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Mechanism and dynamics of fatty acid photodecarboxylase

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Light is important for organisms from all domains of life, serving as an energy resource or carrier of information initiating intra- or intercellular signaling. Photosensitive proteins, endowed with a light-absorbing chromophore, enable this. Detailed insights, including the initial events on the ultrafast time scale, can be obtained by various forms of spectroscopy and computation. However, direct structural information necessary to understand the underlying molecular mechanisms has been inaccessible until recently. The unique properties of X-ray free electron lasers open the sub-ps time domain for time-resolved crystallography using small crystals that can be efficiently photolyzed, thus providing access to the long sought-after excited state and intermediate structures. Photodecarboxylation is a well-established reaction in chemistry; however, no photo-enzymatic equivalent was known until the discovery of Fatty Acid Photodecarboxylase (FAP), a flavin containing photoenzyme [1]. The enzymatic mechanism was investigated in detail by a large interdisciplinary consortium [2]: decarboxylation occurs directly upon reduction of the photo-excited flavin by the fatty acid substrate. Along with flavin reoxidation by the alkyl radical intermediate, a major fraction of the cleaved carbon dioxide unexpectedly transforms in 100 ns into another species, assigned to be bicarbonate based on IR-spectroscopy performed on cryogenic samples. Despite a great deal of insight into the catalytic mechanism and the role of two strictly conserved residues for substrate stabilization and functional charge transfer [2], a number of questions remain. To address these, including the nature of the transiently generated CO₂-derivative we performed a follow-up time-resolved serial femtosecond crystallography experiment at SwissFEL spanning time-delays from ns to ms after photoexcitation. The results will be discussed.

[1] Sorigué et al An algal photoenzyme converts fatty acids to hydrocarbons, *Science* 357: 903-907 (2017)

[2] Sorigué et al Mechanism and dynamics of fatty acid photodecarboxylase, *Science* 372, [eabd5687](#) (2021)

The conservation of protein dynamics on an evolutionary timescale of nearly a billion years

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Proteins are the fundamental building bricks for living organisms. Their structure, dynamics, and function are inherently encoded in their amino acid sequence. In the course of evolution, the conservation of protein sequence, structure, and dynamics is depending on selective constraints and differs from protein to protein [1]. Although the conservation of protein sequence and structure has been extensively investigated in the past, very little is known about the conservation of protein dynamics. Does the conservation in protein structure correlate with the conservation of protein dynamics?

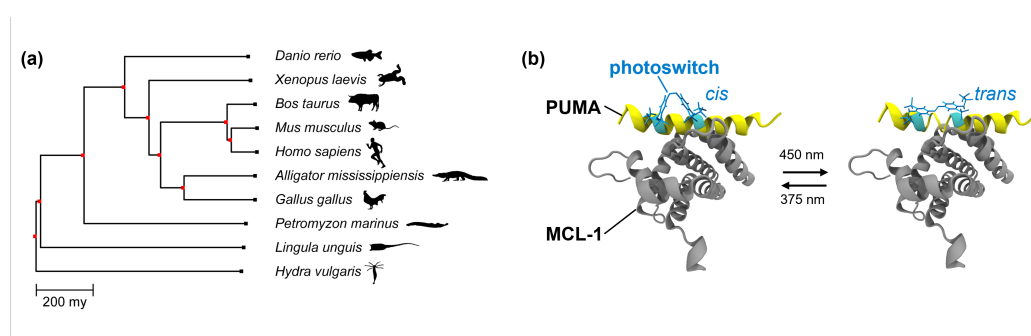


Figure 1: (a) The protein MCL-1, a key player in apoptosis, is present in ten selected species, separated by several hundreds of millions of years in evolution. (b) Ten different photoswitchable complexes were generated, consisting of an MCL-1 homolog and its natural binding partner PUMA. With the help of the photoswitch, an ultrafast perturbation is induced inside the complex and the resulting processes are recorded via transient infrared spectroscopy.

In our current study, we investigate the dynamics of the protein MCL-1 from ten different species, separated by nearly a billion years of evolution (Figure 1a), via transient infrared spectroscopy. MCL-1 is a key regulator in apoptosis, the programmed cell death [2]. Due to its crucial function in apoptosis, MCL-1's structure and function appears to be conserved in all vertebrates and a lot of other animal species. Here, we generated photoswitchable versions of MCL-1 in complex with its natural binding partner PUMA (Figure 1b) to investigate the dynamic response of the protein complex upon photo-induced perturbation [3]. When triggering the photoswitching event in PUMA, we altered PUMA's secondary structure in the binding pocket of MCL-1 and recorded the time scales of molecular response in a time window of pico- to microseconds.

By experimentally determining the dynamic behavior of these ten photo-perturbed MCL-1 homologs, hundreds of million years apart, we detected similar patterns. We found dynamic processes in the nanosecond regime which correlate well with the evolutionary separation of the protein homologs. Our findings help to understand how fast molecular processes change over an evolutionary timescale and which kind of dynamic processes remain preserved.

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Fast Viral Dynamics Revealed by Microsecond Time-Resolved Cryo-EM

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Observing proteins as they perform their tasks has largely remained elusive, which has left our understanding of protein function fundamentally incomplete. To enable such observations, we have recently proposed a novel technique that improves the time resolution of cryo-electron microscopy (cryo EM) to microseconds [1-5]. We demonstrate for the first time that microsecond time-resolved cryo-EM enables observations of fast protein dynamics [6]. We use our approach to elucidate the capsid mechanics of cowpea chlorotic mottle virus (CCMV), whose large-amplitude motions play a crucial role in the viral life cycle [6]. We observe that a pH jump causes the extended configuration of the capsid to contract on the microsecond timescale. While this is a concerted process, the motions of the capsid proteins involve different timescales, leading to a curved reaction path.

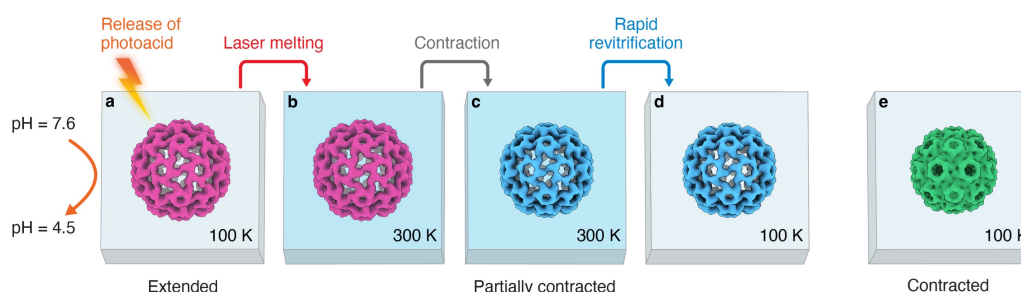


Fig. 1. Microsecond time-resolved cryo-EM of the CCMV contraction — experimental concept.

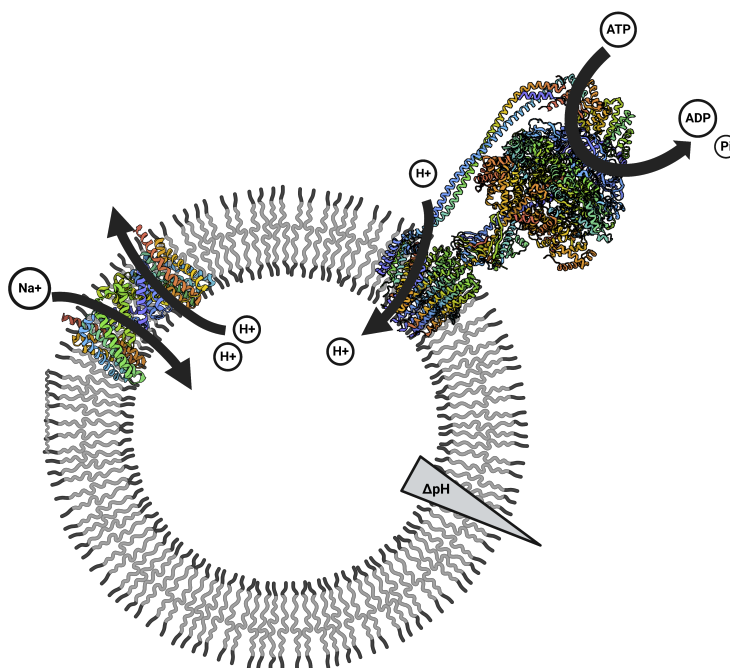
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ATP Synthesis in Giant Unilamellar Vesicles Formed by Double-Emulsion Microfluidics

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The cellular membrane is a key component of a cell, used to maintain homeostasis by blocking toxic materials from entering the cell while allowing the flow of necessary molecules through incorporated channels, receptors, and transporters. Further understanding of the complex composition of the cell membrane, especially how membrane proteins function in conjunction with others, is possible through the formation of a cell membrane mimic. To this end, we present the formation of giant unilamellar polymer vesicles through double-emulsion microfluidics. These vesicles are then functionalized with NapA, a sodium-proton antiporter, and ATP synthase, the enzyme that phosphorylates ADP to form ATP, the energy currency of the cell. Establishing a system where any set of membrane proteins with coupled functions can be investigated in detail allows us to increase our understanding of how the many components of cellular membrane influence each other.



Two-level ordering in nano-rattles for optical propertiesA. Scalabre¹, K. M. Fromm^{1*}¹University of Fribourg, Chemistry Department, Chemin du Musée 9, CH-1700 Fribourg

Yolk-shell nano-particles (also named nano-rattles), are in the center of many studies thanks to their interesting properties in multiple fields ranging from medicine to physics.^[1] These properties come from both, the non-homogeneous composition of the nano-rattles, and also from the particular environment around the core, as it behaves like a nano-reactor. Synthesizing such nano-objects is challenging,^[2] but we decided to take it one step further by organizing them in different ways and levels for optical effects.

In a first part we focused on obtaining a controllable and reversible way of aggregating the nano-particles, using silica spheres as model. The second part focused on the development of anisotropic and magnetic nano-particles and on how to use these as starting point for the synthesis of the desired nano-rattles. Having such a high control over the organization of nano-materials might allow to control opalescent properties of the aggregates.

