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Effects of pressure and temperature on photophysical properties of Sm^{2+} in BaFI crystals

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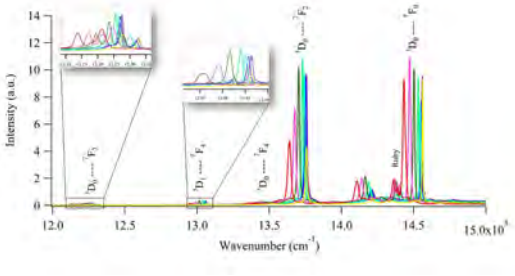
In divalent rare earth (RE^{2+}) ions, the $4f^{N-1}5d$ configuration is much closer in energy to the ground $4f^N$ configuration compared to trivalent rare erath (RE^{3+}) ions. This leads to relatively stronger interaction between the two configurations and larger admixture of parity-allowed 5d orbital into the 4f-4f transitions [1]. Hence, the luminescence properties of RE^{2+} ions are affected by the chemical environement as well as external physical factors including presure. Among the RE^{2+} ions, Sm^{2+} has atracted extensive attention due to its hole burning properties [2]. The lowest-lying excited $4f^55d^1$ configuration of Sm^{2+} is only slightly above the ^5D_J excited state in energy. Upon inducing external presure on BaFI:Sm^{2+} crystals, we were able to tune the energy seperation between the $4f^55d^1$ and $4f^6$ configurations. The energy level of $4f^55d^1$ configuration decreases as the external pressure on the host crystal enhances. This leads to greater interaction of $4f^55d^1$ and $4f^6$ configurations, which in turn results in alternation of optical properties of Sm^{2+}. We present effects of pressure (Figure 1) and temperature on the photophysical properties of Sm^{2+} in BaFI crystals.



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Chemical shift based NMR crystallography directed by unbiased prior constraints

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Structure elucidation of amorphous materials and microcrystalline solids presents one of the key challenges in chemistry today. While techniques such as single crystal diffraction and cryo-electron microscopy are generally not able to characterize such materials, an approach using solid-state NMR in combination with crystal structure prediction (CSP) appears to be succesful.[1-3] The main current downside of this method lies in the high computational cost associated with CSP methods and the required density functional theory (DFT) chemical shift calculations. These bottlenecks currently prevent efficient high throughput structure elucidation by NMR crystallography.

Here we accelerate and guide the CSP procedure by introducing unbiased prior constraints from solid-state NMR. Specifically, the constraints allow us to restrict the CSP search space to the correct single molecule conformer regions. The approach directs the determination procedure from the first steps towards the correct crystal structure, without the need for assumptions. We show that the approach can correctly determine the crystal structures of cocaine, flutamide, and flufenamic acid, with significant acceleration in computational times. Most significantly, we correctly determine the crystal structure of powdered ampicillin, which had not been previously possible using conventional CSP-NMRX methods.

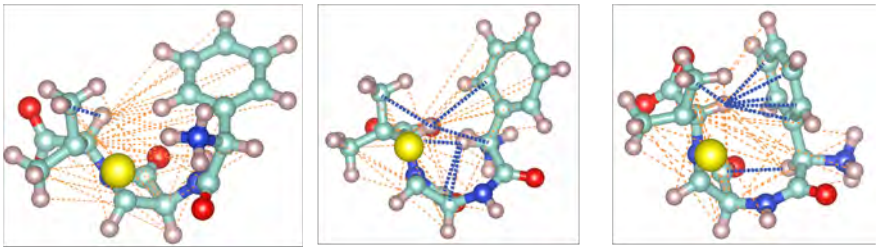

Figure 1. Three single molecule conformers (A, B and C) of ampicillin. The dotted lines correspond to the observed experimental constraints, extracted directly from NMR experiments on the crystalline powder. The orange dotted lines indicate fulfilled constraints and the blue dotted lines indicate violated experimental constraints. Here, conformer A has minimum violations and is selected for the subsequent CSP procedure. B and C are excluded.

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Quantum effects in the electron escape from submicron-sized droplets

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Photoelectron velocity-map-imaging (VMI) studies on submicron-sized droplets have been increasingly important in elucidating the properties of low-energy electrons in the condensed phase [1-5]. An essential step in interpreting such experiments is the understanding of electron escape at the droplet-vacuum interface. The degree of confinement [6] and presence of charge [7,8] are among the factors that can significantly alter the properties of a photoelectron.

In this work, we present a combined experimental and modeling study of the electron escape process from submicron-sized droplets. We recorded photoelectron VMI spectra of size-selected dioctyl phthalate (DOP) droplets while varying their charge distribution in a controlled manner. A probabilistic scattering model [3,9] was extended to include charge-dependent shifts in the binding energy onset, as well as quantum-mechanical effects in the escape process. In particular, the transmission probability was calculated by solving the radial Schrödinger equation for the escaping electron under the interfacial potential, including the charge effects.

We obtained first results pointing towards the importance of quantum phenomena for the electron escape at the droplet-vacuum interface. These findings are relevant for the interpretation of droplet VMI data, especially at very low electron kinetic energies.

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NMR Studies of Hierarchical Protein Dynamics

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A fundamental challenge in biology is to describe and understand the complex interaction between protein motion and function.

Protein motion occurs over a wide range of timescales and plays a crucial role in function. However, the mechanisms that link motion to function are not fully understood, and the capacity to predict function from motion remains elusive. To address this, one approach is to map the underlying energy landscape of the protein. Recently, Lewandowski and coworkers have shown using temperature dependent magic angle spinning multinuclear solid state NMR relaxation measurements, at temperatures ranging from 105 to 280K, how to obtain a window into the energetics of multiple dynamic processes in proteins.[1]Solid-state NMR allows simultaneous access to a wide range of observables (here we observe sixteen different probes within one protein).

Here we extend the measurements to different magnetic field strengths (400, 500, 600 and 800 MHz).[2]This allows us to increase the number of independent temperature dependent data sets from 16 to 25. We show that this allows us to significantly improve the accuracy of the results, and allows us to test the hypotheses underlying the interpretation. The data reveal backbone and side-chain motions, exhibiting low- and high-energy modes with temperature coefficients around 5 and 25 $kJ \cdot mol^{-1}$. The results are compared to variable temperature molecular dynamics simulation of the crystal lattice, providing further support for the interpretation of the experimental data in terms of molecular motion.

We will also show results from a series of proteins (SH3, OmpG, Sendai virus Large protein IDP domain) will be presented and will be compared to understand to what extent the energetic activation processes are common or not between different classes of protein.

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Magnetic selection of neutral alkali-metal doped clusters

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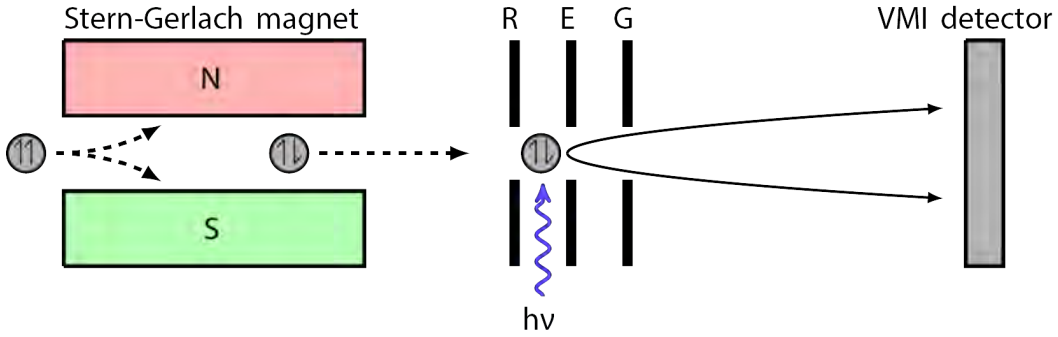
Spin pairing of solvated electrons in alkali metal ammonia bulk solutions is a remarkable example in electron correlation effects in a condensed molecular environment. Such effects of bulk solutions have been probed by magnetic measurements [1-3]. Electron correlation in alkali metal ammonia solutions is not well understood with even the involved species being unknown [4].

We are developing a new experiment to couple a Stern-Gerlach type magnetic deflector to a photoelectron velocity map imaging and cluster ion time-of-flight mass spectrometer for small alkali-metal doped ammonia clusters. We expect these experiments to provide insight into cluster-size and concentration dependent electronic and magnetic properties of these systems. A particularly interesting question is whether spin paired and unpaired solvated electrons can be distinguished in angle-resolved photoelectron spectra. In the current contribution, we present the experimental setup along with its experimental and theoretical characterization. For an effusive beam of alkali metal atoms, the experimentally observed behavior agrees quantitatively with theoretical expectations. For small sodium-doped ammonia clusters, the achieved deflection remains below the theoretical expectations. Issues with the current experimental setup and possible solutions are discussed.



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Protein dynamics by MAS NMR: towards the investigation of posttranslational modifications in tubulin

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Dynamics plays a crucial role in determining protein function. Magic-angle spinning (MAS) NMR is a powerful technique to investigate both structure and dynamics of proteins of variable sizes and in different aggregation states.

We present here recent findings from our group on the characterization of distinct dynamic modes in proteins. We aim to apply these approaches to determine how posttranslational modifications (PTM) affect tubulin dynamics, and therefore its properties. We are optimizing protocols for the production of selected isotypes of tubulin carrying defined PTMs, in yields suitable for MAS NMR experiments.

Polarimetric angle-resolved second harmonic scattering on colloidal TiO_2 nanoparticles in aqueous environments

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Due to it's high physical and chemical stability, titanium dioxide (TiO_2) is a promising candidate for the use in environmental and energy applications. Among others it is extensively studied as photoanode material in photocatalytic water splitting cells.

In this work, we investigate TiO_2 colloids in aqueous environments, as this material possesses relevant characteristics to split water and nanoparticles are an interesting system to study due to their large surface to volume ratio. With the help of surface sensitive nonlinear optical techniques, more specifically polarimetric angle-resolved second harmonic scattering (AR-SHS), we access important parameters such as the nonlinear second order surface susceptibility $X_{s,2}^{(2)}$ as a measure of molecular ordering, and the surface potential Φ_0 of the semiconductor with respect to bulk water. Here we show first results on how the surface molecular orientation of water at the TiO_2 interface and the surface potential change with particle concentration and in different salt and pH conditions.

State-to-State Molecule/Surface Scattering Apparatus Using Bolometric Infrared Laser Tagging Detection

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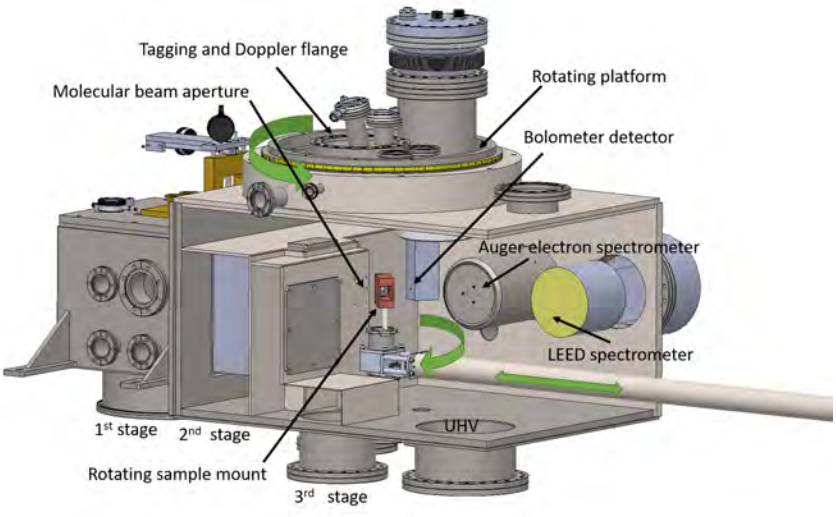
State-to-state molecule/surface scattering experiments which prepare the incident molecules in a specific quantum state and provide information on quantum state distribution of the scattered molecules can be a powerful tool to study molecule/surface interactions. Here, we present a new apparatus designed for state-to-state surface scattering experiments using Bolometric Infrared Laser Tagging detection (BILT) [1], a technique that is more generally applicable than the widely used resonance-enhanced multiphoton ionization (REMPI). The apparatus consists of a molecular beam source with three pumping stages coupled to a UHV chamber where we perform surface characterization and scattering experiments. The seeded molecules in the incident molecular beam will be state-prepared in a specific rovibrational state using infrared pumping by a high power single mode infrared laser. After the collision of the state prepared molecules, the quantum state distribution of the scattered molecules will be interrogated by selectively exciting (tagging) individual quantum states of the scattered molecules using a modulated infrared laser. Lastly, the laser tagged, scattered molecules will be detected by a cryogenic bolometer with quantum state resolution using lock-in detection. The bolometer is mounted on a rotating platform which allows to change the incident and the scattering angles independently in order to explore different scattering geometries. The apparatus also allows to perform Doppler velocimetry measurements of the scattered molecules. Thus, both the internal state distribution and the kinetic energy of the scattered molecules can be measured. This makes our new apparatus a powerful tool to study molecule/surface interactions. BILT detection is applicable to any molecule with rotationally resolved infrared active vibrational modes and will be used to study the scattering of small molecules such as CH_4, CO_2 and NH_3 from catalytically active metal surfaces.



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Gas-liquid Scattering Dynamics in Crossed Beams

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Gas-liquid interfaces are ubiquitous and play a major role in several important physical-chemical processes, and yet there is a dearth of molecular collision studies on water.

We report on the status of an experiment on gas-liquid scattering dynamics, where we will combine a supersonic expansion with a liquid surface inside a vacuum chamber. For low vapour pressure liquids, one can use the well-known rotating wetted wheel. For high vapour pressure liquids, however, this method is not suitable. Here, the most successful approach has been the crossing of a molecular beam with a liquid microjet that allows the preparation of a liquid surface inside a high-vacuum environment.

A single jet with cylindrical cross section was used for the first study of this kind[1]. This approach is very promising, but the size mismatch between molecular beam and microjet makes the method rather insensitive. Moreover, the curved surface makes the analysis of scattering angles very difficult. In our new setup, we overcome these issues by replacing the cylindrical jet with a flat-jet. By colliding two cylindrical microjets, flat leaf-shaped surfaces are obtained under the right conditions.

We are currently in the process of setting up our new experiment. As a critical first step, we are characterizing the water surfaces and vapour environment. This is crucial to understand the collision dynamics of gas molecules with the liquid water interface.

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Non-linear effects in $CsPbBr_3$ perovskite in a strong quantum confinement regime

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Hybrid organic-inorganic and all-inorganic lead halide perovskites have emerged as promising materials for different technological applications, such as photovoltaic devices, LEDs, and Lasers. These semiconductors have been studied in the bulk and in the form of nanoparticles with different quantum confinement geometries (1D to 3D). However, most papers in the literature regarding 3D quantum confined perovskite or quantum dots (QDs) were studied in a weak confinement regime, with particle sizes equal or larger than the exciton Bohr radius. Here, we explored the non-linear properties of perovskites in a strong quantum confinement regime. We synthesized colloidal dispersions of CsPbBr3 perovskite QDs with nanoparticle radius of the order of 2-4 nm. The QDs were characterized by transmission electron microscopy, while their optical properties were studied by steady-state and time-resolved photoluminescence spectroscopy and ultrafast transient absorption spectroscopy. The photoluminescence maximum and first excitonic absorption peak were observed at wavelengths = 450-460 nm, and 420-450 nm, respectively. Based on Poisson statistics for exciton population in QDs, we calculated the absorption cross-section of the material at 3.2 eV to be 2.8 – 5.0 ×10–15 cm–2, depending on the size of the QD. The formation of biexcitons was evidenced by the non-linear optical response of QDs submitted to increasing photoexcitation energy fluences. The biexciton lifetime was found to be extremely fast, about 5 - 8 ps. The biexciton binding energy was derived as being 99 meV. This value are significantly larger than the typical binding energy reported in the literature and is clearly attributed to the strong quantum confinement regime.

Mass accommodation coefficient retrieval through single-particle photoacoustic spectroscopy

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The concept of evaporation and condensation plays a key role in research areas such as aerosol nucleation, electrospraying and drug delivery to the lungs. In 1878 Maxwell introduced the concept of *accommodation coefficient* which describes the probability of an uptake of a molecule into a condensed phase upon collision. This kinetic parameter is crucial for proper description of evaporation and condensation processes. Despite the extensive research in this area for many decades, exact values of these coefficients are still hard to retrieve even for well-studied systems such as water.

We have developed a new experimental set-up that opens an experimental window into accessing mass accommodation coefficients of single optically-trapped aerosol particles in the sub-micrometre to micrometre size range.[1] We study the evaporation and condensation of water on tetraethylene glycol (TEG) aerosols through two simultaneous independent techniques based on light absorption and scattering.

Exposing an optically-trapped particle to a modulated IR laser induces a periodic volume oscillation around the particle's equilibrium state and of the surrounding air. The volume change of the air creates a pressure (sound) wave, while the particle's volume change induces an oscillation in the elastically scattered light. We employ photoacoustic spectroscopy to measure the particle's absorption through detecting the sound wave using a microphone.[2] The elastically scattered light is collected using an objective, projected onto a photodiode and demodulated at the modulation frequency of the incident IR laser.

Photoacoustic signal is composed of its amplitude and phase, which are both measured and used to retrieve the accommodation coefficient. The demodulated scattering technique alongside its mass accommodation coefficient retrieval allows for measuring sub-nanometre to nanometre size changes of an aerosol particle induced by heat expansion and mass flux. Performing measurements at different RH and fitting them to the theory[3] allows for mass accommodation coefficient retrieval from both methods. The two methods seem to be very reliable as they yield overlapping values of the mass accommodation coefficient for water on TEG.

