonds and their strength is the relative downshift of OH stretching frequencies. In fact, this is one criterion of the definition of a hydrogen bond[1]. We attempt to correlate OH stretching frequencies obtained by jet-Raman spectroscopy with the so called asymmetry parameter η, which can be derived from nuclear quadrupole coupling constants obtained with jet microwave spectroscopy. It is sensitive towards the local electronic environment around the quadrupolar nuclei. Hence, η will also change upon the formation of a hydrogen bond towards a quadrupolar nucleus such as chlorine and bromine. By correlating the OH stretching frequencies with η we explored if η can be used to judge the formation and strength of hydrogen bonds. In particular, the intramolecular hydrogen bonds formed in chloro- and bromopropanols[2] as well as 3-X-propane-1,2-diols (X = Cl, Br) have been investigated[3]. Implications for halogen bonding and OD hydrogen bonds (deuterium is quadrupolar) are also discussed.



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The effect of methyl group rotation on ^{1}H-^{1}H solid-state NMR spin-diffusion spectra

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The advent of fast magic-angle spinning (MAS) NMR experiments opens the way for proton-detected NMR studies with a broad range of applications from material science to biomolecules and pharmaceuticals. A recent study [1] reported on the appearance of negative cross peaks in 2D ^{1}H-^{1}H spin-diffusion (SD) based spectra in the solid state, which have been explained by means of higher-order SD effects in which the chemical shifts of the quadruples of nuclei involved must compensate each other.

In this contribution, we discuss the occurrence of negative cross peaks in SD-based spectra observed in a variety of small organic molecules bearing fast-rotating methyl groups. [2] By combining experimental observations with numerical simulations, we have been able to disentangle the occurrence of coherent (third-order SD) and incoherent (cross-relaxation) polarization-transfer pathways contributing to such negative peaks. This contribution sets the stage for a deeper understanding of the origin of negative cross peaks in proton-detected solid-state NMR spectra under fast MAS conditions, opening further avenues for instance in simplified resonance assignment in proteins and organic molecules.

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Surfaces and Interfaces

Resolving the impact of structural defects on the charge carrier transport in (opto)electronics

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Extended structural defects, like grain or domain boundaries in polycrystalline semiconductors, can introduce mid-bandgap trap states, host dopants or lead to electrostatic barriers. The implications of these local defects for charge carriers in materials used for (opto)electronic applications can be manifold: They can act as non-radiative recombination centers, delay or restrict the charge transport or, in some cases, improve the transport properties though a change in doping.

Here, we will discuss how electrical and electromechanical atomic force microscopy (AFM) in combination with complimentary techniques can not only resolve extended defects, but also capture their electronic or (electro)mechanical properties and relate these defects to local changes in charge carrier transport. For instance, using electromechanical AFM, we visualized subcrystalline twin domains present in hybrid organic inorganic perovskites that are applied in photovoltaic devices. With the data analysis exacerbated by the mixed ionic and electronic conductivity of hybrid perovskites, we conducted advanced electromechanical AFM to decouple mechanical and electrostatic crosstalk, which finally revealed the ferroelastic nature of the domains. Correlating to spatial- and time-resolved photoluminescence suggest that the domain walls as extended structural defects delay the charge carrier diffusion by acting as electrostatic barriers.[1] However, the possibility to tailor the arrangement and density of these ferroelastic domains allows engineering a directional charge transport and improved device performance.[2]

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Charge Transfer in Ternary Quantum Dot Sensitized TiO_2 for Photocatalysis Studied by Ambient Pressure Time-Resolved XPS

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Photocatalytic water splitting could serve as an environmentally friendly and low-cost means of hydrogen fuel production [1]. Wide band gap transition metal oxide semiconductors such as TiO_2 are promising candidates for photocatalysts. However, due to the large band gap of 3.2 eV, the absorption of TiO_2 is limited to the UV spectrum, and sensitizing agents, e.g., semiconductor quantum dots (QD) have to be used [2]. The QD can be tuned to absorb visible light [3] before the excited electrons are transferred into the conduction band of TiO_2 enabling the photocatalytic reaction [4]. In order to improve the performance of quantum dot sensitized TiO_2 photocatalysts, a detailed understanding of the electron transfer process and the associated chemical dynamics is needed.

To get an insight into the interfacial electron transfer process, ternary AgInS quantum dots were synthesized, drop-coated on nanoporous TiO_2 substrates, and studied with ultrafast, site-specific, picosecond time-resolved X-ray photoelectron spectroscopy (tr-XPS) at the ALS beamline 11.0.2 [5]. The observed core level shifts show the initial ultrafast charge separation and the following slower recombination dynamics in the picosecond domain. Ambient pressure measurements in a water atmosphere (5-70 mTorr) showed slower relaxation dynamics than in ultrahigh vacuum, indicating the occurrence of a photocatalytic reaction under measurement conditions.