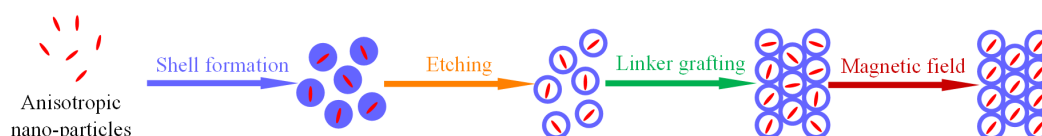


Figure 1. Schematic representation of the different synthesis and organization steps

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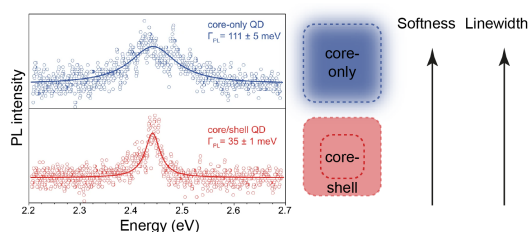
Ultra-narrow room-temperature emission from single CsPbBr₃ perovskite quantum dots

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Within only few years since their first synthesis, colloidal perovskite quantum dots (QDs) have already turned into a commercial product. Their facile synthesis, solution-processability, and narrow-band luminescence, spectrally tunable across the entire visible range, are currently being exploited for classical light-emission applications, such as LEDs and displays, as well as quantum light applications, such as single-photon sources. However, continued progress of perovskite-QD based devices cannot evade the question to which extent the pronounced dynamical disorder of the soft perovskite crystal structure limits further advances in light emission, *e.g.*, the quest for every-smaller linewidths in classical applications and single-photon indistinguishability (via coherence) in quantum applications.

In this talk, I will discuss some of our recent insights into exciton-phonon coupling in perovskite QDs.[1][2] Single-QD PL spectroscopy in combination with *ab-initio* molecular dynamics (AIMD) simulations suggest a sizable coupling of the exciton to low-energy surface phonons via the deformation potential. Smaller QDs exhibit stronger coupling and, hence, overall broader emission. However, mild adjustments of the surface chemical composition successfully reduce the emission linewidth from 70-120 meV to 35–65 meV, on par with the lowest linewidths reported for structurally rigid colloidal II-VI quantum dots.



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Environmental aspects and sustainability in the Chemical/Analytical and Biological/Live Science Laboratory

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Laboratories have a huge plastic consumption. They use much energy, water and chemicals. The instrument live time has become significantly shorter with increasing complexity of applications and features. Labs and equipment suppliers put more and more emphasis on improvement of the situation. Companies' procurement starts identifying the topic as part of the purchase decision. With "Pharma 5.0" sustainability got even more focus. However, solutions are not as easy as it looks from high level. It appears, that the industry is moving on both ends: consumers and suppliers.^[1]

Companies started with reducing the CO₂ footprint in their local production. Some are already officially "neutral". Even if sometimes "green washing" is involved. Instrument design and consumables get an increasing focus on environmental aspects: Footprint (bench space), plastic reduction, optimized packaging for transportation etc. Focus on sustainability throughout the supply chain will follow if it does not have focus yet.

The restriction of PFAS (per- and polyfluoroalkyl substances) as proposed by European ECHA regulators^[2] however, would result in a major analytical disaster if there are no exceptions e.g. for Fluoropolymers for components in analytical instruments. Many instruments use items made of Fluoropolymer materials for the reason why they in focus of the ban discussion: they are resistant, persistent and inert. Scientifically it will be a challenge or impossible to replace them with other material and any replacement must be resistant, persistent, and inert.^[3]

Concepts, including artificial Intelligence and optimised reaction control and monitoring^[4] are another strategy to reduce lab work with chemicals or at least being more targeted with that. Let us put some light on the topics.

[1]

<https://pharmaceuticalmanufacturer.media/pharmaceutical-industry-insights/latest-pharmaceutical-manufacturing-industry-insights/roundtable-accelerating-the-path-towards-sustainable-future-proofed-qc/> Opened 10.6.2023

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Using *in-situ* Terahertz Spectroscopy to investigate Charge Transport in In-plane Oriented Organic Mixed Ionic-Electronic Conductors

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Organic bioelectronics deals with the study of organic electronic devices which are working at the interface of biology and electronics. A type of material that proved to be perfectly suited for this are organic mixed ionic-electronic conductors (OMIECs) as they enable the transport of ions as well as electrons. Other advantageous properties of OMIECs are their soft and flexible nature, versatile processing and synthetic tunability making it possible to span a wide range of applications.¹ In recent years a lot of studies were focused on device fabrication and on the different material options. However, there is still a lack of a more in-depth understanding of the fundamental effects occurring during the functioning of OMIECs.² An organic polymer showing high charge-carrier mobility is PBTBT, its conductivity can be efficiently improved by inserting alkyl side chains with a single ether group as this is facilitating the uptake of ions into the polymer matrix.^{3,4} The charge transport is happening mainly on the backbone of the organic semiconductor. Therefore, in this study we investigated PBTBT-⁸O films, that were oriented using high temperature rubbing, for comparison the same experiments were carried out with a OMIECs model material P3HT, which was already characterized by multiple different research groups.⁵ The alignment of the backbones will further enhance the charge transport as well as help to unravel the fundamental processes of the charge transport.

To study these effects, we used *in-situ* terahertz (THz) spectroscopy, where we measured films with electrochemical and chemical doping, furthermore spectro-electrochemistry and chronoamperometry were carried out. With THz spectroscopy we can detect the scattering frequencies of charge carriers in semiconductors, this allows us to get the intrinsic nanoscale conductivity and short-range mobility of the studied OMIECs, which is not affected by any grain boundaries or electrodes. The analysis of the complex THz conductivity unveils the mobility and density of charges altogether. We were able to get conductivities of more than 1000 Scm⁻¹ for P3HT and PBTBT-⁸O for electrochemical doping. Furthermore, with chemical doping conductivities of more than 2000 Scm⁻¹ were obtained and band like transport behavior was observed for PBTBT-⁸O, showing the large effect of high in plane orientation of OMIECs.

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Symmetry Breaking Charge Separation in a PDI-Based Molecular Cage

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The Photoinduced Symmetry Breaking Charge-Separation (SB-CS) process—in which an electron transfer occurs between two identical chromophores—has received a lot of attention lately due to its applications in solar energy conversion. We have previously shown the first example of a perylene diimide (PDI) cage with delayed fluorescence [1], presumably originating from a reverse SB-CS process. Using transient electronic absorption spectroscopy (TAS) in increasing polarity Toluene/PhCN solvent mixtures, we could evidence occurrence of SB-CS through identification of the transient bands of the PDI radical anion and radical cation, which are absent in low polarity media due to the destabilization of the ¹CS state.

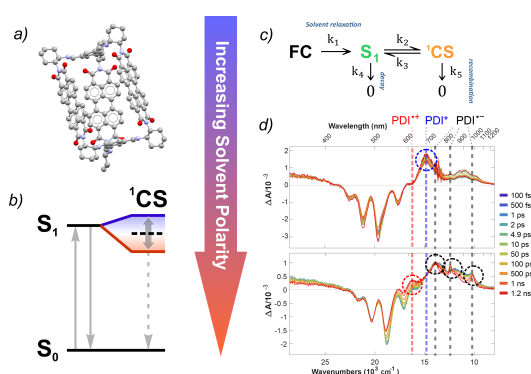


Figure: a) PDI-based cage; b) Stabilization of the ¹CS state with increasing solvent polarity; c) Target model; d) Comparison between toluene (up) and benzonitrile (bottom) transient absorption spectra.

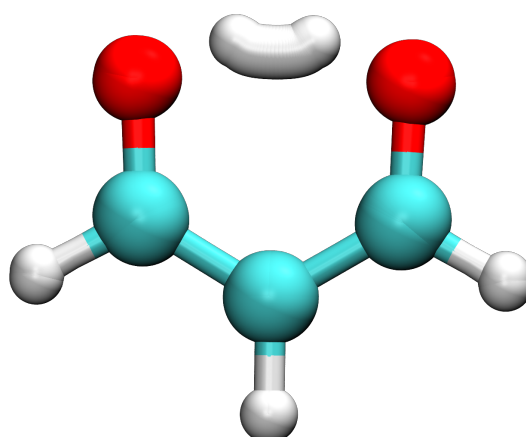
We based our analysis on a five-parameter model that stabilizes the Franck-Condon state, an equilibrium between the S_1 and the ¹CS states, and their respective decay and recombination. Due to its intrinsic complexity, we used additional constraints derived from Ware's model of exciplexes [2]. Our new approach allows us not only to extract distinct Species-Associated Spectra (SAS) but also to obtain relevant kinetic constants from such a complicated scheme while ensuring self-consistency between the TAS and time-resolved fluorescence data. Finally, these kinetic constants allowed us to access the equilibrium constant and the driving force for the SB-CS process.

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Calculation of accurate tunneling splittingsJ. E. Lawrence¹, J. Dusek¹, J. O. Richardson^{1*}¹Laboratory of Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland

We introduce a simple-to-use method for calculating accurate tunneling splittings in molecular systems based on finding the dominant tunneling path (known as the instanton [1]). This can be done straightforwardly using standard optimisation techniques in combination with ab-initio electronic packages [2-3]. In this work we demonstrate how one can go beyond standard instanton theory to include additional anharmonic effects by adding perturbative corrections. This leads to significant improvements both in systems with low barriers and in systems with anharmonic modes. We demonstrate the applicability of our approach to molecular systems by computing the tunneling splitting in full-dimensional malonaldehyde and a deuterated derivative. Comparing to both experiment [4] and recent quantum-mechanical benchmark results [5], we find that our perturbative correction reduces the error from -11% to 2% for hydrogen transfer and performs even better for the deuterated case. This makes our approach more accurate than previous calculations using diffusion Monte Carlo [6] and path-integral molecular dynamics [7-8], while being more computationally efficient and simpler to use by non-experts.