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Calibrating a surface-sensitive molecular ruler with 2D ATR-IR spectroscopy: distance dependence of vibrational energy transfer

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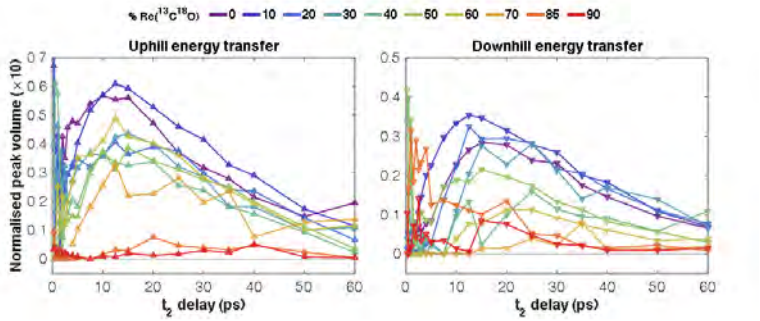
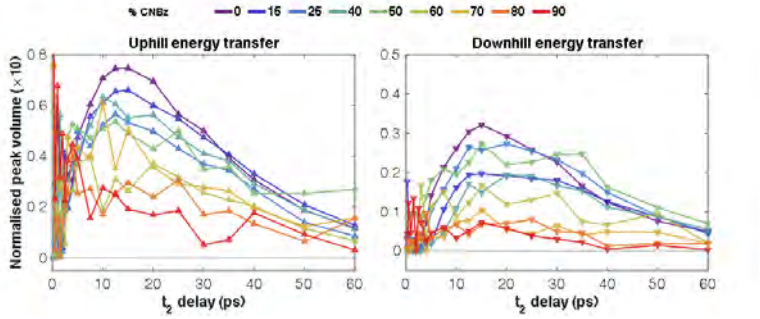
Intermolecular vibrational energy transfer (VET) has been recently reported both in concentrated aqueous solutions,[1] crystals[2] and on surfaces.[3] While it is theoretically expected that this phenomenon has a similar r^{-6} distance dependence like FRET and NOESY (given by the transition dipole-dipole coupling model), no systematic experimental verification of this model has been reported yet. Our model system consists of the ^{12}CO and ^{13}CO isotopologues of [Re(dcbpy)$(CO)_3$Br] (dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid), coadsorbed on a mesoporous TiO_2 layer with 4-cyanobenzoic acid, or a third isotopologue of the complex, Re($^{13}C^{18}O$), as a diluent. With these experiments, we rigorously assess the distance dependence of VET by systematically changing the ratio of the diluent molecule while keeping the ratio of the ^{12}CO and ^{13}CO isotopologues constant and evaluating the effect in the cross-peak dynamics. We observe a significant effect of controlled dilution on a TiO_2 surface on the energy transfer dynamics, and they are discussed in the context of the transition dipole-dipole model.
Upon dilution with the third isotopologue, Re($^{13}C^{18}O$), we observe significant changes in both the amplitude and the peak position of the kinetic traces of the cross peaks in the 2D-IR spectra (Figure 1).



In contrast, when diluting with 4-cyanobenzoic acid, we observe a change only in the amplitudes of the cross peaks, while the kinetics remain largely unchanged (Figure 2). We attribute these results to two different surface morphologies, which are discussed and analysed by deriving qualitative surface model.



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Probing the charge transfer mechanism in pentamethine cyanine dyes

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Cyanine dyes have been exploited for several years as a material for use in organic solar cells [1] as a result of their tuneable absorption wavelength and high extinction coefficients, the latter of which allows for the active layer of the device to be very thin (20 nm). [2]

The dye is typically used alongside a fullerene-based acceptor, such as C60, in a bilayer heterojunction configuration. However, recent studies have shown that high bulk photoconductivity can be seen in pristine pentamethine (Cy5) films without the presence of a D/A interface. [3]

Here, femtosecond transient absorption spectroscopy has been employed alongside other techniques in order to investigate the photophysics of Cy5 systems, and to rationalise the charge transfer mechanism and reduced Langevin recombination that has been reported in the pristine Cy5 film. [3]

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Femtosecond broadband fluorescence upconversion spectroscopy to study vibrational energy relaxation dynamics

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Vibrational energy relaxation (VER) is often the first process occurring after photoexcitation of a molecule in the condensed phase. This process is usually discussed in terms of two consecutive steps: intramolecular vibrational energy redistribution (IVR) and vibrational cooling (VC).[1] The timescales on which these processes occur, make their detailed investigation challenging, as high resolution in both temporal and spectral domains is required. However, thorough understanding of many ultrafast photochemical processes, such as electron transfer is conditioned by a sufficient comprehension of VER dynamics and on how it is affected by the surrounding environment.[1]

We are applying femtosecond broadband fluorescence up-conversion spectroscopy (FLUPS) with sub 100 fs resolution and tunable excitation to follow the time evolution of the fluorescence spectrum of organic molecules in different solvents after photoexcitation with various amount of excess energy.[2] Analysis of the time dependence of the Franck-Condon envelope, based on results obtained from quantum chemical TD-DFT calculations is used to disentangle IVR and VC. Our first results obtained using perylene as the model dye and several of its derivatives in condensed phase will be presented.

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Doubly-excited 3pnd Rydberg Series of the Magnesium Atom: Theory and Experiment

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The Rydberg series of doubly-excited states of alkaline-earth atoms converging to low-lying excited states of the corresponding ion have been the subject of continued interest for the past 40 years [1]. They correspond to states in which one of the two valence electrons is excited to a Rydberg state while the other is excited to a low-lying state. Since they lie far above the first ionization threshold, the doubly-excited states can decay rapidly by autoionization, and their structural and dynamical properties reflect the interplay between the interaction with the Coulomb field of the core and electron-electron correlations, leading in particular to strong Rydberg-series interactions. Of particular interest is the transition from the regime where the outer, Rydberg electron is excited to relatively low-lying states, resulting in a strong interaction between the inner and outer electrons, to a regime where the Rydberg electron is excited to higher-lying states and the interaction between the inner and outer electrons is strongly reduced. In the latter regime, the Rydberg electron is expected to act a spectator and not to perturb any process occurring in the core region.

We have recorded several autoionization spectra of the Mg(3p*n*d) doubly-excited states using the isolated-core-excitation (ICE) technique, with a resolution more than 20 times higher than in previous works [2]. The experiments were carried out using a cold beam of atomic Mg produced in a laser-ablation supersonic-expansion source. Ground-state Mg atoms ($3s^2\ ^1S$) were first excited to a specific 3s*n*d ^1D Rydberg state by (1+1') resonance-enhanced two-photon excitation via the 3s3p ^1P state using two Nd:YAG-pumped pulsed dye lasers. Subsequently, a third, frequency-doubled tuneable dye laser with wavenumber ν_3 was scanned across the 3s - $3p_j$ (j=1/2, 3/2) core resonances and the number of Mg^+ ions produced by autoionization was recorded as a function of ν_3. Spectra of the core transitions were measured for principal quantum numbers of the Rydberg electron ranging from n=31 to n=150. Whereas the spectra observed at low-n values show a complex structure with numerous lines, we observe a gradual coalescence of the complex structure into a single peak as n increases, indicating the progressive reduction of the interaction between the excited-core and Rydberg electrons.

In order to gain insight into the mechanisms governing autoionization and elucidate the complex structure at low n values, we calculated the energy and widths of doubly-excited $3p_jnd$ states and the photoexcitation cross sections corresponding to the measured spectra. The calculations are based on a two-active-electron approximation and a model-potential description of the Mg^{2+} core [1]. The two-electron Hamiltonian is diagonalized within a large *jj*-coupled, configuration-interaction basis built from one-electron orbitals of the Mg^+ ion, the latter being calculated using a finite-element discrete-variable-representation (FEM-DVR) technique [3]. The further use of the exterior-complex-scaling (ECS) technique allows the treatment of autoionizing resonances [3]. Agreement between the calculated cross sections up to n=80 and the measured spectra is excellent, both for the energy and width of the resonances. The autoionization dynamics strongly depend on the total angular momentum quantum number j_2 of the outer electron. We will present a detailed comparison between experimental and theoretical results.

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Semiclassical calculation of the electronic coherences in ultrafast charge migration process

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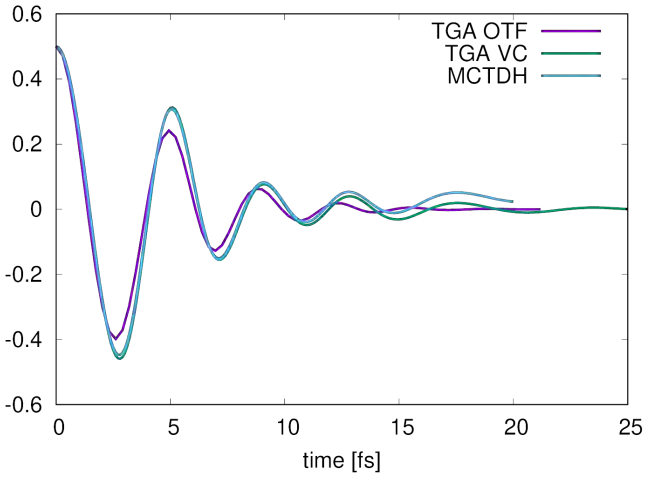
Ionization of molecules very often populates several cationic states launching pure electron dynamics that appear as ultrafast migration of the hole charge throughout the system. A crucial question in the emerging field of attochemistry is whether these pure electronic coherences last long enough to allow for their efficient observation and eventual manipulation with ultrashort laser pulses.

In order to address this question a full quantum treatment of the coupled electron-nuclear dynamics is required. Even though such calculations were recently performed using MCTDH-based approaches for several small molecules [1-3], it is still very case specific and requires construction of global PES, which is a daunting task by itself.

In contrast, approximate semiclassical methods can be used in combination with *on-the-fly* evaluation of the electronic structure which allows to avoid the exponential scaling problem. One of the simplest, yet efficient, semiclassical approaches for molecular dynamics is provided by the thawed Gaussian approximation (TGA) developed by Heller and co-workers [4]. Within this approach, the nuclear wavefunction is described by a single Gaussian wave packet whose time-dependent width is propagated using the local harmonic approximation of the PES.

Here we present a semiclassical TGA calculation of the electronic coherences initiated by outer-valence ionization of propiolic acid molecule. A very good agreement between fully quantum MCTDH calculations and semiclassical TGA results are demonstrated. We argue that simple semiclassical schemes can be efficiently used to support theoretically recent experimental studies of ultrafast electronic dynamics in realistic molecular systems.



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Imaging Chemi-Ionisation Processes

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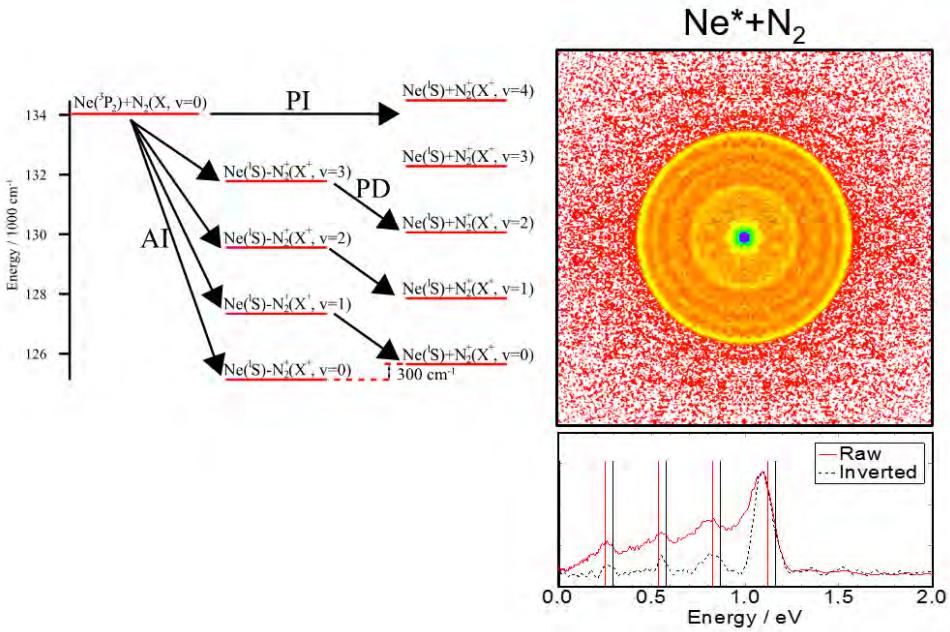
Penning ionisation is an elementary chemical process which results in two neutral specieis generating an ion and an electron. We have performed experiments on metastable neon ($Ne(^3P_2)$) in which the electronic angular momentum of the excited $Ne(^3P_2)$ atom is projected in different directions on the molecular frame by means of an external magnetic field.[1,2] We have demonstrated the ability to control the outcome of the reaction based on the applied field. Upon performing experiments with $Ne(^3P_2)$ and molecular niotogen, we observed a very low cross section for associaitve ionisation events when compared with the Nee*+Ar system.[3] In order to study this, we developed an electoron imaging apparatus in order to measure the kinetic energy and hence the energy levels of the encounter complex from the ionisation reaction. The electrons, just like in photoelecton spectroscopy encode information about the internal energy of the complex at the time of ionisation. One such image is displayed below. The intense central spot is of particular importance. These near zero kinteic energy electrons appear through the v=4 vibrational state of the complex and by reducing the collision energy we can reach below the threshold and probe the Feschback resonance of this state as we increase the collision energy.[4]



The image shows a series of concentric rings each corresponding to ionisation via different reaction channels. By using a novel crossed beam device with a wide tunable velocity range of both primary and secondary molecular beams, we scan the collision energy over the resoaonce and uncover details of the encounter complex and the ionisation mechanism itself.[1]

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How the methyl group position influences the ultrafast deactivation in aromatic radicals

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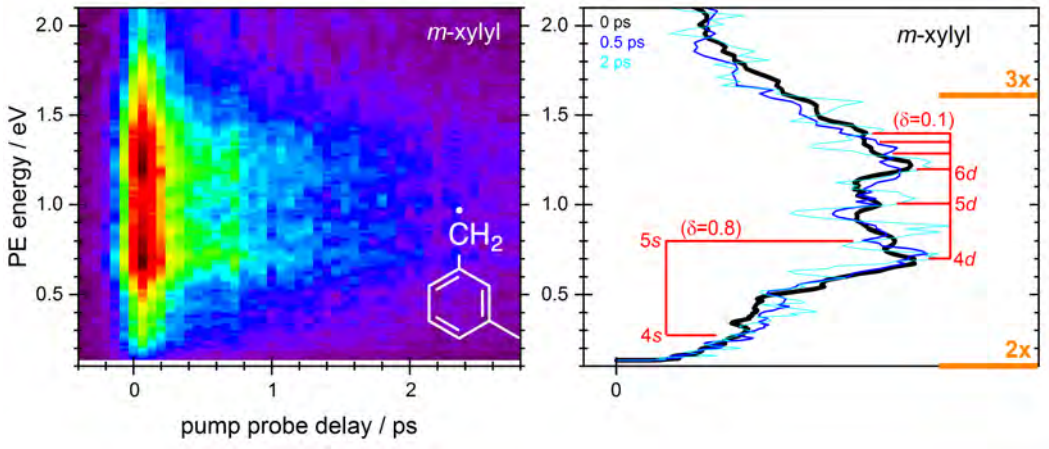
Aromatic xylyl radicals (C_8H_9) exhibit an exceptionally long lifetime in combustion engines and can thus trigger different chemical reactions, which depend on the position of the methyl group. While hydrogen abstraction at the CH_3 group of ortho- and para-xylyl lead to formation of ortho- and para-xylylenes (C_8H_8), the meta- isomer does not produce meta-xylylene due to its biradical character and high C-H bond energy.[1,2]
Recent spectroscopic studies[3] suggested that H dissociation happens on a faster than nanosecond timescale after UV excitation, which motivated us to investigate the deactivation of xylyl radicals using femtosecond time-resolved photoelectron spectroscopy.
The three xylyl radical isomers are selectively generated using flash pyrolysis from xylyl bromide precursors and were excited into the D_3 state (A'') at around 310 nm (4 eV), which can trigger the first hydrogen loss reaction. Multiphoton ionization at 790 nm was utilized as probe step.



While ortho- and para-xylyl exhibit similar lifetimes, the deactivation of the meta-isomer sticks out and depletes twice as fast to the vibrationally hot ground state. We found that a ring deformation mode rather than a methyl pseudorotation enables access to a conical intersection speeding up the deactivation in case of the meta-isomer. Time-resolved photoelectron spectra are structured and can be assigned to Rydberg s- and d-series. Upon absorption of two pump photons (8 eV), ultrafast hydrogen dissociation is triggered, which may indicate isomerization of the meta-isomer. Since the reactivity depends on the position of the methyl group, it can be seen as a sensitive probe to evaluate theoretical predictions and dynamics simulations, which are still scarce for reactive intermediates with open shell structure.

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High-Resolution VUV-Laser PFI-ZEKE Photoelectron Spectroscopy of the $A^+\ ^2\Sigma^+$ state in N_2O^+

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Rotationally resolved pulsed-field-ionization zero-kinetic energy (PFI-ZEKE) photoelectron spectra of several vibrational bands of the $A^+\ ^2\Sigma^+ \leftarrow X\ ^1\Sigma^+$ photoionizing transition of N_2O have been measured in the wave number range from 132100 cm^{-1} to 132500 cm^{-1}. The rotational structures of these bands were analysed using an orbital ionization model [1, 2]. The adiabatic ionization energy was determined to be 132197.70(12) cm^{-1}, which represents an improvement in precision and accuracy by more than one order of magnitude over previous measurements [3, 4].

The experiments relied on a new method to generate tunable, narrow-bandwidth vacuum-ultraviolet (VUV) radiation generated by resonance-enhanced four-wave mixing ($\nu_{VUV} = 2\nu_{UV} \pm \nu_2$) in a pulsed gas expansion of argon, using the $3p^5 4p'[1/2]_0 \leftarrow 3p^6\ ^1S_0$ two-photon resonance of Ar at a wave number of $2\nu_{UV} / c$ = 108722.6194 cm^{-1}. The laser radiation for the two-photon transition ν_{UV} (λ_{UV} = 183.95 nm) was generated by sum-frequency mixing in a prism-coupled $KBe_2BO_3F_2$ (KBBF) crystal device [5] 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 [6] operating at a wavelength of 596.4 nm. In combination with a home-built spectrometer allowing for the detection of ions or electrons, this VUV laser system allows the recording of high-resolution photoionization and photoelectron spectra in the wave number ranges from 55000 cm^{-1} to 95000 cm^{-1} by difference-frequency mixing and from 121000 cm^{-1} to 160000 cm^{-1} by sum-frequency mixing.

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Errors in NMR crystallography

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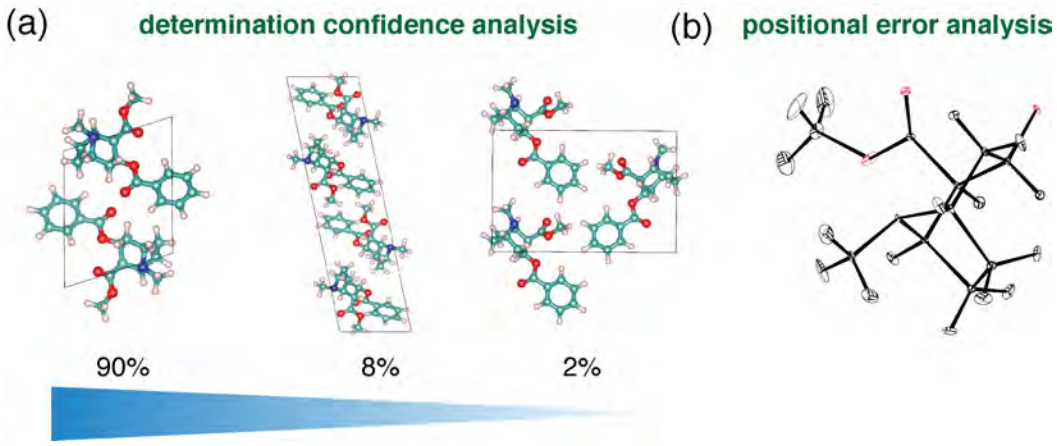
Structure elucidation of amorphous materials and microcrystalline solids presents one of the key challenges in chemistry today. While techniques such as single crystal diffraction and cryo-electron microscopy are generally not able to characterise such materials, an approach using solid-state NMR in combination with crystal structure prediction (CSP) appears to be successful.[1,2] However, until recently there were no approaches to determining the positional uncertainties on the resulting structures, and in that sense they remained models, nor was there a fully coherent approach to the determination of which structure was in best agreement with the data, and what was the reliability of the determination.