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Synthesis of dual emitting dot-in-a-rod nanoparticles made from ZnSe/ZnS/CdS via a sequence of cation-exchange reactions

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Semiconducting nanoparticles exhibit numerous interesting properties and have promising characteristics to be used as light-emitters. Quantum dots that emit a single sharp band of color have already been implemented in TV screens. Currently,two kinds of quantum dots are needed for a display. To streamline the production of those screens, the combination of two emitters into one particle is highly desirable.

To achieve this, an approach to use the widely known CdSe/CdS dot-in-a-rod structures as templates to form ZnSe/ZnS/CdS dot-in-a-rod structures is currently in development.The synthesis starts with the growth of CdSe quantum dots, which are then incapsulated into an elongated CdS shell. After that a series of cation-exchange reactions is carried out to convert the CdSe/CdS first to Cu_2Se/Cu_2S and then to ZnSe/ZnS while retaining the hexagonal lattice structure of the original CdSe/CdS particle. The emission wavelength of the new ZnSe/ZnS particles is highly dependent on the dot size and the completeness of the cation exchange: It redshifts the bigger the dot is and the more cadmium ions are left in the lattice.

To implement a second emitter into the same nanoparticle, a partial cation exchange from ZnS to CdS at the tip of the dot-in-a-rod structure can be carried out. This CdS domain shall be used as the second emitter itself or as an anchor to grow a CdSe tip on top of the dot-in a-rod structure. In this way, a rod shape double dot nanostructure can be created.

In the current state of this work the ZnSe/ZnS dot-in-a-rod nanoparticles have been synthesized. The structural characteristics of the ZnSe/ZnS dot-in-a-rod structures were investigated by TEM, HRTEM, XRD and EDX measurements while the optical characteristics were investigated by absorption and photoluminescence measurements. The following step of implementing the second emitter is still work in progress.

Spectroscopic Fingerprints and Reactivity of Oxygen Radicals on MgO Nanocubes: Theory Meets Experiment

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Oxygen radicals such as O_2^- and O_3^- are important species in a wide range of chemical reactions and applications including cell signalling, sensing and catalysis. Here, we investigate their spectral fingerprints and reactivity on MgO nanocubes, combining UV and electron paramagnetic resonance spectroscopy with quantum chemical calculations on cluster models, periodic surfaces and nanocubes of nanometer size. QM:MM approaches are employed in photochemical calculations, sampling different oxygen radicals position (neat surface, defect, edge, corner…).[1] Upon adsorption of O_2 on MgO nanocubes, broad absorption bands form at ~290 and 410 nm; our calculations show that they correspond to O_2^- and O_3^-, respectively (Figure 1). Surprisingly, their position is hardly influenced by the local environment.[2] Upon reaction with water, mainly peroxides are formed.

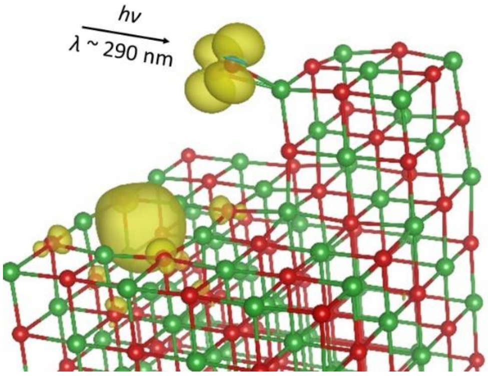

Figure 1 – Model of a superoxide radical, O_2^-, adsorbed on a periodic MgO surface, along with an oxygen vacancy. Spin density is shown in yellow.

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Biological Lipid Hydration: Distinct Mechanisms of Interfacial Water Alignment and Charge Screening for Model Lipid Membranes

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Lipids are the main structural components of biological membranes. The formation of these membranes is mainly driven by the interaction of amphiphilic lipid molecules with the water molecules in the surrounding aqueous phase. In addition to hydrophobic interactions, hydrophilic interactions between the polar headgroups and water play an essential role in membrane formation and function. Indeed, details of the hydrated polar headgroup of the lipid, either zwitterionic or negatively charged in most biological membranes at physiological pH [1,2], are essential for determining membrane properties

In this study we use surface-specific sum-frequency-generation experiments to investigate how model lipids impact water structure and alignment in contact with the monolayer and to what degree the overall charge of a given lipid layer may be screened by charged ions in the aqueous phase

We find that there are two distinct modes through which the lipid structures the water subphase: The first being due to the net charge of the lipid monolayer, and the second due to large dipole fields resulting from zwitterionic headgroups.