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Rovibrational and Hyperfine Structure of the Molecular Hydrogen Ion from Spectroscopy of Rydberg-Stark Manifolds

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H_2^+ is the simplest molecular three-body system, and is therefore of interest from a fundamental point of view. Specifically, precision measurements of rovibrational energies in this system can provide access to fundamental constants such as the proton-to-electron mass ratio or the proton charge radius, by comparison with theoretical results [1]. Because homonuclear isotopologues of molecular hydrogen have no permanent electric dipole, pure rotational and vibrational spectra cannot be measured. Instead, transitions to Rydberg series converging on different rovibrational states of the ion core can be driven in a multiphoton excitation scheme starting from the molecular ground state [2]. Extrapolation of Rydberg series yields the ionic level energies. In this work, we use a combination of high-precision laser spectroscopy and calculations of Rydberg-Stark manifolds including electron and nuclear spins to determine rovibrational and hyperfine intervals in H_2^+ and HD^+ at sub-MHz accuracy.

Experimentally, precise measurements of Rydberg states with a rovibrationally excited core are challenging because of line-broadening effects caused by autoionization. By applying electric fields, states of different values of orbital angular momentum l are mixed, which provides access to the non-penetrating states of high- l character and therefore increases the lifetimes. Additionally, the high- l states have vanishingly small quantum defects and form a nearly degenerate Stark manifold. Extrapolation to zero field yields the zero-quantum-defect positions [3], from which the ionization energy can be determined. By applying the zero-quantum-defect-method to states with the ion core in different rovibrationally excited states, energy differences between these ion core states are determined.

For rigorous comparison with the measurements, we present calculations of Stark manifolds including interactions involving electron and nuclear spins. In particular, because previous studies have shown that the calculated manifold positions are sensitive to the zero-field positions of high- l states [3], we show how these positions can be accurately calculated with a simple polarization model [4] to which spin-orbit, spin-rotation and, if necessary, hyperfine interactions are added.

This contribution focuses on the determination of the fundamental vibrational and the spin-rotation intervals in H_2^+ and the hyperfine splitting in the ground state of HD^+ .

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Quantum-logic control of complex molecular ions for applications in molecular and chemical physics

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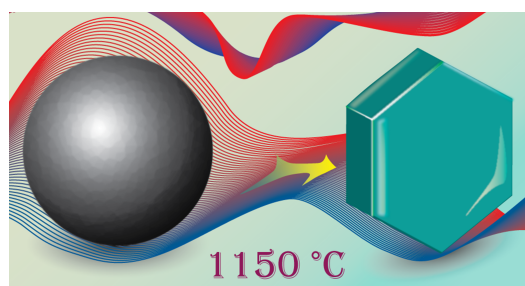
Over the past years, the coherent manipulation of single isolated quantum systems such as atoms, ions, superconducting circuits, and quantum dots has advanced greatly and yielded important applications in the fields of quantum metrology, quantum sensing, and quantum computing. Recently, extending and applying quantum technologies to molecules has become one of the prime goals of the quantum physics community. However, their complex internal structure and lack of cycling transitions makes it difficult to cool, control and manipulate them. In our lab, we co-trap a single molecular ion together with an atomic ion which acts as a coolant to cool the molecule translationally as well as a messenger for the internal state identification of the molecule without destroying it. The information of the complex molecular ion is mapped onto an easily addressable atomic ion from where it is read out [1-5]. I will talk about the quantum-non-demolition detection of the rovibrational state of single nitrogen ions which is a crucial step towards their coherent manipulation. This method allows us to go beyond the state-of-the-art and prepare molecular ions in well-defined hyperfine-Zeeman states. I will also discuss the extension of our technique to polyatomic ions to lay the foundations for the exploration of their spectroscopy and molecular dynamics.

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Crystallization of SrAl₁₂O₁₉ Nanocrystals from Amorphous Submicrometer ParticlesJ. Afshani¹, T. Bürgi¹, H. Hagemann¹¹University of Geneva

The use of advanced tools like transmission electron microscopy (TEM) and modern analysis techniques has greatly advanced our understanding of crystallization, particularly from solution, which is crucial for designing and creating specific crystals. However, there is still limited knowledge about the process of crystallization under high-temperature annealing (HTA) conditions, which is commonly used to obtain metal oxide crystals. While hydro-/solvothermal methods are widely used on a small scale in laboratories, HTA is the preferred method in many industries for large-scale production of metal oxide crystals. Unfortunately, the lack of precise control over the shape and size of these crystals under extreme HTA conditions restricts their applications.

In this study, we employed ex-situ TEM to investigate the transformation of a single amorphous spherical submicrometer precursor particle of SrAl₁₂O₁₉ (SA₆) into a nanosized hexagonal crystal, which is thermodynamically favored, at a temperature of 1150 °C. The sequential steps of this transformation are observed and explained in detail, illustrating the contributions of both kinetic and thermodynamic factors to the evolution of crystal shape and morphology. The findings reveal a nonclassical process of nucleation and growth, involving densification, formation of crystallite domains, oriented attachment, surface nucleation, two-dimensional (2D) growth, and surface diffusion of atoms, ultimately leading to the formation of a hexagonal platelet crystal. The TEM images also provide insights into a parent crystal that influences the crystal lattice and morphological orientation of a network of interconnected platelets.

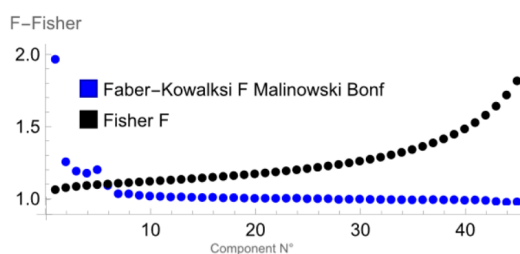


Enhancing Data Understanding: An Integrated Approach using multivariate statistical techniques in Time-resolved Spectroscopy, case of study: Trans-CI-[Ru(X,X')-dimethyl-2,2'-bipyridine)(CO)₂Cl₂].

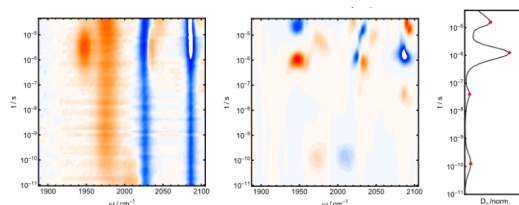
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Since the rise of the computing power, the application of mathematical techniques for data analysis has become indispensable across various scientific disciplines. Prior to engaging in exploratory analysis, a comprehensive understanding of the data is important to mitigate the risk of making wrong conclusions or fabricating data, all of which can undermine the acquisition of meaningful insights. The primary objective of this work is to present Singular Value Decomposition (SVD) as a widely adopted and well-established analytical tool, utilized for several decades. The subjectivity involved in discriminating between chemical and mathematical information can be mitigated through the employment of lesser-known mathematical methodologies that facilitate the imposition of statistical boundaries on such data [1].



Additionally, the Shannon's Maximum Entropy Method (MEM), extensively employed in the deconvolution of individual chemical species spectra [2], is used to extract valuable information from the data. Furthermore, we explore the Lifetime Analysis (LTA) technique, an infrequently utilized method grounded in MEM principle to extract information from the kinetics point of view. These methodologies are exemplified through their application to a series of experiments conducted on a Ruthenium bipyridyl complex employing ultrafast time-resolved pump-probe spectroscopy under varying conditions. The significance of this work extends beyond this specific experimental data, as these tools can be effectively applied to other types of multidimensional datasets encompassing diverse domains such as microscopy images, electrochemical spectra, and multidimensional NMR, among others.



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Effect of solvation on excited state symmetry breaking using transient infrared spectroscopy

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Over the past few years, two-branched symmetric electron donor-acceptor-donor (D- π -A- π -D) chromophores have been shown to undergo excited-state symmetry breaking (ES-SB) in polar environments. During this process, electronic excitation becomes unevenly distributed over the two DA branches and is highly dependent to the solvent polarity and the solvation dynamics [1]. In this work we will present the effects of solvation on the ES-SB, using a DAD chromophore in non-polar/polar solvent mixtures of different volumetric ratios. To do this, we use transient infrared (TRIR) spectroscopy, where we excite the sample at 400nm to the S1 state and probe the $-C\equiv C-$ stretching vibrations of the excited molecule with broadband IR pulses as a function of the delay time.

Our results show that in pure non-polar solvents (CHX), the chromophore is excited to a symmetrical quadrupolar excited-state, where the charge transfer character is the same in both arms. Addition of a polar solvent (ACN), even in tiny amounts, results in a fluctuating solvent field around the chromophore. This leads to an uneven charge distribution around the molecule and a partial breaking of the symmetry, creating an Intermediate state where both antisymmetric and symmetric vibrational modes are visible (Figure 1 second panel). With a higher amount of polar solvent, the chromophore is surrounded by more polar molecules and the field becomes more asymmetric, leading eventually to a full localisation of the excitation in one arm and hence to a dipolar excited state D (figure 1 third panel). In pure polar solvent, the reaction field is even stronger and more asymmetric, the charge transfer only takes place in one arm and only the D state is visible. The time scales associated with the transitions between these states coincide with those of solvation dynamics, which involves significant translational diffusion in solvent mixtures

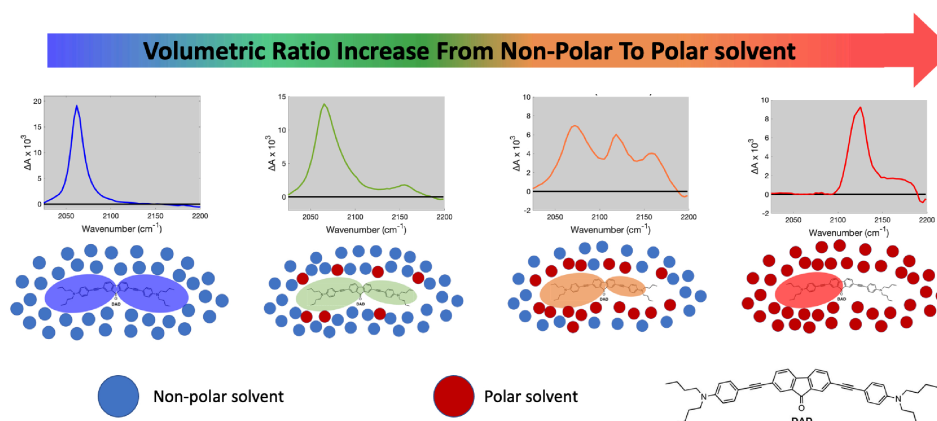


Figure 1. Transient infrared spectra of a DAD chromophore in non-polar/polar solvent mixtures (blue and red circles respectively). From left to right more polar solvent is added to the mixture and dipolar solvation starts taking place. This affects the environment around the chromophore breaking the symmetry, going from a symmetric quadrupolar state to a dipolar one.