We recently introduced a computational method to estimate the correlation between the error in chemical shift space and the positional error for an investigated structure,[3] that allows us to experimentally quantify the positional errors of individual atoms in structures validated or determined by NMR chemical shift based crystallography. Furthermore,we introduce a probabilistic Bayesian model to discriminate between candidates for chemical shift based NMR crystallography. This model allows us to rank and quantify the reliability of determined structures.

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Adiabatic Ionisation Energy of CO_2

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The adiabatic ionisation energy E_I of CO_2, corresponding to the interval between the X $^1\Sigma_g^+$ (v_1, v_2, v_3 = 0, 0, 0), J = 0 ground state of CO_2 and the X $^2\Pi_{g,3/2}$ (0, 0, 0), J^+ = 3/2 ground state of CO_2^+ has been determined to be $E_I = hc \cdot 111112.29(18)\text{cm}^{-1}$ by pulsed-field-ionisation zero-kinetic-energy photoelectron spectroscopy of a low-pressure CO_2 gas sample at room temperature.

The use of a multipulse electric-field sequence for the selective field ionisation of high Rydberg states [1] led to a improved precision and accuracy compared to earlier values [2−5]. Additionally, the use of a stationary gas sample suppressed uncertainties from Doppler shifts.

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Precision measurements of the ionization and dissociation energies of molecular hydrogen

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H_2 and its deuterated isotopomers are the simplest molecules displaying all features of a chemical bond and are as such important systems for the development of molecular quantum mechanics. Their dissociation and ionization energies are benchmark quantities for ab initio calculations. The latest nonadiabatic calculations, which include relativistic and QED corrections, have reached a precision of better than 1 MHz for H_2 [1], which is of the same order of magnitude as the shifts resulting from the finite size of the proton.

We shall present spectroscopic measurements of the ionization energies of H_2 and HD and compare their results with those of the calculations. The ionization energies are determined as a sum of three intervals [2,3], the first between the ground state a low-n (n=2,3) Rydberg state, the second between the selected low-n and high-n (n=50-70) Rydberg states, and the third being the binding energy of the high-n state.

This contribution will focus on the determination of the last two intervals using slow supersonic beams generated by a cryogenic pulsed valve. To avoid the generation of ions in the measurement volume, the low-n Rydberg state is populated by absorption of a VUV photon followed by spontaneous emission. The low-n to high-n interval is measured using a frequency-comb-calibrated cw UV laser. The binding energies of the high Rydberg states and their hyperfine structures are determined by combining millimeter-wave spectroscopy and multichannel quantum defect theory (MQDT) [4], which also enables the determination of the hyperfine structure of H_2^+ and HD^+.

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Merged Molecular Beams to Study Ion-Molecule Reactions at Temperatures down to 300mK

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Merged-beam experiments enable the study of chemical reactions a low temperatures. Ion-molecule reactions are important in low-density gaseous environments, such as cold (3 - 60 K) interstellar clouds. Quantum-mechanical effects start to influence the kinetics of bimolecular reactions when the collision energy approaches zero.

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^+ 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 collision 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 (Figure 1). The collision energy is tuned by adjusting the temperature of the supersonic valve of the ground-state beam or by decelerating the H_2 Rydberg molecules during deflection.

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[2], primarily caused by the influence of the quadrupole moment of the quantized rotation of H_2.[3] The universal approach was also used to determine the ratio of the $H_2D^+ + D$ and $D_2H^+ + H$ channels of the reaction $D_2 + H_2^+$.

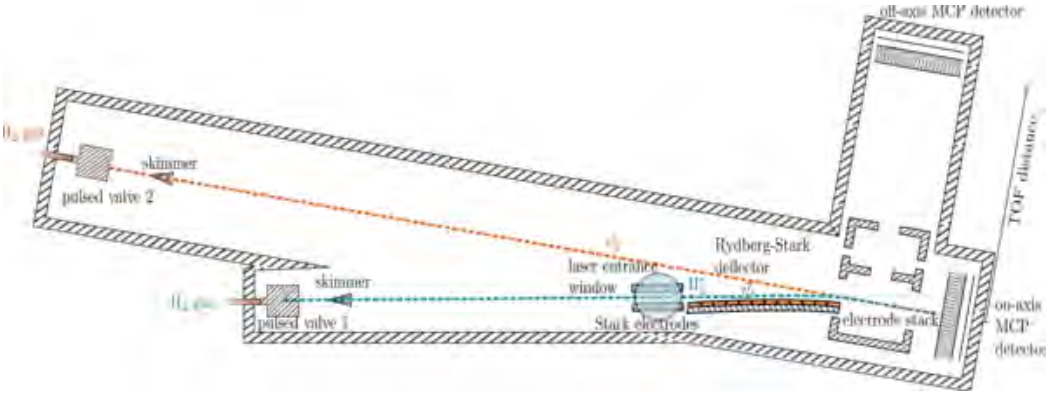

Figure 1: Experimental setup. The lower beam (blue) is deflected by Rydberg-Stark deceleration onto the axis of the other beam (brown) containing H_2 molecules in the ground vibronic state (75% ortho H_2 ($N = 1$) and 25% para H_2 ($N = 0$)). The relative rate constants are determined by monitoring the H_3^+ (or H_2D^+, D_2H^+) reaction products by TOF mass spectrometry as a function of the collision energy.

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Exploring Electron-Nuclear Coupling in Molecules with Multidimensional Electronic Spectroscopy

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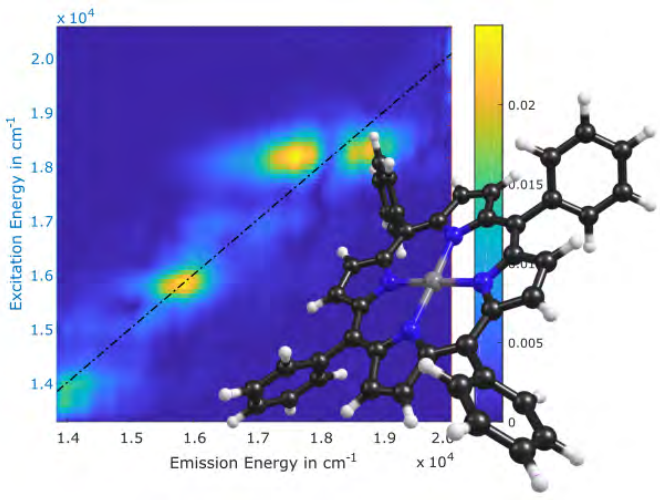
Ultrafast optical spectroscopies have proved a powerful and widely-applicable technique for probing excited state photochemistry. However, for complex molecular systems, spectral congestion in transient electronic absorption spectra can prove a severe hindrance to the extraction of the desired spectral and temporal information. One answer to this is multidimensional electronic spectroscopy, where the ability to resolve optical spectra along both the excitation and detection frequencies make it possible to unravel complex photochemical mechanisms in unprecedented levels of detail. Here, I will detail the development of new, broadband coherent electronic 2D set-up with sub-15 fs time resolution and its application to Q-band energy transfer in a series of porphyrin derivatives. The broadband nature of the excitation/detection pulses in this experiment (400 – 750 nm) make it possible to simultaneously resolve and map energy transfer between the multiple electronic states in this region and disentangle the influence of different metal centres and substituents on the porphyrin's electronic and structural dynamics.



Light-induced peptide unbinding in the RNase S complex

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Understanding the non-equilibrium pathways of protein-peptide interactions remains one of the most intriguing problems in biophysics. Time-resolved techniques (e.g. transient infrared spectroscopy) coupled with ultrafast triggered peptide unbinding can provide a detailed picture of conformational changes that happen as a consequence of the unbinding event. Ultrafast time-resolution of such measurements can clarify the sequence of events offering insight into the unbinding vs conformational responses of the peptide and the protein. Ribonuclease S (non-covalent complex of S-protein and S-peptide) represents an excellent model system used to study protein-peptide interactions[1]. Among five designed photoswitchable S-peptides, complete unbinding was achieved in one S-peptide variant upon light-induced isomerization of the azobenzene based crosslinker. This result represents a starting point for time-resolved measurements.

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High-Resolution Spectroscopy of metastable He_2 and He_2^+

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Having only three electrons, He_2^+ represents a system for which highly accurate *ab initio* calculations are possible. The most accurate potential energy surface (PES) of He_2^+ available in literature does not include relativistic or radiative corrections and treats non-adiabatic effects only partially [1]. We have performed systematic studies of the rovibrational structure of He_2^+ using MQDT-assisted Rydberg-series extrapolation in cold molecular beams of metastable He_2 (He_2*) [2-4]. These measurements indicate a discrepancy between theory and experiment that rapidly increases with the rotational quantum number N^+, both for the rotational levels of the vibrational ground state and first excited vibrational state. Recently, Mátyus obtained more accurate values for the non-adiabatic corrections to the rovibrational levels of He_2^+ using R-dependent rotational and vibrational reduced masses for solving the nuclear Hamiltonian with the PES of Ref. 1 [5]. The work of Mátyus shows that part of the discrepancy in the rotational energies can indeed be attributed to the neglect of non-adiabatic effects, but the non-adiabatic corrections worsened the difference between theory and experiment for the vibrational enegy. In addition to the gross rovibrational structure of He_2^+, we determined the fine-structure intervals of the rotational levels of the vibrational ground state of He_2^+ from the observed fine-structure of high triplet np Rydberg states of He_2 and the rotational fine structure of He_2* [6,7]. Effective fine-structure constants extracted from the observed splittings disagree with the isotopically scaled *ab intio* result for $^3He^4He^+$ [8]. Our measurements may therefore serve as a benchmark to test and improve advanced calculations of three-electron molecules.

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High-Resolution Gigahertz and Terahertz Spectroscopy of the Isotopically Chiral Molecule trans-2,3-dideutero-oxirane (c-CHD-CHDO)

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The rotational spectra of the isotopically chiral molecule trans-2,3-dideutero-oxirane (c-CHD-CHDO) have been measured and assigned in the Gigahertz region between 62 and 112 GHz ($\Delta\nu/\nu = 10^{-11}$) and in the Terahertz range from 25-80 cm^{-1} ($\Delta\nu = 0.00052$ cm^{-1}). The parent isotopomer oxirane (c-C_2H_4O) has been detected by astrophysical spectroscopy in space **[1]**. A small number of lines of trans-2,3-dideutero-oxirane had been previously analyzed in the microwave region **[2]** up to 70 GHz**.** We have recently **[3]** measured and successfully analyzed the rotational spectrum of monodeutero-oxirane between 65 and 119 GHz using our GHz spectrometer **[4],** and in the 0.75 to 2.5 THz range measured with our FTIR setup **[5]** at the Swiss Light Source. Here we discuss our recent study of the spectrum of trans-2,3-dideutero-oxirane. We were able to assign and analyze more than 2500 rotational transitions of the vibronic ground state of trans-2,3-dideutero-oxirane up to J=65. This molecule is also important in the context of molecular parity violation, similar to the related molecule fluoro-oxirane [**6**]. The results of this study are important as they pertain to isotopic chirality and parity violation [**7**], and to the possible astrophysical observation of this molecule.

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Spin and Excited-State Charge Dynamics in Myoglobin

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Nitric oxide (NO) bound to Myoglobins (Mb) exhibits several remarkable physiological functions that are still being explored, e.g. as a neurotransmitter, in signal transduction, etc. The dissociation from and rebinding of ligands to the Fe in the heme (respiration) can be mimicked by photo-dissociating them with a pulse of light and monitoring the recombination with a probe pulse. While several studies of these processes have been carried out using visible, infrared and Raman probes, none is capable of element-specificity and structural-sensitivity at the Fe site. In recombining to the Fe atom, the NO binds in a domed geometry of the heme, as suggested by previous time-resolved resonance Raman studies. [2]. We will present results of our study on MbNO using both X-ray absorption and emission spectroscopy (XAS and XES), which we complemented by X-ray diffuse scattering (XDS), carried out at the EXFEL, SACLA and SwissFEL. The current understanding of respiration in heme proteins is, dissociation and doming occur in a single step, followed by the so called “protein quake” (structural changes in the protein). This serves as the basic mechanism for respiration in all mammals. Contrary to this, our study reveals a 2-step process for the dissociation and doming. XAS and XES show that upon prompt dissociation (< 70 fs), the NO ligand is dissociated, after which doming occurs going through an 3T state into the final quintet state, to which NO recombines in a multiexponential fashion over time scales of a few tens of ps to ~200 ps, which is in agreement with our previous study [1]. Both the XES Kα and the Kβ show a clear signature of the triplet and quintet state and combination with XAS enables correlation to the structural changes around the Fe-atom. XDS instead is sensitive to global structural changes of the protein and the combination of these three techniques can potentially reveal a unique picture of electronic, local and global structural changes of Mb.

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Tracing nucleation on a molecular level

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Nucleation is the first step in many phase transition processes, however its underlying molecular mechanisms are still poorly understood.[1, 2] We have demonstrated how information on the nucleation behavior of CO_2 at high supersaturations can be obtained using mass spectrometry, revealing details of the condensation process on a molecular level.[3]

In our experiment clusters are formed in the uniform post-nozzle flow of a pulsed Laval expansion and detected by soft single photon ionization. The uniformity of the flow enables measurements at constant temperatures and supersaturations and the ionization technique minimizes dissociation of the condensed aggregates. Both are critically important to study the nucleation process in a well defined manner.[4] Experimentally we can directly assess the onset of nucleation by varying the flow temperature and the timing of the measurement.

Here we present data on the onset of homogeneous nucleation of CO_2 in the range between 30 K to 70 K. We also determine number concentrations of clusters which enables us to derive nucleation rates. Our results on the onset of nucleation are in good agreement with measurements from other groups and extend the range of available data for CO_2 towards lower temperatures.[5, 6, 7] In this regime we find a strong indication for the transition from nucleation behavior in the presence of a barrier, to barrier-less condensation.

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Untying the Physico-Chemical Properties of Quinolinium-Based Molecular Knots and Links

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Knots fulfill important tasks in the macroscopic world. They are equally important at the molecular scale and spontaneously occur in DNA, proteins and polymers. Artificial molecular knots and links more complex than the singly interlocked [2]catenane are still difficult to synthesize and therefore systematic studies on the physico-chemical properties of these molecules are scarce.[1] While it has been established that the physical and chemical properties are significantly altered in the knotted structures, detailed knowledge about the exact role played by topology in such complex systems is often limited.

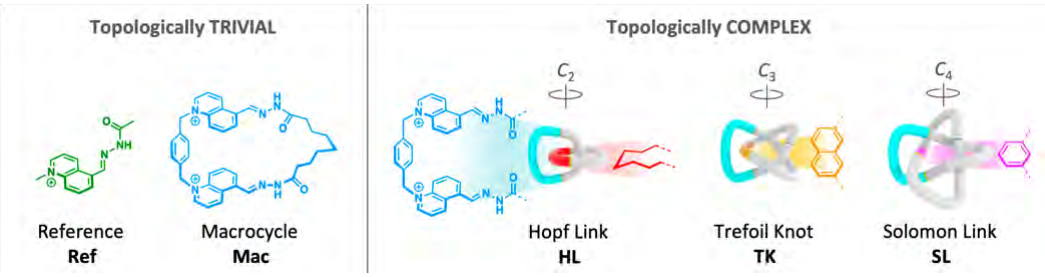

Figure 1. Chemical structures of the molecular knots and links.

Here in, we report on a systematic comparative investigation on the influence of topology on the photophysical and chemical properties of a family of closely-related quinolinium-based knots and links. The compounds are synthesized via self-assembly driven by hydrophobic interactions between the quinolinium moieties and the hydrocarbon linker units in aqueous environment (Figure 1).[2] Using a combination of experimental and computational approaches, we are able to disentangle the effect on the properties due chemical structure and conformational flexibility from that purely arising from the topology. In addition, we will demonstrate how the three-dimensional conformations of these structures and their ability to perform molecular recognition in water can be controlled in a pH-dependent manner.

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Ruthenium-based pyrochlores for oxygen evolution catalysis

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Electrochemically-driven processes, such as water splitting or CO_2 reduction to fuels are promising technologies enabling sustainable energy conversion and storage.[1] The efficiency of these processes is severely limited by the sluggish kinetics of anodic oxygen evolution reaction (OER), which provides protons and electrons required for the reduction half-reaction. In this respect, Ru- and Ir-based electrocatalysts are of particular interest due to their high activity and durability in acidic environment: the mark yet to be achieved by non-noble metal-based catalysts.[2]

In this work, we have investigated a series of A-site substituted pyrochlore oxides, $Y_{1.8}M_{0.2}Ru_2O_{7-\delta}$ (M = Cu, Co, Mn, Fe, Y), to assess the correlations between the OER activity and oxide structural features. By tailoring metal substitution, we could control the oxygen non-stoichiometry (δ) and increase it with the concomitant contraction of a Ru-O bond distance and enhancement of the OER activity. These results point out that surface oxygen exchange kinetics and Ru-O bond covalency are among the key parameters governing the reactivity of Ru-based oxides in OER. Overall, these insights clarify the possible underlying effects of metal substitution in pyrochlores on OER performance, which is instructive for the rational design of the new catalysts for water splitting.

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Extraction of Monomer-Cluster Association Rate Coefficients from Water Nucleation Data Measured at Extreme Supersaturations

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We have recently reported data[1] for water nucleation in the uniform post-nozzle flow of pulsed Laval expansions at flow temperatures of 87 and 47.5 K and high supersaturations of lnS~41 and 104, respectively. The cluster size distributions were measured at different nucleation times by mass spectrometry coupled with soft single-photon ionization at 13.8 eV. The soft ionization method ensures that the original cluster size distributions are largely preserved upon ionization, and allows us to extract monomer association rate coefficients from the measured cluster size distributions. Assuming cluster evaporation to be negligible, we first derived the dimerization rates from experimentally determined nucleation rates, which were approximately $5 \cdot 10^{15}$ cm^{-3} s^{-1} and $2 \cdot 10^{15}$ cm^{-3} s^{-1} for lnS ~ 41 and 104, respectively. We then sequentially determined the association rate coefficients between monomer and cluster *j*, k_{1j}, by fitting cluster concentrations predicted by a kinetic model[2] to experimental values. The fitted results confirmed earlier findings that dimerization is the limiting step for water nucleation at our experimental conditions. The dimerization rate lies 2-3 orders of magnitude below the gas kinetic collision limit and agrees with an earlier prediction based on *ab initio* transition state theory.[3] Other than the dimerization rate, however, the fitted rate coefficients ($k_{1,j>2}$) are on the same order of magnitude as the kinetic collision limit. In particular, the fitted rates are significantly higher than those predicted by transition state theory[3] for j=2, 3 and 5.