While the effect of monolayer surface charge on water orientation is furthermore strongly dependent on the electrolyte concentration, the salinity of the subphase does not impact any dipolar alignment of water molecules.

Notably, the different effects are additive for mixed charged/zwitterionic lipid systems occurring in nature. Specifically, for an E.coli lipid membrane extract, consisting of both zwitterionic and negatively charged lipids, the response of water can be very well approximated by a sum of the separate contributions, despite the system's complexity.

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Interdiffusion of water in waterborne polymer latex films

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Waterborne latex films, obtained from the dispersion of latex particles are of particular interest due to the non-content of volatile organic compounds (VOC), often mandatory under environmental legislation [1]. However, abrupt water penetration inside the films restricting their lifespan and deteriorating the shining of the coating. In order to prepare efficient and solvent-free coatings with the low glass-transition temperature (Tg < the drying temperature) but with higher mechanical strength, we have integrated hydrophilic layers (Acrylic acid/ Poly(acrylamide)) around the hydrophobic cores (mixture of Methyl methacrylate and Butyl acrylate) and also hard shell around the soft core in the latex film. Latex particles with different morphology (hairy layer variants and core-shell particles) have been synthesized using emulsion polymerization [2]. Polymer latex films have been prepared in the next step by evaporating water in a thermo- and humidistatic chamber at temperature 25 ^{o}C. The structure formation of polymer latex films in the dry state (crystallinity) and in re-swelled state (change in crystallinity and whitening or blushing) have been studied to propose a recipe for the preparation of efficient latex coatings. The Small-Angle Neutron Scattering (SANS) study shows the FCC-like structure formation by the latex film, which become more organized with the inclusion of the hydrophilic shell. The hydrophilic shell also promotes the formation of the homogeneously water-swollen film and slows down the development of water "pockets", preventing the deterioration of the latex film over time. On the other hand, the inclusion of hard shell protects the latex films from water whitening and provides additional mechanical strength.

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Studying Molecular Rearrangement of P1 Dye at a Passivating Alumina Surface Using Vibrational Sum-Frequency Generation Spectroscopy: Effect of Atomic-Level Roughness

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This study delves into the intricate relationship between surface roughness and the organization of dye layers in model photoelectrodes with alumina passivation layers. Combining advanced surface sensitive techniques such as Vibrational Sum-Frequency Generation (VSFG) with X-ray Photoelectron Spectroscopy (XPS), and Photoluminescence (PL) measurements, we unveil valuable insights into the molecular ordering, packing density, and electronic states of adsorbed dye monolayers. Our findings show that increasing surface roughness, down to the atomic level, induces disorder in the molecular layer while also leading to higher dye loading.[1] Notably, surface roughness-induced molecular rearrangement profoundly influences the VSFG spectral shape that acts as a signature of molecular orientation and ordering. Furthermore, such altered molecular adsorption/orientation also influences electronic interaction between the surface and the substrate as evidenced by the formation of trapped electronic states resulting from dislocated and tilted molecules.

These results hold significant implications for the development of molecularly functionalized photoelectrodes, particularly in the context of dye-sensitized solar cells (DSSCs). Furthermore, this comprehensive molecular understanding can be extended to benefit a wide array of applications, spanning from optoelectronic devices to surfaces tailored for heterogeneous catalysis.

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Investigation of Initial Phase of Vibrational Energy Pooling of CO adsorbed on NaCl(100)

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Carbon monoxide (CO) adsorbed to NaCl(100) may have the weakest coupling between an adsorbate and a solid surface, thus making it an ideal system to study the interactions between molecules physisorbed to a surface. After saturating the $v = 0 \rightarrow 1$ transition with an infrared laser pulse, CO exhibits vibrational energy pooling (VEP) mediated by dipole-dipole interactions [1]. Here, vibrational quanta are collected in a few CO molecules leading to vibrationally highly excited states up to CO($v = 27$) [2]

$$\mathrm{CO}(n) + \mathrm{CO}(m) \rightarrow \mathrm{CO}(n+1) + \mathrm{CO}(m-1) + \Delta E(n,m).$$

These highly excited CO molecules can undergo isomerization from the C-bound to a metastable O-bound configuration [3].