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Composition-Driven Differences in Active Site Speciation and Behavior in Methane to Methanol Oxidation of Copper Exchanged Chabazite

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Introduction. The wasteful handling of natural gas in the oil and gas sector in combination with the strive for resource efficiency has animated research efforts to identify effective methods to convert retained CH₄ into high-value commodity chemicals such as CH₃OH. [1,2] Direct, low-temperature CH₄ oxidation by Cu exchanged zeolites via chemical looping has proven to be a particularly promising technology as a result of its scale flexibility and exceptional CH₃OH selectivity. Among the different zeolite topologies, Cu exchanged chabazite (Cu-CHA) is of special interest due to its superior CH₃OH yield. [3] However, attempts at industrial implementation are impaired by the lack of knowledge regarding the influence of the Si/Al ratio and the Cu-loading on the Cu active site speciation governing the redox behavior and CH₃OH selectivity of the material. This is further aggravated by the fact that information about the site-specific kinetic properties is missing. The present work aims at identifying the composition dependent Cu speciation by determining characteristic spectroscopic fingerprints and at elucidating their distinct kinetic behavior. Structure-activity relationships are established by correlating these results to the redox activity and CH₃OH selectivity of the bulk material.

Experimental/methodology. Four Cu-CHA materials differing in Cu speciation were prepared by deliberately varying the Si/Al ratio and Cu-loading. The results of plug flow reactor (PFR) reactivity tests were correlated to *in situ* X-ray absorption near edge structure (XANES) and *in situ* Fourier-transform infrared (FTIR) spectroscopy experiments. The observed differences in redox behavior and CH₃OH selectivity of the samples were linked to the variation in Cu speciation, which was established by means of *in situ* FTIR of adsorbed NO as well as *ex situ* Raman, *ex situ* photoluminescence (PL), *operando* ultraviolet-visible diffuse reflectance (UV-Vis), and *operando* electron paramagnetic resonance (EPR) spectroscopy.

Results and discussion. Samples exhibiting a low Si/Al ratio and Cu content predominantly host monomeric Cu²⁺ species such as bare Cu²⁺ ions or [CuOH]⁺ sites. At high Si/Al ratio and/or Cu-loading, oxygenated multinuclear Cu centers including [Cu₂(μ-O)]²⁺ and [Cu(μ-1,2-O₂)]²⁺ species are formed. Compared to dimeric Cu-Oxo compounds, materials containing predominantly monomeric Cu²⁺ active sites are characterized by a slower reaction rate as well as a shift of the redox activity profile to higher reaction temperatures. Simultaneously, these active centers feature a higher CH₃OH-based Cu efficiency and CH₃OH selectivity than their multinuclear counterparts. This indicates that the high activity of [Cu₂(μ-O)]²⁺ and [Cu(μ-1,2-O₂)]²⁺ moieties comes at the expense of material selectivity. These findings highlight the influence of the composition on Cu active site speciation, which ultimately determines the material's redox properties and behavior in CH₄ oxidation.

Acknowledgements

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Can IR substitute X-rays? Quantitative analysis of vibrational spectra powered by machine learning

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Vibrational spectroscopies are widespread techniques for operando characterization of heterogeneous catalysts. Being sensitive to the vibrational structure of the adsorbed molecules, they are often used to identify chemisorption sites, reaction intermediates etc. At the other hand, evolution of the structural parameters of the catalyst itself, which often affects the catalyst's performance, often require bulk sensitive techniques, such as X-ray absorption spectroscopy (XAS), application of which is troublesome due to the demand for synchrotron radiation sources. In this work, we demonstrate how vibrational spectra can be used as a source of quantitative structural information by applying machine learning (ML) algorithms. Focusing on the palladium hydride phase formation in the supported palladium nanoparticles (Pd/Al₂O₃), which can occur during numerous industrially relevant hydrogenation reactions, we collected, under exactly identical conditions, XAS and diffusive reflectance infrared Fourier-transformed spectroscopy (DRIFTS) data in a wide range of temperatures and partial hydrogen pressures in presence of CO as a probe molecule. Then, ML algorithm was trained on the dataset made of experimental XAS and DRIFTS data, showing that it is possible to predict structural parameters of Pd nanoparticles from DRIFTS spectra of the adsorbed CO and revealing perspective descriptors of both structural parameters of palladium nanoparticles and DRIFTS data. The experimental results were supported by the density functional theory (DFT) calculations modelling the change in vibrational modes upon the formation of hydride phase.

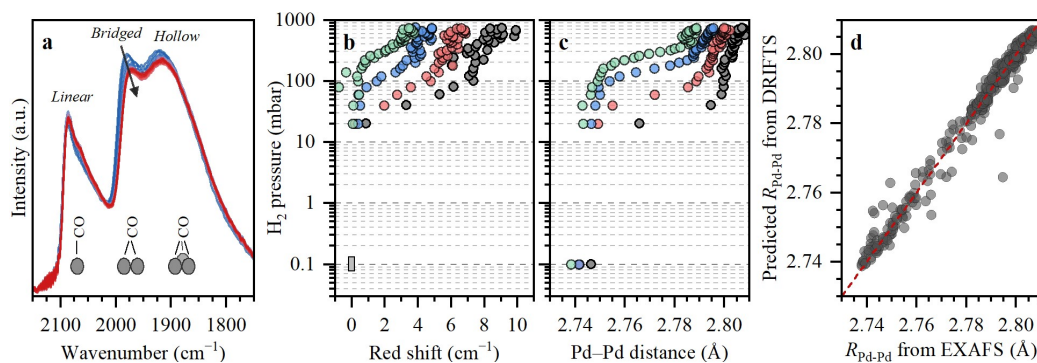


Figure 1. (a) Evolution of DRIFTS spectra in the region of CO vibration upon increase of the H₂ partial pressure (from blue to red) at 30 °C. (b) Red shift observed for bridge CO vibration upon increase of the H₂ partial pressure at 30 (black), 50 (red), 70 (blue) and 90 (green) °C. (c) Pd-Pd distance from EXAFS data measured under identical conditions. (d) Pd-Pd distance predicted from DRIFTS based on the absolute positions of three CO peaks versus true distance obtained from EXAFS.

Phase transition detection of CO₂ through near infrared spectroscopy

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Near infrared (NIR) spectroscopy is a widely used analytical method for online monitoring of chemical processes. Often, combination with chemometric methods is required to capture actual changes that elude inspection by eye during processes, such as chemical reactions and phase transitions, or to quantify components within complex spectra. Temperature changes may result in shifts in position and changes in the intensity of absorption bands. It is, therefore, possible to analyze these spectral changes and correlate them with actual chemo-physical properties, such as variations in the state of aggregation, thus to phase transitions.

In this work, we studied the behaviour of carbon dioxide at high temperature and pressures in an autoclave. The low critical point for CO₂ allowed us to span from vapor phase to supercritical phase. An immersion probe was installed in the autoclave and connected to the spectrometer through optical fibers. Spectra were acquired continuously every 30 s in temperature ramp. The spectra in Figure 1a collected during heating were analyzed with Principal Component Analysis (PCA) without data pre-processing. The score plot of PC1 vs. PC2 (explaining 99.8% of the total variance, Figure 1b) revealed the separation of the data into three different clusters attributable to different states of aggregation. The changes in the score plot are associated with changes in temperature and in peak shape and area. In particular, the three clusters identified by PCA characterize the different phases of CO₂ during heating from liquid phase to supercritical phase.

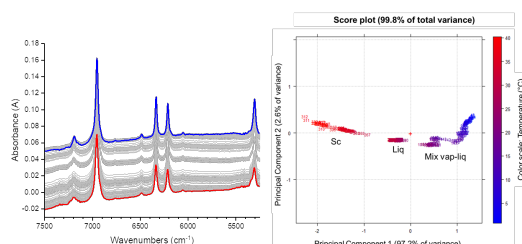


Fig 1: a) NIR spectra obtained during heating liquid CO₂ from cold (blue) to high temperature (red). b) Score plot of the entire dataset identifying three main data clusters.

Precision spectroscopy of transitions from the metastable 2^3S_1 state of ^4He to high np Rydberg states

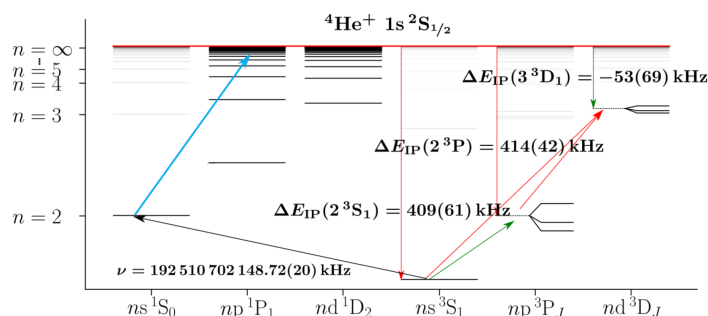
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The metastable He ($(1s)^1(2s)^1$) atom in its singlet (1S_0) or triplet (3S_1) states is an ideal system to perform tests of *ab-initio* calculations of two-electron systems that include quantum-electrodynamics and nuclear finite-size effects. The recent determination of the ionization energy of the metastable 2^1S_0 state of ^4He [1] confirmed a discrepancy between the latest theoretical values of the Lamb shifts in low-lying electronic states of triplet helium [2] and the measured $3^3D \leftarrow 2^3S_1$ [3] and $3^3D \leftarrow 2^3P$ [4] transition frequencies. This discrepancy could not be resolved in the latest calculations [5,6].