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Operando Identification of Active Centers of Nickel Iron Catalysts for Water Splitting and the Role of Iron in the Catalytic Activity

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Efficient water splitting is imperative in the carbon neutrality process, as hydrogen is the primary energy carrier for the proposed hydrogen economy.[1] One of the major performance losses in the electro/photocatalytic water splitting is owing to the large overpotential required on the anode side for the oxygen evolution reaction (OER).[2] Nickel (Ni)-Iron (Fe) based materials are among the most promising earth-abundant competitors for catalyzing the OER in alkaline media. However, the nature of active centers at Ni-Fe based catalysts are still under debate. Moreover, the amount of Fe determines the activity of mixed Ni-Fe compounds. It is known that even trace amounts of Fe existing in the electrolyte noticeably enhance the activity of pure Ni oxide hydroxide.[3]

Fundamental understanding of the active centers under operando conditions is essential to the development and practical applications of NiFe catalysts. By using a recently demonstrated technique of direct identification of catalytically active centers using electrochemical STM under reaction conditions, one can map the activity distribution at the catalyst surface. It is based on the concept that, during catalytic reactions, electrochemical STM can capture 'unexpected' disturbances in the tunneling current on active centers while scanning, which correlate the location of active centers on the sub-nanometer scale.[4]

In this work, two-dimensional Ni and NiFe layered double hydroxides (LDHs) immobilized on inert substrates prepared by the method described elsewhere[5,6] have been used as the samples for electrochemical STM investigations. Fe-containing and Fe-free KOH aqueous electrolytes are utilized in order to reveal the actual mechanism that increases the OER activity of pure Ni catalysts caused by the Fe in the electrolyte. Furthermore, morphological factors (e.g., defects, terraces) that affect the OER activity are tracked in this operando study.

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Ultrafast photoreduction of solvated iron compounds probed by VUV photoelectron spectroscopy

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Transition metal complexes can exist in high-spin (HS) or low-spin (LS) configuration [1], whose equilibrium depends on oxidation state, nature of the ligands and coordination number. Light interaction triggers ultrafast electronic and structural dynamics such as bond cleavage, symmetry rearrangement, spin-crossover (SCO), and charge transfer [2]. These compounds can hardly be isolated, hence photochemistry of solutions is studied, where solvent plays a relevant role [3]. A good example is ferric trisoxalate $[Fe^{III}(ox)_3]^{3-}$ (ferrioxalate), that upon UV excitation experiences ligand dissociation because of forerunner processes yet to be clarified. The final photoproduct lacks of a ligand and the iron is reduced [4]. This implies a ligand-to-metal charge transfer (LMCT) process, a ligand-field strength reduction and a possible SCO. Recent X-ray studies at the iron K-edge concluded fragmentation within 3 ps [5]; other IR measurements demonstrated ligand bond breakage within the first ps [6]. Though, it is not yet clarified whether the metal reduction is a consequence of the cleavage or not, and how structural and electronic dynamics interplay at early times. We present a time-resolved study of photoexcited ferrioxalate aqueous solution by means of photoelectron spectroscopy (PES) [7-8], which is the only technique that provides the whole accessible electronic structure of the sample [9]. This allows us to simultaneously track electronic and structural dynamics of photoexcited solvated molecules. Upon 266 nm-wavelength excitation, we observe the Fe 3d photoelectron signal to shift towards the ferrous spectral position (see figure), i.e. metal photoreduction is prompt (<50 fs), which ascertains the LMCT as primary and driving mechanism. Furthermore, the transient photoelectron iron signal does not undergo peak narrowing whithin our probe range (5 ps), otherwise expected in case of HS to LS SCO [10]. These results, together with previous infrared [6] and X-ray studies [5], yield a complete picture of the photoinduced dynamics.

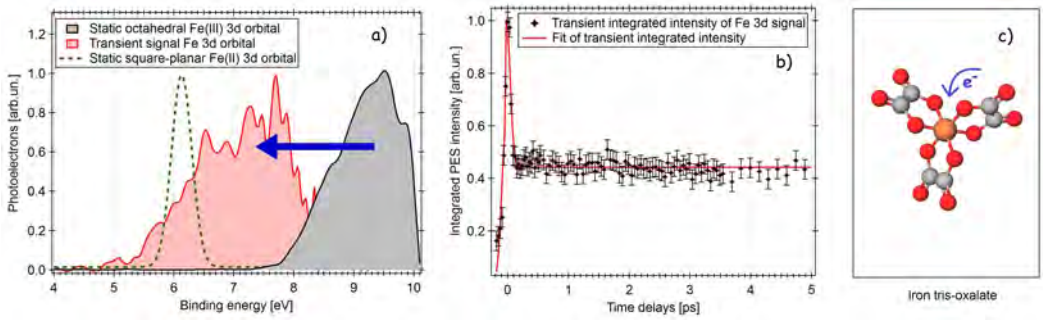

Figure: a) Static PES signal of Fe(III)oxalate iron 3d orbitals (black), and transient Fe(II) upon 266 nm excitation (red) shifting towards the final product Fe(II) spectral signature (dashed); b) the integrated PES Fe(II) transient intensity rises and remains constant; c) sketch of ferrioxalate with LMCT mechanism.

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Mechanism of universal fluorescence quenching of organic dyes by water

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Fluorescence spectroscopy and imaging have become standard tools to address biological questions. Extrinsic fluorescent probes are typically selectively attached to biomolecules of interest in order to enable their detection. When it comes to choosing the fluorophore, it is however often overlooked that water, which is ubiquitous in biological environments, quenches the emission of many fluorophores. Frequently, fluorescence is restored in aprotic and deuterated solvents and we previously showed that single-molecule based super-resolution imaging significantly benefits from replacing H_2O by D_2O [1, 2].

Whereas the mechanism leading to fluorescence quenching by water has been discussed in detail for inorganic ions in coordination complexes [3], its nature remains elusive for organic fluorophores surrounded by loose water as the solvent. In this contribution, we systematically explore the quenching of 40 organic fluorophores by water and other solvents. We observe that quenching by solvents is stronger for red-emitting fluorophores and depends on the spectral overlap between fluorophore emission and overtones of solvent O-H vibrational modes. We further relate the quenching efficiency to the number of water molecules in the first fluorophore coordination sphere and show that this strategy can be used to quantify the water amount in contact with the fluorophore, for example at a protein interface.

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Long-term trapping of Stark-decelerated polar molecules

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Trapping particles for extended durations is a key factor for high-resolution spectroscopic measurements and successful collision experiments in the cold regime (T_{trans} < 1 K), especially in cases where densities are low. Such experiments allow to study fundamental interactions between particles and to get insight into their quantum nature. While hybrid systems of trapped cold atoms and ions have been proven to provide a suitable basis for these experiments, the focus is now shifting towards molecular systems due to their increased versatility [1, 2].

Here, we report on the trapping of cold OH radicals under cryogenic conditions. The radicals are produced via a pinhole discharge of H_2O in a supersonic expansion, and are slowed down with a Stark decelerator from 425 m/s to 29 m/s. A final stopping field is applied close to the center of a magnetic trap, which results in an average velocity of 6 m/s or a nonthermal translational temperature of 37 mK. Successful trapping of OH is confirmed via laser-induced fluorescence and 1/e trap lifetimes close to half a minute were achieved under cryogenic conditions [3]. The magnetic trap is part of a hybrid system that further employs a radiofrequency ion trap and allows to mechanically shuttle the neutral molecules to the ion trap. Thus, studies of elastic, inelastic and reactive collisions between quantum-state selected cold polar molecules and atomic/molecular ions are possible. We further present the development of an improved version of the hybrid trap system that eliminates the need for a shuttle motor.

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Study of the Structural and Luminescent Properties of Inorganic Crystals doped with Rare Earth Elements

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The alkaline earth metal oxyhalide $Sr_4OCl_6:Eu^{2+}$ is characterized by good thermal stability and a tiny chromaticity shift. It emits efficiently in blue upon excitation with a near-UV LED chip [1],[2].

In this work, inorganic crystals of M_4OX_6 (M= Sr, Ba, Ca and X= Cl, Br) doped with Eu^{2+} are synthesized, characterized and their luminescent properties are studied. Low temperature and high pressure measurements are used to have a deeper understanding of the relationship between the environment of the luminescent center and its emission properties in this type of hosts.

Periodical DFT calculations have been performed in order to have an accurate spectroscopic signature of these systems. Also, it helped us investigate the validity of the unusual description of the structure using anion-centered tetrahedra as independent subunits.[3]

The last part of this work is the investigation of the optical properties and the crystal field analysis of Terbium (III) in borohydride compounds.

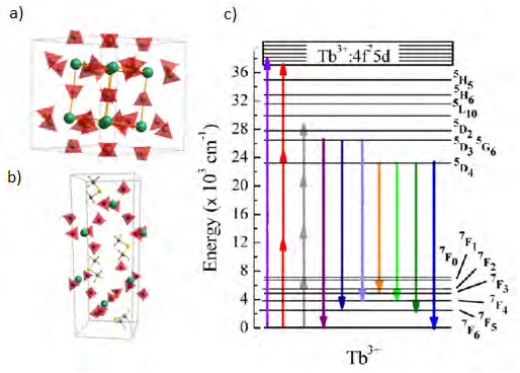

Figure: a) Crystal structure of α-$Tb(BH_4)_3$ b) $Tb(BH_4)_3$-DMS c) Energy diagram of Terbium (III). Taken from reference [2].

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A set of temperature-controlled sources as biophysical tools for native mass spectrometry

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Understanding how noncovalent interactions drive the folding of biomolecules and their interactions constitutes an important challenge in biophysics. On the one hand, to get access to the respective stabilities of biomolecular species, one can perform isothermal titration experiments. On the other hand, kinetics give access to the mechanism and allow the study of intermediates and kinetic traps.

Many common biophysical techniques are suitable for the investigation of thermodynamically stable states or to monitor kinetics. However, all these techniques are performed in solution and usually struggle when more than two species coexist. Using mass spectrometry and its ability to separate these coexisting species, it is possible to study equilibria of noncovalent complexes. These mass spectrometric experiments are however typically performed at room temperature and only provide thermodynamic or kinetic constants at room temperature.

Here, we present a set of two temperature-controlled electrospray ionization (ESI) sources for mass spectrometers. The first one, following a design by other groups [1]-[3], consists in a temperature-controlled copper block in which is embedded an ESI emitter filled with the solution of interest. We monitored the relative energy levels of several coexisting species as a function of temperature and demonstrate that thermal denaturation even of simple complexes can be quite complicated [4]. The second source is suitable to monitor fast kinetics at different temperatures. In a typical experiment, a solution containing a complex of interest is flown through a capillary embedded inside two independent temperature-controlled copper blocks. First, an equilibrium at the temperature of the first block is reached. This equilibrium is then perturbed by a sudden change in temperature when the solution enters the second block. By varying the flow rates, different time scales can be accessed and kinetics can be recorded.

To demonstrate the capabilities of the sources, we recorded the thermodynamics and kinetics of formation of a DNA triplex at multiple temperatures. Using the transition state theory, we mapped the full potential energy surface for the formation of this complex. This work illustrates how native mass spectrometry, supplemented by the right tools, can become a major biophysical method to study biomolecular interactions.

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Surface Characterization of Colloidal Silica Nanoparticles by Second Harmonic Scattering: Surface Potential and Interfacial Water Order

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Surface properties of colloidal nanoparticles (NPs) are key to a large number of industrial applications, in particular those related to heterogeneous catalysis. However, buried interfaces and surfaces of particles in solution are challenging to probe selectively as the bulk contribution often dominate, and in many cases the surface properties of a colloidal system cannot be inferred from studies of the corresponding planar surface.

Here we show that the electrical double layer of silica NPs in solution can be probed with polarimetric angle-resolved second harmonic scattering (AR-SHS). This nonlinear optical technique selectively probes the interfacial region and offers an all-optical alternative to surface-sensitive techniques that usually require more sophisticated resources, as for example x-ray photoelectron spectroscopy. Furthermore, AR-SHS gives access to quantities such as surface potential and molecular orientation at the interface, two parameters not easily obtained experimentally, without the use of any labeling molecule or *a priori* models for the structure of the interface. The AR-SHS data can thus be used to monitor surface changes as a function of pH and salt concentration, and provides an accurate description of the interface of colloidal NPs in water.

Mimicking nacre through magnetically driven self-assembly of colloids

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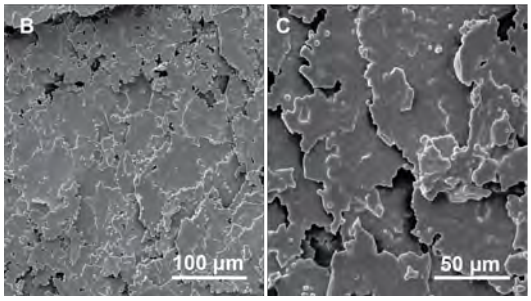
Nature’s intelligent design of composite materials leads to enhanced mechanical properties compared to the individual constituents, which can for example lead to a combination of high stiffness and toughness [1]. Nature design principles have inspired scientists to fabricate reinforced synthetic materials by mimicking the architecture of biological systems. Nacre is one of the most studied systems [1,2]. It is a composite material formed of alternating layers of inorganic aragonite platelets intercalated by a biopolymer. Nacre displays remarkably high mechanical properties going far beyond the rule of mixture of its constituents.We tried to mimic this layered composite structure using silica as inorganic material. In order to obtain a layered porous and anisotropic silica network, we modified the conventional sol-gel process, which leads to porous silica monoliths, by adding superparamagnetic iron oxide nanoparticles (SPIONS) and applying an external rotating magnetic field during the sol-gel transition [4]. The magnetic nanoparticles will self-assemble into layered structures in the presence of a high frequency rotating field, aligned in the plane of rotation of the field. Silica having an affinity for the iron oxide nanoparticles will nucleate on them adopting the same structure as the SPIONS, which act as smart templates to dictate the final structure of the monolith, which is permanently fixed after gelation. The final inorganic-organic nacre inspired composite is created by filling the porous structure with a polymer. Compressions tests of the platelet-structured composite show the desired increase of the mechanical properties of the silica monolith.



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The link between energy relaxation and structural dynamics: A refined mechanistic picture of the [Pt(ppy)(μ-^{t}Bu$_2$pz)]$_2$ photophysics

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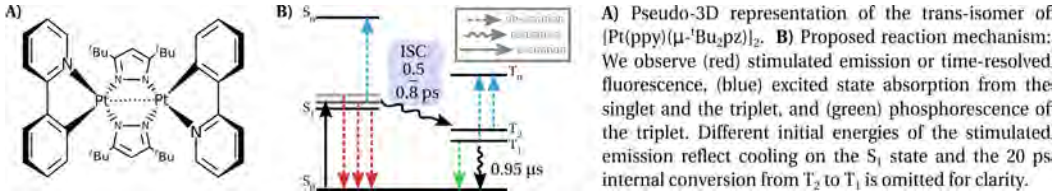
Adressing the connection between molecular structure, electronic properties and reactivity is fundamental for rational molecular design and beneficial for applications such as photovoltaics, light emitting diodes, catalysis, etc. Here, we investigate the photophysics of [Pt(ppy)(μ-^{t}Bu$_2$pz)]$_2$ (ppy: 2-phenylpyridine, ^{t}Bu$_2$pz: 3,5-di-tert-butylpyrazolate, Fig. 1), a model from the family of d^8-d^8 di-metal complexes, whose structural dynamics and electronic relaxation channels are intimately linked,[1] leading to the breakdown of the Born-Oppenheimer approximation.



A) Pseudo-3D representation of the trans-isomer of [Pt(ppy)(μ-^{t}Bu$_2$pz)]$_2$. **B)** Proposed reaction mechanism: We observe (red) stimulated emission or time-resolved fluorescence, (blue) excited state absorption from the singlet and the triplet, and (green) phosphorescence of the triplet. Different initial energies of the stimulated emission reflect cooling on the S_1 state and the 20 ps internal conversion from T_2 to T_1 is omitted for clarity.

The common motif in these complexes is that optical excitation of their lowest electronic state promotes an electron away from a σ*-antibonding orbital, resulting in the shortening of the metal-metal distance. In [Pt(ppy)(μ-^{t}Bu$_2$pz)]$_2$ the electronic transition is of metal-metal-to-ligand charge-transfer (MMLCT) character and the relaxation to the triplet MMLCT state (^{3}MMLCT) occurs on an ultrafast time scale. The details of this intersystem crossing (ISC) has been subject of debate[2,3] and here we unambigously identify the mechanism using ultrafast spectroscopy. Particularly, transient absorption anisotropy measurements allow to disentangle the congested transient absorption spectra. ISC occurs in 0.5-0.8 ps and the ground- and excited state vibrational coherences of the Pt-Pt mode dephase before ISC. With the help of *ab initio* calculations we identify a weak signal corresponding to the internal conversion process $T_2 \rightarrow T_1$, and show that the ISC occurs between S_1 and T_2, since the direct $S_1 \rightarrow T_1$ ISC is symmetry forbidden.

Our and previous[4] studies suggest that the charge-transfer character of the excited state likely plays a more general role in mediating the ISC when direct spin-orbit coupling is symmetry forbidden. This improved mechanistic picture proves advantageous when tuning the electronic properties of molecules and complexes via deliberate structural modifications.

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From Molecular Modulation to Supramolecular Engineering for Hybrid Perovskite Solar Cells

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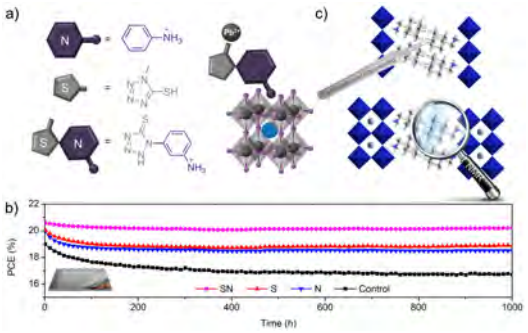
Hybrid perovskite solar cells attract considerable attention due to their remarkable power conversion efficiencies. However, their limited stability and molecular-level engineering remain challenging.[1–4] In contrast to three-dimensional perovskites, their layered analogues have demonstrated promising stabilities.[5-6] They comprise organic spacer layers connecting the hybrid perovskite slabs. In order to benefit from their enhanced stabilities without compromising the performance, we demonstrate a supramolecular strategy based on fine-tuning noncovalent interactions complemented by structural adaptability in the design of molecular modulators[3–4] and organic spacers.[5-6] These systems are devised to interact with the perovskite surface in a manner uniquely assessed by solid-state NMR spectroscopy at the atomic level.[3-4,6] As a result, we obtain solar cells with superior properties based on formamidinium lead iodide compositions with efficiencies surpassing those of the state-of-the-art formamidinium-based perovskites, accompanied by enhanced stabilities.[4-6] This has been investigated using a combination of techniques to unravel the design principles and exemplify the role of supramolecular engineering in advancing perovskite solar cell research.



Schematic representation of the (a) modulated perovskite structure with the (b) evolution of the performance of the corresponding solar cells over time and the (c) layered hybrid perovskite prototype.