We report on time resolved pump-probe vibrational sum frequency generation (VSFG) and infrared transient absorption (IRTA) studies where for the first time the initial phase of VEP is investigated with a resolution of 25 ps. The observed pooling process turns out to be >8 times faster than previously determined from kinetic-Monte Carlo (KMC) simulations with rate constants derived from perturbation theory [2]. Furthermore, the initial vibrational energy transfer between buried monolayer and isotopically varied overlayer [4] has been investigated to find that the energy transfer efficiency is determined by the phonon density of states of the overlayer.

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Probing the Interfacial Molecular Structure of a Co-Prussian Blue In-Situ by Vibrational Sum Frequency Generation Spectroscopy

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Molecular-level insight into the interfacial composition of electrodes both at the solid-electrolyte and the solid-electrode interface is essential towards understanding the charge transfer processes, which are key for electrochemical (EC) and photoelectrochemical (PEC) applications. Over the years, research efforts have predominantly focused on characterizing bulk properties of individual materials, overlooking the pivotal role of interfaces in dictating device operation. While ex situ techniques have furnished valuable insights, they often fall short of capturing the dynamic nature of real operating conditions.

Here, we use *in-situ* surface sensitive vibrational sum-frequency generation (VSFG) spectroscopy for the first time to directly access the interfacial structure of a cobalt containing Prussian blue analogue (Co-PBA) in contact with the electrolyte and TiO_2/Au surface [1-3]. Co-PBAs represented with the general molecular formula, ($K_xCo^a[Fe^b(CN)_6]_y.zH_2O$, where a, b are formal oxidation states and x, y and z are stoichiometric coefficients) are acknowledged as robust, effective, and inexpensive electrodes for sodium/potassium-ion batteries and electrocatalytic processes including water and alcohol oxidation processes. We studied structural and compositional changes of the Co-PBA layer during electrochemical oxidation by monitoring the stretching vibration of the CN group. At open circuit potential, VSFG reveals a non-homogeneous distribution of oxidation states of metal sites in the Co-PBA film: Fe^{III}-CN-Co^{II} and Fe^{II}-CN-Co^{III} coordination motifs are dominantly observed at the Co-PBA|TiO_2 interface, while it is only the Fe^{II}-CN-Co^{II} unit at the electrolyte interface. Upon increasing the potential, we observe the partial oxidation of Fe^{II}-CN-Co^{II} to Fe^{III}-CN-Co^{II}, followed by its transformation to Fe^{II}-CN-Co^{III} via charge transfer and finally the formation of Fe^{III}-CN-Co^{III} species at the interface with TiO_2 and the electrolyte. Our molecular-level analysis of the electrolyte/electrode interface provides the basis for a variety of scientific and technological applications, including energy storage and electrocatalysis.
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Single Nanoparticle Charging Dynamics in the Gas Phase

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Nanoparticles (NPs) possess unique size-dependent properties and can be utilized in a wide range of applications, including heterogeneous catalysis and optoelectronics. [1] In order to gain access to the intrinsic properties of NPs without influence of their physical and chemical heterogeneity or a supporting surface, it is important to perform experiments on single NPs. Our approach to single NP characterization is based on quasi-continuous, non-destructive mass determination in a cryogenic split-ring electrode trap. [2] Recently, we demonstrated the feasibility of single NP action spectroscopy to measure UV/vis absorption spectra indirectly by monitoring adsorption/desorption of messenger molecules as a function of the irradiation wavelength. [3]

Here, we probe the charging dynamics of a 100 nm diameter SiO_2 NP by controlled manipulation of the NP charge state (500-1200 e). We investigated the influence of buffer gas pressure, its ionization potential and the charge state of the NP on the charging dynamics, both on positively and negatively charged NPs. A better understanding of processes taking place on the NP is the first step towards modelling its behaviour and the energy balance. We further report on the current progress to systematically characterize ad- and desorption as well as the NP surface temperature to facilitate modelling of sorption kinetics. Elucidating the relationship between the different experimental parameters is a prerequisite to enhance experimental control and quantitative data interpretation.

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Theory and Data Science

GP3-xTB: A general purpose self-consistent Tight-Binding Quantum Chemical Method

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We present our third-generation extended tight-binding (xTB) model named GP3-xTB. It aims at general-purpose (GP) applicability in chemistry going beyond the special-purpose parametrization for geometries, frequencies, and non-covalent interactions (GFN) of previous xTB-versions [1,2]. The centerpiece of the new method is the adaptive minimal valence basis set q-vSZP [3], which allows for a different radial expansion of basis functions on symmetry-distinct atoms in a molecule. Together with its deep contraction and special optimization on molecular DFT calculations, it substantially improves on previously employed minimal basis sets. Beyond improvements to the basis set, the GP3-xTB Hamiltonian is augmented by three main features: (i) approximate non-local Fock exchange to emulate the behavior of range-separated hybrid DFT, (ii) atomic correction potentials (ACP [4]) to introduce anisotropy into the minimal basis, and (iii) a complete range-dependent expansion of the electrostatic interactions up to third-order to improve the description of charged species. Preliminary results indicate that GP3-xTB approaches DFT accuracy more closely and for a wider range of chemical properties such as barrier heights, ionization potentials, or thermochemistry, than previous semi-empirical methods at only slightly increased computational cost.