Currently, we focus on the development of a new experimental method for the determination of the ionization energy of the 2^3S_1 state of ^4He via the measurement of transitions from the 2^3S_1 state to np Rydberg states. Extrapolation of the np series yields the ionization energy with sub-MHz accuracy.

In this poster, we present the progress in the development of our experimental setup, which involves (i) the preparation of a cold, supersonic expansion of helium atoms in the 2^3S state, (ii) the development and characterization of a laser system for driving the transitions to the np Rydberg states and (iii) the implementation of a new sub-Doppler, background-free detection method. We present this new spectroscopic method, with which we cancel the 1st-order Doppler shift and illustrate its power with a new determination of the ionization energy of 2^3S_1 metastable He.



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Properties of γ D-crystallin undergoing Liquid-Liquid Phase Separation studied by EPR and *In-situ* Raman spectroscopy

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Liquid-Liquid Phase Separation (LLPS) describes the demixing of a homogeneous protein solution into a dense protein-rich and a diluted protein-depleted two-phase system. This sub-compartmentation in the complex environment of the cell creates a confined domain crucial for a manifold of biological processes like the formation membraneless organelles or the recruitment of proteins involved in the assembly of the cytoskeleton.¹

In contrast to the intrinsic disorder associated to most proteins undergoing LLPS, γ D-crystallin is a globular protein with a mass of 20,6 kDa, ubiquitously expressed in the eye lens of vertebrates, which forms molecular condensates in aqueous solutions at relatively high concentration and low temperatures. The presence of co-solutes such as polyethylene glycol and TMAO were shown to stabilize the phase separated state thereby increasing the onset temperature of LLPS.²

Here, we used γ D-crystallin as a model protein undergoing LLPS, to elucidate the effects of molecular crowding on its dynamics and to address the changes in solvation and protein density upon droplet formation in the presence of co-solutes. In an integrative approach we investigate the effects of co-solutes on the phase diagram by UV-vis spectroscopy, the dynamics and the local protein density of γ D-crystallin in the condensed phase by continuous wave and pulsed EPR spectroscopy and we used *in-situ* Raman spectroscopy to address local protein concentration in the two phases, partitioning of co-solutes and changes in protein hydration.

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Excited State Dynamics of Electron Injection and Hole Shift in a Dye-Sensitized Photocatalytic System

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Abstract : The development of renewable and environmentally friendly energy sources is of key importance for a sustainable society¹. In this context, dye-sensitized photo electrocatalytic cells (DSPECs) comprising an organic photosensitizer (PS) co-adsorbed with a hydrogen evolution catalyst (HEC) onto an n-type semiconducting (n-SC) nanoparticles (NPs) is a promising strategy. However, a better understanding of the photoinduced charge transfer process is necessary to improve the photocatalytic efficiency of DSPECs. Ultrafast spectroscopy is a highly powerful technique to assess the dynamics of photogenerated carriers in the photocatalytic systems. Here, the electron injection, hole shift and charge recombination dynamics of a DSPEC system with a dye chemisorbed on TiO₂ NPs and associated with a TEMPO (2,2,6,6-tetramethyl-1-piperidine N-oxyl) catalyst for the selective oxidation of alcohol into aldehyde have been studied using steady-state and time-resolved spectroscopies. Upon visible excitation of the PS, the electron is injected from the excited state of the dye to the conduction band (CB) of the n-SC on the fs-ps time scale. Femtosecond transient absorption measurements allow to identify the generation of the radical cation of the dye after the fast electron injection. Further, the hole shift from the dye cation to TEMPO catalyst and the regeneration of the dye are probed by nanosecond transient absorption spectra. Transient absorption in the mid-infrared region is used to probe the absorption of the injected electrons in the conduction band of the n-SC. To understand the hole diffusion within the dye molecules, transient absorption anisotropy measurements are also performed for the dyad on TiO₂ on the fs-ps and ns-ms time scales. This study reveals that the functionalization of the dye with TEMPO catalyst could lead to a more efficient photocatalytic system.

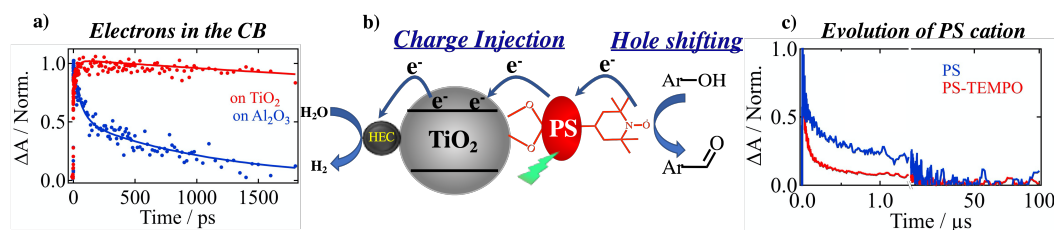


Fig. 1 a) The IR TA dynamics of electrons in the CB of TiO₂ and Al₂O₃ after electron injection from the dye, b) schematic representation of the working processes occurring in the DSP system and c) TA dynamics of the radical cation of the dye after photoexcitation.

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Influence of translational and rotational energy on the rate of ion-molecule reactions near 0 K: $D_2^+ + NH_3$ and $D_2^+ + ND_3$ R. Hahn¹, V. Zhelyazkova¹, D. Schlander¹, F. Merkt^{1*}¹Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland

Ion-molecule reactions are important reactions in atmospheric chemistry, astrophysics and plasma physics [1]. Reliable values for the reaction rates are key to modelling the relevant reaction networks, but are difficult to study in the collision energy range relevant for astrophysics because ions are very easily heated up by stray electric or magnetic fields.

To study the reactions $D_2^+ + NH_3$ as well as $D_2^+ + ND_3$ at low collision energy, we replace D_2^+ by D_2 in a Rydberg state (of high principal quantum number $n \geq 30$). The distant Rydberg electron shields the ion core from external fields without influencing the ion-molecule reaction within its orbit. We use a Rydberg-Stark deflector to merge a beam of D_2 Rydberg molecules with a supersonic beam of NH_3 or ND_3 and tune the collision energy E_{coll} from $\sim k_B \cdot 150$ mK to $\sim k_B \cdot 70$ K [2]. Short (~ 20 μs) gas pulses ensure a high collision-energy resolution.

We observe two reaction channels for the reaction with NH_3 : $NH_3^+ + D_2$ and $NH_2D^+ + D$, but these two channels are not resolvable by mass spectrometry for $D_2^+ + ND_3$. The rate coefficients deviate strongly from Langevin rates and increase sharply below 2 K, which is explained by rotationally adiabatic capture calculations as arising from the linear Stark effect of the two inversion tunneling components of ammonia in the electric field of the ion [3-6]. We study the influence of the rotational temperature (14 K or 39 K) of NH_3 and ND_3 using pure ammonia beams and beams of ammonia seeded in helium and measure the rotational states populations with (2+1) REMPI spectroscopy. We compare these results with those obtained for the $He^+ + NH_3$ [6] and $Rg^+ + NH_3$ ($Rg=Ar, Kr, Xe$) reactions [7].

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Accessing Higher Vibrational States of He_2^+ through Multi-Step Excitation

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The precise measurement of highly excited vibrational states of small molecular systems such as H_2^+ , H_2 and He_2^+ is of significant interest as benchmark to *ab-initio* quantum-chemical calculations [1]. In the case of He_2^+ , only the first few vibrational levels of the electronic ground state $X^+ \ ^2\Sigma_u^+$ were precisely measured [2-3]. In this poster presentation, we propose a method to access the higher vibrational states of He_2^+ $X^+ \ ^2\Sigma_u^+$ using a multi-step excitation scheme.

Our approach involves the production of a molecular beam of He_2 in the long-lived metastable $a \ ^3\Sigma_u^+$ state [4] through an electric discharge. We then utilize a high-intensity laser to promote the system to the electronic state $c \ ^3\Sigma_g^+$ in an excited vibrational level with v in the range 3-5. This state predominantly decays radiatively to the $a \ ^3\Sigma_u^+$ state with $v' = v$ because of favorable Frank Condon factors.

A second laser is then employed to induce a transition from the vibrationally excited metastable state $a \ ^3\Sigma_u^+(v')$ to the ion state $X^+ \ ^2\Sigma_u^+(v^+ = v')$. This method offers the prospect of studying the structure and dynamics of highly excited vibrational levels of He_2^+ that are typically challenging to access.

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Precision Spectroscopy and Coherent Manipulation of a Single Molecular Nitrogen IonR. Karl¹, A. Shlykov¹, M. Roguski¹, M. Sinhal¹, P. Paliwal¹, S. Willitsch^{1*}¹Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

Within the rich energy level structure of molecules, transitions with advantageous properties for precision studies and molecular quantum technologies can be found. However, without closed cycling transitions and frequencies ranging from MHz for hyperfine transitions to GHz in rotational transitions and THz in ro-vibrational transitions, efficient cooling of translational degrees of freedom as well as coherent state preparation, manipulation, and readout becomes challenging. We produce a single N₂⁺ ion in its internal ground state using threshold photoionization and use Doppler, Sideband, and EIT laser cooling on a co-trapped calcium ion to reach the motional ground state. With a quantum-logic protocol that uses the calcium ion as a probe for the molecular state, we achieve quantum non-demolition state detection with fidelities over 99%. Our current efforts go towards precision-spectroscopy on non-dipole-allowed rotational and ro-vibrational transitions using frequency sources that are referenced to the Swiss primary frequency standard at METAS. Beyond precision-spectroscopy, the methodologies that we develop pave the way for the implementation of molecular qubits, for establishing new frequency standards in the mid-IR regime, and for investigating state-to-state dynamics of chemical reactions.