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Towards parity violation in chiral molecules: High resolution FTIR spectroscopy of 1,3-difluoroallene, anharmonic calculations and ro-vibrational analysis of its CF-symmetrical ν_4 and asymmetrical ν_{12} stretching bands

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According to ordinary quantum chemistry including only the electromagnetic interaction the ground state energies of enantiomers of chiral molecules are exactly equal by symmetry. However, this symmetry is broken by the electroweak interaction and a slight energy difference $\Delta_{PV}E$ is introduced between the ground states of the two enantiomers, the accurate theory and measurement of which being the goals of our studies [1-7]. We show some experimental results on 1,3-difluoroallene calculated to be a possible candidate for the parity violation experiment [8]. The molecule is stable and gaseous at room temperature. As a starting point for our studies of parity violation in this molecule using the experimental setup reported in [9] we present here high resolution IR-spectroscopic results as outlined in the title.

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Towards Measuring the Parity Violating Energy Difference ($\Delta_{PV}E$) between the Enantiomers of Chiral Molecules: Theory and Spectroscopic Experiment

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According to the traditional point of view, the ground state energies and all the corresponding excited quantum states of the enantiomers of chiral molecules are exactly identical by symmetry. However, because of the electroweak parity violating interaction known from the Standard Model of Particle Physics (SMPP) a very small 'parity violating' energy difference $\Delta_{PV}E$ between the enantiomers of chiral molecules is predicted by theory. This might be measurable according to [1,2]. Theoretical progress in our group in the 1990s has shown that the values of $\Delta_{PV}E$ are typically one to two orders of magnitude larger than previously anticipated. This has been confirmed by calculations in other groups (see the reviews in [3-5] for the current status). A typical value is about 100 aeV (or 10^{-11} J/mol) as calculated for the prototypical chiral molecule CHFClBr [6], but strongly depends upon the molecule. However, experimental confirmation is still missing and this remains one of the major open questions in physical-chemical stereochemistry, related also to the open question of the evolution of biomolecular homochirality [5] and to consequences for fundamental symmetries in physics [4,7]. We provide in this poster a guided tour through the basic idea of the experiment [1,2], theoretical calculations on promising candidate molecules for the experiment [3-5,8,9,10,11] and high resolution FTIR spectroscopic experiments, providing some ground work for the laser spectroscopic experiments [8, 12]. We show the currently existing set-up with an experimental proof of principle for the achiral molecule ammonia NH_3, demonstrating that energy differences as small as 100 aeV are measurable [13]. These differences are zero for NH_3 (see also the complete theoretical simulation for ClOOCl [11]).

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No incorporation of dimethylammonium into the black perovskite phase of $CsPbI_3$ evidenced by solid-state NMR

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The black all-inorganic $CsPbI_3$ 3D perovskite is attracting attention owing to its considerably higher thermal stability, as compared to methylammonium- and formamidinium-based materials. However, it is thermodynamically unstable and spontaneously transforms to yellow δ-$CsPbI_3$ which hinders its use in PV device fabrication.[1] One of the strategies to stabilize the black phase of $CsPbI_3$ consists in using hydriodic acid, which was hypothesized to lead to the formation of $HPbI_3$ as an intermediate precursor.[2] This has been recently shown not to be the case – rather, the addition of HI leads to hydrolysis of DMF, which is present in the precursor solution as a solvent, and the formation of a new cation – dimethylammonium (DMA) – whose purported incorporation into the $CsPbI_3$ perovskite lattice has been suggested to stabilize the black phase.[3] We have recently shown that solid-state NMR provides a versatile means of probing cation incorporation and phase segregation in lead halide perovskites.[4-6] Here, using solid-state cesium-133 and carbon-13 magic angle spinning (MAS) NMR, we show that DMA is not incorporated into the 3D perovskite lattice of $CsPbI_3$. Our results demonstrate that the stabilization of DMA-doped $CsPbI_3$ is caused by physical screening of the perovskite crystallites rather than a change in the underlying atomic-level microstructure.

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Transient Absorption study of dilute small molecule organic solar cells

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Organic photovoltaics have been a rich source of study in recent years with a myriad of variables effecting the properties and performance of solar cells. These organic small molecules are especially interesting because of their highly tunable optoelectric properties and the ability to control morphology of active layers through molecular engineering. Traditional ideas about the necessity of both percolated and phase separated donor and acceptor regions has been challenged by the observation of efficient charge separation in fullerene based solar cells with <10% donor concentration. The mechanisms and underlying principles of these dilute cells are yet to be completely illuminated, and so significant research still needs to be done in order to fully understand and take advantage of these systems.

This study looks at a C_{60} acceptor-based system with dilute and equal ratio small molecule donors. The donors in the system being α-Sexithiophene (α6T) and 1,1-bis-(4-bis(4-methyl-phenyl)-amino-phenyl)-cyclohexane (TAPC) created using vacuum deposition techniques. A low fluence femtosecond transient absorption (TA) study is made comparing the effect of different concentrations of donor on charge generation properties, and how these change in the different small molecule donor systems. Further TA studies compare these results to those of pure C_{60}, bilayers and full devices, comparing at the charge generation and recombination processes in different configurations of dilute and undiluted systems.

Capturing the ultrafast evolution of excited state chirality with time-resolved CD in the deep ultraviolet

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For understanding the functioning of many photo-driven molecular machines, it is crucial to capture the temporal evolution of their chirality and thus structure upon photo-excitation. This is especially relevant for understanding, e.g. the biological systems, such as photo-active proteins and the kinetics of novel synthetic machines, such as unidirectional molecular motors. Steady-state circular dichroism (CD) has become a standard analytical tool to obtain solution-phase structural information via a molecule's chiral properties. Especially in the deep ultraviolet (UV) spectral range (< 300 nm), it is sensitive to the UV-transitions in proteins and many organic ligands in functional chiral complexes. However, pushing CD spectroscopy into the time-domain to directly capture the ultrafast evolution of chirality of the photo-excited systems has remained a challenge, with only few isolated reports with sub-nanosecond resolution (1).

Here, we present the first time-resolved CD spectrometer in the deep-UV region (250–370 nm) with sub-picosecond time-resolution (2). Due to its unique broadband detection scheme with unprecedented sensitivity, it is now possible to extract the CD spectra of photo-excited states and map their temporal evolution with femtosecond resolution. We benchmark the set-up through the characterisation of the structurally well-defined photo-excited triplet metal-to-ligand charge transfer (MLCT) state in enantiopure samples of $[Ru(bpy)_3]^{2+}$. This lets us proceed to the more complicated dynamics of excited supramolecular systems: $[Fe(bpy)_3]^{2+}$ is configurationally labile in solution and its configuration needs to be controlled by supramolecular complex formation with enantiopure counterions; the diastereomeric interactions within the ion pair leading to a preferential Λ or Δ configuration (3). Here, we study the transfer of this interaction to the photo-excited neutral quintet state, which couples to an accompanying ultrafast expansion of the metal-ligand distances.

The achieved combination of temporal and spectral resolution in the deep-UV demonstrates, that the measurement of ultrafast chirality changes in photo-active functional complexes and biological systems is now feasible, opening an avenue that was previously not accessible in chiroptical spectroscopy.

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NMR-Based Determination of the 3D Structure of the Ligand-Protein Interaction Site without Protein Resonance Assignment

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X-ray crystallography molecular replacement (MR) is a highly versatile tool for the detailed characterization of lead compound and binding modes in the pharmaceutical industry. The two major limitations of its application to drug research are (i) the availability of a similar protein structure, and (ii) obtaining well-diffracting crystals of the ligand-protein complexes of interest. While nowadays the first point is often not a limitation anymore, obtaining well-diffracting crystals might be difficult. In such situations structure determination of protein-ligand complexes by liquid-state NMR is a good option. Unfortunately, the established standard structure determination protocol is in general time-consuming, and a shortcut using available structural data as in the case of MR in X-ray crystallography is not available.

Here, we present *N*MR^2 (**NMR M**olecular **R**eplacement), a MR-like approach in NMR to determine the structures of the binding pockets of ligands at atomic resolution. The calculation of structures of protein-ligand complexes relies on the collection of unassigned semi-quantitative inter-molecular NOE distance restraints and on previously solved structures.[1] The *N*MR^2 method uses a high throughput structure calculation protocol, rather than a docking-scoring simulation. It is fast since it requires only a few days of measuring time and bypasses the time-consuming sequential assignment steps for the protein.

We will present multiple *N*MR^2 applications covering several ligand topologies ranging from peptidomimetic to small molecules that bind strongly or weakly to protein receptors. We also report how *N*MR^2 can make use of partially labelled protein using methyl-specific isotope labelling. Our findings demonstrate that *N*MR^2 may open an avenue for the fast and robust determination of the binding pocket structure of ligand-protein complexes at atomic resolution.

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Catalytic Fast Pyrolysis of Lignin Model Compounds by Detecting Reactive Intermediates

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Lignin is one of the three main components of lignocellulosic biomass and has high potential as a feedstock for bulk and fine chemicals.[1, 2] The most promising method to depolymerize its structure and to get sustainable fuels is probably catalytic fast pyrolysis (CFP).[3] However, there are only a few mechanistic studies on CFP of lignin or its model compounds, due to the complexity of the lignin structure and the limitation of analytical instrumentation to detect elusive and reactive species. To overcome these issues, reactive intermediates in catalytic fast pyrolysis can be directly detected using imaging Photoelectron Photoion Coincidence Spectroscopy (iPEPICO). This technique provides spectroscopic insight to isomer-selectively assign reactive intermediates in complex reaction mixtures ranging from combustion to catalysis.[4, 5, 6]

CFP of two benzenediols, catechol and resorcinol, was investigated in a newly build catalytic reactor using molecular beam sampling and iPEPICO techniques at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source. Our results show that catechol was much more reactive than resorcinol. While the fulvenone ketene was found as the central reactive intermediate during the HZSM-5 catalyzed CFP of catechol, no reaction intermediates or products were observed in the exact same reaction using resorcinol. Mechanistic insights will be discussed in this contribution.

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Heteronuclear 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 results in oscillatory potentials that may support bound states of long-range diatomic molecules in case of a negative s-wave scattering length. In alkali metal dimers, the spins of the Rydberg electron and the valence electron of the ground-state atom pair either in a singlet or triplet configuration. 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 structure. We will present studies on the formation and dynamics of homo- and heteronuclear long-range Rydberg molecules in ultracold caesium and potassium Rydberg gases using high-resolution photoassociation spectroscopy. These studies improve our understanding of the binding mechanism and represent a stringent test ab-initio low-energy electron-atom scattering phase shifts [9].

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Magic Rydberg-Rydberg transitions in electric fields

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Rydberg states of atoms and molecules are very sensitive to electric fields. This property makes them ideal electric-field sensors [1-4] but is detrimental to applications of Rydberg states in quantum-optics, quantum-information processing and quantum simulation because of inhomogeneous Stark broadening and the resulting loss of quantum coherence [5-12]. We demonstrate, with the example of Rydberg states of ^{39}K, the existence of Rydberg-Rydberg transitions with extremely small differential dc Stark shifts, which we call *dc-field-magic Rydberg-Rydberg transitions*.

These transitions hardly exhibit any Stark broadening, even when the electric-field strength varies by as much as 10 Vcm^{-1} over the experimental volume. We present a systematic study of dc-field-magic Rydberg-Rydberg transitions combining experiment and calculations, and classify them in three main types, which should also be encountered in the other alkali-metal atoms, in alkaline-earth-metal atoms, and even in molecules. The observed insensitivity to dc electric fields does not reduce the interactions between Rydberg atoms, even if they are dominantly electric dipole-dipole in nature. Rydberg states coupled by dc-field-magic Rydberg-Rydberg transitions therefore have great potential as qubits.

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Supramolecular encapsulation of metastable-state photoacids

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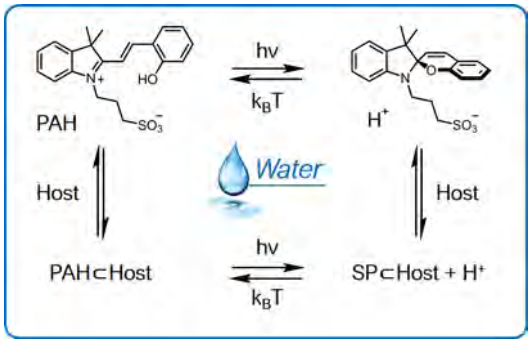
Metastable-state photoacids[1] (PAHs) are a specific class of molecular switches capable of releasing protons through visible light absorption and uptake them spontaneously under dark conditions (Figure 1). These compounds impact many different fields of research, as they offer the opportunity to make use of a chemical potential for controlling reversibly any acid-sensitive system. In recent years, they have found applications that span from polymer science[2] and supramolecular chemistry[3] to nanotechnology[4] and pharmaceutical sciences[5]. However, when using water as the solvent, severe limitations persist: solubility and chemical stability are generally low, whereas dark acidity – i.e., the acidity of MSPs in the absence of light – is not as weak as it is in organic solvents. All these factors, together with moderately short lifetimes, limit the extent and the reliability of proton release in aqueous solutions. Herein, we show how suitable cucurbit[n]uril and cyclodextrins – macrocyclic host molecules well known for their binding capabilities – can bind PAHs (Figure 1), tuning their light-driven operation in water.



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Determination of Size, Shape, Mass and Concentration of Single Aqueous Supersaturated Aerosol Particles

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Aerosol particles offer a unique opportunity to study various chemical and physical processes in pico- to attoliter samples. In particular, aqueous salt particles are a suitable system for studying phase transitions like the efflorescence, where a new phase nucleates inside a supersaturated droplet. This process has been under intense investigation for decades, but open questions still remain [1,2]. A prerequisite of any successful investigation of this phase transition is the precise monitoring of the particle's properties.

Recently we demonstrated methods to retrieve simultaneously key particle properties like size, refractive index and chemical composition of spherical, optically trapped particles ranging from submicrometer to micrometer size [3]. Current work focuses on two additional measurement techniques to obtain complementing particle data. The first method is based on a modulated optical trap where the particle is forced into a quasi-harmonic motion. The mass of the particle is retrieved from the measured resonance frequency and damping ratio of the oscillation. Simultaneously, we use a digital in-line holography setup for imaging of the particle [4]. From this, the particle size and morphology are obtained with high spatial and temporal resolution (770nm, 240µs).

The combined setup is used to characterize aqueous salt particles, in particular in the supersaturated regime that is reached upon drying of an undersaturated droplet. This data is needed to better understand the efflorescence phase transition of micron and submicron sized aerosol particles.

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The chemical nature of CO_2 adsorption on zeolites

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Adsorption-driven CO_2 capture is one of the most promising carbon capture and storage (CCS) technologies, which aim to remove CO_2 from N_2 in post-combustion flue gas. Nano-porous zeolites are of particular interest to adsorption applications because of their CO_2 capacities and selectivities, robustness, and often low costs. The nature of CO_2 adsorption is various. The process may act as physical adsorption with intermolecular interactions of the van der Waals type or as chemisorption with a significantly perturbed electronic structure of CO_2 and the formation of CO_3^{2-} and HCO_3^- species.[1]

Adsorption-driven processes can be implemented only if highly functional adsorbent materials have been developed. Zeolite A is one of the most successful adsorbents. Rzepka *et al.*[2] broadly discussed the potential enhancement of the selectivity of CO_2 over N_2 and CH_4 by replacing Na^+ with larger monovalent cation e.g. K^+ in the pore windows of zeolite A. Figure 1 shows the cations positioned at the 4- and 6-rings and the 8-ring apertures of the aluminosilicate framework of zeolite A. K^+ ion was favored at the 8-ring sites, and also gradually substituted the 6-ring sites with increasing x in $|Na_{12-x}K_x|$-A.[2] Large cation did not fit the mirror plane of the 6-ring and was placed on its both sides.[2] Cations sitting in 8-rings and 6-rings appear to tailor the size of main pore windows.

The effective pore size was shown to depend on the K^+ content and to separate small CO_2 molecules from large N_2 and CH_4 due to differences in their diffusivities. Various compositions of $|Na_{12-x}K_x|$-A demonstrated gradual decline of CO_2 uptake with x and a total exclusion of N_2 and CH_4 already for low x.[2] Most of already absorbed CO_2 molecules were revealed to bridge adjacent 8-ring sites (Figure 1). They are relatively weakly physisorbed, and therefore most of the working capacity of CO_2 adsorption is related to this site.[1] On the other hand some of CO_2 molecules coordinated to a cation in the 8-ring plane (the second most populated site of CO_2 adsorption) demonstrated perturbed electronic structure.[1] These chemisorbed carbonate species cannot be removed by simple evacuation.[1]

Rzepka *et al.*[2] also reported that adsorbed CO_2 molecules displaced the cations into the a-cages and resulted into a slight contraction of the overall distribution of extra-framework cations in zeolite structure upon the adsorption of CO_2.[2] 4- and 8-ring sites cations are attracted by CO_2 molecules and shifted towards the center of zeolite cavities.[2] The time-averaged repositioning stands in an agreement with the “trapdoor” mechanism reported also for zeolites Rho, X and chabazite.

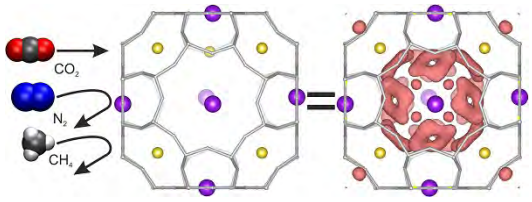

Figure 1. Selective adsorption of CO_2 on $|Na_9K_3|$-A (left). Na^+ and K^+ positions represented by yellow and magenta balls. Nuclear densities of adsorbed CO_2 molecules (right).

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Study on NO+O and N+O2 collision on 2A', 4A' and 2A'' potential energy surfaces.

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In atmospheric chemistry the study of high temperature (10000-20000 K) non-equilibrium reactions is of great importance. In particular the study of reactions involving NO + O or O2 + N, which are present in thin shock layer regions like the ones created by hypersonic vehicles.

In this work we study the forward and reverse reaction using QCT (quasi-classical trajectory) reaction dynamics calculations. For this purpose, we have constructed a full dimensional potential energy surfaces (PES) for the 2A', 4A' and 2A'' electronic states of NO2. Over 30000 ab initio points are calculated at the MRCI+Q/aug-cc-pVTZ level. Following a reproducing kernel Hilbert space approach [1] a full dimensional surface is constructed. State to state cross section, rate coefficients and equilibrium constant have been computed over a wide range of temperature (600 - 20000 K). Our results of cross section and total rate coefficients are compared with available theoretical [2,3,4,5] and experimental results [6,7] reported in literature. Our reported value of equilibrium constant, can serve as wide temperature benchmark for this reaction.

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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 ($v \leq 300$ m s^{-1}) 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^{-1} to 50 - 100 m s^{-1} [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 precision measurements of *n*p-2s transition frequencies.