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An exciton coupling scheme based on simplified time-dependent density functional theory

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The computation of excited states of systems with about 10.000 atoms remains a challenging and mostly unsolved task. Many biomolecular aggregates and polymers fall into this regime, rendering the development of efficient computational methods for this purpose necessary. For systems up to 200 atoms, single determinant approaches as time-dependent density functional theory (TD-DFT) or its Tamm-Dancoff approximated variant (TDA) are commonly employed. [1] A decade ago, simplified variants of TD-DFT and TDA, sTD-DFT [2] and sTDA, [3] have been developed, which utilize semiempirical monopole approximations for the computation of two-electron integrals and reduce matrix dimensions through the selection of relevant configuration state functions (CSFs) up to a desired threshold. [3] While these methods enable computation of excited states beyond the scope of conventional TD-DFT, their application to very large systems is still limited. A promising strategy to expand the current limitations of these methods are exciton coupling (ExC) schemes. Here, a subdivision of the complete system into smaller (excitonic) fragments is done. Guided by this idea, we present a new and highly efficient ExC approach based on sTD-DFT and sTDA to enable the computation of electronic spectra of very large (bio-)molecular systems. By neglect of interfragment charge transfer excitations and transformation into the fragment exciton basis, the ExC eigenvalue problem is constructed and solved at considerably reduced computational cost compared to its parent sTD-DFT/sTDA method. The performance of the ExC method is demonstrated on large molecular clusters and biomolecules, and the effect of electrostatic embedding [4] is addressed to improve the accuracy of the model considerably.

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Constraints-Based Orbital-Optimized Excited States Method

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We present a novel method to directly optimize the electronic excited states based on constraint density functional theory (cDFT) [1]. In contrast to other previously proposed methods based on cDFT [2,3], only a single, state-specific constraint is required.

Our method shows a stable and rapid convergence behavior and no collapse to the ground-state like delta-SCF or similar methods like the maximum overlap method (MOM) [4]. Furthermore, the optimized excited states follow the Aufbau principle, so that the regular toolbox for electronic ground states can be readily applied to the resulting eigenstates.

We present first benchmark results of our constraints-based excited state method and analyze the electronic structure of the excited states by comparison with conventional methods.

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Structural Diversity of a Pseudo-ionic Liquid: Investigating Mixtures of [Li][NTf$_2$] and Triglyme

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In the search for improved energy storage devices, lithium batteries still offer great opportunities due to their high energy density. However, many current electrolyte-systems often show undesirable properties like a high combustibility.[1] Therefore, possible alternatives to conventional electrolytes are searched for. Combinations of lithium salts and glymes, which are known to form so called pseudo-ionic liquids for certain mixing ratios [2], could be one possibility.

To investigate their structure and dynamics in detail, several mixtures of [Li][NTf$_2$] and triglyme (H-(CH$_2$-O-CH$_2$)$_4$-H) were analysed by means of molecular dynamics simulations at temperatures between 300 K and 480 K. We could show that the structural motifs in the lithium coordination sphere depend almost exclusively on the mixing ratio of triglyme and ion pairs (and water) but do not show a significant temperature dependence. By adding triglyme to [Li][NTf$_2$], the lithium salt changes from contact ion pairs to solvent-separated ion pairs. By this, the cations are spatially separated from their counterions and the mixture acts as a pseudo-ionic liquid.

As a consequence of the structural changes, the transport properties of the system change significantly. While self-diffusion coefficients of all components increase, the viscosity decreases. Meanwhile, the percentage of charge carriers is lowered which impacts the mixture’s conductivity. Hence, the mixture composition has to be chosen carefully with regard to possible applications.

