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High Resolution Spectroscopy of Monodeuterooxirane from the GHz and THz to the IR Range (n_8 Fundamental)

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Monodeuterated ethylene oxide c-C_2DH_3O (D_1-oxirane), is a small cyclic molecule, an asymmetric top and an excellent example of a simple isotopically chiral molecule. Normal oxirane (c-C_2H_4O) has been detected in SgR B2N [1]. In previous work, D_1-oxirane had been analysed in the microwave region [2] up to 70 GHz and rotational constants of D_1-oxirane were calculated *ab initio* [3]. We report new results on the rotational spectrum of D_1-oxirane between 65 and 119 GHz using our GHz spectrometer [4] and in the 0.75 to 2.4 THz range measured with our FTIR setup [5] at the Swiss Light Source. The infrared spectrum has been recorded at an instrumental resolution of 0.0015 cm^{-1} using the Bruker IFS HR Zürich spectrometer [6]. Spectroscopic parameters for the vibrational ground state and n_8 fundamental level (CH_2 twist, n_c=896.025 cm^{-1}) have been determined. Our results will be discussed in relation to isotopic chirality and parity violation, and also in relation to monofluorooxirane [7] and the broader context of fundamental symmetries and symmetry violations [8].

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From Monomers to Stacks: From “simple” photophysics to complex sub-populations

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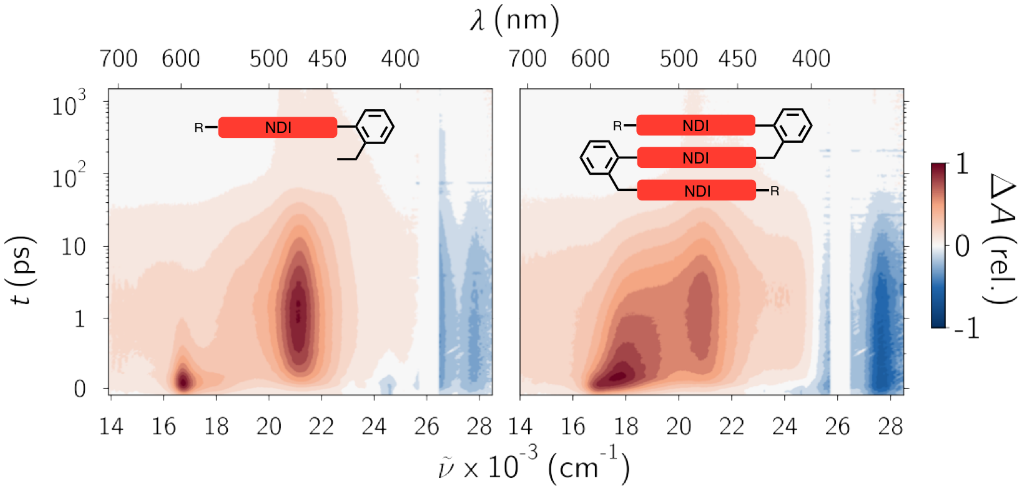
Close proximity of two or more chromophores modifies their photophysical and redox properties compared to the isolated monomers, as indicated by changes in their electronic absorption and/or fluorescence spectra. These differences can be accounted for by the formation of aggregates or donor-acceptor complexes in the ground state, and by a delocalisation of the excitation over multiple constituents. If the chromophores are covalently linked to stacks, they are forced to be in close proximity and the impact of the coupling between a discrete number of chromophores can be studied at a predefined distance.



In this communication, we will compare the ultrafast photophysics of 1,4,5,8-Naphthalene Diimide (NDI) monomers to those of cofacially stacked dimers, trimers and tetramers. Based on the results obtained from transient absorption spectroscopy in the UV and IR spectral range, we will discuss the electron transfer from the benzyl linker and the delocalization of the excitation throughout the stack. Furthermore, we will show the excitation wavelength dependent population of sub-ensembles differing by the amount of excitonic coupling.

Crystal Structure Prediction & NMR Powder Crystallography

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Structure activity relationships are the basis of development in modern chemical sciences, which depends on the capacity for atomic-level characterization. While it is straightforward to determine structures from single crystals, when the sample is a powdered solid, in many cases structure determination is difficult if not impossible. This is a major handicap in the development of complex materials. For example, the drug delivery properties of a pharmaceutical compounds are governed by the three-dimensional packing in the crystal structure, and the overall architecture of the formulation.

Over the past few decades computational crystal structure prediction (CSP) methods have seen great improvement and have been successfully used to predict and confirm single and multicomponent systems [1]. Recently they have been combined with solid-state NMR and DFT chemical shift calculations to provide a tool for structure determination in powders [2-4]. The main bottleneck for these methods today is the computational cost that grows sharply as the systems get bigger and more complex.

We present how solid state NMR measurements can be used to accelerate CSP. As an example we correctly determine the crystal structure of the medium-sized organic molecule ampicillin, where the ordinary approach fails to determine the correct structure.

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2D Raman–THz Spectroscopy of water and heavy water near the freezing point

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Two-dimensional Raman-THz spectroscopy, recently developed in our group, interrogates the low-frequency intermolecular modes of liquids (below 400 cm^{-1}) consecutively through impulsive Raman and direct THz excitation providing, in principle, an equivalent information accessible by conventional third-order echo-based spectroscopies [1]. The new approach has the ability to monitor the extent of the inhomogeneity of intermolecular motions of liquids through the relaxation dynamics of the vibrational echo signal measured along the correlated coordinate $t_1=t_2$ in the 2D response (Fig. 1a). Recently, we demonstrated that in aqueous salt solutions the extent of such an echo-like feature correlates with the viscosity, confirming the structuring abilities of “kosmotropic salts” on the molecular level [2]. In the current contribution, we explore further how the change in macroscopic properties of the liquid water projects on the echo coordinate of the Raman-THz response. Specifically, the response and the corresponding diagonal cuts were measured for both H_2O (Fig. 1b) and D_2O as the sample was cooled down. Figure 1c shows a gradual increase in the decay along $t_1=t_2$ coordinate as function decreasing temperature for H_2O and D_2O. There is a clear thermal offset of about 4 K in relaxation times between the two isotopes which fits the increase of 3.82 K in the melting point of water upon deuteration. Moreover, the ratio of the relaxation times between the two isotopomers follows closely their square root mass ratio of 1.05, providing a molecular level insight on the connection of structural and dynamical properties in bulk water.

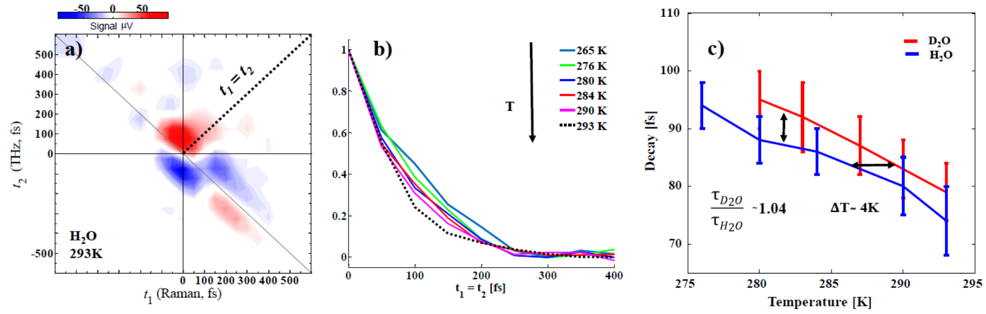

Fig. 1 a) Experimental 2D Raman-THz signal of H_2O at room temperature. b) Diagonal cuts along $t_1=t_2$ of H_2O response as a function of temperature. c) Single exponential decay along $t_1=t_2$ in fig. 1b as a function of temperature for D_2O (red) and H_2O (blue).

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Photo-controlling protein allostery in PDZ3 domain

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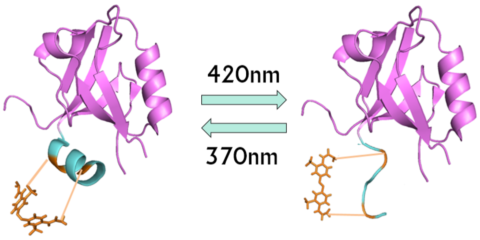
Function of many proteins is modulated by allosteric regulation of their activity. PDZ3 domain from the protein postsynaptic density-95 (PSD-95) has been shown to be allosterically regulated via destabilization of distal third helix [1]. Naturally occurring phosphorylation of tyrosine residue in the third helix leads to destabilization of this secondary structure which, in turns, affects binding affinity of the system [2]. It has been shown that by covalently cross-linking ultrafast reversible azobenzene photoswitch to a helical peptide resulted in photo-controlled helix folding/unfolding [3]. Our current work focuses on applying the same principle to PDZ3 domain protein, and photo-inducing the destabilization of the allosteric element – the third helix.



Photoswitch in *cis* – helix folded

Photoswitch in *trans* – helix unfolded

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Gas-Liquid Scattering Dynamics in Crossed Jets

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We report on an experiment to study reaction dynamics at the liquid–gas interface which is currently being set up. Our liquid target is a flat (planar) microjet in vacuum which is created by colliding two cylindrical water mircojets. Molecules interacting with the aqueous-solution flat jet are introduced by a molecular beam. Here we present several molecular systems that will be studied, and we describe the various spectroscopic methods that will be used to fully characterize the reaction and scattering processes and also our methods to characterise the flat microjet itself.

Synthesis and self-assembly of amphiphilic PEO-b-PEHOx polymers into multicompartment micelles

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Preparing well-defined amphiphilic block copolymers with tuneable properties has become a main focus of modern research.[1-2] We present here the synthesis and self-assembly of poly(ethylene oxide)-*block*-poly(2-ethyl-3-heptyl-oxazoline) (PEO-*b*-PEHOx), a new amphiphilic diblock copolymer obtained via microwave-assisted polymerization of EHOx using a new nosylated PEO macroinitiator.[3] Kinetics of the polymerization in different solvents were performed and monitored by ^{1}H NMR and gel permeation chromatography to optimize the synthesis. Differential scanning calorimetry was conducted and proved that PEO-*b*-PEHOx has a glass transition temperature of -29°C, making it suitable for a wide range of self-assembly methods. Self-assembly of PEO-*b*-PEHOx was then performed using two different techniques: film rehydration and solvent exchange. In both cases, we were able to prove the formation of multi-compartment micelles by light scattering, TEM and Cryo-TEM. Our results show that PEO-*b*-PEHOx is a meaningful addition to the canon of self-assembling block-copolymers.

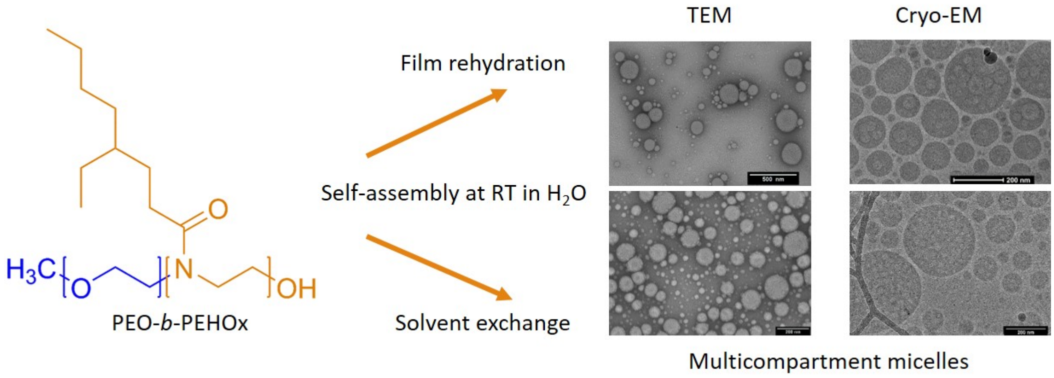

Figure 1 - Amphiphilic diblock copolymer PEO-*b*-PEHOx self-assembling into multicompartment micelles as shown by TEM and Cryo-EM images.

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Lipid transmembrane asymmetry probed by vibrational sum-frequency scattering

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Natural lipid membranes are asymmetric in terms of lipid composition of the two leaflets which has a biological significance. Recent developments enabled the synthesis of asymmetric liposomes using cyclodextrin-mediated lipid exchange. This opens a way for studying the structure and kinetics of lipids in more realistic models of lipid membranes. Vibrational sum-frequency scattering (VSFS) is ideally posed to study such asymmetric membranes as it probes vibrational resonances of molecules in non-centrosymmetric arrangements. The advantage of this approach lies in dispensing with unnatural labeled lipids and solid membrane supports both of which deviate from real behavior. Transmembrane asymmetry is achieved by using isotopically-labeled acyl chains in one leaflet of the membrane or by using lipids with different head groups. Measurements performed on $d_{62}DPPC^{(in)}:DPPC^{(out)}$ show a small but stable asymmetry. In contrast, asymmetric liposomes composed of $POPS^{(in)}:d_{62}DPPC^{(out)}$ seem to undergo phase-separation within the leaflets, leading to a large enhancement of VSFS response.

2D IR spectroscopy of Insulin: a combined experimental-computational study

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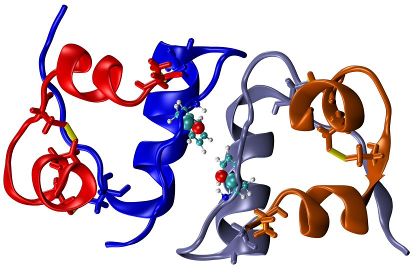
Manipulation and control of the dissociation of the Insulin dimer to two monomeric units (i.e. the functional form of the protein) is of great therapeutic importance. Recently, two-dimensional infrared spectroscopy (2D IR) – a technique that operates at the femtosecond-picosecond timescale – was used to investigate the dissociation dynamics of the Insulin dimer, systematically varying the temperature and concentration of the hormone [1]. Interpretation of such experimental spectra is often challenging and estimating the monomer/dimer composition is non-trivial. While at higher temperatures (e.g. 339K), essentially only monomers are present, it is difficult to isolate the dimeric form. Even at lower temperatures (e.g. 283K), only 50-80% of the composition is estimated to be the dimer. However, “pure-monomer” and “pure-dimer” spectra can be easily calculated computationally. In the most recent investigations, Tokmakoff *et. al.* use isotopically labeled insulin to explore the dimerization process. In parallel to this, we have explored the process using a complementary, computational approach, exploiting molecular dynamics (MD) and normal mode analysis. This builds on our previous investigations of the vibrational relaxation of N-methylacetamide, a small organic molecule that mimics peptide bonds in proteins [2].



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Temperature dependence of water-water and ion-water correlations in bulk water and electrolyte solutions probed by femtosecond elastic second harmonic scattering

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The temperature dependence of the femtosecond elastic second harmonic scattering (fs-ESHS) response of bulk light and heavy water and their electrolyte solutions is presented. We observe clear temperature dependent changes in the hydrogen (H)-bond network of water that show a decrease in the orientational order of water with increasing temperature. Although D_2O has a more structured H-bond network (giving rise to more fs-ESHS intensity) the relative temperature dependence is larger in H_2O. The changes are interpreted in terms of the symmetry of H-bonds and are indicators of nuclear quantum effects. Increasing the temperature in electrolyte solutions decreases the influence of the total electrostatic field from ions on the water-water correlations, as expected from Debye-Hückel theory, since the Debye length becomes longer. The effects are, however, 1.9 times (6.3 times) larger than predicted for H_2O (D_2O).Since fs-ESHS responses can be computed from known molecular coordinates, our observations provide a unique opportunity to refine quantum mechanical models of water.