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Investigation of Mirror-Image Breakdown in the Stationary Electronic Spectra of 9,10-Bis(phenylethynyl)anthracene by Ultrafast Broadband Fluorescence

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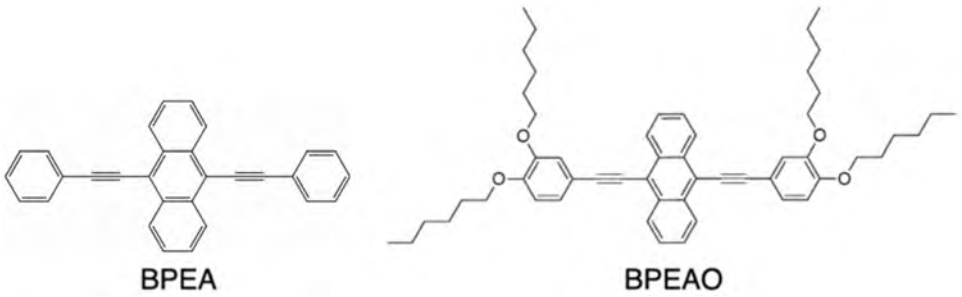
In this study we inspect the mirror-image inconsistency in the electronic spectra of 9,10-bis(phenylethynyl)anthracene (BPEA, Fig. left), using broadband fluorescence upconversion spectroscopy (broadband FLUPS). Fluorescence dynamics is the only clear and direct way of monitoring this process and to our knowledge this is the first time this method is used for this purpose. In previous studies, visible transient absorption spectroscopy[1] and single wavelength detection fluorescence spectroscopy[2] have been utilized. In the latter case, the spectra have been reconstructed by the single wavelength decays, with all the shortcomings ensuing this method[3].



This mirror-image breakdown has been studied in the past for oligomers[2] and was explained in terms of a planar geometry in their excited state with respect to a torsional disordered ground state configuration owing to lower rotational barrier. Structural relaxation of the excited state to the planar geometry is expected to cause a significant evolution of the emission spectrum. BPEA appears to be an excellent candidate for this study using broadband FLUPS considering its high oscillator strength and solubility in numerous organic solvents. To examine further this planarization process, we also used a bulkier compound, BPEAO (Fig. right). These measurements reveal broad and structureless early time emission spectra for both compounds, compared to the late time and stationary spectra. Results obtained using different pump wavelengths, i.e., upon photoexcitation of molecules with different extent of torsional disorder, will also be presented.

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Comparative studies on $LiNi_{0.5}Mn_{0.5-x}Co_xO_2$ ($0 \leq x \leq 0.5$) cathode materials for lithium-ion batteries

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Lithium-ion batteries are one of the best power sources for applications such as electric vehicles.[1] The most commonly used cathode materials in Li-ion batteries are layered lithium metal oxides ($LiTMO_2$, TM is transition metal) due to their large theoretical capacities (280 mAh/g). Among the layered cathode materials, lithium nickel manganese cobalt oxides ($Li(Ni_xMn_yCo_{1-x-y})O_2$ or NMC) exhibit promising electrochemical properties, which primarily depends on the atomic composition of Ni, Mn and Co in the structure.[2] Several NMC compositions such as NMC 111, 442, 532, 622 and 811 (the three numbers denote the ratio of Ni to Mn to Co) have been studied extensively. Among them, NMC 532 shows some decent properties that are desirable to industrial applications including electric vehicles. Hence, this study focuses on cathode material compositions of the series $LiNi_{0.5}Mn_{0.5-x}Co_xO_2$ ($0 \leq x \leq 0.5$) that includes $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ or NMC 532. The main goal of this study is to understand the effect of Co/Mn as well as the morphology on the electrochemical behaviour of cathode materials.

In this study, cathode materials were synthesized by systematically varying the concentrations of Mn and Co but keeping the nickel content constant. The as-synthesized compounds of the series $LiNi_{0.5}Mn_{0.5-x}Co_xO_2$ - NMC 550, NMC 541, NMC 532 and NMC 523 were structurally characterized using X-ray diffraction. By constructing coin-cells and testing, their electrochemical properties were compared. Results showing their electrochemical behaviour such as their voltage profile and cyclability will be presented. For the same atomic composition, two morphological variants were made, and their respective properties were also compared. The results of this study will reveal (a) whether NMC 532 is superior in the series $LiNi_{0.5}Mn_{0.5-x}Co_xO_2$ ($0 \leq x \leq 0.5$) or not, (b) if true, what reason makes NMC 532 superior and (c) how morphology affects the properties of cathode materials with respect to their chemical compositions.

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Precision Spectroscopy, Coherent Manipulation and State-to-State Chemistry of Single Molecular Ions

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Recent progress in laser technology, frequency metrology and molecule optics have enabled ultra-precise measurements of molecular frequencies [1 - 3]. We are developing a complete experimental and theoretical toolbox for non-destructive spectroscopy of single molecular ions using quantum-logic techniques [4 - 8]. In a first stage, we target relative measurement accuracies of order 10^{-14} – 10^{-15}; an improvement of several orders of magnitude in comparison to the present state of the art of 10^{-9} [1, 2]. These advancements will pave the way for using molecules as new high-precision frequency standards and clocks, for addressing fundamental physical problems such as the proton-radius puzzle and a possible temporal variation of fundamental physical constants [9, 10] and for precision tests of quantum electrodynamics. It will also enable the observation and control of chemical reactions of single particles on the quantum level. The dramatic advancement in measurement accuracy targeted here is enabled by the implementation of new spectroscopic methodologies based on quantum technologies [4] and by the development of ultra-narrow & ultra-stable quantum-cascade laser sources tailored to the current needs. We present a detailed discussion of our approach and a characterisation of the quantum-logic readout of single molecular ions for spectroscopy.

We use N_2^+ as a prototype molecule in this work, although our methods can be extended to a general class of diatomic and polyatomic molecules. The electronic ground state of N_2^+ features narrow electric-dipole-forbidden transitions and insensitivity to Stark & BBR shifts to the first, rendering N_2^+ an attractive candidate for precision spectroscopy [3, 4].

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Effect of Ionic Liquids on the Excited-States Dynamics of Malachite Green at Dodecane/Water Interface

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The interfaces between two isotropic media have gained considerable attention over the past decades as they play a crucial role in many areas of science.[1] For example, interfaces with a room temperature ionic liquid (RTIL) as one of the phases could have promising applications in extraction processes and air treatment but remain largely unexplored.[2-3] A major experimental difficulty for investigating interfaces is that the signal from the interfacial region is completely hidden by that originating from the bulk when conventional spectroscopic methods are used. We are investigating liquid-liquid interfaces using a surface specific technique, surface second harmonic generation (SSHG). This technique is based on the second order non-linear response, which within dipolar approximation originates from the interfacial region only.

Here in, we present an investigation on the influence a room-temperature ionic liquid (RTIL) on the excited-state properties of an organic dye, Malachite Green (MG), at water/dodecane interface. MG is positively charged and its properties at the interface are modulated by the presence of ions.[4] First, we will show the SSHG response at different concentrations of MG at neat water/dodecane interface. Second, the influence of the RTIL on the SSHG signal is described. Information about the interfacial charge, i.e. which of cation or anion has the highest affinity for the interface, will be discussed.

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Broadband Fluorescence Up-Conversion Spectroscopy : A Powerful Tool to Assess Ultrafast Dynamics of Charge Carriers and Excitons in Lead Trihalide Perovskites

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Time-resolved fluorescence spectroscopy is a powerful tool to investigate the photo-luminescence dynamics of semiconductor systems on the femtosecond timescale. Available experimental techniques, such as those based on the use of streak cameras or time-correlated single photon counting (TCSPC) are limited by a temporal resolution of a few picoseconds [1]. A resolution of at most 0.2-0.5 ps, however, is deemed necessary to monitor the early events occurring during the relaxation of hot carriers and the formation of excitons in direct bandgap materials. To allow for such a time-resolution, the emission of the sample can be upconverted (gated) by sum-frequency mixing with an ultrashort pulse in a nonlinear optical crystal.

Here, we are presenting a new broadband (λ = 420-750 nm) fluorescence up-conversion setup (FLUPS) developed by Ernsting et al. [2], which allows single-scan pump-gate measurements. The time resolution of the FLUPS instrument is only limited by the gate pulse duration and has been found to be < 200 fs for our setup. A spectral discrimination of less than 50 cm^{-1} is achieved, moreover, using an unfolded Czerny-Turner spectrometer for signal detection.

We demonstrate the ability of FLUPS by investigating the early-time evolution of the fluorescence of two-dimensional lead trihalide perovskites. The rise of the photoemission of such 2-D films has been found to be of the order of 0.9 ps to 1.2 ps, depending on the cation and fluence, which is well above the experimental response function. A deeper analysis of the kinetics of the fluorescence rise will provide insights into the dynamics of the charge carriers and pseudo-particles upon light excitation of low-dimensionality perovskites of various compositions and architectures.

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Kinetics of exon unbinding in group II introns by single-molecule FRET and molecular dynamics

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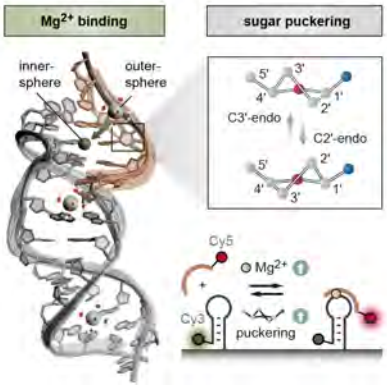
Formation of stable RNA tertiary contacts is inextricably linked to metal cations to compensate the electrostatic stress and guide RNA folding. Self-splicing group II introns establish long-range tertiary interactions between domain 1 and the upstream exon to accurately position the 5'-splice site within the ribozyme's active core.[1] Here we use single-molecule FRET and computer simulations on a model RNA hairpin to monitor the kinetics of exon recognition and release in response to K^+ and Mg^{2+}.[2]



We find that exon unbinding rates are heterogeneous as a result of degeneracy in the FRET states which in turn originates from the presence or absence of specifically coordinated Mg^{2+} ions.[2-5] We solve the rate system by hidden Markov modeling and identify the structural origin of the kinetic heterogeneity. While metal ion binding locks the RNA tertiary contact in a rigid conformation, molecular dynamics simulation show that strain on the sugar phosphate backbone is alleviated through fast sugar puckering. Switching between pucker conformations is pronounced in DNA exons which explains their lower affinity towards group II introns.

Financial support by the Swiss National Science Foundation (RKOS), the UZH Forschungskredit (FDS and RB) and the University of Zurich is gratefully acknowledged.

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Excited-state symmetry breaking in novel pyrrolopyrroles - The effect of the position and the strength of the acceptor group

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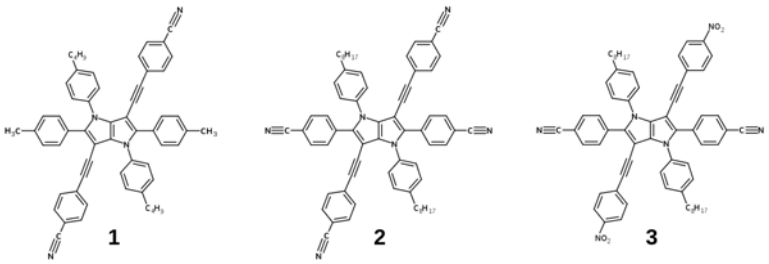
Excited-state symmetry breaking (ESSB) in centrosymmetric acceptor-donor-acceptor (ADA) or DAD type molecules has attracted a large amount of attention over the past few years. These compounds are characterised by a large two-photon absorption cross section which makes them attractive for many applications.

Their electronic ground-state is purely quadrupolar, but their excited-state behaviour points to a strongly dipolar character. Whilst, in apolar media, the symmetry of the electron distribution is retained upon excitation, in polar solvents, the symmetry breaks and the molecules become dipolar. It was recently shown that this process is triggered by the instantaneous asymmetry of the surrounding solvent field and enhanced by solvent relaxation.[1]

Here, we investigate ESSB in three novel pyrrolopyrrole derivatives[2] (see graphic). The effect of the position and strength of the electron withdrawing groups is studied by time-resolved infrared (TRIR) spectroscopy. The changes of the electronic structure after the excitation are monitored by looking at the C≡N and C≡C stretching modes. We will show that weak quadrupolar interactions with the solvent suffice to break the symmetry of the excited-state electronic structure.



Acknowledgement: The authors are grateful to Prof. D. T. Gryko for providing the investigated compounds.

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Towards cold dipole-dipole collisions in 3D-printed merged electric guides

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Merged beam experiments on neutral molecules recently allowed for first molecular beam studies of reactive scattering below 1 K. In these experiments, a magnetically guided beam was merged with a direct expansion or an electrically guided beam of polar molecules[1]. We have designed a new merged beam setup that permits to study cold collisions between two beams of polar molecules, thus giving access to the investigation of dipole-dipole interactions in the sub-Kelvin range.The Stark effect can be used to manipulate polar neutral molecules in an electrostatic guide but the electrode structure necessary to merge two polar molecular beams is complicated because one beam cannot be inserted into the guide of the other beam in the same manner as is done in previous merged beam experiments. The required structure is highly complex and difficult to build by traditional means. The 3D printing-metal coating approach, developed in our group[2], makes possible the production of an Y-shaped electrostatic guide. In this setup two bent quadrupoles guides are smoothly merging in an hexapole guide.A series of simulations has been performed to estimate the transmission of the guide as a function of the velocity in order to design the merged beams experiment. The correct functioning of the device is demonstrated by studying ND_3-ND_3 scattering.

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Site-selective and bond-specific dissociation of methane molecule

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Steam reforming process is used in the formation of hydrogen from methane at industrial level. The rate limiting step in this reaction is the dissociation of methane. Therefore, studying this step in detail would give us a better understanding of the process. In our lab, we study surface dynamics of gas-solid interactions. Currently, our studies mainly revolved around understanding the dissociation of methane using vibrational spectroscopies (RAIRS). In our experiments, we try to control as many parameters as possible in the rate limiting step of the steam reforming process and understand how the different parameters contribute to the efficiency of methane dissociation. The surface that we used for our study is Pt. We worked on the different surfaces of Pt because exposing different planes to a beam of methane molecules means that molecules come into contact with different type of surface atoms. For example Pt(211) surface has three types of surface atoms which are step atoms, terrace atoms and corner atoms. Meanwhile, Pt(111) only has one type of surface atom available for the interaction of the incident methane molecules which is the terrace atom.

We found interesting results when we directed a molecular beam of methane onto different Pt surfaces. For example, the dissociation of methane is more effective on the step sites of Pt(211) surface compared to the terrace atoms of the same surface. This is due to the lower dissociation activation barrier on the step atoms compared to the terrace atoms. Meanwhile, the corner atoms have very high activation barrier that no dissociation takes place there. This experiment was an evidence for the site-selectivity of the dissociation of methane molecules on Pt.

Apart from the above information, the incident molecules that we use are prepared in a specific ro-vibrational state with laser excitation. The ability to prepare our molecules in a specific quantum state allows us to carry out experiments which are quantum-state resolved. An experiment that we did in the lab includes preparing the incident deuterated methane molecules, CH_3D with excitation of the antisymmetric C-H bond. This allowed us to study the bond-selectivity in the methane dissociation. We found that the single quantum excitation was enough to cause bond-selective dissociation in the dissociation of methane molecules.

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Plasmon-induced slow Electron Injection of Gold nanoparticles into titanium dioxide

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By using the core-shell Au/TiO_2 nanoparticles (NPs), we monitor the electron injection into anatase TiO_2 under plasmon excitation of the gold using broadband deep-ultraviolet (deep-UV) transient absorption spectroscopy. We observe a significantly long-lived bleach of the TiO_2 excitonic resonance at ~325 nm which is due to the injected electrons. The temporal behaviour of the bleach shows that the plasmon-induced electron injection occurs on two timescales: a prompt regime within ~320 fs, and a larger one over 171.7 ps which represents the dominant channel.

Autoionization rates of core-excited magnesium Rydberg atoms in electric fields using the core fluorescence as a reference

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$[M^{+*}]nl$ core-excited Rydberg states of the alkaline-earth metal atoms can decay by electronic autoionization ($[M^{+*}]nl \rightarrow M^+ + \varepsilon l'$) or by fluorescence of the core ($[M^{+*}]nl \rightarrow [M^+]nl + h\nu$) [1]. The two processes can be detected separately by monitoring the prompt M^+ autoionization yield and the delayed pulsed-field-ionization yield of the $[M^+]nl$ Rydberg states. Whereas the former process strongly depends on the principal (n) and orbital angular-momentum (l) quantum numbers, the latter is independent of n and l because it is essentially a property of the ion core. We present an experimental study of the competition between autoionization and core fluorescence in $[Ne]3p_{3/2}nl$ core-excited Rydberg states of Mg atoms and of its dependence on n and weak electric fields [2]. We analyze the experimental results using a kinetic model, from which we extract the electronic-autoionization rates by using the Mg^+ $3p_{3/2} - 3s_{1/2}$ core fluorescence (τ_{fl} = 3.8 ns [3]) as an internal clock. The autoionization rate of the $3p_{3/2}nd_{3/2}$ (J = 3) and of the fully Stark-mixed $3p_{3/2}nk$ (m = 0, ±2) series are $(1.9 \cdot 10^{16}\ (n^*)^{-3}\ )\ s^{-1}$ and $(8(3) \cdot 10^{15}\ n^{-4}\ )\ s^{-1}$, which would translate for the lowest Rydberg states (3d with n^* = 2.62) to autoionization rates of $\sim 10^{15}\ s^{-1}$ and $\sim 10^{14}\ s^{-1}$, respectively, as fast as Auger decay processes [4].

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Towards parity violation and tunneling in chiral molecules: An experiment in the mid-infrared range using a pulsed slit jet expansion.

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[1]Laboratorium für Physikalische Chemie, ETH Zürich

In our scheme proposed to measure the parity violating energy difference between the enantiomers of chiral molecules [1], a pure parity state has to be prepared in a two photon process in which the molecules are excited to a rovibrational state with an excitation energy close to or above the barrier for the interconversion of the two enantiomers [2]. For the preparation step a complete understanding of the IR-spectrum in this energy region where tunneling splittings are large is essential. To measure such infrared spectra with high accuracy a new setup has been built to investigate polyatomic molecules of moderate size in the required spectral range from 2500 to 5000 cm^{-1} using an OPO referenced to a frequency comb reaching an accuracy better than 10 kHz for the mid-IR laser frequency. The spectra are measured in a slit jet molecular beam expansion using cavity ring-down spectroscopy [3, 4]. Due to the Doppler shift the effective frequency uncertainty is about 1 MHz. We will present test results for ammonia (NH_3), which is also of general interest as a prototype tunneling molecule [5], as well as for nuclear spin symmetry (see [6] and Refs. cited). The results of the experiments are consistent with nuclear spin symmetry conservation in seeded supersonic jet expansions providing cooling to temperatures below 7 K. In the achiral molecule NH_3 one also has effective parity conservation [2]. Results on potential chiral candidates for measuring parity violation will be presented as available at the time of the meeting.

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Transient infrared response of a PDZ2 domain protein upon light induced ligand perturbation

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A photo-controllable peptide ligand[1] was employed to promote a non-equilibrium structural transition of a PDZ2 domain which has been recorded by transient infrared spectroscopy. With the help of isotope labelling strategy, a heavier ($^{13}C^{15}N$) PDZ2 domain version was expressed by which the PDZ2 domain amide I response was isolated from the one of the photo-controllable peptide ligand. Photo-induced isomerization of the latter leads to ca. 4 fold difference in affinity towards the PDZ2 domain. The transient infrared spectra reveal rearrangements of the protein structure happening on many timescales which is in agreement with the results previously obtained for a similar model system[2].