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Vibrational Spectroscopy from Machine Learning Molecular Dynamics by Accurately Representing the Atomic Polar Tensor

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Vibrational spectroscopy is a key technique to elucidate microscopic structure and dynamics. Without the aid of theoretical approaches, it is, however, often difficult to understand such spectra at a microscopic level. Ab initio molecular dynamics has repeatedly proved to be suitable for this purpose [1, 2, 3], but the computational cost can be daunting; in particular when electronic structure methods beyond GGA DFT are required. Here, a new route to calculate accurate IR spectra from machine learning molecular dynamics is presented, utilizing the atomic polar tensor [4]. The latter can be trained *a posteriori* on existing molecular dynamics simulations using the E(3)-equivariant neural network *e3nn* [5] and is a most fundamental physical observable. The introduced methodology is therefore general and transferable to a broad range of systems. Besides benchmarking the method against explicit ab initio molecular dynamics, I will also present applications utilizing a atomic polar tensor neural network at the hybrid DFT level. These demonstrate that it has the potential to significantly contribute toward novel physical findings, especially where large-scale molecular dynamics simulations or expensive electronic structure calculations are required.

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The Path of Water in MOF-303

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Water scarcity is an ever more pressing problem around the world. Metal-organic frameworks (MOFs) have emerged as promising candidates to supply drinking water by extracting it from the humidity of air. However, to efficiently utilize these novel materials, it is crucial to understand how water molecules interact and move within the pores.

Computational methods are indispensable to gain detailed insights into the structure and dynamics of water and will help to pave the way for the design of increasingly powerful materials. Our goal is to identify the pathways for the diffusion of water molecules between clusters of water in MOF-303 (Al(OH)(PZDC), where PZDC is 1-*H*-pyrazole-3,5-dicarboxylate). [1] This material with exceptional water-harvesting properties was developed by our experimental collaborators in the group of Omar M. Yaghi. We conduct density functional theory (DFT) calculations with VASP. To study how water molecules move, we apply a Nudged Elastic Band (NEB) algorithm implemented in MonaLisa [2] for two loadings: 3.5 water molecules per asymmetric unit (low loading) and 8.5 H_2O/asym. unit (high loading).

Our results show that water diffusion between clusters is a multi-step process involving several (probably short-lived) intermediates for both loadings. On average, the high loading diffusion pathway has higher barriers compared to the low loading case. This may indicate different types of diffusion depending on the loading.

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SHNITSEL: A Science-Driven Photochemistry Database

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Photochemistry is arguably the most sustainable type of chemical transformation, but the ultrafast nature of light-induced reactions often complicates their precise understanding and leads to rather speculative structure-property relationships. Quantum chemistry is an indispensable tool which, in combination with non-adiabatic molecular dynamics simulations, provides unparalleled insights into the time-dependent evolution of excited states. However, the accuracy of the simulations is limited by the high cost of quantum chemical methods, which restricts their practical use.

This is where the application of science-driven machine learning (ML) [1] enters: This kind of ML relies on existing quantum chemical data, such as energies and forces in various excited states and their non-adiabatic couplings, related to educts, intermediates and reaction products. Ultimately, ML-predictions of such properties are employed to accelerate non-adiabatic molecular dynamics simulations by orders of magnitude while maintaining *ab initio* accuracy [2–4].

In this talk, we provide an overview on how ML can be used to access properties of interest, *e.g.*, energy barriers and reaction rates and introduce **SHNITSEL** [5], a database that encompasses computational data for a series of photochemical reactions including, among others, [2+2]-cycloadditions [2], roaming [3], and *cis/trans* isomerizations [4]. We address the challenges of efficiently defining and curating datasets from the community while ensuring robust and far-reaching capabilities in developing ML models.

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Non-Adiabatic Path Integral Monte Carlo Simulations of FeH$^+$

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Quantum statistical mechanics simulations of many-body systems are fundamental to our understanding of physical reality and at the core of emerging quantum technologies. In this context, path integral (PI) simulations based on Feynman's imaginary time PI have proven to be a powerful method by giving numerically exact results with respect to quantum Boltzmann statistics within the canonical ensemble. This is achieved by discretizing the path integral into discrete time intervals and mapping the quantum mechanical problem onto a classical one, whose statistical behaviours are identical. Now, it is usually assumed that this isomorphic system evolves on a single potential energy surface (PES); however, for systems including heavier atoms, it is known that multiple low-lying excited states are populated due to spin-orbit interaction and need to be considered for an accurate sampling of the configuration space.

Here, we propose an approach based on the mean-field PI sampling of Alexander [1] to accurately consider multiple PES including non-adiabatic effects, where the simple picture of a classical isomorphic system still holds and thus can be efficiently sampled by a Markov-chain Monte Carlo algorithm. As this approach uses the potential in the diabatic basis, a diabatization protocol that includes spin-orbit coupling is first applied to the adiabats, as obtained from high-level quantum chemical calculations like multi-reference configuration interaction (MRCI).