Understanding the structural and chemical changes of SnO_2 nanoparticles during CO_2 electro-catalysis derived from operando XAS and Raman Spectroscopy

A. Dutta*[1], A. Kuzume[2], V. Kaliginedi[1], M. Rahaman[1], I. Sinev[3], B. R. Cuenya[3], S. Vesztergom[4], P. Broekmann[1]*

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In this present study we probed structural and chemical changes of Sn(IV) oxide NPs supported on reduced graphene oxide (rGO) during an ongoing CO_2 electrolysis by means of operando XAS and Raman spectroscopy. To achieve sufficiently high reaction rates it is necessary to apply high cathodic electrode potentials. Under such conditions, however, not only CO_2 is electrochemically reduced, but also the catalyst particles themselves may be transformed from the initial Sn(IV) state to the Sn(II) state or, in an extreme case, to metallic Sn. While Sn(II) species still favor CO_2 electroreduction, yielding formate as a primary product, on metallic Sn CO_2 reduction is disfavored with respect to the competing hydrogen evolution reaction (HER). Interestingly, at -1.1 V, the formate production efficiency (FEs) is ~ 80 % on as the synthesized catalyst (4-8 nm) where the mixed oxidation state of Sn (Sn(II), and Sn (IV)) (SnOx ($1 < x < 2$)) was observed by operando Raman spectroscopy. On the other hand, the operando XAS, a robust technique yielding bulk-sensitive information averaged over a large surface area is a very expedient method that can detect the reduction of SnO_2NPs@rGO to metallic Sn, provided that the catalyst is applied at a high enough loading. XAS can thus be used to establish an optimum potential for the electro-reduction in practical electro-lysing cells. It takes, however, a more surface-sensitive method offered by operando Raman spectroscopy to detect certain reduction intermediates such as the Sn(II) state that remains undetectable for ex situ methods. Moreover, Raman spectroscopy may also find further use when investigating the recovery of catalyst particles following exposure to extreme reducing conditions.

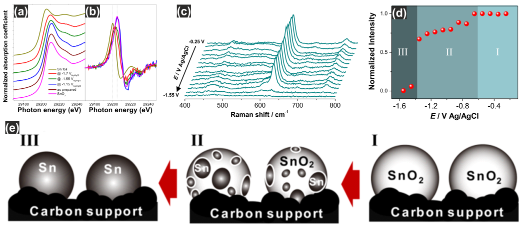

Fig.1 Sn K-edge XANES (a) and their first derivatives (b) acquired on a graphene oxide supported SnOx. (c-d) In operando Raman studies at varied potentialof the Sn (IV)-related A1g. (e) Scheme of partially reduced compound of mixed oxidation state , and completely reduced metallic Sn.

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Compositionally variant CuAg bimetallic foam: Towards electrochemical CO2 conversion into selective Ethanol

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The electrochemical reduction of CO_2 into products of higher value (in the following referred to as CO_2RR) offers the unique chance to make a significant contribution to the closing of the anthropogenic CO_2 cycle and is therefore currently in the focus of research activities worldwide. Energy needed for such electro-conversion processes might originate from excesses of renewables like hydro, wind and solar energy (power to value concept). This work describes a new tailored design of bimetallic Cu-based CO2RR catalysts that are co-alloyed with Ag (Fig.1). Various binary CuAg alloy foams differing in their compositions were synthesized by a template-assisted electrochemical co-deposition process. Furthermore, the electro-deposited alloy foams were subjected to an extra 12 h thermal annealing at 300 °C in air. The different compositions of non-annealed (referred to as NA) and annealed (referred to as 'AN') catalysts were characterized by means of XRD, HRSEM, EDX and XPS techniques. The electro-catalytic reduction of CO2 on these NA-CuAg and AN-CuAg bimetallic catalysts was systematically studied, thus leading to a clear correlation between the catalytic activity and the surface composition of the bimetallic electrocatalysts. Most intriguingly, it was found that the ethanol and ethylene production on the NA-CuAg and AN-CuAg are tunable by systematically changing the atomic Ag/Cu ratio. The NA-CuAg and AN-CuAg catalysts exhibited the optimum selectivity for C_2H_4 and C_2H_5OH at −1.1 V vs RHE, with faradic efficiencies (FE) of ~35.6% and ~30-35%, respectively. This tunable catalytic selectivity will be discussed on the basis of variations in the binding strengths of COOH and CO intermediates, which might be influenced by the surface electronic structure of the bimetallic alloy foams.

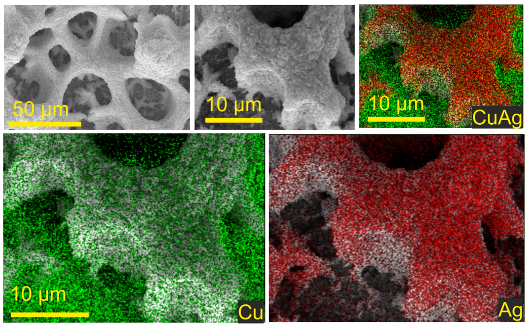

Fig.1. SEM images and elemental mapping of hydrogen template assisted electrochemical co-deposited CuAg binary-alloy, designed for CO_2RR

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Label-free Nonlinear Microscopy of Model Biological Membranes with Incorporated Ion Channels

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[1]Laboratory for fundamental BioPhotonics (LBP), EPFL

The present research project is dedicated to second harmonic (SH) imaging of lipid bilayer membranes. A lipid bilayer membrane is a perfect model system of a biological membrane that is a natural boundary of all living cells (1). Consisting of only 2 parallel monolayers of lipid molecules, typical width of a bilayer is only several nanometers (5-10 nm) (2). That is why it is crucial to implement non-invasive and label free techniques for investigating bilayers in its own hydrated environment. Our technique allows to image structural and dynamical properties of membranes by the mean of oriented water molecules. In such a model system, the orientation of water molecules is determined by ether by charge-dipole interaction between charged lipids and the dipole moment of water or by the external transmembrane electrical bias.

In this work, we are particularly interested in SH-imaging of symmetric neutrally charged lipid membranes (such as DPhPC) that incorpotare artificial ion channels. An ion channel is a pore forming protein or a protein complex that can self-assemble inside a membrane. The reason we are studying ion pores is that they play an important role in a real cell membrane being responsible for the transmembrane ion transfer that establishes membrane potential which allows the membrane to react on and transfer electrical signals and etc.

The second part of the work is dedicated to characterisation of hydrophobic oil behaviour inside horizontal freestanding bilayers A freestanding lipid membrane is self-assembled in a hole punched in a teflon film. In this process, the area around the aperture should be firstly pre-painted with hydrophobic oil such as hexadecane, squalene, heptadecane, decane or etc (3). In this work we examined different oils with different alkane chains on appropriateness to use them as pre-painted solutions. Using white light, two-photon fluorescence and SHG techniques we showed that squalene, in contrast to hexadecane oil, tends to stay in the middle of the membrane. Moreover, analysis of SH and two-photon fluorescence images of oil edges indicates that squalene extends further in the middle of a bilayer than hexadecane do.

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Measurement of Long-Range Heteronuclear Coupling Constants Using the Peak Intensity in Classical 1D HMBC Spectra

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In this contribution, we show that the magnitude of heteronuclear long-range coupling constants can be directly extracted from the classical 1D HMBC spectra, as *all* multiplet lines of a cross peak always and exclusively vanish for the condition $\Delta = k/{}^{n}J_{CH}$. To the best of our knowledge this feature of the classical HMBC has not yet been noticed and exploited. This condition holds true, irrespective of the magnitude and numbers of additional active and passive homonuclear ${}^{n}J_{HH'}$ couplings. Alternatively the ${}^{n}J_{CH}$ value may also be evaluated by fitting the peak's intensity in the individual spectra to its simple $\sin(p\,{}^{n}J_{CH}\Delta)\exp(-\Delta/T_{2eff})$ dependence. Compared to the previously proposed *J*-HMBC sequences that also use the variation of the cross peak's intensity for extracting the coupling constants, the classical HMBC pulse sequence is significantly more sensitive.

Peter Bigler, Julien Furrer, *Magnetic Resonance in Chemistry,* **2018***,* 5, 329-337***.***

Why is HMBC superior to LR-HSQC? Influence of homonuclear couplings $J_{HH'}$ on the intensity of long-range correlations

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Long-Range Heteronuclear Single Quantum Correlation (LR-HSQC) experiments may be applied as an alternative to Heteronuclear Multiple-Bond correlation **(**HMBC) experiments for detecting long-range correlations, but has never enjoyed popularity for that purpose. To the best of our knowledge, the exact reasons have not yet been fully established. For both experiments it is widely accepted that the evolution of proton-proton homonuclear couplings $J_{HH'}$ during the polarization transfer delays Δ leads to significant losses, and that the intensity of the observable coherence is zero when $J_{HH'}$ matches the condition D = $0.5/J_{HH'}$. Here, we analyze the influence of $J_{HH'}$ on the intensity of long-range correlations in HMBC and LR-HSQC spectra. We show that for both experiments long-range correlations *will not* be canceled because of homonuclear couplings $J_{HH'}$. Our theoretical and experimental results definitely establish and validate the superiority of HMBC-based experiments among the family of heteronuclear long-range correlation experiments: (i) the overall cross peak's intensity is higher, and (ii) in LR-HSQC experiments the intensity of the long-range cross peaks is additionally influenced in an unwanted way by the magnitude and number of passive homonuclear proton-proton couplings $J_{HH'}$.

Hydrogen evolution reaction on metallic electrodes in acidic solutions

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Cathodic hydrogen evolution reaction (HER) is one of the most studied electrochemical phenomena. It plays a key role in a variety of technologically relevant processes, e.g., the production and storage of clean energy, the corrosion and electrodeposition of metals, etc. and also deserves attention as one of the most important parasitic reactions of other cathodic processes, such as the electroreduction of CO_2. In aqueous solutions, HER can occur in two alternative ways: either by the reduction of H^+ ions or, if these are not abundant, by the reduction of water molecules. In moderately acidic solutions ($1.5 < pH < 3.5$), where the concentration of H^+ ions is limited, both these reactions can take place. In such cases the respective rates of the two processes are determined by the applied electrode potential and by the rate and means of mass transfer in the electrolyzing cell. Accordingly, the stationary polarization curves measured on rotating disk electrodes in moderately acidic solutions show three characteristic regimes (Figure 1). At not very negative potentials we observe a mostly charge transfer-controlled section corresponding to the reduction of H^+ ions (I). This is followed by a flat plateau region (II) that is governed by the rate at which H^+ ions can approach the electrode surface. At more cathodic potentials we notice an additional increase of the current (III), due to the onset of direct H_2O reduction. In this work, we measured stationary polarization curves on metallic electrodes in mildly acidic solutions. Furthermore, we developed an analytical model that can fully describe the obtained curves at various values of pH and rotation rates, based on one global parameter set. This model accounts for both electrode reactions: the reduction of H^+ ions and that of water molecules, the latter yielding OH^- as a product. The model assumes a strong coupling between the concentrations of OH^- and H^+ ions due to the autoprotolysis of water and utilizes a quasi-steady state approximation.

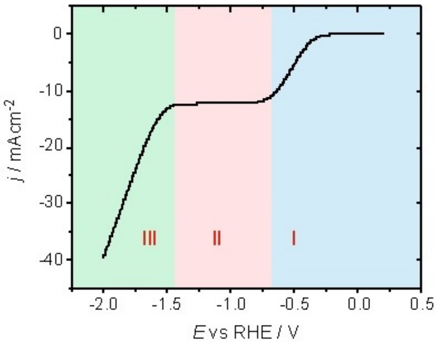

Figure 1. A stationary polarization curve of a polycrystalline gold rotating disk electrode, measured in a pH = 2.5 $HClO_4$ solution (supporting electrolyte: 0.1 M $NaClO_4$). Rotation rate: f = 2500 min^{-1}.

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Stereodynamics of cold chemi-ionisation

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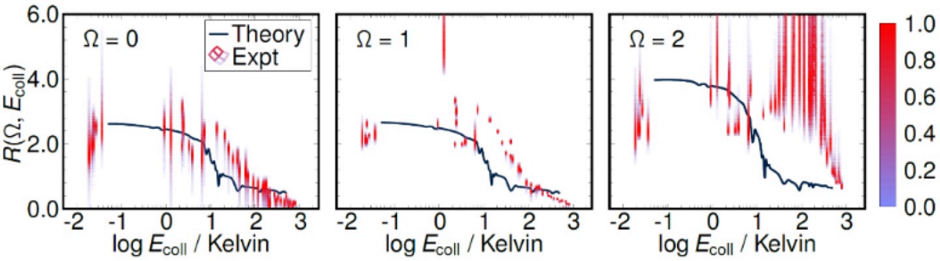
The stereodynamics of the Penning and associative ionisation processes has recently been studied using a merged molecular beam apparatus. [1,2,3] The experiment uses a curved magnetic hexapole to polarize a beam of incident metastable Ne(3P2) [Ne*] atoms into an interaction region which features a set of magnets that adiabatically orient the Ne*. The beam of Ne* is merged with neat Ar which allows us to determine the reactivities of each Ω state, where Ω is the projection of J onto the interatomic axis. The Penning and associative ionisation reaction channels both have Ω state specific cross sections which can be determined by scanning the ion yield of both channels, IAI;PI as a function of the angle of the magnetic field with the relative velocity.

We observe the complete dominance of the associative ionisation channel irrespective of the orientation direction and hence Ω state in the cold regime, as shown in Figure 1. We also observe the total loss of the Penning channel at these low collision energies. As the collision energy is slowly increased, the steric effect makes a return at approximately 10K, indicating a possible change of mechanism as the collision energy reaches this level. Newly calculated theory in the relevant collision energy range provided by Brumer *et al*. allows comparison to our experimental data across the 6 order of magnitude energy range.



Merged beam reactivities obtained from the experiment (red) compared to theory (blue).

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2D/3D Hybrid Perovskites for Stable and Efficient Solar Cells

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Three-dimensional (3D) methylammonium lead iodide perovskite solar cells are undoubtedly leading the photovoltaic scene with their power conversion efficiency (PCE) >22%, holding the promise to be the near future solution to harness solar energy [1]. Tuning the material composition, i.e. by cations and anions substitution, and functionalization of the device interfaces have been the successful routes for a real breakthrough in the device performances [2]. However, poor stability (= device lifetime), mainly due to material decomposition upon contact with water, is now the bottleneck for the widespread of this technology. Diverse technological approaches have been proposed delivering appreciable improvements, but still failing by far the market requirements demanding 25-years lifetime. In this talk, I will show a new concept by using a different class of perovskites, arranging into a two-dimensional (2D) structure, i.e. resembling natural quantum wells. 2D perovskites have demonstrated high stability, far above their 3D counterparts. However, their narrow band gap limits their light-harvesting ability, compromising their photovoltaic action. Combining 2D and 3D into a new hybrid by interface engineering 2D/3D heterostructures will be discussed as a mean to boost device efficiency and stability together. The 2D/3D composite self-assembles into an exceptional gradually organized structure where the 2D perovskite anchors on the TiO_2 substrate, templating the growth of a highly ordered 3D perovskite on top. This results in Mesoporous solar cells leading to 12.9% PCE [3]. Aiming at the up-scaling of this technology, we realize 10x10 cm^2 large-area solar modules using a fully printable, hole conductor free device configuration (i.e. where a carbon electrode is used to replace the organic hole transporter and Gold). The module delivers 11.2% efficiency stable for more than 10,000 hours with no degradation under accelerated testing conditions, leading to a record one-year stability. On the other side a 3D/2D interface will be also presented, where 2D layer lies on top of the 3D as a mean to protect the 3D underneath while also blocking the electron hole recombination at the perovskite/hole transporter interface. This results in enhanced stability without compromising the efficiency, leading to PCE=20% stable for 1000 h [4].