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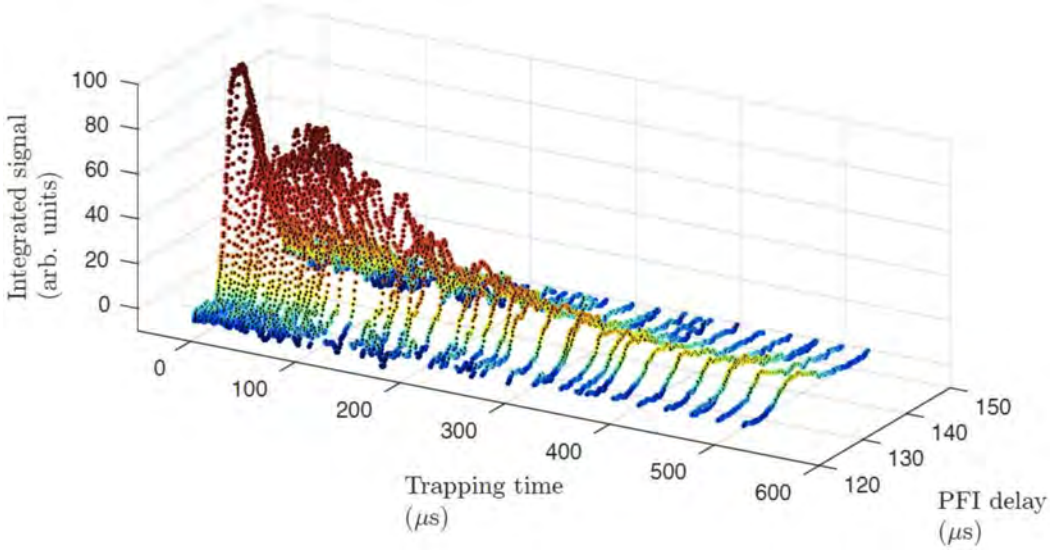
Fluorescence-lifetime-limited trapping of Rydberg He atoms on a chip

M. Zesko[1], V. Zhelyazkova[1], J. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]Laboratorium für Physikalische Chemie, ETH Zürich

The manipulation of atoms above surfaces is an important objective in atomic and molecular physics, in cavity QED [1], in cold chemistry [2], or atom interferometery [3]. If the neutral atoms are in highly excited Rydberg states, they can serve as substitutes for ions because the mean radius of the excited-electron orbit is very large and scales with the square of the principal quantum number n. In this work, we report on experiments in which cold metastable (1s)(2s) $^3S_1$ He atoms generated in a supersonic-beam source were excited to Rydberg states in the n = 27 – 30 range, subsequently decelerated by a surface-electrode decelerator in a cryogenic environment, and then held in traps above its surface. The atoms were decelerated to zero velocity over a distance of 33 mm in 75 µs and kept trapped for times in the 0 – 525 µs range, after which they were re-accelerated for detection by pulsed-field ionisation (PFI).

The long trapping times achieved in this work result from two improvements over previous He trapping experiments [4]: (i) an in-house-built valve producing gas pulses of about 20 µs duration enabled the reduction of losses from collisions with atoms in the trailing part of the gas pulse, and (ii) cooling the environment suppressed losses from blackbody-radiation-induced processes. At 4.7 K, the excited-atom losses from the trap were found to come almost exclusively from the fluorescence of the Rydberg states. Increasing the temperature of the environment to 100 K reduced the trapping times because of transitions stimulated by blackbody radiation.



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Studying ion-molecule reactions at low temperatures with a merged-beam set-up

V. Zhelyazkova[1], M. Zesko[1], J. A. Agner[1], H. Schmutz[1], F. Merkt[1]*

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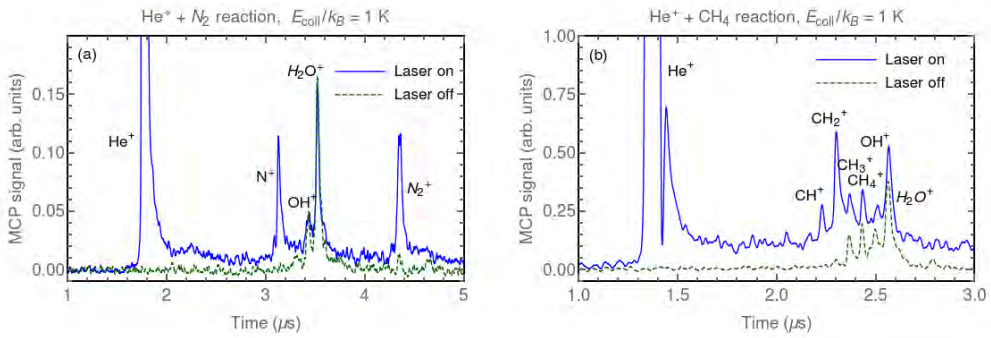
Reactions involving highly reactive species, such as ions or radicals, often proceed without an activation barrier and readily take place even at low temperatures with large rate coefficients (~10^{-9} cm^3/s). Reactions involving the helium ion in particular have importance in astrochemistry [1] and atmospheric physics [2].
Studying ion-molecules reactions at low temperatures is experimentally challenging - stray electric fields as small as 2 mV/cm cause ion-heating of $k_B \cdot 12$ K and at high ion sample densities heating because of Coulomb repulsion can arise.
Here we present the results of experiments in which ion-molecule reactions involving the helium ion are probed at temperatures in the 0 - 40 K range. To avoid heating of the ions by stray electric fields, we excite the He atoms to high Rydberg states and study the reaction within the orbit of the Rydberg electron [3]. The Rydberg electron acts as a spectator and does not significantly affect the outcome of the reaction. We use the large dipole moments of the He Rydberg states to deflect a He-Rydberg-atom beam with a curved 50-electrode chip device and merge it with a ground-state beam of either N_2 , CH_4 or CH_3F. The principle can be extended to study reactions between the helium ion and a wide range of molecules.



The helium atoms are produced in a home-built pulsed supersonic valve that can be temperature-stabilized in the 35 - 100 K range. A dc electric discharge at the valve orifice populates the metastable (1s)(2s) $^3S_1$ state of helium, from which the atoms are excited to Rydberg-Stark states with principal quantum number $n = 30$. The velocity of the He-Rydberg-atom beam can be set to a value in the 600 – 1200 m/s range. After the He-Rydberg-atom beam is merged with the ground-state molecular beam, the two beams traverse a reaction zone and the product ions are detected with a microchannel-plate detector.
The energy of the collision, E_{coll}, is determined by the relative velocity of the Rydberg and ground state beams and the reduced mass of the system. By integrating the product ion yield as a function of E_{coll}, it is possible to determine the energy dependence of the relative reaction rate at collision energies below $k_B \cdot 1$ K.
Because of the well-defined velocity and compact spatial extent of the Rydberg atoms transported by the chip-device, it is possible to achieve an energy resolution of better than $k_B \cdot 1$ K.

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Sub-picosecond charge transfer in polymer/non-fullerene heterojunction

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The recent development of non-fullerene acceptor (NFA) has taken the organic photovoltaics (OPV) community by storm. The remarkable efficience not only derives from better absorption spectrum of NFA, but also due to high open circuit voltage coming from low interfacial driving force. Yet the excact relationship between energitic driving force and charge transfer at polymer/NFA interface is not clear. Some reports show slow charge transfer takes place at low driving force, setting fundamental trade-off relationship between obtaining higher Voc and efficient charge generation.We herein show that charge transfer in polymer/NFA system has 2 seperate pathways. On one hand, electron transfer from polymer to NFA remains ultrafast irrespective to driving force, while hole transfer is driving force dependent but remain relatively fast (<1 ps) even driving force is approaching zero. Such results indicate theoratical framework of Marcus thoery can not be applied to such solid interface, possibly duo to strong interaction. More practically, interfacial driving force can be minimized to enhance Voc of the device, pushing efficiency of OPV to a higher level.

We herein show that charge transfer in polymer/NFA system has 2 seperate pathways. On one hand, electron transfer from polymer to NFA remains ultrafast (

Nanographene Favors Interactions with the Electron Acceptor Rather Than the Electron Donor in a Planar Fused Push-Pull Conjugate

P. Zhou[1], M. Volland[2], L. Wibmer[1], R. Häner[1]*, S. Decurtins[1], T. Feurer[3]*, S. Liu[1], D. Guldi[2]

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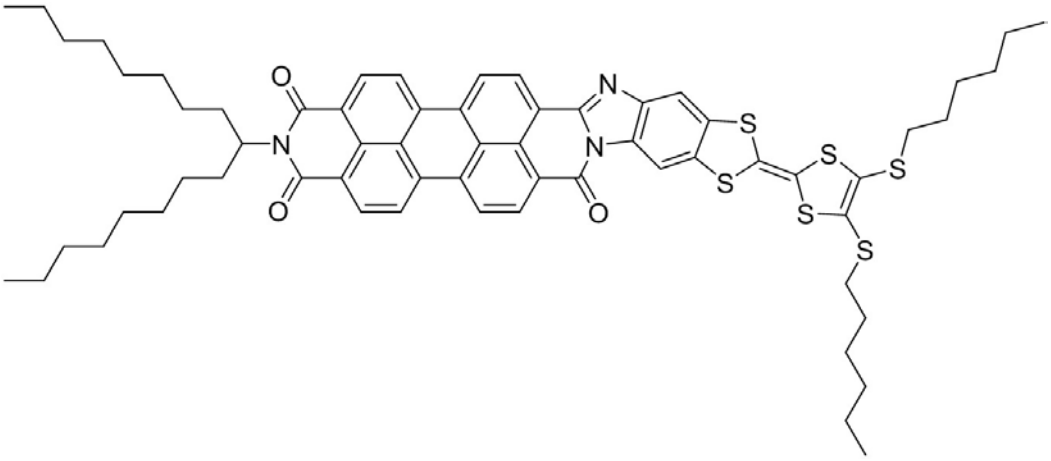
Graphene films have attracted a lot attention due to their potential application in nanoelectronic devices.[1] Noncovalent functionalization of graphene does not disrupt the extended π-conjugation. Incorporation of intercalators in the form of redox- and/or photoactive building blocks enables the usage of electron donor-acceptor (D–A) interactions. Accordingly, the noncovalent functionalization of nanographene (NG) or graphene sheets with either aromatic electron donors or acceptors, as demonstrated in the case of carbon nanotubes, is widely exploited in contemporary research.[2] Herein, we report the exfoliation of graphite via intercalation and immobilization of planar p-conjugates tetrathiafulvalene–perylenediimide (TTF–PDI). The resultant nanohybrids have been characterized by complementary spectroscopic and microscopic techniques.[3]



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Sub-Kelvin stereodynamics study of the Ne($^3P_2$) + N_2 reaction

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We here report the first experimental stereodynamics study of a polyatomic collision system at collision energies below 1 K. The reaction between Ne($^3P_2$) and ground state N_2 was studied in a range of collision energies between 60 mK and 700 K. Ne($^3P_2$) is paramagnetic and can be oriented by an external magnetic field, and the orientation affects the branching ratio between Penning ionization (formation of N_2^+) and associative ionization (formation of NeN_2^+).[1-3] In previous studies we investigated the Ne($^3P_2$) + N_2 reaction at high collision energies, and the results indicate that predissociation takes place after collision when a product ion NeN_2^+ is formed in a vibrationally excited state. This can distort the extracted branching ratios because different pathways lead to the formation of N_2^+. [2,3]

From the experimental data we extract, by accounting for predissociation, energy-dependent relative reaction cross sections for states that differ only in Ω, the projection of the neon total angular momentum vector on the inter-particle axis. At the lowest collision energies, we observe a re-orientation of Ne* to the end where no steric effect can be observed. We find that associative ionization products, NeN_2^+ predissociate close to 50% except in an energy range around 450 K where we expect a vibrational Feshbach resonance.

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Many-body elastic scattering of exciton polarons in organic-inorganic hybrid perovskites

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Owing to both electronic and dielectric confinement effects, two-dimensional organic-inorganic hybrid perovskites sustain strongly bound excitons at room temperature. The intrinsic optical lineshape reflects multiple excitons with distinct binding energies, each dressed differently by the hybrid lattice. Given this complexity, a fundamentally far-reaching issue is how Coulomb-mediated many-body interactions --- elastic scattering such as excitation-induced dephasing, inelastic exciton bimolecular scattering, and multi-exciton binding --- depend upon the specific exciton-lattice coupling. We report the intrinsic and density-dependent exciton pure dephasing rates and their dependence on temperature by means of a coherent nonlinear spectroscopy. We find exceptionally strong screening effects on multi-exciton scattering relative to other two-dimensional single-atomic-layer semiconductors. Importantly, the exciton-density dependence of the dephasing rates is markedly different for distinct excitons. These findings establish the consequences of particular lattice dressing on exciton many-body quantum dynamics, which critically define fundamental optical properties that underpin photonics and quantum optoelectronics in relevant exciton density regimes.

Hot Carrier Dynamics in Lead Halide Perovskites from a THz Mobility Perspective.

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Ultrafast time-resolved terahertz spectroscopy (TRTS) allows for the direct probing of charge carriers and quasi-particles in semiconductors. The sensitivity of the technique to both the carrier mobility and its density can help elucidate the mechanisms of their temporal evolution. The use of gas photonics provides short, ultra-broadband THz pulses and, thus, offers an improved time-resolution.

Here, we present a study of the early steps of the charge carrier dynamics in lead halide perovskite thin films from the point of view of the THz mobility. Taking advantage of a 200 fs time-resolution, we were able to temporally follow the cooling of hot carriers through the observation of a change in their mobility. This change is understood as resulting from a modification of the carrier effective mass [1].

Our results are compatible with a hot carrier cooling mechanism implying LO phonon emission. This is subjected to a phonon bottleneck [2], and competes with a dynamic screening process, which time-constant was identified as being due to polaron formation [3]. While the screened hot carriers take longer to cool down [4], the dynamic screening process does not produce a change in mobility when only cold carriers are involved.

Measurements applied to perovskite samples of various compositions are compared to elucidate the role of cations and anions in both processes.

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Underestimated Effect of a Polymer Matrix on the Light Emission of Single $CsPbBr_3$ Nanocrystals

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Lead-halide perovskite $APbX_3$ (A=Cs or organic cation; X=Cl, Br, I) nanocrystals (NCs) are subject of intense research due to their exceptional properties as both classical[1] and quantum light sources.[2-4] Many challenges often faced with this material class concern the long-term optical stability, a serious intrinsic issue connected with the labile and polar crystal structure of $APbX_3$ compounds. When conducting spectroscopy at a single particle level, due to the highly enhanced contaminants (e.g., water molecules, oxygen) over NC ratio, deterioration of NC optical properties occurs within tens of seconds, with typically used excitation power densities (1-100 W/cm^2), and in ambient conditions.

Here,[5] we demonstrate that choosing a suitable polymer matrix is of paramount importance for obtaining stable spectra from a single NC and for suppressing the dynamic photoluminescence (PL) blueshift. In particular, polystyrene (PS), the most hydrophobic amongst four tested polymers, leads to the best optical stability, one-to-two orders of magnitude higher than that obtained with poly-(methyl methacrylate) (PMMA), a common polymeric encapsulant containing polar ester groups. Molecular mechanics simulations based on a force-field approximation corroborate the hypothesis that PS affords for a denser molecular packing at the NC surface. These findings underscore the often-neglected role of the sample preparation methodologies for the assessment of the optical properties of perovskite NCs at a single-particle level and guide the further design of robust single photon sources.

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What determines the open circuit voltage of Perovskite solar cells?

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Despite the rapid increase in the efficiency (PCE) of perovskite solar cells, their open circuit voltage (V_{oc}) limits their commercialization. Contradictory results exist in the literature concerning the dependence of the V_{oc} on the ionization energy (IE) of the hole transporting layer (HTM) while different timescales have been reported concerning the injection of photogenerated holes from CH3NH3PbI3 even towards the same HTM. Here, we present a series of fully evaporated devices employing HTMs with different IEs. The V_{oc} of the devices along with the processes of hole injection and trapping are studied in terms of ideality factors and fs-transient absorption (TA) spectroscopy. We prove that the V_{oc} is mainly determined by the bulk and surface recombination rather than by the energetic offset between the valence band (VB) of the perovskite and the IE of the HTM. Furthermore, we find that hole injection competes with carrier thermalization and takes place from hot states in the VB independently of the IE of the HTMs. Finally, the observed difference in the timescale between hole injection and interfacial trapping is found to contribute to the high efficiency of the studied HTMs when employed in solar cell devices. Our results provide an understanding of the origin of the V_{oc} and point to other crucial factors that should be considered when searching for novel HTMs rather than their IE.

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Bulk hyperpolarization of inorganic materials

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Solid-state NMR can be used to obtain atomic level structure and dynamics of inorganic materials, but its application is sometimes limited by its relatively low sensitivity. Impregnation dynamic nuclear polarization (DNP) is a strategy that can be used to improve sensitivity in solid-state NMR experiments of powders, provided that hyperpolarization that is generated close to the particle surface can be relayed towards the bulk by spontaneus ^{1}H spin diffusion.

Here we show how the relayed DNP method can be extended to proton-free inorganic materials, by using a combination of impregnation DNP, cross-polarization, and slow spin diffusion between weakly magnetic nuclei such as ^{119}Sn and ^{31}P.[1] The method is demonstrated to provide a sensitivity gain of a factor 50 for the ^{119}Sn spectra of SnO_2, with an additional factor of 3.5 when the magic-angle-spinning rate is modulated during the experiment.[2] This correponds to acceleration of up to a factor of 30 000 in acquisition times, allowing access to materials that were previously unfeasible. We also show how the pathways of spin diffusion can be probed with multi-dimensional experiments.

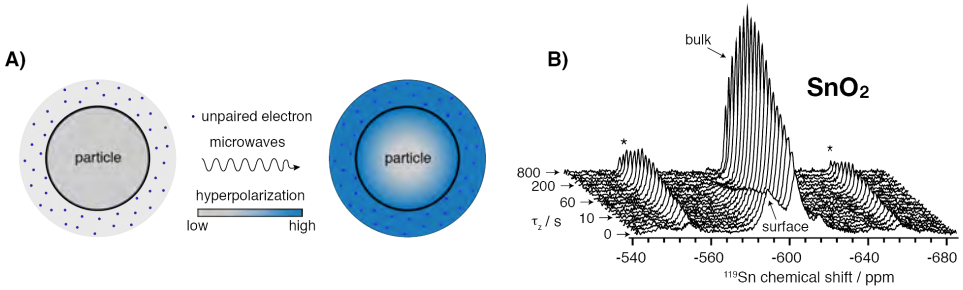

Figure 1. A) Impregnation DNP of a powdered solid. B) Spontaneus ^{119}Sn-^{119}Sn spin diffusion relays hyperpolarization from surface to bulk in the ^{119}Sn spectrum of SnO_2.