Accordingly, we want to demonstrate in the case of FeH$^+$, which is expected to be present in the interstellar medium, that including multiple PES is necessary to capture the full extent of its quantum mechanical behaviour due to several low-lying electronic states.

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ωB97M-3c: A small basis set composite DFT method for the computation of large systems

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We introduce a new “-3c” composite density functional (DFT) method called ωB97M-3c. Almost 10 years after the release of the first 3c method (HF-3c [1]), we are circling back to the application of a minimal AO basis set for a substantial speed-up in computation time, while preserving the accuracy of more recent approaches. The method is based on the popular ωB97M-V range-separated hybrid density functional [2] together with the D4 dispersion correction [3]. The employed minimal basis set has been specially optimized in molecular DFT calculations and provides atom-in-molecule adaptive basis functions by pre-computed effective atomic charges [4]. Computationally expensive polarization functions can be avoided using atomic correction potentials (ACP) as proposed by Prasad et al. [5], which are implemented in standard quantum chemistry codes. The method enables, e.g., the computation of protein structures and supramolecular complexes at a hybrid DFT level and offers great potential in the application of QM/QM embedding approaches.

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On the Relevance of Active Learning for Accurate Machine Learning Potentials

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Machine learning potentials trained on *ab initio* data allow us to perform molecular dynamics simulations of larger systems and longer time scales than accessible with *ab initio* molecular dynamics, while maintaining the level of accuracy of the *ab initio* method. Active learning is a strategy to construct the data set used to train the machine learning potential, often in the context of reducing the number of expensive *ab initio* calculations. Today, it is taken for granted that active learning should be used when training a machine learning potential. However, the efficiency of active learning across different systems is not well-understood. We study an active learning strategy based on committee disagreement [1] for the training of a high-dimensional neural network potential [2, 3] for bulk liquid water at ambient conditions. We investigate in detail the performance of active learning, at the level of computational requirements, train and test errors, and the quality of the final potential.

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One stone, two birds: using high electric fields to enhance the mobility and the concentration of point defects in ion-conducting solids

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Improving the ionic conductivity of outstanding, composition-optimised crystalline electrolytes further is a major challenge. Achieving increases of orders of magnitude requires, conceivably, highly non-linear effects. One known possibility is the use of high electric fields to increase the point-defect mobility.

In this study, we investigate quantitatively a second possibility, that high electric fields can increase substantially point-defect concentrations. As a model system we take a pyrochlore oxide ($La_2Zr_2O_7$) for its combination of structural vacancies and dominant anti-Frenkel disorder; and we perform molecular-dynamics simulations with many-body potentials as a function of temperature and applied electric field.

Results within the linear regime yield the activation enthalpies and entropies of oxygen-vacancy and oxygen-interstitial migration, and from three independent methods, the enthalpy and entropy of anti-Frenkel disorder. Transport data for the non-linear regime are consistent with field-enhanced defect concentrations and defect mobilities. A route for separating the two effects is shown, and an analytical expression for quantitative prediction of the field-dependent anti-Frenkel equilibrium constant is derived.

In summary, we demonstrate that the one stone of a non-linear driving force can be used to hit two birds of defect behaviour.

Transport and Storage

Triple-conducting $BaZrO_3$-$BaFeO_3$ solid solution series - why the middle is not the optimum

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Oxides with mixed oxygen vacancy, proton, and electron hole conductivity ("triple conductors") are needed as oxygen electrode materials for protonic ceramic fuel and electrolysis cells.[1] One possible approach is to explore solid solution series between $Ba(Zr,Y)O_{3-z}$ protonic electrolyte materials and $BaFeO_{3-\delta}$ perovskites with mixed oxygen vacancy and hole conduction. Proton uptake occurs through the hydration reaction of water incorporation into oxygen vacancies $V_O^{\cdot\cdot}$: $H_2O + V_O^{\cdot\cdot} + O_O^x \leftrightarrow 2\ OH_O^{\cdot}$ forming protonic defects $OH_O^{\cdot}$ (OH^- ions on O^{2-} site).