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High-Resolution Spectroscopy in the Vacuum-Ultraviolet exploiting a new KBBF Prism-Coupled Device

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In this contribution, we present high-resolution photoelectron spectra of small molecules and their ions in the vacuum ultraviolet (VUV, $\lambda < 200$ nm) range of the electromagnetic spectrum. Narrow-band coherent VUV radiation is generated by resonance-enhanced degenerate four-wave mixing ($\tilde{\nu}_{\mathrm{VUV}} = 2\tilde{\nu}_{\mathrm{UV}} \pm \tilde{\nu}_2$) in a pulsed gas expansion of argon, using the two-photon resonance of Ar $3p^5 4p' [1/2]_0 \leftarrow$ Ar $3p^6\,{}^1S_0$ at a wavenumber of $2\tilde{\nu}_{\mathrm{UV}}$ = 108'722.6194 cm^{-1}. $\tilde{\nu}_{\mathrm{UV}}$ (λ_{UV} = 183.95 nm) is generated by sum-frequency mixing in a prism-coupled $KBe_2BO_3F_2$ (KBBF) crystal device [1] using the 4th harmonic of an injection-seeded pulsed Nd:YAG laser (λ = 266 nm) and the output of a pulsed-amplified single-mode continuous-wave ring dye laser [2] operating at a wavelength of 596.4 nm. This scheme enables the generation of tunable, narrow-bandwidth VUV radiation in the wavenumber ranges 72'500 cm^{-1} - 95'000 cm^{-1} by difference-frequency mixing and 123'000 cm^{-1} - 145'000 cm^{-1} by sum-frequency mixing and to record high-resolution (0.1 cm^{-1}) pulsed-field-ionization zero-kinetic energy (PFI-ZEKE) photoelectron and photoionization spectra of cold molecules in supersonic expansions. Results obtained on the photoelectron spectrum of methanol near the adiabatic ionization threshold at ~87'430 cm^{-1} [3] and on the photoelectron spectrum of H_2 near the $X^+\,{}^2\Sigma_g^+$ ($v^+ = 3$) ionization threshold at ~130'610 cm^{-1} will be presented.

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Determination of the Lowest Rovibrational Intervals in H_2^+ with 10^{-9} Accuracy

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H_2^+ is the simplest of all molecules and as such an important system for the development of molecular quantum mechanics. The rovibrational energy-level structure of this one-electron system can be calculated extremely precisely by quantum-chemical methods [1]. By comparison with the results of precise spectroscopic measurements of rovibrational intervals, fundamental constants or particle properties, such as the proton-to-electron mass ratio or the proton size, can be determined [2]. Because the rotational and vibrational transitions of H_2^+ are electric-dipole forbidden, the experimental data on its energy-level structure are limited.

We present the determination of vibrational, rotational and spin-rotational intervals in H_2^+ at a relative accuracy of 5E-9 from high-resolution measurements of the Rydberg spectrum of H_2 and Rydberg-series extrapolation using multichannel quantum defect theory [3]. For the excitation of Rydberg states, a resonant three-photon excitation scheme was employed, using pulsed VUV and VIS laser sources to reach selected intermediate valence states and a continuous-wave near-infrared laser source for the excitation to the Rydberg states. Suitable double-well valence states, characterized by long lifetimes and favorable Franck-Condon factors for excitation to different vibrational states in the ion, allow us to excite Rydberg series that converge on selected rovibrational levels of H_2^+ and to overcome the limitations imposed by angular momentum selection rules or vanishing intensities in the direct spectroscopy of the ion. The valence state - Rydberg state intervals could be measured with a relative accuracy of 3E-10 using an optical frequency comb for the frequency calibration of the cw laser and relying on the systematic reduction of uncertainties [4].

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Examining the Ultrafast Ligand to Metal Charge Transfer in Ferricyanide

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The photoinduced dynamics of the prototypical metal complex, ferricyanide ($[Fe(III)CN_6]^{3+}$), have been studied using a variety of experimental and theoretical techniques.[1,2] In particular, infrared markers of the ligand to metal charge transfer (LMCT) processes were identified, indicating formation of ($[Fe(II)CN_6]^{3+}$) species.[1] Back electron transfer from the Fe to CN ligands was also observed to be relatively slow and solvent dependent, occurring on a 0.5 ps timescale in H_2O and D_2O and 1.2 ps in ethylene glycol. Here we extend these studies to the UV-visible and establish spectroscopic markers of the LMCT processes. This allows us to investigate systematically the solvent dependence of the back electron transfer which we discuss in terms of solvent properties.

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Modulating S-protein/S-peptide interactions in RNase S complex by light

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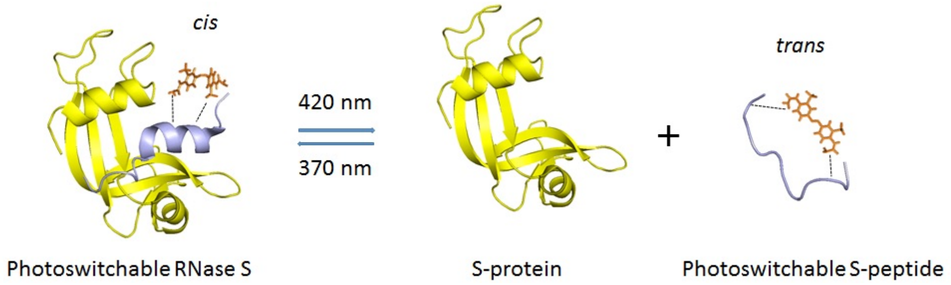
Photocontol has been recognized as a valuable tool for external manipulation of numerous *in vitro*, as well as *in vivo* processes with advantages of high spatio- and temporal resolution and selectivity, with possible biocompatibility of the wavelengths used[1]. In this study we modulate coupled binding and enzymatic activity of non-covalent ribonuclease S complex (RNase S). RNase S represents a product of limited subtilisin hydrolysis of ribonuclease A, enzyme from bovine pancreas. Under controlled conditions, subtilisin can cleave single peptide bond in RNase A and yield RNase S complex composed of S-peptide (1-20) and S-protein (21-124). Complex possesses full enzymatic activity and its three dimensional structure is the same as the one of intact ribonuclease A[2]. S-peptide fragment adopts α-helical structure when it is bound to the S-protein, but it is essentially unfolded when isolated in solution[3]. There are speculations that S-protein undergoes structural changes upon peptide unbinding, as well. In order to induce modulation of binding affinity by light, photoswitchable S-peptide variants were designed by crosslinking of azobenzene-based molecule into the S-peptide structure. Upon illumination azobenzene chromophore undergoes reversible *cis* to *trans* isomerization around central diazene double bond. Isomerization changes the geometry of azobenzene molecule and leads to perturbation of α-helical structure[4]. Our results have shown significant modulation of S-protein/S-peptide binding affinity which leads to a consequent modulation of enzymatic activity. Goal of our further study is to follow conformational changes induced in this model system upon light-triggered perturbations in time-resolved manner.



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Spectroscopic Parameters and Electronic Relaxation of Paramagnetic Gadolinium Complexes

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Electron paramagnetic resonance (EPR) is a valuable tool in the study of the electronic and magnetic properties of paramagnetic complexes. The relation of the magnetic properties to the electronic wave function and the configuration of the surrounding nuclei with non-zero nuclear spins provide unique information on the electronic structure, dynamics and spatial distribution of the paramagnetic centers. Lanthanide ions combine fast electronic relaxation and high paramagnetic susceptibility promoting fast nuclear longitudinal and transverse relaxation of the protons in close vicinity. As stable complexes, this makes them promising candidates as MRI contrast agents and spin tags in EPR as well as paramagnetic NMR spectroscopy. A prominent example are the complexes of Gd(III), which have been successfully used in clinical practice[1] as well as in NMR[2] and EPR[3] studies. However, their design requires an understanding and ideally a priori prediction of their electronic properties.

In this contribution, we want to demonstrate what information can be obtained by pulsed EPR experiments on Gd(III) complexes in frozen glassy solutions. We study the relaxation behavior in the solid state at different magnetic field strength from 0.35 to 3.5 T and investigate the influence of the surrounding ligands on the electronic relaxation times for five different complexes. Interactions of the Gd(III) ion with the surrounding ligands, the electron-electron dipole coupling in spin systems with $S > 1/2$, as well as some relativistic effects cause the so-called zero field splitting (ZFS) interaction. We show the current precision of extracting zero-field splitting (ZFS) values in aqueous frozen solutions from multi-frequency EPR measurements. Finally, we discuss possible correlations between molecular structures of the Gd(III) complexes and their experimental designed ZFS parameters distributions based on superposition modeling of pairwise Gd(III)-ligand atom interactions.[4]

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Ligand dissociation and recombination of Nitrosyl-myoglobin in physiological media studied by ultrafast X-ray spectroscopy and X-ray Diffuse Scattering

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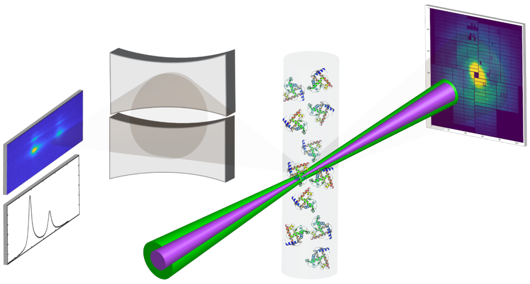
Myoglobin is a small protein consisting of a single polypeptide chain and a heme as its active center. It plays a central role in many biological functions based on detection, transport, release and/or binding of molecular ligands such as O_2, CO, NO, CN, etc. Nitrosyl-Myoglobin (MbNO), in particular, is not entirely understood despite its biological relevance in controlling various neurophysiological responses. The ultrafast photodissociation of low spin, planar MbNO leads to the high-spin deoxyMb. However, the recombination occurs on multiple timescales (from sub-ps to 100s ps) and formation of a high-spin domed ligated MbNO is accepted as one of the intermediates on the way back to the planar form. Previous X-ray absorption studies with 70 ps resolution supported the latter hypothesis [1], but the nature of the earlier time kinetics is unclear. In particular, is the relaxation back to planar a cascade via spin states or is it due to steric hindrances? In order to elucidate these aspects, we combined femtosecond Fe K-edge X-ray absorption spectroscopy (XAS) with X-ray emission spectroscopy (XES) and X-ray diffuse scattering (XDS) at the FXE beamline of the European-XFEL (Hamburg) and at SACLA (Japan). The setup at the European-XFEL is shown below, laser (green) and x-rays(purple) overlap on a round jet, behind XDS and perpendicular XES is detected.



XAS probes the unoccupied density of states (DOS) and the local structure around the Fe atom, while XES the occupied DOS and the spin state of the intermediates. XDS allows to unravel structural changes of the protein structure. We will present our results from these measurements and cast them in the context of on-going studies of biosystems at XFELs.

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Enhanced electrocatalytic CO_2 conversion on nanostructured silver electrodes in ionic liquids

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The development of efficient catalytic system for elctroreduction of CO_2 to intermittent energy fuels has received noticeable attention from the scientific community all over the globe. Ag-based catalysts have drawn great attention due to its product selectivity towards CO formation in CO_2 reduction reaction (CO_2RR) [1]. On the other hand, the use of room-temperature ionic liquids (ILs) can decrease the CO_2RR overpotential[2]. Herein, we demonstrated the enhanced catalytic activity of a novel nanostructured Ag electrode in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]). The nanostructured and highly porous Ag catalyst was prepared via additive assisted electrodeposition approach. Deposition was done galvanostatically for 20 s at current density of –3 Acm^{-2}. The Ag catalyst was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). It represented a Ag foam, consisting of nanorods (NRs) with diameters in the range of 50 to 100 nm (Fig. 1). The activity of the Ag NRs electrode was demonstrated by cyclic voltammetry (CV) to be significantly increased as compared to a Ag foil electrode in pure IL and with water addition (X_{H2O}~20%). Using Ag NRs, we achieved highly selective CO production (Faradaic efficiency FE_{CO} was nearly 100%) in a relatively broad potential window of 0.4 V in [BMIm][BF_4]. Furthermore, to check the stability of the catalyst, we performed long-term electrolysis. For 5 hours, current density did not change and FE_{CO} remained ca. 100%. No structural changes in Ag NRs were revealed by identical location SEM characterization that was done before and after the electrolysis.

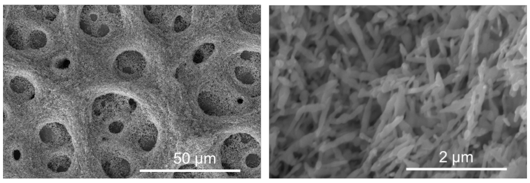

Fig.1. SEM images of Ag foam, consisting of nanowire

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How to accelerate diffusion of CO2 in ionic liquids for its electrochemical conversion

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The electrochemical reduction of carbon dioxide (CO_2) currently receives global interest as one of the most promising approaches to mitigate and utilize CO_2 gas, which is regarded as one of the major contributors to the greenhouse effect.[1]Ionic liquids (ILs) have gained attention for CO_2 reduction due to several unique advantages: (i) ILs exhibit a selective and relatively high absorption of CO_2; (ii) ILs suppress the parasitic hydrogen evolution reaction; (iii) ILs decrease the overpotential of CO_2 reduction via stabilization of CO_2 radical anion intermediate.[2] So, ILs are proposed as the next generation of effective solvents for CO_2 capture/sequestration and its conversion. However, the mass transport of CO_2 in ILs is typically slow due to the relatively high viscosity of ILs. Recently we demonstrated that dilution of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]) with water improved the mass transport properties and boosted CO_2 reduction reaction (CO_2RR) to carbon monoxide (CO) on a silver electrode. Now we compare the mass transport properties of CO_2 and CO_2RR in [BMIm][BF_4] with those in ILs, 1-ethyl-3-methylimidazolium tricyanomethanide ([EMIm][TCM]) and 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIm][TCB]), which have significantly lower intrinsic viscosity (Fig. 1). A pulsed-gradient spin-echo (PGSE) NMR spectroscopy is used to determine the concentration and diffusion coefficients of CO_2 and other solution components. The effect of water addition is explored in the diffusion-controlled CO_2RR in IL/water mixtures by means of voltammetry, chronoamperometry and rotating disc electrode techniques. The diffusion coefficients obtained from PGSE-NMR are compared with those obtained from electrochemical measurements. The formation of CO in CO_2 electroreduction is confirmed by online gas chromatography.

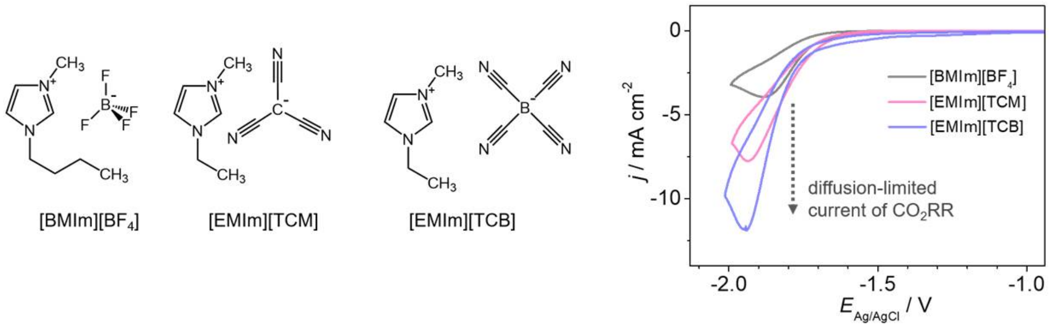

Fig. 1. Left: ILs under study. Right: Cyclic voltammograms of Ag in CO_2-saturated ILs compare diffusion-limited currents of CO_2RR

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Selective Reaction of Phosphonate with Strained Siloxane Bridges on Silica Surfaces via ^{31}P Solid-State NMR and DNP-SENS

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The preparation of heterogeneous catalysts and advanced nanoscale fabrications necessitates molecular level control and precision. Thus, a molecular-level understanding of surfaces and their chemistry is essential. In this context, Surface Organometallic Chemistry (SOMC) has emerged as a powerful route for the understanding and the development of heterogeneous catalysts, imaging and microelectronic devices through a stringent control of surface hydroxyl by the means of a dehydroxylation process, the first step for the control incorporation of metal centres and dopants on surfaces via grafting.[1] On silica, the OH density is typically controlled via a thermal treatment under vacuum and/or an inert gas. This process generates an increasing proportion of isolated OH groups with higher thermal treatment, and it is accompanied with the formation of siloxane bridges, which can be highly reactive 4-membered siloxane bridges when very high temperatures are used (> 600 °C).