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Towards time-resolved laser T-jump/X-ray absorption probe spectroscopy

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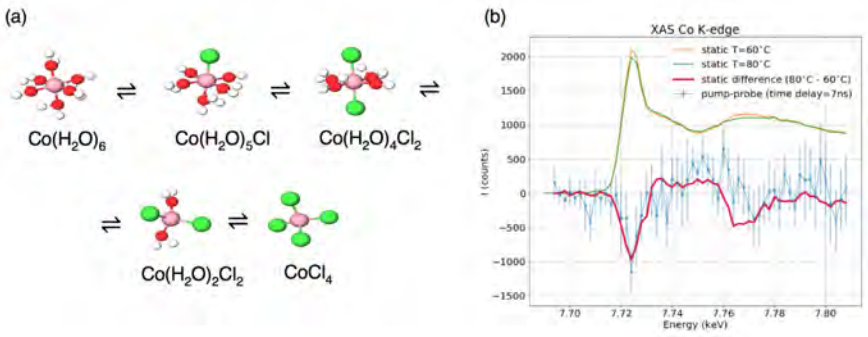
Most of (bio)chemical reactions in Nature and in industrial processes are driven by thermal effects that bring the systems above the barrier for reaction. This process can also be triggered by the Temperature-jump (T-jump) method. The latter is ideal in aqueous solvents, where, by directly exciting the water high frequency vibrational and/or bending modes,[1-3] it leads to an ultrafast (2-5 ps) increase in the temperature of the irradiated volume, locally triggering chemical reactions. Implementing the laser T-jump method with X-ray techniques in the picosecond time domain would add element-specificity and structural-sensitivity, helping the identification of the intermediates of reactions. Here we demonstrate the laser T-jump/X-ray absorption probe method to probe the sequential substitution process of a Cobalt center from the octahedral aqueous complex to the tetrahedral chlorinated species: $[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$. This reaction had previously been investigated in the optical domain [4], and it proceeds via several intermediate steps (Fig.1(a)) through equilibria that can be controlled by changing the temperature and/or the chloride concentration [5].



The experiments were carried out at the Swiss Light Source (SLS), pumping the aqueous solution at 1064 nm and probing the samples (consisting of an aqueous solution of $CoCl_2$ at a concentration of $[Co^{2+}]$=500mM and $[Cl^-]$=8M) by Co K-edge absorption spectroscopy. Given the jet speed (6 m/s) and the laser and X-rays spot sizes (laser spot: 70x60 μm^2, X-rays spot: 50x50 μm^2), the laser repetition rate was set to 65 kHz to avoid multiple pumping of the same volume of solution and to increment the energy per pulse deposited onto the sample. Under these conditions, the local T-jump, estimated according to ref. [1], corresponds to a ΔT=0.3K when using a laser fluence of 240 mJ/cm^2. Figure 1(b) shows the steady-state Co K-edge spectra of the solution at 2 different temperatures, along with the transient spectrum at 7 ns time delay of a 60˚C solution. The difference of the steady state spectra is shown in red and it reproduces nearly all the features of the transient (blue line). This shows that even a mild increase in temperature can be monitored with great sensitivity by X-ray absorption spectroscopy. Further details of this study will soon be published [6]. The implementation of the T-jump method for time-resolved X-ray probing is not limited to X-ray absorption spectroscopy but it also includes X-ray emission and X-ray scattering. Given the ultrafast (2-5 ps) time scale of the laser heating in aqueous solutions, the present results open very promising perspectives for the investigation of temperature-driven biochemical processes at X-ray Free electrons lasers.

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Structural Dynamics of an Excited Donor-Acceptor Complex: Ultrafast Polarized Infrared Spectroscopy and Mixed Quantum/Classical Simulations

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In solution, particular combinations of donor and acceptor molecules can form ground-state pairs that exhibit a new, red-shifted, electronic absorption band not present in the individual donor or acceptor spectra. This new absorption is termed a ‘charge-transfer’ (CT) band and corresponds to excitation from the HOMO of the donor to the LUMO of the acceptor, effecting nearly instantaneous transfer of one electron from donor to acceptor. Charge-recombination (CR) then occurs in concert with solvent and vibrational relaxation and structural dyamics of the ion pair (IP). Due to the large distribution of ground-state complex structures, the excited state of the system is a composite of many different species. Although the thermodynamics and CR processes of such complexes have been the subject of intense study, the structural dynamics of the pairs and their relation to CR are still poorly understood.

We will present results of ultrafast visible (visTA) and infrared (TRIR) transient absorption experiments on the benzene/tetracyanoethylene (Bz/TCNE) pair in addition to a mixed quantum/classical computational study of the system. Population dynamics from the visTA and TRIR experiments reveal complex sub-10 ps dynamics followed by CR on a 55-60 ps timescale. Polarized TRIR anisotropy measurements reveal rich structural dynamics involving large-scale reorganization of Bz/TCNE radical ion pairs following excitation. A detailed computational study of the system combining quantum chemical calculations and classical molecular dynamics simulations was able to reproduce the experimental electronic absorption lineshape and TRIR anisotropy dynamics, allowing for a more detailed interpretation of the structural dynamics. We find that neither the ground nor excited state of the Bz/TCNE pair can be described using a single well-defined structure, and that the IPs convert from predominately face-to-face π stacks to edge-to-face T-shaped structures. Given the sensitivity of charge-transfer processes to donor/acceptor orientation, theoretical descriptions of the recombination dynamics must take into account the structural diversity and evolution of the excited state.

Signatures of intra-/intermolecular vibrational coupling in halogenated liquids revealed by 2D Raman-THz spectroscopy

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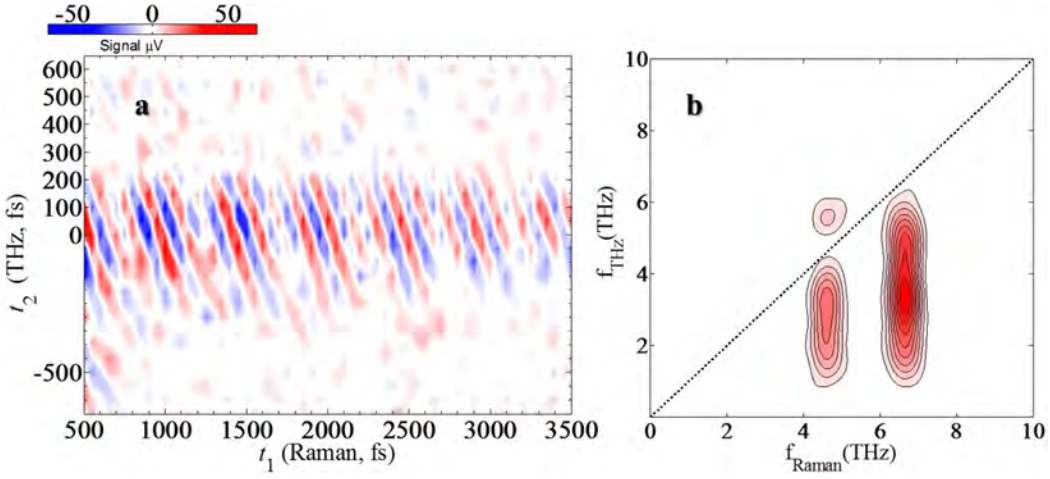
The spectral properties of liquids in the terahertz (THz) region play an important role in chemistry, as they reflect motions of large molecules and molecular complexes which, in turn, govern chemical reactivity and processes like solvation. These specific properties of liquids can be addressed either via resonant THz spectroscopy or Raman spectroscopy. However, due to the ultrafast dynamics and the large anharmonicity of intermolecular modes, low frequency one-dimensional spectra (both Raman and THz) are mostly blurred and indistinct. Multidimensional spectroscopy can enhance spectral resolution by spreading spectra in more than one frequency dimension, thus increasing significantly the amount of information that is possible to extract [1].

Here, we demonstrate the unique capabilities of 2D Raman-THz spectroscopy, a novel 2-dimensional spectroscopic technique developed in our group [2], of measuring coupling between low-frequency vibrational modes, information that are not present in a 1D linear spectrum. To that end, we recorded the 2D Raman-THz responses in the spectral range between 1 and ~ 8THz of liquid bromoform and dibromomethane. The spectra reveal cross peaks which we attribute to the coupling between the relatively sharp intramolecular modes and the much broader intermolecular degrees of freedom of these solvents.



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Solvation in a Propyl Acetate/Butyronitrile Mixture

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Solvation dynamics play an important role in many ultrafast photochemical reactions in solutions. [1] In particular, dielectric stabilization can significantly influence the driving force of chemical reactions involving charged intermediates or products, such as electron and proton transfer reactions. [2] Solvent mixtures of varying dielectric constant enable systematic studies on the influence of solvent stabilization on such reactions. Ideally, other solvent parameters such as viscosity and refractive index should remain constant in the mixture. To investigate the effect of solvent stabilization on these ultrafast photochemical reactions, we use broadband femtosecond (fs) fluorescence up-conversion technique, [3] which provides the entire fluorescence spectrum as a function of time with fs time resolution.

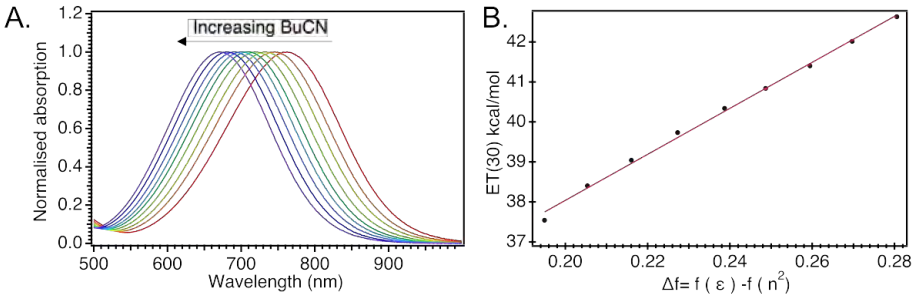

Figure. Absorption of Reichardt's dye in solvent mixtures. (A) Absorption spectrum shift of RD with increasing butyronitrile concentration (B) Reaction field factor ($f(x) = (x-1)/(2x+1)$) versus $E_T(30)$

A binary mixture between propyl acetate and butyronitrile is ideally suited for investigating the effect of dielectric stabilization. The dielectric constant (ε_r) increases from 6 to 24.7 upon increasing fraction of butyronitrile from 0 to 1 whereas the viscosity and refractive index remain constant. However, a thorough characterization of the dielectric stabilization in the mixture is necessary before detailed studies on ultrafast reactions. Here in, we present simple and reliable ways for the purification of the solvents and characterize both the static and dynamic dielectric stabilization in this mixture. The static dielectric stabilization is investigated by measuring the steady-state absorption energies of Reichardt's dye whereas the dynamic solvent effects are monitored from the time-resolved fluorescence of standard push-pull dyes. Last, we will demonstrate the influence of dielectric stabilization on both ground- and excited-state acid-base reactions between a photoacid and organic bases in these mixtures.

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Using IRPD-spectroscopy for onium ions serving as a molecular balance for the estimation of non-covalent interactions

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London dispersion, which is a part of the famous van der Waals potential, may be an important element of structural stability, and thus affects chemical reactivity and selectivity[1]. Recently we have shown that attractive, non-covalent interactions in the gas phase are largely, but not entirely, screened out in solution[2]. Comparing experimental gas-phase bond dissociation energies and dispersion-corrected DFT or local coupled-cluster methods results, we showed that the weakest point in the computational models is the treatment of solvation. As an independent test, we have performed the experiment in the gas phase at temperatures of 4-50 K using an IR action spectrometer with a cryogenic Penning trap that was recently tested in our group (FT-ICR-MS)[3] In particular, we have measured CIVP-spectra of pyridines, quinolones, and pyridinium dimers. The frequency of the N-H-N asymmetric stretching mode is strongly red-shifted relative to that for an unperturbed N-H stretch in a non-hydrogen-bonded pyridinium. The N-H stretch of a pyridinium cation is not involved in an ionic hydrogen bond is 3370 cm^{-1}. When it is hydrogen-bonded, our computational studies suggest the frequency drops to around 2200 cm^{-1} (Figure 1). If the hydrogen bond is bent, the proton tends to localize and the frequency shifts back towards 3370 cm^{-1}, depending on how much the N-H-N angle is bent. If a proton-bound dimer is built with side chains that can interact by dispersion, then the molecule serves as a molecular balance. The stronger the non-covalent interaction is, the more the proton-bound dimer's hydrogen bond is bent, and the more the frequency shifts to higher energy.

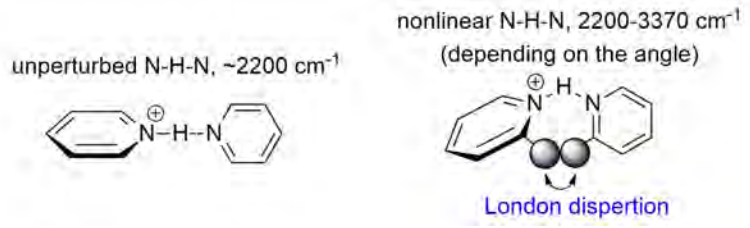

Figure 1. Experimental design in which the N-H-N frequency of the ionic hydrogen bond is used as a probe for the strength of the noncovalent interactions between two substituents, whose interaction is balanced against the bending potential of the N-H-N linkage.

Therefore, the proton-bound dimer acts as a molecular balance where the attractive dispersion force is weighed against the bending potential of the N-H-N moiety. Thus the IRPD spectrum becomes a sensitive measure of gas-phase geometry and, in turn, a quantitative measure of the dispersion interactions between the substituents.

The conducted experiment will help to resolve the discrepancy between theory and experiment in the dispersion contribution to bond dissociation energies in large molecules as well as to fill the gap in the estimation of solvent effects in calculations.

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Photochemistry of single optically trapped organic aerosol droplets: The photodegradation of oleic acid by oxygen

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Organic aerosols represent 20 to 90 % of the total terrestrial aerosols at continental mid-latitudes and therefore impact the climate, air quality and health [1]. During their lifetime, they undergo transformations that alter their physical properties and they are exposed to sunlight and chemical species which can lead to complex chemical evolution [2]. These processes are known as aerosol aging. Nevertheless, the temporal evolution of the aging process is not well understood.

We present a method to study the chemical aging of organic aerosols. Particles are optically trapped in air with a counter propagating tweezer with a laser wavelength of 532 nm [3]. The chemical aging of the particle can be induced by light or by a surrounding gas. The monitoring of the elastically scattered light gives information on the temporal size evolution of the trapped droplet [4]. The inelastic scattered light is monitored to give time dependent Raman spectra which provide in-situ information on the droplet's chemical composition. With this approach, we are able to study the temporal evolution of size and chemical composition of the aging particle.

In this work, we apply our method to study the photodegradation of isolated oleic acid droplets induced by 532 nm light. The trapping laser wavelength matches the excitation wavelength of ground state oxygen to singlet oxygen ($^1O_2$) [5]. The produced $^1O_2$ reacts with oleic acid leading to the production of volatile compounds resulting in a decrease of droplet size. The temporal Raman spectra are used to identify the degradation of chemical bonds and retrieve reaction rates of the photoreaction of oleic acid. We study the influence of the excitation light power and oxygen concentration on the reaction path and its kinetics. Furthermore, a kinetic-multilayer model was developed to qualitatively support the experimental results giving insight into the mass transport and production rates of the volatile compounds in the droplet.

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High Resolution Infrared Spectroscopy of Monodeuterated Ethylene Oxide c-C_2DH_3O: Analysis of the Infrared Spectrum of several Ring Deformation and Stretching Fundamentals

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Monodeuterated ethylene oxide c-C_2DH_3O (D1-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]. Several ro-vibrational bands of the parent species have been examined by other investigators [2]. Only a few lines of D1-Oxirane have previously been analysed in the microwave region [3] up to 70 GHz. The rotational constants of D1-oxirane have been calculated *ab initio* [4]. We have obtained an extensive analysis of our new results [5] including ground state constants and energy levels obtained from the analysis of the rotational spectrum of D1-oxirane from 65-119 GHz using our GHz spectrometer [6] and in the 0.75-2.4 THz range measured with our FTIR setup [7] at the Swiss Light Source. Here we report the infrared spectrum recorded at a resolution of 0.0015 cm^{-1} using the Bruker IFS HR ZP2001 Zürich prototype spectrometer [8]. Spectroscopic parameters for the vibrational ground state and the ν_{12} and ν_{13} fundamentals (ν_{12} = 896.025 cm^{-1} and ν_{13} = 837.354 cm^{-1}) have been determined. We have expanded the range of study into the region of the stretching fundamental vibrations near 3000 cm^{-1} and shall present first results of this analysis. Our results will be discussed in relation to isotopic chirality and parity violation, as they relate to monofluorooxirane [9] and in the broader context of fundamental symmetries and symmetry violations [10].

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Reaction kinetics of trapped molecular ions with conformer- and isomer-selected neutral molecules

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The experimental challenges in preparing pure samples of individual molecular isomers and conformers have thus far precluded a characterization of their distinct chemical behavior. Recent progress in manipulating polar molecules using electrostatic fields has made it possible to select and spatially separate different conformers and rotational states of molecules in supersonic molecular beams [1,2]. By combining this technology with a stationary reaction target of Coulomb-crystallized ions in a linear quadrupole ion trap [3] we have recently explored conformer selected molecule-ion reaction dynamics and observed that reaction-rate constants can strongly depend on molecular conformation [4,5]. More recently, we have extended this method to the separation of different nuclear-spin isomers for studies of ion-molecule reactions with control over the rotational and nuclear-spin state of the neutral reaction partner.

Water is one of the fundamental molecules in chemistry, biology and astrophysics. It exists as two distinct nuclear-spin isomers, *para*- and *ortho*-water, which do not interconvert in isolated molecules. We have successfully studied the proton-transfer reaction of the spatially separated ground states of *para*- and *ortho*-water with cold ionic diazenylium (N_2H^+), an important molecule in astrochemistry. We found a 23(9)% higher reactivity for the *para* nuclear-spin isomer which we attribute to the smaller degree of rotational averaging of the ion-dipole long-range interaction compared to the *ortho*-species [6]. This finding is in quantitative agreement with a modelling of the reaction kinetics using rotationally adiabatic capture theory [7] and highlights the ramifications of nuclear-spin symmetry on chemical reactivity.

Despite their significance in organic synthesis, the mechanistic details of Diels-Alder cycloadditions, in which a diene and a dienophile react to form a cyclic product, still remain an extensively discussed question. The ionic variants, polar cycloadditions, have proven to be a particularly efficient route to form cyclic compounds, but it has proven difficult to determine whether only the *cis* conformer (concerted mechanism) or both *cis* and *trans* conformers (stepwise mechanism) of the involved diene react to form the cyclic product [8]. In order to shed light on these questions we are currently investigating the ionic cycloaddition reaction of 2,3-dibromo-1,3-butadiene with ionic propene. Having successfully verified the separation of the two conformers using soft vacuum-ultraviolet ionization we are now able to perform experiments that directly test the underlying mechanism of polar cycloadditions.

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