We study $BaZr_{0.88-x}Fe_xY_{0.12}O_{3-\delta}$ perovskites using XRD, thermogravimetry, conductivity measurements, and x-ray spectroscopy to elucidate the evolution of defect concentrations and transport with increasing iron content.[2] Already low Fe contents $x \geq 0.1$ strongly decrease the proton uptake. This can be understood from the fact that the strong covalency of the Fe-O bonds decreases the basicity of six adjacent oxide ions, and thus disfavors the hydration reaction.[3] For materials with high Fe content, the presence of redox-inactive, oversized dopants such as Y^{3+} is beneficial for proton uptake, because the induced lattice distortions lower the Fe-O covalency.[4]

As a consequence of the large lattice parameter and local lattice distortions, the mobility of electron holes in $BaFeO_3$-based perovskites is comparably low. Thus, rather high Fe contents $x \geq 0.7$ are needed to obtain an electronic conductivity $\sigma_{eon} \geq 1$ S/cm.

Materials in the middle of the $BaZr_{0.88-x}Fe_xY_{0.12}O_{3-\delta}$ series suffer not only from low proton concentration and σ_{eon}, but are affected by defect interactions (trapping; locally modified migration barriers) which act on $V_O^{\cdot\cdot}$ as well as on protons.[2,5] Therefore, perovskites with high Fe content ≥ 0.7 offer the best combined transport properties. This study demonstrates the capabilities but also challenges encountered within single phase perovskites for combined $V_O^{\cdot\cdot}$/proton/hole conductivity. Thus, also multi-phase materials should be explored to further improve the oxygen electrode performance.

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Alkali Ion Transport in Lithium Borate Glass: New Insights from a sequential Double-CAIT experiment

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Glasses are characterized by the lack of long-range order and a distribution of binding lengths and angles. As a consequence, site energies of mobile ions in glasses are specific to their position and have a distribution [1]. Experiments on the basis of the Charge Attachment Induced Transport (CAIT) technique [2,3] suggest that in homogeneous glasses the site energy distribution (SED) can be quantified and can be often described by a unimodal Gauss function to a good approximation [4-6]. The width of the distribution is characteristic for the glass system under investigation.

CAIT experiments generate concentration-depth profiles through incorporation of foreign ions into a sample. The concentration-depth profiles are then analyzed within the Nernst-Planck-Poisson (NPP) transport formalism. The analysis provides concentration-dependent diffusion coefficient of the native ion which encodes the SED. In a previous study [7], we presented the results of K^+-, Rb^+- and Cs^+-CAIT experiments on $Li_3B_7O_{12}$ glass from which the quantification of the native SED was derived. Conceptually, it is clear, that the CAIT replacement experiment involves the formation of two different populations, one for the native and one for the foreign ion. The pivotal question right now is, on what time scale these populations equilibrate.

To find an answer, a new experiment has been devised, which aims to quantify the populations resulting from the CAIT experiment mentioned above. Here, the populations generated by a (mono-) Rb^+@$Li_3B_7O_{12}$ CAIT experiment are probed by a subsequent Cs^+@Rb^+@$Li_3B_7O_{12}$ experiment, constituting a sequential Double-CAIT experiment.

Several Double-CAIT experiments have already been performed. The concentration depth profiles measured by means of ToF-SIMS exhibit a very clear – but complex – competition of electric field versus chemical potential gradient driven transport including forward and backward components relative to the direction of the Mono-CAIT experiment. An extensive analysis of these profiles by means of Onsager-Nernst-Planck-Poisson transport concepts is currently being performed. The progress will be reported on in this contribution.

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Vacancy-mediated ion diffusion in biaxially strained $CsPbBr_3$

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Perovskite structured halides are approximately an order of magnitude softer than their oxide counterparts. While this property (among others) makes them promising candidates for e.g. flexible (opto-)electronic devices, there is a strong correlation between mechanical strain and the material's stability, which has been attributed to changes in the activation barriers for ion diffusion with strain, and for anion diffusion in particular [1,2]. On the other hand, the interplay between strain and ion transport could be exploited to for e.g. memristive applications [3]. While there exists computational evidence that anion diffusion barriers are lowered in the presence of tensile strain and increased in the presence of compressive strain [4], a detailed atomistic analysis of this interplay is currently lacking, and cation migration has not been considered at all.

Therefore, we carried out a DFT-based study on the effects of imposing biaxial strain on Cs^+ and Br^- ion diffusion in a model perovskite halide, orthorhombic (space group *Pnma*) $CsPbBr_3$. Our results indicate that the relationship between imposed strain and ion diffusion is significantly more complex than previously thought – in particular, activation barriers may either increase or decrease with the magnitude and 'sign' of the imposed strain, and the plane in which it is imposed, and moreover, the relationship is often non-monotonic. Furthermore, we find that the correlation between strain and diffusivity are significantly stronger for Cs^+ than for Br^-, suggesting that the dependence of perovskite-halide stability on stress/strain might be due to cation migration, rather than anion migration, in contrast to common assumption.

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