In the context of the development of microelectronic devices, achieved with the selective phosphorous doping of silicon wafers,[2] we have been interested in understanding the reaction of phosphonate, a prototypical phosphorus precursor for the doping of metal oxide surfaces, with silica used as a high surface area model of the substrate. Herein, we describe the characterization of surface species resulting from the reaction of $P(O)(OEt)_2(CH_2Ph)$ with the surface of SiO_2 partially dehydroxylated at temperature ranging from 300 to 900 °C. Phosphorus-31 DNP surface enhanced solid-state NMR spectroscopy[3, 4] combined with computational studies shows that phosphonates are readily physisorbed on silica and that grafting does not occur on surface silanols, but only on strained siloxane bridges generated at high temperatures.

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Towards hybrid trapping of cold molecules and cold molecular ions

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Hybrid systems of trapped atoms and ions in the cold regime (< 1 K) have been studied extensively over the last few years [1]. The high degree of control makes them ideal candidates for the study of cold collisions and reactions. Recent research focuses on the extension of these systems to neutral molecules and molecular ions [2].

Here, we report on the development of a hybrid system of trapped cold OH radicals and atomic/molecular ions. Packages of translationally cold OH molecules (< 1 K) are produced with a Stark decelerator, which allows to slow down polar molecules with inhomogeneous electric fields. The decelerated molecules are stopped with electric fields in order to load them into a magnetic trap. Successful trapping of the molecules is confirmed via laser-induced fluorescence.

Our system will allow to superimpose both the magnetic trap and a radiofrequency ion trap in order to study collisions between these particles. This will make it possible to perform quantum-state selective investigations of elastic, inelastic and reactive collisions at low temperatures. Initial experiments will focus on OH + Ca^+, OH + N_2^+ and OH + H_2O^+ as collision systems.

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Probing the CPEB3 RNA structure by NMR

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This work is aimed at the investigation of the NMR solution structure and folding mechanism of the cytoplasmic polyadenylation element binding protein 3 (CPEB3) ribozyme to better understand its catalytic activity. Ribozymes are naturally occurring catalytic RNA molecules. The CPEB3 ribozyme is until now the only confirmed small ribozyme in mammals but its role remains still elusive.[1] As RNA function is directly linked to structure, structural studies are the basis to understand RNA function.

The CPEB3 belongs to the Human Delta Virus (HDV)-like family of self-cleaving ribozymes.[2] Therefore it is suggested that its mechanism of self-cleavage is very similar to the known mode of action the HDV ribozyme. The cleavage reaction of the HDV follows a Mg^{2+} facilitated acid-base mechanism that is based on a perturbed pK_a of the conserved cytosine C75 within its catalytic core. In analogy to C75 of HDV, the CPEB3 ribozyme contains a conserved cytosine C57 that might directly participate in the cleavage reaction. Therefore we started to determine the pK_a value of C57 in the absence and in the presence of Mg^{2+}. The first pH-titrations with the chimp CPEB3 construct did not show any elevated pK_a value, independently of the Mg^{2+} concentration applied.

Another goal of this work is the elucidation of the NMR solution structure of the CPEB3 ribozyme. Using various truncated constructs, different labeling schemes and a number of multinuclear and multidimensional NMR experiments, a large fraction of resonances could be unambiguously assigned. Further, by introducing 5-Fluoro-uridine into the CPEB3 RNA using *in vitro* transcription ^{19}F-NMR spectroscopy was now applied to support and facilitate the assignment of our construct, on the one hand, and on the other hand, to directly follow the folding of the CPEB3 into its active state upon Mg^{2+}. These results are the basis to understand the individual steps of the ribozyme function on a structural level and to enlighten the biological role of the CPEB3 ribozyme.

Financial support by the University of Zurich and the Swiss National Science Foundation are gratefully acknowledged.

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Molecular Engineering Towards Highly Efficient and Stable Perovskite Solar Cells

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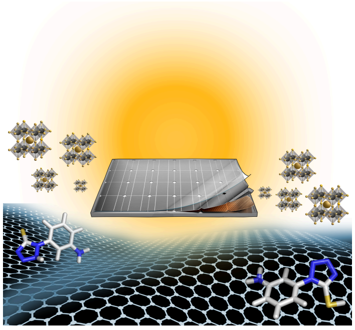
The increasing energy demands pose a requirement for sustainable resources, which can be met by relying on light harvesting photovoltaic technologies. Perovskite solar cells present one of the most prominent photovoltaic technologies with extraordinary efficiencies exceeding 22%.[1–2] However, their stability, scalability, and engineering at the molecular level remain challenging.[2–4] We demonstrate a new molecular modulating concept of scalable and operationally stable perovskite solar cells that exhibit exceptional solar to electric power conversion efficiencies. The molecularly designed modulator SN links the mercapto-tetrazolium (S) and phenylammonium (N) moieties, which passivate the defects, while improving the morphology and electronic quality of the $FA_xCs_{1-x}PbI_3$ (FA = formamidinium) perovskite formulation.[3] We investigated the properties of the material and the corresponding devices by relying on the state of the art methodology, involving X-ray diffraction, scanning electron microscopy, cathodoluminescence, solid state NMR, as well as photoluminescence spectroscopy. The molecular modulation greatly enhanced solar cell performance with efficiencies exceeding 20% for active areas above 1 cm^2, which was accompanied by outstanding operational stability under ambient conditions.[3] These findings reveal a prototype that inspires the advanced molecular design of a new generation of molecularly engineered organic agents,[4–5] unveiling a path to realize efficient and stable, large-scale perovskite solar cells in the near future.



Schematic representation of a perovskite solar cell with the models of molecular modulators

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Discerning γ-Alumina Surface Sites with Nitrogen-15 Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy of Adsorbed Pyridine

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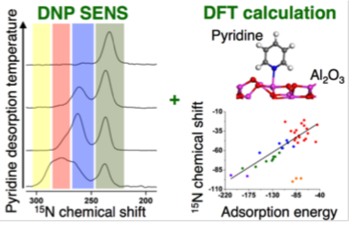
Transition aluminas, in particular γ-Al_2O_3, are of great interest due to their broad range of applications. In catalysis, they serve as catalysts by themselves or catalytic supports [1]. Today, the most advanced studies have focused on understanding the role of specific surface sites and facets in the reactivity of γ-Al_2O_3 [2]. ^{15}N NMR of adsorbed pyridine has been shown to be a powerful tool to probe the surface of solids [3]. The large ^{15}N chemical shift range of 100 ppm between free pyridine and protonated pyridine (pyridinium) should in principle provide a sufficient resolution to discriminate surface sites of different acidity, but the NMR experiments have to be carried out at low temperature to avoid rapid exchange between surface sites, that averages chemical shift values and can thereby lead to misassignment.



Here, we explore the use of low-temperature ^{15}N dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS) [4] and ^{15}N labeling for probing the specific surface sites of γ-Al_2O_3. This technique allows extracting the chemical shift anisotropy parameters within acceptable experimental time thanks to increase of the NMR sensitivity through DNP using exogenous dinitroxyl radicals [5]. Based on the results of DNP SENS with complementary *in-situ* IR measurements and DFT calculations on periodic models of alumina surface, we propose the assignment for the observed NMR and IR signals and rationalize the relationship between ^{15}N chemical shift and adsorption energy of pyridine.

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Excited state dynamics of helicene dimers

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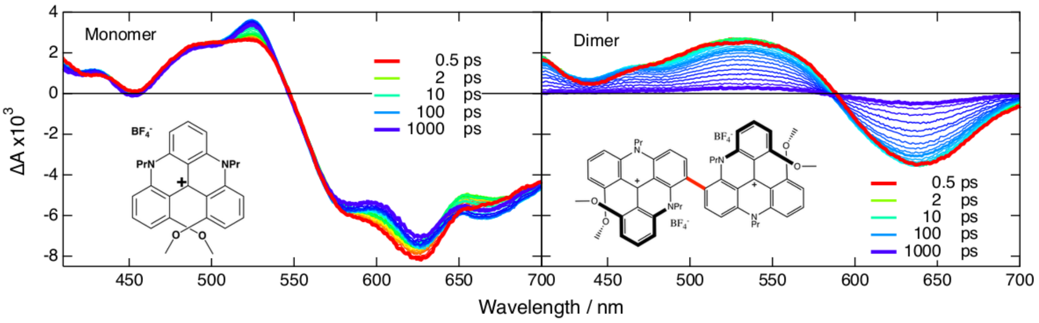
Organic helicenes may find applications in several areas like in blue light emitting diode or in bio-imaging. The photophysical properties of chiral [4]helicenes cations[1] and functionalized cationic [4]helicenes were discussed in detail previously[2]. Here we will present an investigation of the excited state dynamics of an [4]helicene dimer, consisting of two directly-linked [4]helicenes. Two isomers of the dimer, which differ by the mutual orientation of the subunits, have been studied. Contrary to the monomers, which have fluorescence quantum yields up to 0.55, the dimers are hardly fluorescent.

To understand the origin of this quenching, a variety of spectroscopic measurements, including fluorescence up-conversion and transient absorption experiments were carried out.



Transient absorption data (see figure) point to a substantially shorter excited lifetime of the dimer (460 ps) compared to the monomer (< 1ns). This shortening depends on the solvent polarity, as wheel as on the mutual orientation of the chromophores suggesting the occurrence of a charge transfer process between the two helicene subunits. Additionally, occurrence of other processes such as excitation energy hopping has been detected.

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Mechanosensitivity of polydiacetylene with a phosphocholine headgroup.

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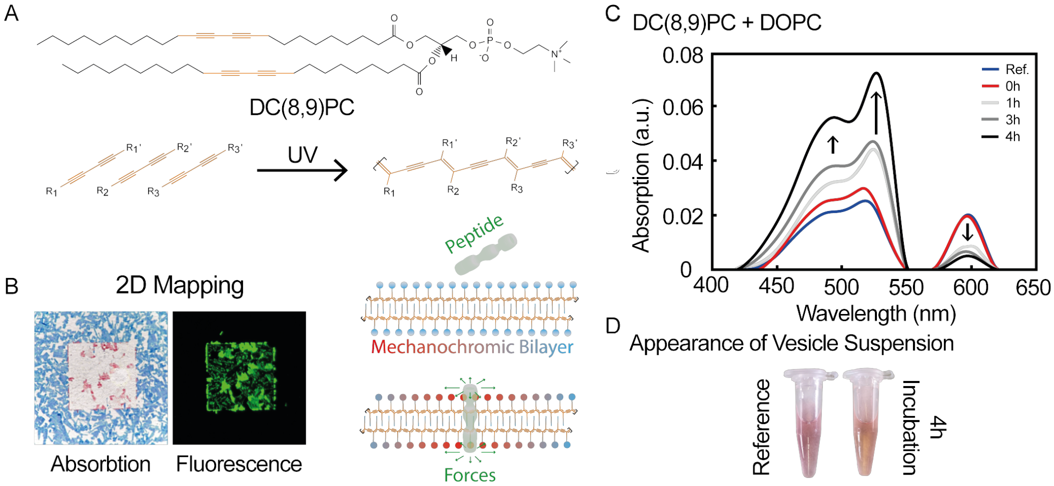
Membrane forces play pivotal roles in numerous physiological processes such as endocytosis, cell mutations and calcium signaling.Currently used characterization methods such as atomic force microscope (AFM) or optical tweezers allow for the controlled force application but not for the detection of the forces applied to the bilayers. Micro-aspiration of giant unilamellar vesicles (GUV) enables the quantification of surface tension, however, its conversion into local forces is difficult.



We are developing a mechanosensitive membrane probe that enables direct measurement of molecular forces applied within lipid bilayers. We employ a mechanochromic polymer polydiacetylene (PDA, Figure 1A) that changes its color and fluorescence intensity upon application of forces (Figure 1B-C). As a first step, we demonstrated a PDA vesicle assay that detects melittin, a transmembrane peptide from bee venom. First we fabricated PDA vesicles by self-assembling the lipid monomer and subsequently crosslinking by UV. Figure 1C shows the absorption spectra before (blue) and right after (red) addition of melittin to the PDA vesicle solution. These spectra overlap, suggesting no immediate colorimetric response due to the addition of melittin. However, we found that the spectra shifted over the next several hours (Figure 1C). After 4 hours, the shape of the spectra changed completely, as the color change was clearly visible also by naked eyes (Figure 1D). The slow response from our PDA sensor against melittin is different from what has been reported with other types of PDA sensors[1] [2]. In this work, we further analyze the unexpectedly slow interaction kinetics, fluorescence spectra of PDAs, and discuss possible origin of the slow kinetics[3].The developed assay proved that DiynePC PDA is sensitive to mechanical stimuli. The advantage of our PDA sensor is that it has a phosphocholine head group that mimics cell membranes. Its combination of sensitivity and the biocompatibility will allow us to incorporate this probe in live cells in future, providing us a further possibility to investigate force distribution during mitosis, cell migration, and interactions with medical implants etc.

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Time-resolved element selective probing of the photo-induced charge carriers in inorganic lead perovskites

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[1]Laboratoire de Spectroscopie Ultrarapide (LSU) and Lausanne Centre for Ultrafast Science (LACUS), Ecole Polytechnique Federale de Lausanne (EPFL), 1015 Lausanne, Switzerland, [2]Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA, [3]ETH Zürich, Laboratory of Inorganic Chemistry, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland

Lead halide perovskites represent promising candidates for the next generation of solar materials, due to their low cost fabrication and outstanding optoelectronic performances. Despite the large research efforts in recent years, microscopic details of the charge carrier formation and relaxation are still missing. In this perspective, time-resolved X-ray absorption spectroscopy (TR-XAS) represents an ideal tool to investigate this multi-element material.

Previous time-resolved experiments performed at the Swiss Light Source (SLS) on the Br K-, the Pb L3- and the Cs L2-edges of CsPbBr3 nanocrystals in toluene (optical pump 355 nm) have pointed out to localization of the holes at Br sites, which leads to formation of a small polaron in the valence band (VB) within 100 ps. The results also suggested that the electrons remain either delocalized or form large polarons in the conduction band (CB). [1,2]

Recently, these investigations were pursued at the Advanced Photon Source (APS, Chicago). The Br K-edge energy spectra at different time delays have been recorded to probe the local structural modification in the EXAFS region and kinetic traces at the pre-edge, edge and post-edge were collected, in order to determine the relationship between the electronic dynamic at Br sites and the structural changes of the local environment. Furthermore, high energy resolution fluorescence detection (HERFD) was implemented at the Pb L_3-edge XANES, yielding finer details of the broad featureless absorption. The study allows to obtain further insights about the charge carrier relaxation process and relates the spectral features at the Pb centers with the nuclear and electronic changes of the Br sites.

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Long-range Rydberg molecules bound by electron-atom scattering

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In 1934, Amaldi and Segré [1] observed pressure-dependent shifts and broadenings in Rydberg spectra. The pressure shift results from interactions of the Rydberg electron with ground-state atoms lying within the Rydberg electron's orbit. Fermi [2] explained this interaction as arising from the s-wave scattering of the slow Rydberg electron with the ground-state atom.

As first predicted by Greene et al. [3] and first observed by Bendkowsky et al. [4], the interaction can be treated using oscillatory potentials that may support bound states of long-range diatomic molecules in case of a negative s-wave scattering length. For the alkali metal atoms, the triplet scattering length is negative whereas the singlet scattering length is very small or even positive. Singlet and triplet scattering channels are, however, mixed by the hyperfine interaction in the ground-state atom [5]. This mixing allowed for a first determination of the zero-energy singlet s-wave scattering length of caesium [6].