Analysis of the Infrared Spectrum of *trans-c-2,3*-di-deutero-oxirane and further isotopomers

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The concept of isotopic chirality is of fundamental interest because it introduces a completely new isotope effect arising from the parity violating weak nuclear force [1–3]. It also has possible astrophysical applications. Oxirane (ethylene oxide *c*-C₂H₄O), detected by astrophysical spectroscopy in Sgr B2N [4], has two isotopically chiral isotopomers, monodeuterooxirane (*c*-C₂H₃DO) and *trans-c-2,3*-dideuterooxirane (*c*-CHD-CHDO). We have previously reported the analysis of high resolution GHz and THz spectra of monodeuterooxirane in the context of a possible first astrophysical observation of an isotopically chiral species [5, 6]. Following this work, Müller et al have reported a tentative detection of *c*-C₂H₃DO and the achiral *c*-CD₂CH₂O toward IRAS 16293-2422B [7]. There have also been ab initio calculations on the spectra of monodeuterooxirane and oxirane [8]. We have previously reported high resolution GHz and THz spectra of *trans-c-2,3*-dideuterooxirane [9]. Here we report new results of the detailed analysis of the infrared spectrum of *trans-c-2,3*-dideuterooxirane (*c*-CHD-CHDO), which we have recorded up to 3600 cm⁻¹ with a resolution of 0.0015 cm⁻¹ using the Bruker IFS 125 HR Zürich Prototype (ZP 2001) Fourier Transform spectrometer. The instrumental bandwidth is significantly less than the Doppler width of the compound in this region at room temperature. We have used the molecular parameters obtained from our analysis [9] of the ground state of *trans-c-2,3*-dideuterooxirane (*c*-CHD-CHDO) and have carried out the rovibrational analysis of regions of interest in the infrared spectrum using Watson's A reduced effective hamiltonian in the I' representation, including up to sextic centrifugal distortion constants. The results will be discussed as they pertain to isotopic chirality and molecular parity violation.

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High-Resolution Fourier Transform Infrared Spectrum of 1,3-Difluoroallene: a Candidate for the Detection of Molecular Parity Violation

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According to traditional quantum chemical theory, the ground state energies of enantiomers of chiral molecules would be identical by symmetry, whereas “electroweak quantum chemistry” including the parity violating weak nuclear force predicts them to be different by a very small parity violating energy difference $\Delta_{pv}E$ on the order of sub-feV to feV. This small effect has not yet been measured: such experiments constitute a major challenge of physical-chemical stereochemistry with possible importance both for fundamental physics in the standard model of elementary particles, and for the evolution of biomolecular homochirality in the origin of life [1,2]. An important step towards such experiments, according to the approach following [3], is the analysis of high-resolution spectra of suitable candidate molecules. We have identified chiral allenes in general and 1,3-difluoroallene in particular as possible candidates for such experiments [1-5] (see Table 2 of [2]). Here we report the high-resolution Fourier Transform Infrared (FTIR) spectroscopy and detailed analysis in the range of the antisymmetric CF-stretching fundamental $\nu_{12} = 1087.138308(32) \text{ cm}^{-1}$ and the symmetric stretching fundamental $\nu_4 = 984.9027(3) \text{ cm}^{-1}$ of FHC=C=CHF. The experimental results will be discussed in the context of possible further efforts towards measuring the parity violating energy difference in chiral molecules [6–9].

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High-resolution spectroscopy of the ground and low-lying excited states of MgNe^+ and MgXe^+

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Diatomic molecules RgM consisting of a rare-gas atom Rg and an alkaline-earth-metal atom M and their singly and doubly-charged cations RgM^+ and RgM^{2+} have unusual chemical properties related to the low first and second ionization energies of M and the high ionization energy of Rg . The second ionization energy of Mg is lower than the first ionization energy of Ar . Consequently, MgAr^{2+} is thermodynamically stable and Rydberg series of MgAr^+ can be observed that converge on the $X^{2+} \ ^1\Sigma^+$ ground state of MgAr^{2+} [1]. Similar behavior is expected in MgNe because of the even higher first ionization energy of Ne . In MgKr and MgXe , however, the second ionization energy of Mg is higher than the first ionization energy of the rare gas, and MgKr^{2+} and MgXe^{2+} are predicted to be metastable. In this contribution, we focus on the two extreme cases MgNe and MgXe . We present the results of spectroscopic investigations of MgNe^+ and MgXe^+ in their ground and low-lying electronically excited states that extend earlier studies of these cations [2,3].

PFI-ZEKE photoelectron spectra of the $X \ ^2\Sigma^+$ ground state were recorded from the $a \ ^3\Pi_0$ metastable state. Spectra of the lowest vibrational levels of MgNe^+ and MgXe^+ enabled the determination of the adiabatic ionization energy of metastable MgNe and MgXe . With a resonant two-photon ($1 + 1'$) excitation scheme, the PFI-ZEKE photoelectron spectrum of the $X \ ^2\Sigma^+$ state starting from the $X \ ^1\Sigma^+$ ground state of MgNe was recorded as well, giving access to the adiabatic ionization energy of the neutral ground state and the lowest singlet-triplet interval in the neutral molecule. Using isolated-core multiphoton Rydberg dissociation spectroscopy [4], transitions to electronically excited states of MgNe^+ and MgXe^+ were observed that are associated with the $\text{Rg} + \text{Mg}^+ (3p)$ dissociation limit. These states are the lowest members of Rydberg series converging on the ground state of MgNe^{2+} and MgXe^{2+} . These studies represent the first steps towards studying the doubly charged cations MgNe^{2+} and MgXe^{2+} .

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A Pinch of Sodium: Rapid CO₂ Uptake with MgO-based CO₂ sorbents upon promotion with Na₂CO₃ seeds

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There is an urgent need to develop and engineer functional materials that can capture and release CO₂ on demand. Solid oxide materials such as MgO and CaO constitute a promising family of materials for CO₂ capture, utilization, and storage, considering their favorable thermodynamics, high theoretical CO₂ uptake capacities and earth-abundance. However, despite favorable carbonation thermodynamics, MgO suffers from a limited CO₂ uptake due to very slow carbonation kinetics. The carbonation kinetics can be enhanced by adding an alkali metal nitrate promoter such as NaNO₃, which dissolves surface carbonates in the form of [Mg²⁺...CO₃²⁻] ion pairs and thereby facilitates MgCO₃ crystallization.^{1,2} Moreover, it was found that the addition of Na₂CO₃ seeds to NaNO₃-promoted MgO further increases the CO₂ uptake rate by a factor of 10.³ We investigated the promotional effect of Na₂CO₃ via in situ synchrotron-based X-ray powder diffraction (XRD) with a high time resolution (1 s) complemented by electron microscopy characterization. We demonstrate that Na₂CO₃ rapidly transforms into Na₂Mg(CO₃)₂ in the presence of MgO, CO₂, and NaNO₃. The Na₂Mg(CO₃)₂ phase acts as an effective nucleation seed that boosts MgCO₃ growth. Our In-situ XRD measurements prove that MgCO₃ nucleates onto the Na₂Mg(CO₃)₂ seeds while TEM imaging of the Na₂Mg(CO₃)₂-MgCO₃ interphase reveals that the Na₂Mg(CO₃)₂ seeds promote MgO dissolution and thereby facilitate MgCO₃ growth. Taken together, the insights obtained here will help the development of more effective MgO-based CO₂ sorbents.

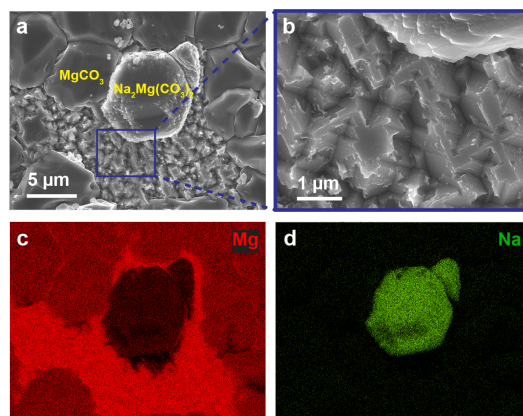


Figure 1. SEM-EDX analysis of a carbonated NaNO₃/Na₂Mg(CO₃)₂-promoted MgO(100) single crystal. (a) SEM image of a Na₂Mg(CO₃)₂ crystals surrounded by MgCO₃ crystals. (b) zoom focusing on the etching pits formed in the MgO(100) surface. (c) Corresponding Mg and (d) Na elemental maps.

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Determination of fundamental photophysical parameters of gold nanoclusters

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Atomically precise metal nanoclusters (NC) in general and gold nanoclusters (AuNC) specifically have many advantages which allows their uses in areas such as photocatalysis, biosensing, or solar energy conversion [1]. A comprehensive description of their photophysics will strongly benefit all these three branches of applications. However, the basic photophysics of AuNC is currently not clearly understood, according to the previously published results in the area. This work intends to achieve such a level of understanding of their photophysical properties. To this end, the absorption and fluorescence spectra (steady-state and time-resolved) were obtained for the most commonly studied cluster, Au₂₅PET₁₈. A series of deviations from conventional molecular photophysics was observed, in particular the discrepancy between absorption and luminescence excitation spectra, the violation of Kasha's rule (i.e. a strong dependence of emission spectra and lifetimes on excitation energy) and clearly multi- or nonexponential behavior for the ns- μ s emission decays. A tentative Jablonski diagram and kinetic scheme are proposed to explain these findings.

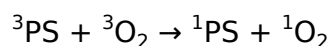
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Using Instanton Theory to Study Quantum Effects in Photosensitization

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Photosensitization of O₂ is widely made use of in organic synthesis, photovoltaic cells and is a key step in photodynamic therapy. Despite its significance, its comprehensive mechanism is still unknown.