The often neglected p-wave contribution is known to lower the potential barrier towards smaller internuclear separations [7,8]. The excited molecules may therefore decay by tunnelling through the potential barrier. Measurements of the lifetimes of the molecules can provide a sensitive probe of the potential-energy curve. We will present studies on the formation and dynamics of long-range Rydberg molecules in an ultracold caesium and potassium Rydberg gases using high-resolution photoassociation spectroscopy and an outlook towards future experiments with heteronuclear molecules.

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The Use of Peptide Bonds for Cold Ion Spectroscopy

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UV absorption by aromatic residues in cold, gas-phase peptides is extremely sensitive to their structure. Combined with vibrational spectroscopy (IR-UV double-resonance[1]and IR-IR-UV hole-burning[2, 3]techniques) it provides detailed information for accurate validation of calculated geometries, while together with high-resolution mass spectrometry (2D UV-MS[4]) it allows for an identification of isoforms of biomolecules. These photofragmentation techniques require presence of aromatic amino acids in the peptide sequence.

Alternatively, peptide bonds can be used as chromophores. In solution, peptides and proteins exhibit strong π→π* and a weak n→π* absorptions below and above 200 nm, respectively. However, their UV absorption in the gas phase has never been characterized. We report the first UV photofragmentation spectrum of a protonated dipeptide, a model system with one peptide bond, in a wavelength region above 192 nm. We explore the effect of IR pre-excitation on electronic spectrum of cold ions and demonstrate the applicability of all-conformer IR-UV gain and conformer-selective IR-IR-UV hole-burning techniques to peptides that do not contain aromatic residues.

Local interactions in peptides affect spectroscopic fingerprints of individual peptide bonds. In particular, hydrogen bonds disturb the planar orientation of the peptide bonds, which results in the increase of the π→π* transition intensity. We demonstrate that the fragment-specific UV spectroscopy of a model helical peptide reveals such transitions and intensities of these transitions correlate with local structural preferences of the peptide, reported previously. We therefore suggest that the 2D UV-MS spectroscopy can be used as a local structural probe for peptides and proteins.

This work was supported by the Swiss National Science Foundation (grant IZLRZ2_163865).

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Novel Oxide Derived Zn Nano-Catalysts for Efficient Conversion of CO_2 to Formate

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Oxide derived Zn nano-catalysts were prepared via sequential catalyst synthesis and activation processes. First, dendritic Zn catalysts were prepared by a template assisted electrodeposition approach followed by a thermal annealing at 200°C for 5h thus leading to a thick Zn(II) oxide precursor layer covering the catalyst surface. The Zn oxide layer was subsequently reduced to metallic Zn nanocrystals by applying an potential of -0.9V vs RHE for 1500 s. These nano-crystals were applied as efficient catalyst in electrochemical CO_2 reduction reaction (in the following denoted as CO_2RR). The catalysts characterization was performed by means of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDAX), X-Ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) methods. Electrolysis was carried out in CO_2 saturated aqueous 0.5 M $KHCO_3$ electrolyte. Products were analyzed by means of gas chromatography (GC) and ion chromatography (IC) techniques. CO and $HCOO^-$ were identified as primary CO_2RR products. Our analysis demonstrates a clear switching of the product selectivity from CO to $HCOO^-$ when going from lower to higher applied overpotentials. A maximum in the faradaic efficiency of 44% was obtained for $HCOO^-$ at -1.2V vs RHE (Fig 1). Our study demonstrates that a template assisted catalyst deposition approach followed by thermal annealing can fundamentally change the product distribution and transform a primarily CO forming catalyst into a formate producing one.

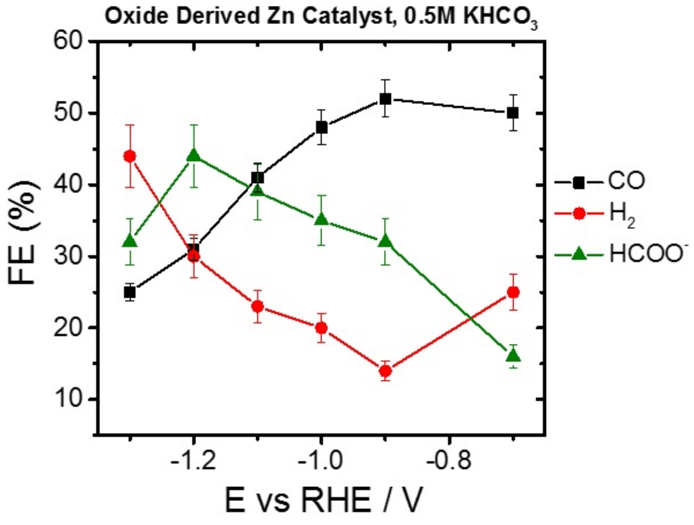

Fig. 1 Faradaic efficiency (FE) plot of oxide derived Zn catalyst representing the selective formate formation at higher overpotentials.

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Understanding OECT; The new THz ATR spectroscopic option

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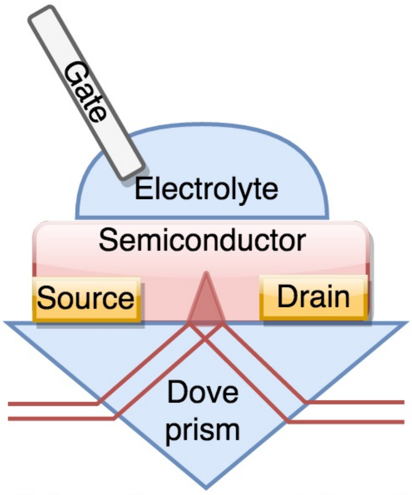
[1]Department of Chemistry and Biochemistry, [2]Department of Chemistry and Biochemistry, Universi, [3]Department of Chemistry and Biochemistry,

Organic biosensing and bioelectronics is a young, dynamic and exciting field, uniting researchers from highly diverse backgrounds – life sciences, synthesis, physical chemistry, solid-state physics, materials science and device engineering.[1] One prominent example in bioelectronics are OECTs (organic electrochemical transistors) were ions from an aqueous environment penetrate an organic semiconductor film and affect its electric conductivity. Such devices can be integrated with living cells, tissues and organs to monitor cellular activity.[2] So far, an in-depths understanding of the underlying fundamental processes and working principles of OECTs is still lacking. The vision of ours research project is to bring sophisticated spectroscopic studies into this emerging field. We expect that ion penetration strongly affects the visible and terahertz absorption of the polymers film. However, the strong THz attenuation by water renders the use of THz spectroscopy on OECTs problematic. To overcome this difficulty, we want to apply THz spectroscopy in an attenuated total reflection (ATR) geometry, where the sample interacts with the evanescence wave travelling along the surface of a Dove Prism



Schematic representation of an OECT in an ATR geomerty

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Broadband Ultrafast Spectroscopy and Molecular Dynamics Simulations of Electron Donor/Acceptor Complexes

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In solution, particular combinations of donor and acceptor molecules can form ground-state complexes that exhibit a new, red-shifted, absorption band in the visible not present in the individual donor or acceptor spectra. This new absorption is termed a ‘charge-transfer’ (CT) band and corresponds to visible absorption coupled directly to transfer of a full charge from donor to acceptor. Following such charge separation an ultrafast charge-recombination (CR) process occurs in concert with structural dynamics of the newly formed ion pair (IP). Due to the large distribution of ground-state complex structures, ranging from tightly bound complexes to loosely bound, solvent separated, pairs, the excited state behavior of the system is a composite of many different species. Although the thermodynamics and CR processes of such EDA complexes have been the subject to decades of study, the structural dynamics of the EDA complexes and their relation to the CR process in this system are still poorly understood.

In order to describe how structural dynamics influences the CR process in EDA complexes we will present results of ultrafast time-resolved infrared (TRIR), transient visible absorption (visTA), and broadband fluorescence upconversion (FLUPS) experiments on the benzene (Bz)/tetracyanoethylene (TCNE) EDA complex. The TRIR experiment permits us to measure the nitrile vibrational frequency of the TCNE radical ion (formed upon CT excitation) during the CR process, giving us insight into the structural dynamics of the complex. The visTA and FLUPS experiments report on the CR process directly and allow us to probe the recombination dynamics of the excited complexes and IPs. In addition to the experiments, we will report molecular dynamics simulations of donor/acceptor pairs and EDA complexes. Such simulations give us direct insight into the structural dynamics of these systems and also allow for calculation of energetic parameters important to describing the electron transfer process. This unique combination of multiple spectroscopic techniques and simulations give us a unique view into the interplay between structural dynamics and charge recombination in EDA complexes.

Scattering study of C(^{3}P)+NO(X$^2\Pi$) collisions on 2A′, 2A″ and 4A″ potential energy surfaces

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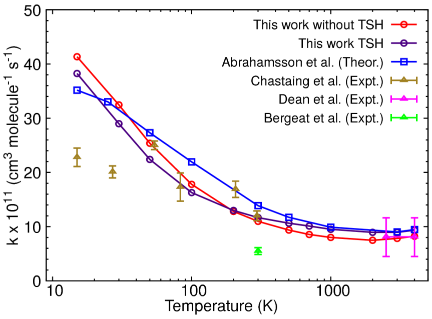
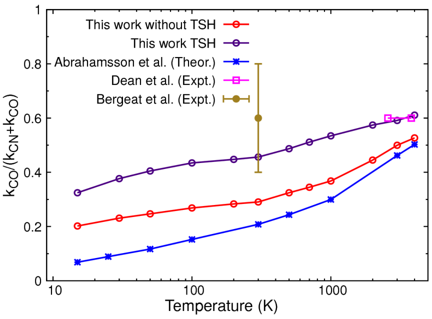
Studies involving the collisions between C, N and O containing species are potentially important in the area of low temperature reactions in the interstellar medium and high temperature combustion chemistry. In this work, full dimensional potential energy surfaces for the 2A′, 2A″ and 4A″ electronic states of CNO system have been constructed following a reproducing kernel Hilbert space approach [1]. For this purpose, more than 50000 ab initio energies are calculated at the MRCI+Q/aug-cc-pVTZ level of theory [2]. The dynamical simulations for the C(^{3}P)+NO(X$^2\Pi$) → O(^{3}P) + CN(X$^2\Sigma^+$), N(^{2}D/^{4}S) + CO(X$^1\Sigma^+$) reactive collisions are carried out on the newly generated surfaces using quasiclassical trajectory calculation method [3]. Trajectory surface hopping (TSH) method is used within the Landau-Zener formalism to investigate the effect of nonadaibatic transitions on the title reaction [4]. Reaction probabilities, cross sections, rate coefficients and branching ratios are calculated for the title reaction and compared with available theoretical [5,6] and experimental results reported in literature [7–9]. Rate coefficients and branching fractions calculated in this work are in a good agreement with the experimental [7–9] results. A new set of rate coefficients are calculated for the first time at temperatures relevant to hypersonic flight regime (5000-20000 K).





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Small-Molecule Reactions : NO_2 case

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Processes involving atom-diatom, diatom-diatom reactive collisions under extreme external conditions are highly relevant for the hypersonic flight regime of spacecraft and other solid bodies such as meteorites reentering the atmosphere. The chemistry around such objects is governed and directly influenced by non-equilibrium conditions. With vibrational and rotational temperatures reaching several thousand Kelvin. At these temperatures, controlled experiments providing the necessary molecular detail are very difficult if not even impossible to carry out. Therefore, validated computational investigations become a valuable complementary tool.

A detailed quasi classical trajectory and reaction dynamics are explore for NO + O and CO + O for different electronic states, based on ab-initio potential-energy surfaces. The study is aimed at generating accurate potential energy surfaces for both systems. Additionally, cross sections and rate constants were obtained and were compared to show good agreement with the available experimental data [1] and quasi classical calculations [2,3,4,5].

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Inorganic Perovskite Nanocrystal Antennae for Photocatalytic Applications

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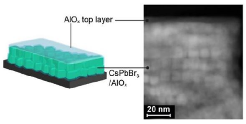
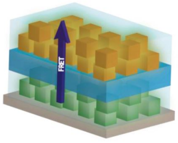
Efficient solar-to-chemical energy conversion is one of the most compelling challenges currently faced by the scientific community. Inspired by the natural photosynthetic mechanisms, realizing an energy conversion devices based on Forster Resonance Energy Transfer (FRET) could provide a potential solution. Thanks to their tunable optical properties, colloidal quantum dots could be ideal candidates to exploit such a concept, if the compositional and structural parameters leading to high efficiency are unveiled.

The recently discovered all-inorganic perovskite nanocrystals (PeNCs) exhibit size-and composition dependent bandgap, large absorption coefficients and very high quantum yields superior to previously studied metal-chalcogenide nanocrystals, particularly in the blue and green region of the visible spectrum.[1] Despite their exceptional optical properties, PeNCs suffer from a number of drawbacks that hamper their implementation in FRET-based architectures, such as: photodegradation, fast anion exchange and water instability.

In this contribution, we will briefly describe the deposition of a low-temperature aluminium oxide(AlOx) matrix that protects PeNCs films against water and photodegradation, while also enabling the assembly of a multilayered structure with angstromic control over the interlayer distances. [3] With the use of this method, the spectroscopic study of such multilayered PeNC structures are made possible. A distance-dependence study is conducted to elucidate the dynamics of energy transfer between PeNC layers of different compositions. In a similar approach, the interaction mechanism between the light-absorbing PeNC layer and the final layer of catalyst has been investigated. One of the most appropriate choice of catalyst has been envisaged to be metallic nanoparticles, such as Ag, Au and Cu, due to their activity for CO_2 reduction and their plasmonic absorption, that can form the basis of an exciton (PeNC)-plasmon (metal NP) energy transfer system





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Cold ion spectroscopy of non-covalent complexes for identification of isomeric glycans

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Oligosaccharides play an important role in biological processes, because, as a result of posttranslational modifications, about half of all proteins in living organisms contain oligosaccharide chains. The qualitative and quantitative structural analysis of glycans is challenging due to their high isomeric diversity, where glycans of the same mass can differ in the isomeric forms, positions and attachment points of their monosaccharide units. Regarding this isomeric complexity, there is currently no a comprehensive analytical technique for structural identifications of olygosaccharides, which is comparable in its power to the standard sequencing technologies, developed, for instance, for proteins and DNA.

Over the last few years our group has demonstrated the successful use of a combination of high-resolution UV photodissociation spectroscopy with high-resolution mass spectrometry (2D UV-MS) for library-based identification and quantification of drugs and model isomeric peptides as a complementary method/alternative to the LC-MS approach. A use of this approach for identification of glycans is severely complicated by the fact, that saccharides have no UV chromophore groups and absorb only in the deep UV region. One known way to solve the problem of “invisibility” of glycans employs their chemical labeling by chromophore groups. This approach requires a timely chemical pre-processing of an oligosaccharide analyte, however. In this work we propose and explore a use of non-covalent complexes of glycans with protonated chromophores for qualitative and quantitative analysis of the glycans by 2D UV-MS techniques. The poster presents some preliminary results of the study.

Tailored photocleavable peptides: a strategy for charge control in high vacuum

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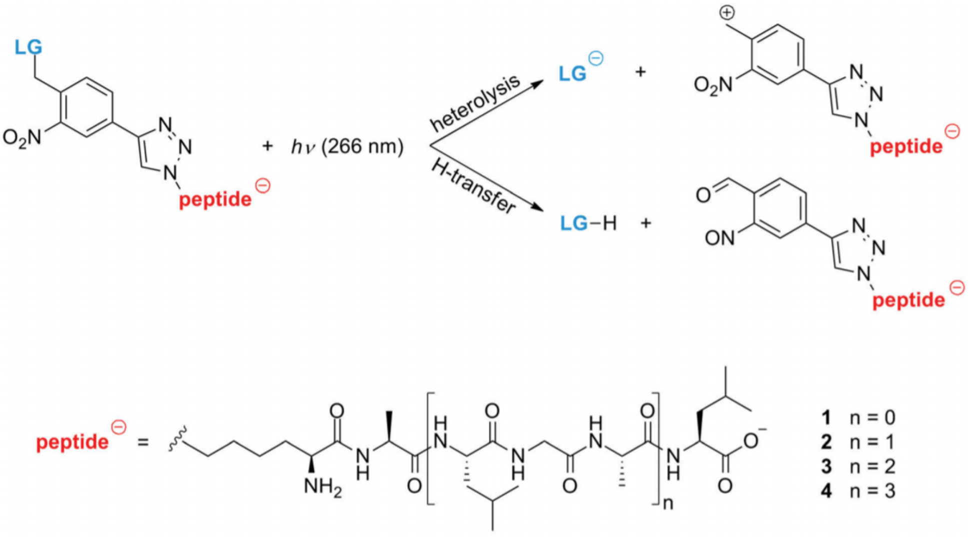
Controlling and manipulating the charge of molecules in the gas phase is an important requirement for quantum interference experiments and related metrology. Photocleavable tags (PCT) based on *ortho*-nitroarylethers were designed and studied to manipulate small biomolecules post-launch. We investigated the photocleavage of electrosprayed oligopeptides, functionalized with our photo-tag under laser-UV irradiation (266 nm) in high vacuum. Upon irradiation, two alternative cleavage channels were observed leading to i) either the formation of a negatively charged leaving group and a charge neutral peptide fragment or ii) a negatively charged peptide fragment and a charge neutral leaving group. We investigated how peptide length, the nature of the leaving group and the position of the nitro group (*ortho* vs. *para*) favours one channel over the other. A *para*-nitro substituted benzylic ether showed heterolytic cleavage in the gas phase, whereas the same compound did not cleave in solution, indicating that the cleavage path differs markedly from established solution phase behavior.



Scheme 1: Photocleavable tags (PCT), reaction scheme and oligopeptides used in this study. Upon irradiation with 266 nm UV light the functionalized peptides can undergo either heterolytic cleavage or dissociation with simultaneous proton transfer. The functionalized peptides differ in their amino acid sequence Lys-Ala-(Leu-Glu-Ala)n-Leu and in their leaving group (LG).

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Manipulating the translational and internal degrees of freedom of hydrogen atoms

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The first experiments designed to control the translational motion and the internal state of the hydrogen atom were performed almost 100 years ago by Rabi [1] using the beam methods developed by Gerlach and Stern [2]. We present a method with which paramagnetic atoms and molecules can be generated in a specific magnetic sublevel of a selected internal state and with which the atom or molecule velocity can be manipulated at will. The selected magnetic state and velocity is achieved by multistage Zeeman deceleration [3,4].

Of particular interest are slow beams ($v < 100$ m/s) of cold hydrogen atoms in view of precision frequency measurements of fine- and hyperfine structure intervals as well as intervals to high-Rydberg states, which are relevant in the context of the proton charge-radius puzzle [5,6]. In our experiment we generate the hydrogen atoms by photodissociation of NH_3 in a capillary mounted at the orifice of a pulsed valve. The hydrogen atoms are entrained in the supersonic expansion and enter a 12 stage Zeeman decelerator, with which they are slowed down from initially ~500 m/s to 50-100 m/s [7]. After leaving the decelerator they are photoexcited to Rydberg states in a 2+1' resonant three-photon excitation sequence via the 2s $^2S_{1/2}$ intermediate state and detected by pulse field ionization. We will report on our experimental progress on the measurements of *n*p-2s transition frequencies.

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Excited-State Dynamics of BODIPY Decorated Phenylethynylen Dendrimers

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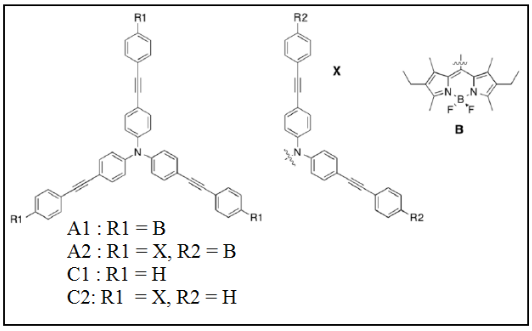
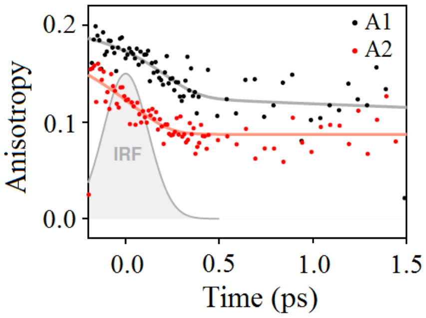
Deep understanding of how nature captures and funnels energy towards the reaction centers of photosynthetic organisms remains a major challenge. Here, we present a study of the excited-state dynamics of two multichromophoric arrays, synthesized as simple mimicks photosynthetic antennae (Fig. left).[2] Both arrays comprise a dendritic core composed of three (C1) and nine (C2) diphenylethynyl branches connected via nitrogen atoms. The two cores are decorated at their periphery with 3 (A1) and 6 (A2) boron-dipyrromethene (Bodipy - B) units, playing the role of energy sinks.





A variety of time resolved techniques has been utilized to unveil the complex excited-state dynamics of these two arrays. Using fluorescence up-conversion measurements under magic angle and anisotropy conditions, we were able to monitor the energy redistribution within the cores (ultrafast depolarization of fluorescence – Fig. right), as well as the energy migration from the high-energy cores to the low-energy Bodipy ends. Transient absorption measurements in the fs to ns timescale not only support the above findings, but evidence the occurrence of other processes occurring in parallel or after those mentioned above, i.e. charge separation and recombination processes.

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High-resolution spectroscopy of the a $^3\Sigma_u^+$ state of $^4He_2$ using Zeeman-decelerated spin-polarized molecular beams

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Metastable $^4He_2$ in the a $^3\Sigma_u^+$ state (He_2^*) is a four-electron molecule and its properties can be calculated *ab initio* with high accuracy [1]. He_2^* has a lifetime of about 18 s and a magnetic moment of two Bohr magneton that can be used to slow down supersonic beams of He_2^* using the technique of Zeeman deceleration [2]. The decelerated He_2^* samples offer a collision-free environment and enable long measurement times, which is ideal for precision spectroscopy. In previous works, the fine-structure intervals of the N=1, 3, 5, 7 - 11 and 25 - 29 rotational states of He_2^* were measured by radio frequency (rf) spectroscopy [3, 4, 5, 6] and included in a global analysis of the a $^3\Sigma_u^+$ state [7].

We present a new measurement of the fine structure of all rotational levels between N=1 and 21 of the a $^3\Sigma_u^+$ (v=0) state. The J=N fine-structure components, which are high-field seeking in magnetic fields, are first eliminated during the multistage Zeeman-deceleration process, and then repopulated from the low-field-seeking J=N±1 components using rf radiation prior to detection by excitation to Rydberg states followed by pulsed-field ionization. The low velocity of the Zeeman-decelerated beam [2, 8] enabled interaction times of the molecules with the rf radiation up to ~500 μs and therefore a reduction of the transit-time broadening down to 3 kHz (FWHM), allowing the transition frequencies to be determined very accurately. The fine structure has been analyzed using an effective Hamiltonian to obtain improved values of the spin-spin and spin-rotation coupling constants for the a $^3\Sigma_u^+$ (v=0) metastable state of $^4He_2$ with unprecedented precision.

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Towards Interpretation of the 2D-Raman-THz Spectrum of Water by Systematic Modification of a Polarizable Water Force Field

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Spectroscopy in the THz range directly probes motions of the hydrogen bonding network of liquid water. Recently, 2D-Raman-THz spectroscopy was successfully applied to water [1]. This method potentially has the ability to resolve structural inhomogeneity of water.
In order to interpret the experimental 2D signal, we need the support of molecular dynamics simulations.
The polarizable TL4P model [2] was amended with charge transfer across hydrogen-bonded dimers as well as an anisotropic polarizability in order to correctly reproduce the THz and Raman spectra [3]. The so obtained force fields can be used to distinguish contributions of these bands to the 2D-Raman-THz spectrum.

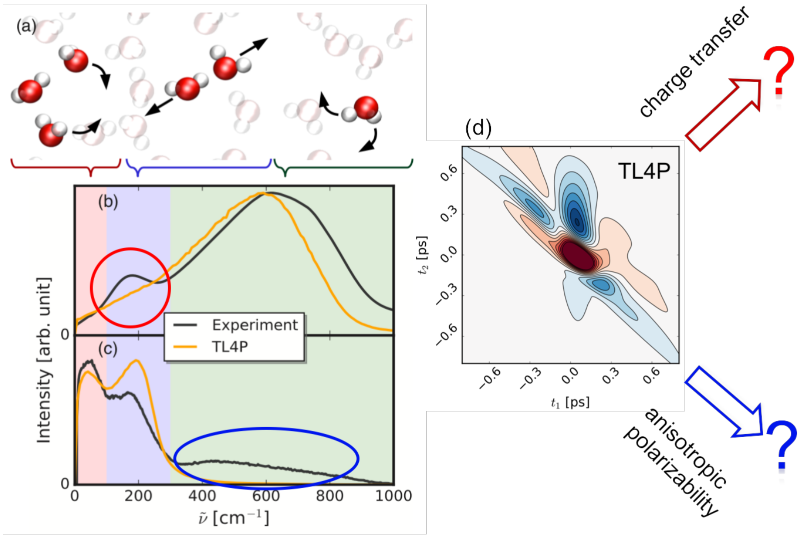

Figure: (a) Illustration of the vibrational modes associated for the three bands visible in the THz range. (b) Experimental THz absorption spectrum of water at 25°C (black), compared to that calculated from the TL4P model (orange). (c) The same for the anisotropic Raman spectrum measured by optical Kerr effect spectroscopy. (d) Simulated 2D-Raman-THz signal from the TL4P model at 25°C.

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Quantum-Logic Spectroscopy of Molecular Ions

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The application of quantum-logic techniques[1] to the spectroscopy of trapped atomic ions has enabled the determination of atomic properties at unprecedented levels of precision[2]. Molecules have been proposed as suitable candidates for testing possible time-variation of fundamental constants[3-9], e.g. m_p /m_e - ratio, and as long-coherence-time qubits[10]. Our efforts focus on N_2+ which has recently been identified as a promising candidate system for precision spectroscopy[3]. We are currently establishing a complete toolbox for high-precision spectroscopy of single molecules using quantum-logic methods, their initialisation, coherent manipulation and non-destructive interrogation by coupling them to a co-trapped single atomic ion. We have laid the experimental and theoretical foundations for hyperfine-state initialisation of the molecular ions and addressing the suitable extremely narrow infrared transitions[11-14].

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Effect of structural disorder on excited-state symmetry breaking in D-A-D quadrupolar molecules

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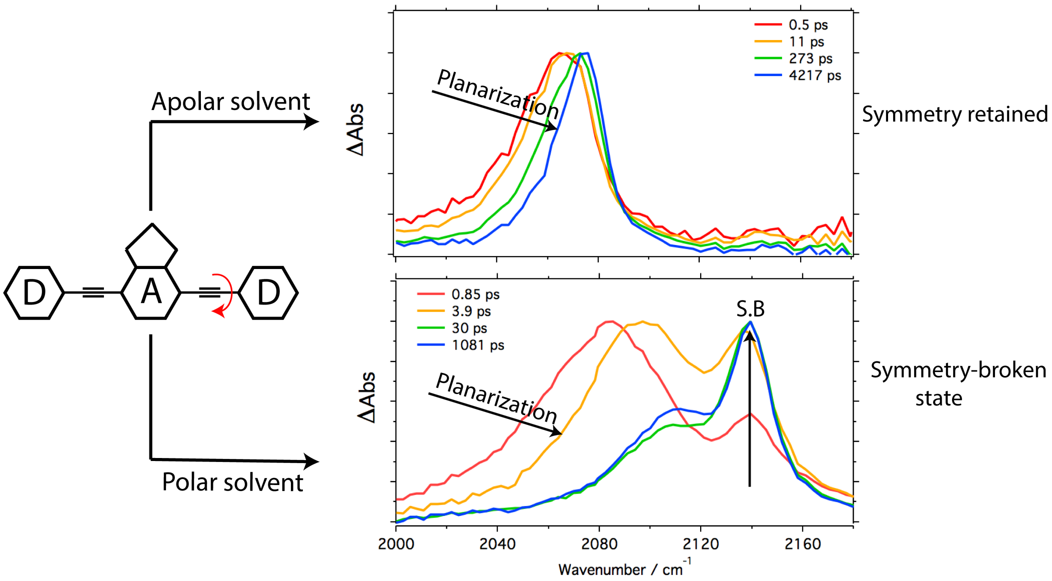
Quadrupolar dyes comprising a central electron acceptor or donor moiety flanked by two branches (D-A-D or A-D-A), are characterised for a strong two photon absorption cross-section, which finds use in a variety of applications ranging from deep-tissue photodynamic therapy to 3D photopolymerization. Upon photoexcitation in polar environments, these symmetric molecules have been shown to become strongly dipolar – a phenomenon known as excited-state symmetry breaking (S.B) [1]. The mechanism of S.B is often discussed in terms of solvent fluctuations and asymmetric solvent field around the two flanking branches. However, structural fluctuations have recently been proposed to as primary reaction coordinate for S.B [2]. We investigated on the role of structural asymmetry on S.B, using Time-Resolved Infrared spectroscopy (TRIR) and complementary quantum mechanical calculations. In the ground state, the studied D-A-D molecule is flexible and exists in +/- 40 deg. distribution of dihedral angles between the D and A planes. Conversely, it is rigid and planar in the excited state. Both planarization and S.B can be directly visualized by TRIR spectroscopy. We will show that torsional disorder in the ground state has no effect on S.B and that this process is entirely driven by solvation.



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Dye sensitization of photoelectrodes with copper based sensitizer molecules

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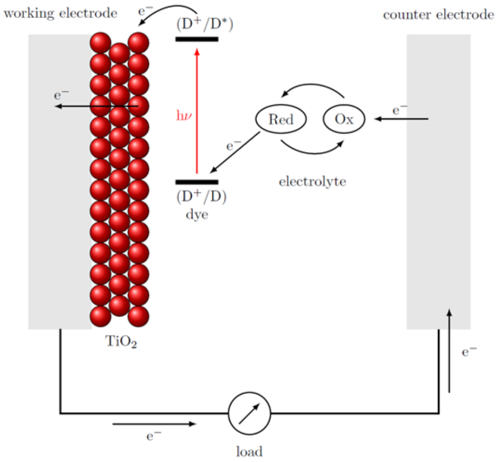
[1]Laboratory for High Performance Ceramics, Empa, [2]Department of Physics and Photon Science, GIST, [3]Department of Chemistry, University of Basel, [4]Ertl Center for Electrochemistry and Catalysis, GIST

Today, photovoltaic modules are based on silicon. An alternative technology—Dye sensitized solar cells (DSSC)—was pioneered by O'Regan and Grätzel in 1991. [1] They consist of a wide band gap semi-conductor sensitized by a dye. Ruthenium is a favourite component in high performance dye molecules.

Because of the low abundance and high cost of ruthenium, our research focusses on copper(I) based dye molecules. [2]

For DSSCs, the charge transfer between dye molecules and semiconductor photoelectrode is very important. We show how we determine the electronic structure of the metal oxide–dye interface operando with ambient pressure photoelectron spectroscopy and NEXAFS for electronic structure determination, and electroanalytical methods for determination of the charge carrier dynamics.



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Bulk nuclear hyperpolarization of inorganic solids using dynamic nuclear polarization

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Incipient wetness impregnation dynamic nuclear polarization (DNP) is an NMR method for hyperpolarizing nuclei in bulk organic solids but relies upon the efficient transport of nuclear magnetization by spontaneous proton spin diffusion. We report here impregnation DNP strategies for bulk hyperpolarization of nuclei in proton-free inorganic solids. The key principle is to maintain a low spin temperature of surface nuclei. Provided that nuclear spin-lattice relaxation is inefficient, even the relatively slow spin diffusion between weakly magnetic nuclei is then capable of transporting enough magnetization from the surface such that the sensitivity of a conventional magic-angle spinning (MAS) NMR experiment can be exceeded. To do this, we have introduced a multiple-contact cross-polarization method, pulse cooling. With pulse cooling we demonstrate sensitivity enhanced NMR of several proton-free inorganic materials at MAS rates up to 12.5 kHz. Ways in which we have further improved sensitivity with this strategy are also described.