A previous theoretical study calculated O₂-photosensitization rates by thiothymines (2-thiothymine, 4-thiothymine and 2,4-dithiothymine) and found a speed up by several orders of magnitude when rates were calculated from Fermi's golden rule (FGR) compared to Marcus theory, thus establishing the importance of quantum effects in driving photosensitization [1]. However, even the smallest photosensitizers (PS) are too large for a quantum approach to be tenable. The gap between the need to account for quantum effects and computational cost can be bridged by semiclassical instanton theory (SCI), in particular, its extension to the inverted regime in the golden-rule limit [2]. SCI has been shown to give excellent results for ISC reactions [3]. While rate constants calculated from SCI are in excellent agreement with experiment, its central contribution is the elucidation of the reaction mechanism by locating the optimal tunnelling pathway [3]. For O₂-photosensitization, we start by extending SCI to a model system, which best describes the process, and obtain near-perfect agreement with exact (FGR) rates. Then, before applying the developed methodology to a real system, we take a closer look at the PSs – the thiothymines – themselves. This is because the mode which promotes photosensitization has been identified to be the one along which intersystem crossing (ISC) of the PS takes place [1]. Our calculations have shown evidence of room-temperature heavy-atom tunnelling in the ISC pathways of 4-thiothymine and 2,4-dithiothymine, while the tunneling effect in 2-thiothymine is negligible. We then extend the calculations to the O₂-photosensitization reaction by thiothymines.

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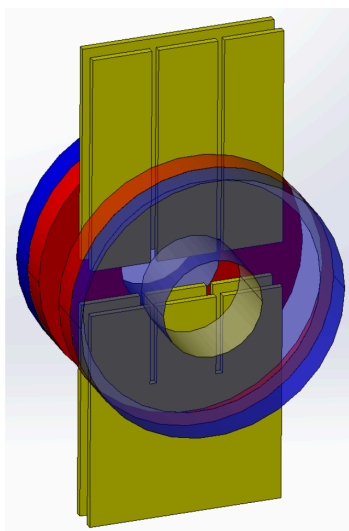
Laser cooling of trapped ions in strongly inhomogeneous magnetic fields

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We demonstrate laser cooling of Ca^+ ions confined in a segmented linear Paul trap in presence of a strongly inhomogeneous magnetic field generated by two permanent ring magnets (see figure below). We show that by employing two cooling lasers with properly adjusted wavelengths and polarizations, the trapped ions can efficiently be cooled to millikelvin temperatures despite strong position-dependent Zeeman shifts. The cold ion structures, also called Coulomb crystals, can additionally be used to visualize the position dependency of the Zeeman effect around the trapping centre. All experimental results are complemented by a theoretical analysis [1].

This setup is an essential prerequisite for a hybrid trapping experiment in which cold collisions and reactions between ions and neutral molecules can be studied.



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Studying rotational-state and conformational effects in chemi-ionisation reactionsA. Mishra¹, L. Ploenes¹, P. Stranak¹, C. He¹, S. K. Kim², S. Willitsch^{1*}¹University of Basel, Department of Chemistry, Klingelbergstrasse 80, 4056 Basel, Switzerland, ²KAIST, Department of Chemistry, Daejeon 34141, Republic of Korea

Conformers are the dominant isomers of complex molecules. The conformation of a molecule can have pronounced effects on its chemical reactivity. However, because they often interconvert into one another under ambient conditions, individual molecular conformations are difficult to isolate. Consequently, only sparse experimental data exists on the chemical properties of distinct conformers [1]. Over the past years, we have developed experimental methods to study conformational effects in ion-molecule reactions under single-collision conditions [2,3]. We have recently built a new crossed-molecular-beam setup to extend our methodology to neutral-neutral reactions [4]. This setup is equipped with an electrostatic deflector which enables the spatial separation of different conformers or individual rotational states of molecules based on their effective dipole moments. As the first application of this new method, rotational-state-dependent chemi-ionisation reactions of carbonyl sulfide (OCS) with metastable neon atoms were investigated. A pronounced state-specific effect on the product branching ratio was observed. Our result suggests that OCS molecules in the rotational ground state $J = 0$ are a factor of 2.5 more reactive for dissociative ionisation than Penning ionisation compared to the $J = 1$ state [4,5]. Moreover, for heavier molecules, the disentanglement of conformational and rotational-state effects can be difficult to analyse due to the involvement of several rotational states [5]. Choosing conformers that can be chemically separated and have high interconversion barriers could disentangle the conformational and rotational state dependencies. Therefore, we chose to study the chemi-ionisation reaction of 1,2-dibromoethylene (DBE), the conformers of which can be chemically separated [6,7]. Additionally, in a collaboration with the Korean Advanced Institute of Science and Technology (KAIST), we are also currently undertaking a comparative study of the photochemistry, photoionization, and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene (DBE) as a prototypical system [8]. These investigations aim to gain a comprehensive understanding of the role of molecular conformations in unimolecular and bimolecular reactivity.

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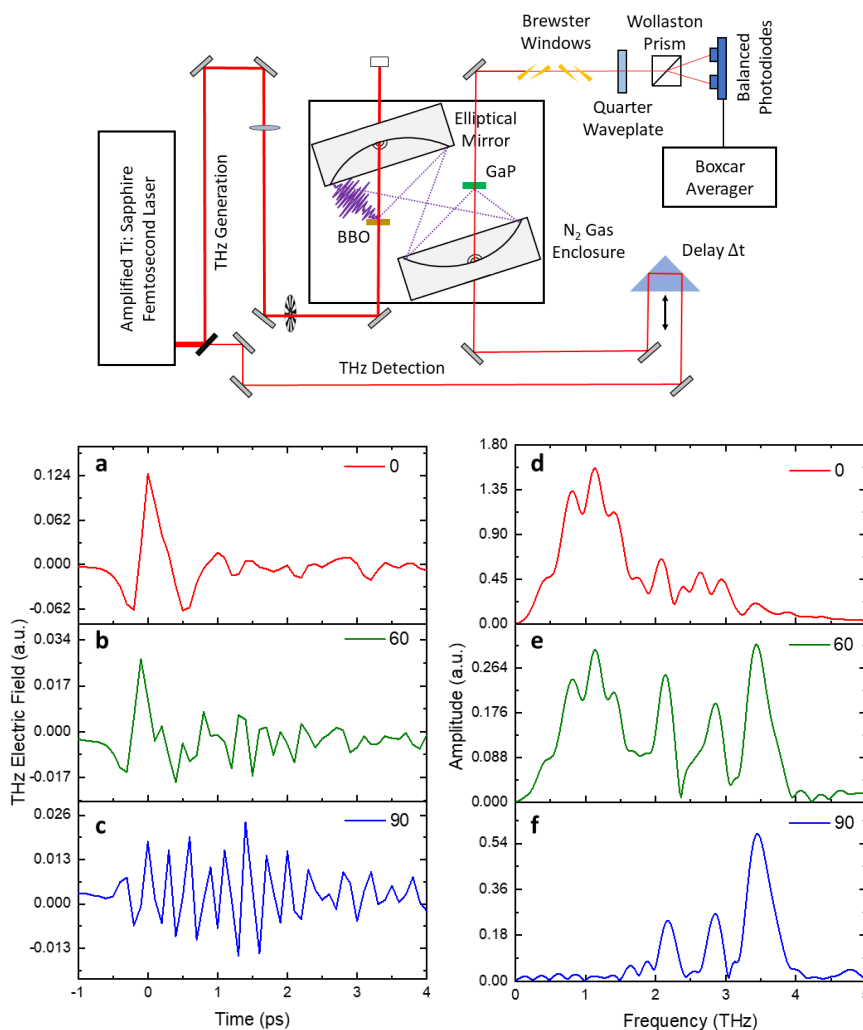
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Single-cycle and multi-cycle terahertz pulse generation in beta barium borate (β -BBO)

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In this work, we present the generation of both single-cycle broadband and multi-cycle narrowband terahertz (THz) radiations from a Y-cut beta barium borate (β -BBO) crystal excited by 100 fs laser pulses at a central wavelength of 800 nm. Additionally, we demonstrate that by adjusting the azimuth angle of the crystal, it becomes feasible to generate a THz field that exhibits both single-cycle and multi-cycle components simultaneously. Finally, we discuss the mechanism responsible for the generation of both broadband and narrowband THz emissions in β -BBO [1-3].



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Real-time tracking of the ultrafast chirality and energy transfer in a chiral OLED complex with circularly-polarized luminescence

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Circularly-polarized luminescence (CPL) has promising applications in the fields of optical data storage, biomedical diagnosis and for the creation of more efficient OLED displays. [1] In this respect, chiral lanthanide complexes have gained a lot of attention as CPL emitters due to their sharp and intense emission lines, long emission lifetimes and above all, due to their high degree of circular polarization. However, despite the impressive progress in the synthesis of metallo-organic CPL complexes, the underlying excited state dynamics of their chiral luminescent states have thus far remained inaccessible due to a lack of ultrafast spectroscopic techniques with sufficient chiral sensitivity.

To address this gap, we have developed a novel ultrafast circular dichroism instrument that combines ultra-sensitive broadband detection with sub-picosecond time resolution. [2] We now apply this technique to resolve the CPL mechanism of the prototypical CsEu((+)-hfbc)₄ (hfbc = 3-heptafluoro-butylyrylcamphorate), which displays a record CPL emission with 85% of the photons being left-circularly polarized at 595 nm. [3] Although its luminescent transitions are metal-centered (MC), the chiral ligands play a crucial role in the CPL mechanism. First, they act as photosensitizers providing efficient energy transfer to the dipole-forbidden MC transition. Second, theoretical models predict that the high degree of luminescence dissymmetry arises from a transient coupling of ligand-centered electronic transition dipoles to the active MC transition of the Eu(III) ion, thereby creating the chiral luminescent excited state. [4,5]

Combining ultrafast circular dichroism with transient absorption and anisotropy measurements from the visible to the deep ultraviolet, we now present the first experimental investigation of the ultrafast energy and chirality transfer of a CPL complex, thereby providing a complete picture of the excited state CPL mechanism.

More generally, our results highlight that with ultrafast circular dichroism it is now possible to capture the evolution of chiral excited states in real-time, opening a new path to the direct investigation and optimization of enantioselective photochemical processes in their native solution phase.