High-resolution laser spectroscopy of Mg Rydberg states in a supersonic beam

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To study the photoionization and photoelectron spectra of Mg-containing species we have developed a pulsed laser-ablation source of Mg based on the design of Ref. [1]. The ablated species are entrained in a carrier gas to form a pulsed supersonic beam and are characterized by time-of-flight mass spectrometry.

We shall present resonant multiphoton excitation spectra of neutral Mg atoms Mg^+ ions using various intermediate levels. In this way, numerous Rydberg series of Mg and Mg^+ can be excited, including series converging on excited states of Mg^+. The series are analyzed with the goal of characterizing (i) Rydberg states of Mg^+, (ii) doubly excited electronic states of Mg, and (iii) double Rydberg states with the focus on states in which one of the Rydberg electron is excited to a state of principal quantum number $n >> 100$ and the other Rydberg electron occupies a lower n orbit.

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A new approach to quantitative analysis of oligosaccharides

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Glycans, or oligosaccharides, are challenging to characterize due to a wide range of stereoisomers, regioisomers and the possibility of branching. Understanding their covalent structure, from the simplest monosaccharides to the most complicated branched oligosaccharides, is essential for fully understanding their biological activity [1].Current mass-spectrometric techniques for carbohydrate characterisation are time-consuming and cannot distinguish all of the different types of isomers.

We take a multidimensional approach by combining ion mobility, cryogenic ion spectroscopy, and mass spectrometry [2]. Drift tube ion mobility spectrometry (IM-MS) separates ions due to their charge, size and shape, and from the drift times we determine collision cross sections (CCS) of an underivatised polysaccharide molecule. Cryogenic messenger-tagging spectroscopy, using N_2 or He as the tag molecule, adds an additional dimension by providing infrared fingerprint (i.e., vibrational signature) of the mobility-selected ions to further characterise them. By measuring CCSs and vibrational fingerprints of standard oligosaccharide molecules, we seek to develop a database that will allow us to identify and quantify bioactive oligosaccharides within mixtures.

In this particular study, we aim to determine where the measured IR spectra can quantitavely determine relative glycan concentrations from a mixture. We measured IR spectra of three disaccharides: the b-and a-anomer of GalNAc(1-3)Gal, and the b-anomer of Gal(1-3)GalNac with He tagging at 3.5 K. Standard solutions of each glycan in a 50:50 water: methanol mixture were prepared and electrosprayed into our custom-made setup. Concentrations and composition of the constituents were varied to see how well the measured spectra track the relative concentrations.

These experiments help us to determine the conditions we should use for developing a database for glycan identification. The immediate next steps are to do extensive concentration studies on larger species and to improve the signal-to-noise ratio.The ultimate goal is to make our technique as an analytically reliable, and broadly available tool for the glycan studies.

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Rydberg-Stark Deceleration of Helium Atoms on a Chip for Merged-Beam Experiments in Low-Temperature Ion-Molecule Chemistry

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We present an experiment designed to study reactions of the He^+ ion with CO and N_2 at low temperatures (1 - 100 K). The study of ion-molecule reactions at temperatures below 10 K is challenging because of the presence of stray electric fields which invariably heat the ions. This problem can be circumvented by using a highly excited Rydberg atom instead of the ion. The excited electron serves as a spectator during the reaction because the radius of its orbit is much larger than the interaction distance of the collision complex [1]. Moreover, Rydberg atoms can be accelerated, decelerated or guided along a desired trajectory with inhomogeneous electric fields [2]. This allows us to study the He^+ CO/N_2 reactions by using a Rydberg helium beam merged with a supersonic CO/N_2 beam by deflecting the helium beam with a curved chip-based device.

We present the results of experiments in which the velocity of Rydberg helium atoms is varied from a starting velocity of 700 m/s (mean velocity of the CO/N_2 beam) to final velocities in the 200 - 1200 m/s range. The helium atoms are excited with an electric discharge to the metastable (1s)(2s) $^3S_1$ state and then a UV photon is used to further excite them to a Rydberg state with the principal quantum number *n* between 25 and 32. By scanning the final velocity of the Rydberg atoms around the mean velocity of the ground-state beam, collisional energies below $k_B \cdot 1$ K can be achieved. The fact that the chip delivers a spatially compact Rydberg-atom packet also allows us to probe different sections of the pulsed supersonic beam containing the CO/N_2 molecules and so achieve a high energy resolution.

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Trapping Rydberg helium atoms above a chip device

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Atoms and molecules excited to Rydberg-Stark states possess very large electric dipole moments (e.g., for $n = 27$ the maximal electric dipole moment is approximately 2700 D) and are thus amenable to translational manipulation with inhomogenous time-dependent electric fields. In particular, deceleration and trapping of H, D, H_2 and He samples generated in supersonic-beam sources and excited to Rydberg-Stark states in the vicinity of $n = 30$ has been demonstrated in experiments using 3D electrode structures [1,2], as well as chip-based printed circuit-board-devices [3].

We present the results of experiments in which Rydberg helium atoms produced in a supersonic beam are decelerated and trapped above the surface of a 44-electrode chip kept at a cryogenic temperature. A fraction of the atomic population survives as long as 0.5 ms in the trap, an order of magnitude longer than in previous studies [3]. The helium atoms are excited from the metastable 1s2s $^3S_1$ state to a low-field-seeking Rydberg-Stark states of the $n = 27$ manifold (typically $|n,k,m\rangle = |27,+19,1\rangle$, where k labels the Rydberg-Stark state), in the presence of an electric field. After excitation, the atoms fly over the 44-electrode chip, kept at 4.7 K, where they are captured in a moving quadrupole trap and brought to rest from an initial velocity of 880 m/s in approximately 112 µs and a deceleration distance of 36 mm.

After approximately 75 µs of trapping time, during which the atoms fill up the available phase space, we measure a trap lifetime of approximately 180 µs, significantly longer than the fluorescence lifetime of the $|27,+19,1\rangle$ state of 48 µs. This prolonged trap lifetime could be attributed to *m*-changing collisions of the atoms inside the trap, as described in Ref. [2]. We further investigate the *n* - dependence and temperature dependence of the trap lifetime.

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Stereodynamics of the Ne($^3P_2$) + X (X = Rg, N_2) reactions

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We have recently studied the stereodynamics of metastable Ne($^3P_2$) reacting with ground state atoms (Kr, Xe, Ar), as well as with the N_2 molecule in a crossed molecular beam experiment.[1,2] Because Ne($^3P_2$) is paramagnetic it can be oriented in an external magnetic field, and the orientation has an influence on the branching ratio between Penning ionization and associative ionization. In the present study we investigated this reactivity as a function of the angle between the neon angular momentum and the relative velocity of the reactants in a range of collision energies between 320 cm^{-1} and 500 cm^{-1}. From these data we extract energy-dependent reactivities for states that differ only in Ω, the projection of the neon total angular momentum on the inter-particle axis. Results are explained by a model involving a long-range mechanism and a short-range interaction mechanism. Here we also discuss the predissociation effect for Ne($^3P_2$)-N_2 system where the deduction of AI can be well explained.

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Spinning-disc confocal microscopy in the second near-infrared window (NIR-II)

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Fluorescence microscopy in the second near-infrared optical window (NIR-II, 1000-1350 nm) has become a technique of choice for non-invasive *in vivo*imaging. The deep penetration of NIR light in living tissue, as well as minimal or complete absence of tissue autofluorescence within this range, offers increased resolution and contrast with even greater penetration depths. Here, we present a custom-built spinning-disc confocal laser microscope (SDCLM) that is specific to imaging in the NIR-II. The SDCLM achieves a lateral resolution of 0.5±0.1 µm and an axial resolution of 0.6±0.1 µm, showing a ~17% and ~45% enhancement in lateral and axial resolutions, respectively, compared to the corresponding wide-field configuration. We furthermore showcase several applications that demonstrate the use of the SDCLM for *in situ*, spatiotemporal tracking of NIR particles and bioanalytes within both synthetic and biological systems.

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Cold Chemistry in Merged Neutral Beams

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I will present our research on fundamental aspects of gas-phase chemical reactions. In the past years we have developed a technique that allows us to merge two supersonic expansions using strong electric and magnetic fields. This gives us access to very low relative reactant velocities and thus to collision energies approaching 0 K. At such low energies one can access purely quantum mechanical effects in chemical reactions that are not visible at room temperature. We combine the merged beam technique with methods to orient the reactants and were recently able to study, for the first time, sub-Kelvin stereodynamics.

Faster than Diffusion? Surface Effects on the Electron Transfer Quenching of Re(I) Carbonyls on Metal Oxide Surfaces

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Rhenium(I) carbonyls have been studied as both photosensitizers and CO_2 reduction catalysts in the past [1]. A recent study has shown the non-innocence of a TiO_2 semiconductor film in the complex electron (back-)transfer dynamics of these systems [2], making the study of the specific quenching mechanisms an interesting topic. We present time resolved optical-pump-IR probe spectroscopy of photocatalytic surfaces and focus on the electron transfer quenching of the triplet excited state of a surface-attached metal carbonyl complex. The excited state of $[Re^{I}(bpyBP)(CO)_3Cl]$, with bpyBP = [2,2'-bipyridine]-4,4'-diylbis(phosphonic acid), **RePOH** is quenched by sacrificial and reversible electron donor molecules in aqueous and polar organic solvents within its lifetime (10 ns). We compare the effects of different quenchers on the dynamics of this process also on different surfaces where electron injection from the complex into the conduction band can take place (TiO_2), or not (ZrO_2). Transient IR absorption spectra (**Fig. 1**) show the signatures of the ground state bleaches and a positive band at ca. 2045 cm^{-1}. The decay kinetics of each of the species are followed, and their dependence on the quencher concentration and its interaction with the substrate surface are discussed.

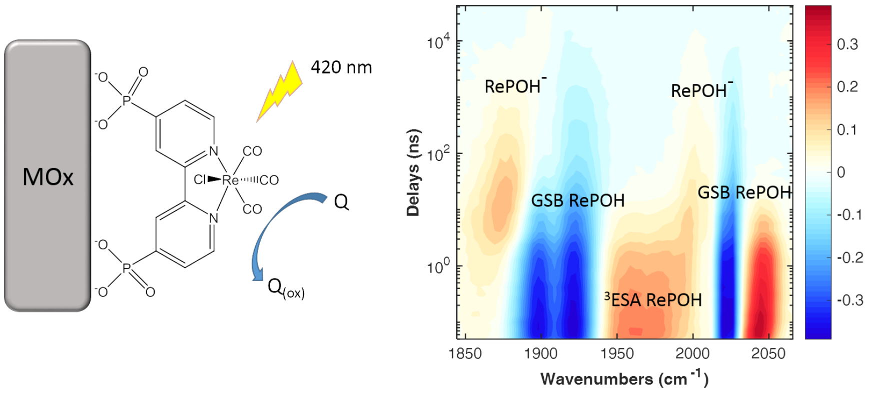

Figure 1: Left: Experimental Principle: Upon excitation with a visible pump pulse the excited state of the **RePOH** photosensitizer is quenched by a (sacrificial) electron donor Q and probed with IR light; Right: Time resolved IR data of **RePOH** on ZrO_2 with 100 mM phenothiazine as quencher in EtOH solution under Ar.

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Exciton dynamics in DNA oligomers studied by broadband deep-UV transient absorption spectroscopy

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Excited state dynamics in DNA oligomers are complex due to the interactions between the chromophores. Using ultrafast broadband deep-UV transient absorption spectroscopy [1] on Deoxyadenosine monophosphate oligomers of various lengths, we observe the effect of π-π stacking.

In dAMP we observe a GSB signal centered at 255 nm and an ESA signal centered at 275 nm. Both GSB and ESA decay mono exponentially with $\tau \approx 0.9$ ps (fig. 1a). Going to $(dA)_2$ we identify the effect of the stacking interaction. The ESA and the GSB dynamics have a bimodal behaviour [2] with the same time constants for both the ESA and the GSB signals: $\tau_1 \approx 0.9$ ps and $\tau_2 \approx 400$ ps. The first few picoseconds are dominated by a monomer-like spectral change. The new channel and the associated broad ESA feature are due to the stacking interaction and are thus a signature of a two-base exciton. Supressing stacking with a methanol sultion confirmes this (fig. 1a). We observe a broad plateau-like spectral shape spanning from approximately 280 to 355 nm (FWHM, fig. 1a,b). In $(dA)_{20}$ excitons spanning more than two bases can form [2,3]. The ESA signature is significantly broader in the 20-mer compared to that of the dimer (1c) and $\tau_2 \approx 200$ ps in the 20-mer. We assign these spectral and temporal differences to excitons spanning more than two bases. This suggests that the exciton states spanning more than two bases may not decay to a two base exciton as a gateway state to the ground state.

Two-dimensional deep-UV (2DUV) pump-probe experiments have been performed and are currently analysed to resolve the evolution of the two-dimensional line shape of this feature and disentangle the structural dynamics of the formed excitons.

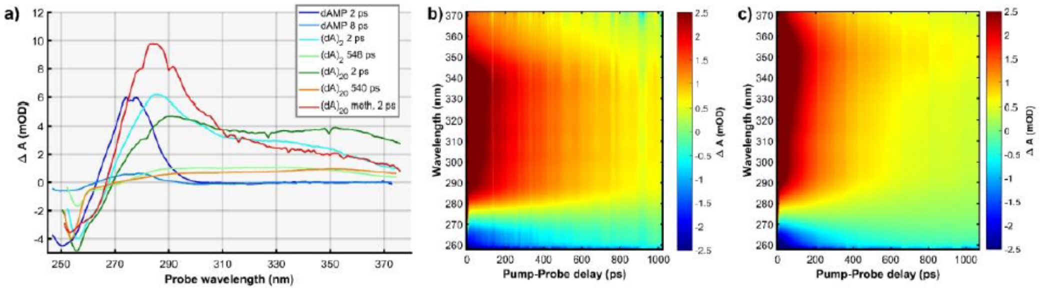

Fig. 1: Spectrally-resolved transient absorption signals of different samples at different time delays in aqueous solution (a), in part taken from the time-wavelength plots of $(dA)_2$ (b) and $(dA)_{20}$ (c). Samples are pumped at 266 nm and have an absorption of 80% at 260 nm.

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Shedding new light on complex porous materials with positron spectroscopy

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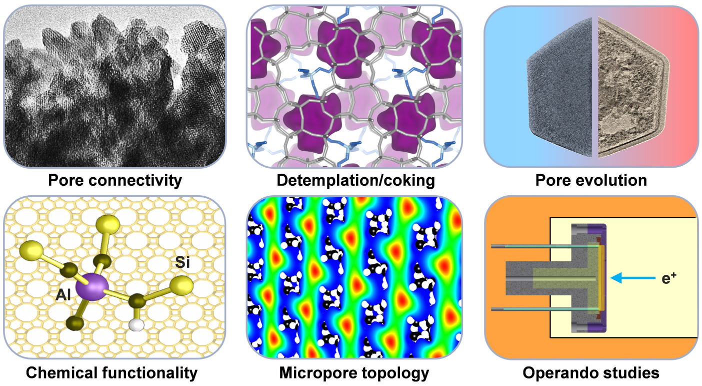
The development of improved tools for the structural analysis of nanostructured materials is of continued interest because of the potential usage of more precise descriptors in guiding the design of materials with enhanced functionality. Positron annihilation spectroscopy (PAS) has attracted interest due to its ability to dynamically probe open volumes, which can provide complementary insights into the properties to those gained through more widespread equilibrium techniques for porosity analysis, such as gas sorption. For example, the formation of metastable *ortho* -positronium species, which can diffuse through pore networks and be annihilated with a lifetime characteristic of the pore size, originates unique sensitivity to the effectiveness of hierarchical pore networks in enhancing transport properties.[1] Similarly, the specific sampling of extended micropore frameworks by *ortho*-positronium provides a unique fingerprint to differentiate crystalline solids with the potential to contribute to structure determination.[2] In addition, the influence of chemical effects on the annihilation response can give insights into the bulk composition and surface functionality.[3] Another interesting facet is the potential to interrogate porous catalysts under *operando* conditions. This contribution summarizes recent approaches in the study of porous materials with PAS, describing the observed interactions, and identifying promising directions for future research (Figure 1).



Pore connectivity **Detemplation/coking** **Pore evolution**

Chemical functionality **Micropore topology** **Operando studies**

Figure 1 Scope of PAS for the structural analysis of nanostructured materials.

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Formation of molecular oxygen in astrochemical conditions.

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Most of the knowledge that we have of interstellar media (ISM) comes from telescopic observations and direct observation using space probes. Due to limited economical resources and the high number of difficulties in data collection and analysis, computational methods play a key role in the study of this phenomena. The oxygen molecule is considered the most important oxygen atom source in most of the reaction networks for the formation and accretion of complex organic molecules, but there are just few observations in the circumstellar shells (and none outside the Milky Way galaxy). The aim of this work is to find a qualitative justification for the existence of this molecule and of the reason why it is not easily observed.

In our hypothesis, O_2 is synthesized on the interface between surface grains or in its bulk, via diffusion of two atoms in local thermal equilibrium in the same region. As the solid phase, amorphous solid water is chosen, due its ubiquity in the ISM and the high number of experiments

This problem is investigated using *Ab-Initio* calculations and Molecular Dynamics (MD) simulations using Gaussian [1] and CHARMM [2] respectively. The calculations are needed to parametrize, via simplex or differential evolution algorithm, the interaction between water molecules with O_2. MD simulations are performed using the Multi Surface Adiabatic Reactive Molecular Dynamics (MS-ARMD [3]) using two different surfaces for the two unbounded oxygens and for the molecule (in this case a RKHS interpolation scheme is used for the bound interactions).

The single atoms have a high mobility, and are able to explore the whole surface within 100 ns at 50 K. Jumps between different sites are observed even for temperatures around 10 K. Another interesting point is that the process cannot be described by an Arrhenius-like equation but needs a model that includes the roughness of the surface itself, as the one proposed by Zwanzing in 1988 [4].

The formation times, both in bulk phase and on top of the surface, with or without a flexible model for the water, is on the ps timescale, with 80% of samples reacting during the first 20 ps of the simulations. In contrast, relaxation time are slow, around three or four order of magnitudes. The reason of this is that there is minimal coupling between the vibrational mode of the oxygen and the ASW, especially in case of rigid water. Part of the relaxation is recovered using a flexible water model, thanks to the coupling with the water bending mode.

The minimal coupling between translational and vibrational motions prevent desorption of the newly-formed molecule, trapping it in the grain for its lifetime.

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Manipulation of molecular hydrogen on a chip to study quantum effects in chemical reactions at low temperature

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Quantum-mechanical effects start to influence the kinetics of bimolecular reactions when the collision energy approaches zero. The quantized angular momentum of the relative motion leads to a discretization of the centrifugal barriers associated with the different collision partial waves. The barrierless and strongly exothermic ion-molecule reaction $H_2 + H_2^+ \rightarrow H_3^+ + H$ provides the opportunity to observe quantum effects at collision energies below $k_B \cdot 1$ K. In past experiments, the cross section could be measured down to collision energies of $k_B \cdot 60$ K, limited by the presence of stray electric fields, which heat up the ions [1]. To avoid this effect, we substitute the H_2^+ reactant by the H_2^+ ($v^+ = 0$, $N^+ = 0$) core of a hydrogen molecule excited to a high Rydberg state. The Rydberg electron does not influence the reaction for states with a principal quantum number $n \geq 20$ but provides electric neutrality. To reach very low energies, we exploit a curved Rydberg-Stark surface-electrode deflector to merge two supersonic beams, one containing the deflected Rydberg H_2 molecules, the other containing H_2 molecules in the ground vibronic state (75 % ortho H_2 in the $N = 1$ rotational level and 25 % para H_2 in the $N = 0$ rotational level). The collision energy is tuned by adjusting the temperature of the supersonic valves or by tuning the parameters of the Rydberg-Stark deceleration [2]. We measure the cross section at collision energies from $k_B \cdot 60$ K down to temperatures below $k_B \cdot 1$ K, where deviations from predictions based on the classical Langevin capture model are observed, primarily caused by the influence of the quadrupole moment of the quantized rotation of H_2 [3]. Recently, we have completely redesigned the experimental setup to improve the collision-energy resolution of the measurements. The results obtained with this new setup will be presented and compared with the results of recent calculations [4].

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Conquest of the high DOS problem – spectroscopy on the individual quantum state

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Quantum-sized transition metal systems are the key element to many of the most relevant processes in chemistry, biology and physics. Still, the high density of states (DOS), which is emerging on their excitation, so far hindered both experimental and computational insight into the interplay of the underlying quantum states. While high resolution spectroscopy commonly fails by just revealing an impenetrable thicket of overlapping features, quantum chemical *ab initio* methods do not scale sufficient to handle an active space of the required size. In this work, we used two-color resonant four-wave mixing spectroscopy to study the neutral copper dimer in gas phase. We already demonstrated the applicability of the method by adding to the picture of the low-lying electronic states,[1] and also gained some knowledge on unperturbed high-lying features.[2] However, here, we finally present the deperturbation of the full studied range in the deep UV. By utilizing the double resonance selection rules to pin the rotational quantum number in the ground state, we could unambiguously assign more than thousand individual rovibronic transitions. These not only revealed the known bright states, but also about ten vibronic levels of perturbing dark states, just visible at their intersections with bright states. Figure 1 exemplary shows the intersections of two dark states with a bright state (left) and a simulation of a one-color spectrum based on the obtained constants (right).

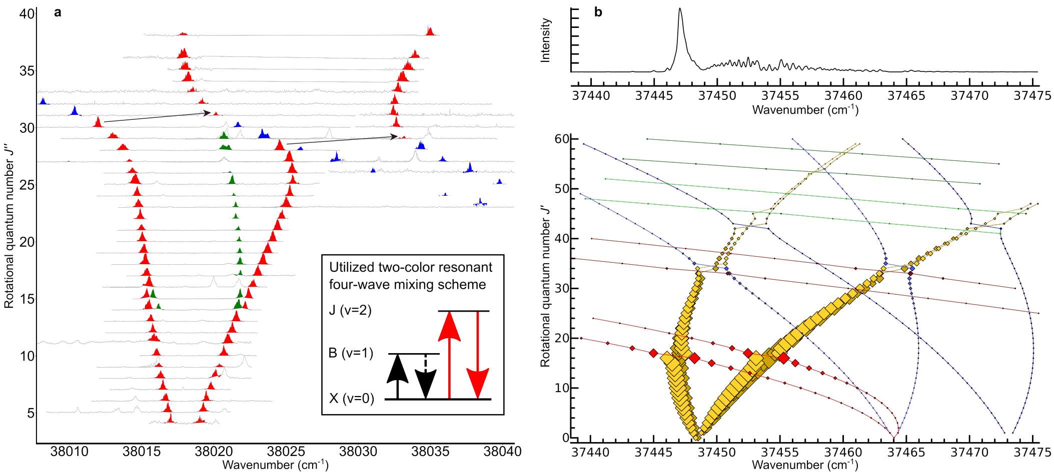

Figure 1: **a**, shows two-color spectra of ^{63}Cu^{65}Cu, ordered by the assigned rotational quantum numbers *J*" of (2-0) J-X transitions (red). Green resp. blue highlighted regions contain lines assigned to a weakly resp. strongly perturbing dark state. **b**, illustrates how the two most abundant isotopologues ^{63}Cu$_2$ (dark colors) and ^{63}Cu^{65}Cu (light colors) form a one-color spectrum of the (0-0) J-X transition, perturbed by 3 dark states.

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Orthogonal Spin Labelling Approaches for the Study of Protein Oligomerisation by Pulsed Electron Paramagnetic Resonanc

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The regulatory function of the human splicing factor hnRNP A1 is believed to be mediated by oligomerisation of the protein via an intrinsically disordered domain (IDD) that interacts with long RNA molecules [1]. A core feature of such complex assemblies is a large heterogeneity of the protein-protein, and protein-RNA interactions. Site-Directed Spin Labelling (SDSL) in combination with pulsed Electron Paramagnetic Resonance (EPR), in particular the Double-Electron-Electron Resonance (DEER) experiment [2], offers the possibility of measuring inter-, and intramolecular distance distributions in such disordered systems. A large range of distances (~1.5-8 nm) is accessible by this technique, and most importantly, the method reports the distribution of distances, which contains valuable information for the accurate modelling of disordered systems [3]. The additional use of orthogonal (i.e. spectroscopically distinguishable) spin labels provides a way of monitoring multiple interactions (such as protein-protein and protein-RNA) within one sample [4]. Our modelling approach combines these restraints to generate an ensemble model. The algorithm also allows including data from additional biophysical methods, such as small angle scattering.

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THz Science in Polymer:Fullerene Blends for Organic Photovoltaics

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To explore the fundamental properties of organic polymer:fullerene blends used in thin film solar cells, we use a combination of ultrafast THz spectroscopic techniques. Our scope is to address questions concerning their transport properties, charge separation and excited-state electronic dynamics, which are crucial for their application in photovoltaic devices. We present an optical-pump-THz-probe (OPTP) study on the organic semiconductor PBTTT:PCBM in different well-controlled phase morphologies. We show the time evolution of the frequency-dependent THz mobility within the first few hundred picoseconds after photoexcitation.

Additionally, we are interested in the first few picoseconds upon photoexcitation and resolve these by exciting an electrically biased sample with an ultrashort excitation pulse. This leads to the emission of a light pulse in the THz frequency range. We show that THz emission spectroscopy gives us access to the generation process and transport in polymers, organic semiconductors and perovskites.

Early Charge Carrier Dynamics in Lead Halide Perovskites

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Solution processed lead halide perovskite materials have become one of the dominant topics in solar energy research, thanks to their outstanding performance and facile processability. A record solar power conversion efficiency of 22.7% has been achieved in merely 5 years with perovskite photovoltaic devices.[1] This outstanding achievement has spurred a rush for the study and understanding of the peculiar properties of these materials that makes them ideal, while improving their stability. A large effort is indeed devoted to the investigation of the photophysical characteristics of lead halide perovskites of various compositions. Ultrafast time-resolved spectroscopy, in particular, has been instrumental in the study of the early dynamics of photogenerated charge carriers [2,3].

The development of gas photonics for the generation and detection of THz pulses has opened the possibility to use ultra-broadband pulses with bandwidths in the tens of THz. This allowed simultaneously to improve the time-resolution of optical pump-THz probe spectroscopy and to access a broader domain for spectral analysis.[4-6] We present here a thorough study of the early dynamics of photogenerated charges in perovskite materials. Using ultra-broadband time-resolved THz spectroscopy, we were able to probe the effects of photon excess energy and compositional variations on the hot carrier mobility and its temporal evolution.

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Time-resolving molecular chirality in the gas phase

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Chirality is an important concept in chemistry and other natural sciences. Recently, molecular chirality in isolated, i.e. gas-phase molecules, has become accessible using photoionization of a chiral molecule and subsequent angle-resolved photoelectron detection, revealing the phenomenon of photoelectron circular dichroism (PECD) [1]. In PECD, the ionized electron shows an asymmetric angular distribution, depending on the helicity of light and the chosen enantiomer. This anisotropy is a signature of molecular chirality, providing a sensitive tool to study the stereo-chemical and electronic structure of a chiral molecule [2]. PECD experiments have already evolved from synchrotron-based static measurements to laser-based sources utilizing femtosecond time-resolution [3, 4, 5].

In this contribution, I will present the first TR-PECD experiments with circularly polarized high harmonics, thereby introducing a general experimental scheme for chiral femtochemistry. Photoelectrons are ionized in a 1 + 1’ pump-probe scheme involving linearly polarized 266 nm and circularly polarized 133 nm pulses. Femtosecond time resolution is achieved with a cross-correlation between pulses below 100 fs. Electron images are recorded using velocity map imaging (VMI) technique.

Our work focuses on one of the simplest chiral molecules – CHFBrI and discusses its molecular dynamics and time-dependent chirality during its photo-dissociation along the C-I bond. Experimental results are supported by high-level ab initio calculations of potential energy surfaces along the dissociation coordinate.

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Pump-Pump-Probe spectroscopy to study ion pair dynamics

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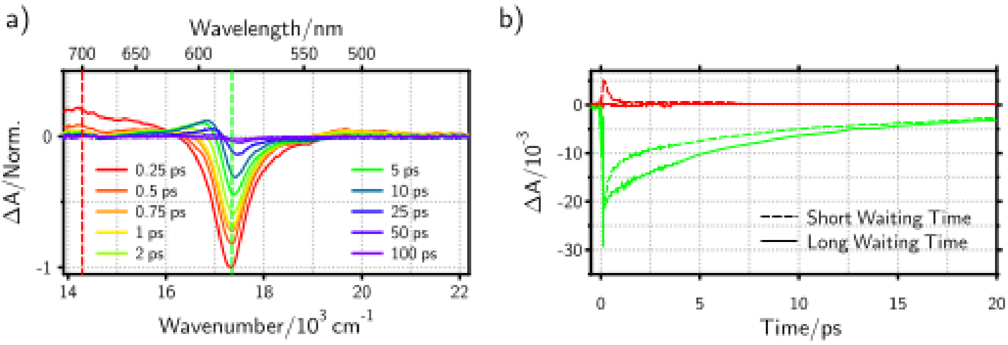
We are interested in studying the excited-states of radical ions as a means of understanding the nature of the product in photoinduced charge separation (CS) – i.e. ion pairs. The change in the nature of the CS product from tight/contact ion pairs to free ions has been suggested as an intermediate step in bimolecular CS, but is difficult to observe using visible pump-probe spectroscopy.[1] We wish to determine if the radical ion excited-state reports on the change of the distribution of the CS product from largely tight/contact ion pairs to free ions.



We accomplish this by using pump-pump-probe vis-TA (PPP) spectroscopy. In our experiments, we first pump to trigger photoinduced CS, then after a defined time delay we use a second pump pulse to photoexcite the generated radical ion. Then, the resulting transient species is probed using whitelight - in essence, one does transient absorption spectroscopy on the radical ion generated in the transient experiment.[2] Figure a shows an example of these data. We will present a series of experiments where we probe various photo-generated anions after different waiting times between the two pump pulses. We will show that these experiments report sensitively that as one changes the distribution in ion pair distances, the excited-state dynamics of the radical anions are changed. Figure b clearly shows this - as one changes from long to short waiting times, an additional spectral component arises in the red and the bleach decay kinetics change. This implies that one can use the dynamics of the radical excited states after CS as a pseudo-“molecular ruler”.

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The structure of protonated serine octamer

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Mass spectrometry has shown protonated serine octamer to be a strong “magic number” with a high degree of homochiral preference [1]. Despite many experimental and theoretical studies, the Ser_8H^+ structures proposed thus far provide no clear reason for its unusual stability, its homochirality, or the facile substitution of two serine units. Previous spectroscopic studies performed at room temperature by IRMPD revealed broad vibrational bands, which were not sufficient to determine a precise structure [2]. We have obtained a highly resolved infrared spectrum of He-tagged serine octamer in a cryogenic octopole ion trap. Sequential substitution with cysteine shifts the frequency of certain oscillators, which we track in the vibrational spectrum. In combination with simulated annealing ab initiomolecular dynamics, we find a structure of the serine cluster that is ~25 kcal/mol more stable than the previous most stable published structure and which explains both the homochiral preference and the facile exchange of two amino acid units.

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