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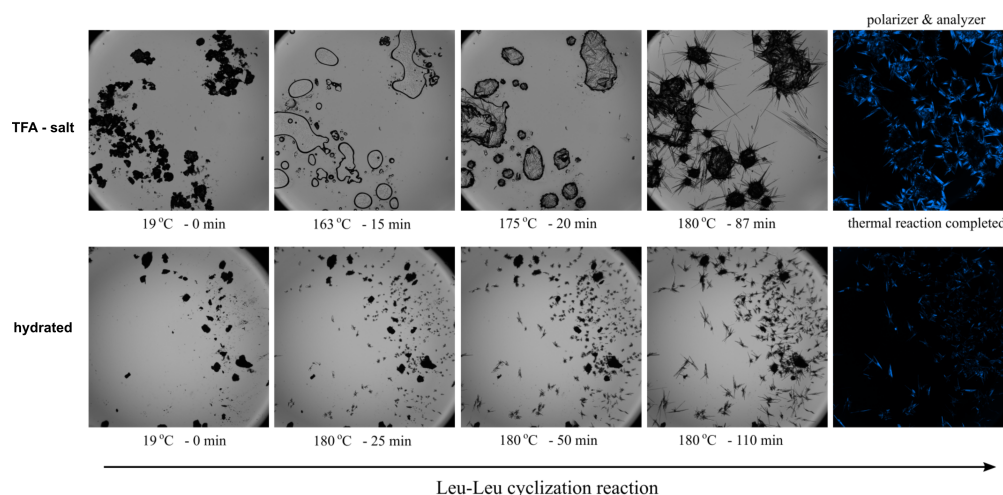
Unveiling the Impact of Trifluoroacetic Acid on Phase Transitions in Solid-State Synthesis of Cyclo Leu-Leu: Revelations and Implications

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Oligopeptides, short chains of amino acids, have a unique ability for self-assembly, a feature widely exploited in the nanomaterials sector [1]. Their self-assembly into diverse nanostructures enables various applications, including biosensing technologies, organic semiconductor production, and targeted drug delivery systems [2-4]. The supramolecular structure and chirality of oligopeptides, which are intricately linked to the absolute configuration of the amino acid monomers, play a crucial role in this self-assembly [5]. Some oligopeptides, like the linear dipeptide (L)Leu-(L)Leu, can undergo a cyclization process when exposed to heat [6,7]. In this presentation, I will present a detailed analysis of cyclo Leu-Leu's solid-state synthesis, divided into three parts focusing on the role of the counterion during the synthesis, morphological changes, and the preservation of chirality.

Initially, we will focus on the role of the TFA counterion in the synthesis, using transient absorption infrared (IR) spectroscopy to analyze the dynamic changes over time. The second part will investigate the morphological changes during synthesis using optical microscopy (figure below), Raman spectroscopy, and X-ray powder diffraction for detailed structural analysis. Finally, we will conclude with an assessment of chirality conservation during the process using vibrational circular dichroism.



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Production cross-section measurements of the medically relevant radionuclide thulium-167 using an 18-MeV medical cyclotron

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Auger electrons have gained significant attention for their potential capability of targeting individual tumor cells due to the deposition of a highly localized, cytotoxic radiation dose. By employing these particles in Targeted Radionuclide Therapy (TRT), healthy tissues could be spared from excessive radiation-induced damage, thereby, reducing potential severe, long-term side effects. Thulium-167 (100 % EC decay, $t_{1/2} = 9.25$ d, $E_{\gamma} = 207.8$ keV (42 %) [1]) is a promising candidate for TRT with Auger electrons due to its substantial emission of low-energy electrons [2]. In addition, the emission of an intense low-energy gamma ray, allows imaging by means of Single Photon Emission Computed Tomography (SPECT). This capability was previously demonstrated when thulium-167 was employed as a bone-scanning agent [3]. However, the understanding of the radiobiological effectiveness of Auger electron emitters is in its infancy, thereby, justifying the urgency for production to ensure systematic investigations. To achieve this objective, the knowledge of production cross sections of relevant thulium radioisotopes is essential to obtain high activities and assess radionuclidic purity of the radionuclide produced. Consequently, this study is aimed at measuring the cross sections of the proton-induced reactions producing thulium radioisotopes using enriched erbium-167 and erbium-168 in the chemically-stable oxide form.

The cross-section measurements were performed using the 18-MeV medical cyclotron in operation at the Bern University Cyclotron Laboratory, equipped with a Beam Transport Line (BTL). In this study, thin targets of erbium oxide were irradiated using nano-ampere (nA) proton currents with varying energy. The production cross sections of thulium-165, thulium-166, thulium-167, and thulium-168 were assessed over an energy spectrum ranging from 6.8 MeV to 18.2 MeV and compared with theoretical predictions obtained from the TENDL 2019 library. To validate the experimental cross-section data, a series of production tests bombarding thick targets were conducted employing the BTL. The production yields of each relevant thulium radioisotope were evaluated using the measured cross sections. This evaluation aimed to identify the optimal proton beam energy yielding maximum thulium-167 production. The theoretical predictions were compared to the corresponding experimental results.

Good agreement is found between the experimental cross-section measurements and the predictions by TENDL 2019. In addition, the production tests successfully validated the measured experimental cross-section data. According to experimental evidence, thulium-167 production yields were determined to be 2.4 MBq/ μ Ah and 8.4 MBq/ μ Ah when using 12.7 MeV and 18.2 MeV proton energies and $^{167\text{enr}}\text{Er}_2\text{O}_3$ and $^{168\text{enr}}\text{Er}_2\text{O}_3$ as target materials, respectively.

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Influence of the collision Energy on the Reaction Rate of the D_2^+ + H_2O Ion-Molecule Reaction near 0 K

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Ion-molecule reactions are important reactions in atmospheric chemistry, astrophysics, and plasma physics.^[1] Reliable values for the reaction rates are key to modelling the relevant reaction networks. This poster focusses on the reactions of water with D_2^+ at the low temperatures in the range of 0-50 K of interstellar molecular clouds.^[1-2] For technical reasons D_2^+ is instead of H_2^+ .

Because ions are easily accelerated by (stray) electric fields, high Rydberg states ($n \approx 30$, $v^+ = 0$, $N^+ = 0$) are utilised as proxies for the ionic reaction partner, because the Rydberg-electron does not significantly affect the reaction but shields it from electric fields.^[3-4] We use a merged-beam approach featuring a Rydberg-Stark deflector and decelerator to access the collision-energy range below $k_B \cdot 10$ K. The molecular beam of water is characterised.

The reaction rates are modelled with an adiabatic capture model inspired by earlier work in Refs. [5-7] which is constructed by modifying the Langevin model with the rotational-state-specific energy of the neutral molecules in the field of the ion.^[5-8] For Maxwell-Boltzmann rotational-state distributions below 100 K the model predicts an increase of the reaction-rate constant at low collision energies.

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Characterisation of The Ground and Low-Lying Excited States of MgO^+ by PFI-ZEKE Photoelectron Spectroscopy

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We report on the characterisation of the rovibrational structure of the ground and first excited electronic states of MgO^+ by high-resolution pulsed-field ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. Rotationally cold ($T_{\text{rot}}=5$ K) MgO molecules in the $X^1\Sigma^+$ ($v = 0-2$) levels were generated in a supersonic expansion of a 0.1% $\text{N}_2\text{O}:\text{He}$ gas mixture following laser ablation off a magnesium (Mg) rod [1]. The rovibrational ionization thresholds corresponding to both spin-orbit components ($\Omega=1/2, 3/2$) of the $X^+ 2\Pi_{\Omega}$ ($v^+ = 0-10$) states as well as to the first excited $A^+ 2\Sigma^+_{1/2}$ ($v^+ = 0-10$) state were reached in a resonant 1+1' two-photon excitation sequence via the rovibrational levels of the $F^1\Pi$, $E^1\Sigma^+$, $G^1\Pi$ and $3^3\Pi_2$ intermediate levels of MgO studied previously by Breckenridge and coworkers [2, 3]. Our new results include accurate values for the adiabatic ionization energy of MgO and for the dissociation energies of the $\text{MgO } X^1\Sigma^+$ and $\text{MgO}^+ X^+ 2\Pi_{\Omega}$ and $A^+ 2\Sigma^+_{1/2}$ states. This work is carried out in the context of our studies of the rovibrational structure of doubly charged dications by high-resolution PFI-ZEKE spectroscopy of singly-charged cations following the approach recently taken to characterise the ground state of the thermodynamically stable dication MgAr^{2+} [4]. The talk will present a roadmap towards characterising the ground state of MgO^{2+} by resonant multiphoton excitation via electronically excited states of MgO^+ . The experiments will reveal whether MgO^{2+} is thermodynamically stable as predicted in Ref. [5] or metastable as predicted in Ref. [6].

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2D-Raman THz Spectroscopy of Ionic Liquids

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2D Raman-THz spectroscopy is a novel spectroscopic method that measures the 2D response of intra and intermolecular degrees of freedom of liquid samples in the low frequency range (below 300cm^{-1}) Fig. 1(a). It has been successfully used to study the dynamical heterogeneity in liquid water and various aqueous salt solutions [1,2]. The current work aims to extend the application of this technique to study ionic liquids, such as 1-Allyl-3-methylimidazolium dicyanamide (AMI) Fig. 1(b).

Room temperature ionic liquids (RTILs) are an interesting class of salts that are liquids at or below room temperature, and their modularity allows for a wide range of desirable properties, making them a promising candidate for various industries such as energy storage, chemical synthesis, CO₂ capture, and green chemistry. The presence of charges in the chemical structure of ionic liquids might facilitate heterogeneity in the structural dynamics, and 2D Raman-THz spectroscopy is expected to provide new insights into the dynamics of these materials. Fig. 1(c) shows a response of AMI liquid obtained by means of our recently developed fast acquisition single shot 2D Raman-THz spectrometer [3] where extent of the signal beyond the strong instantaneous response along $t_1 = t_2$ diagonal (dashed line) encodes inhomogeneity of the liquid.

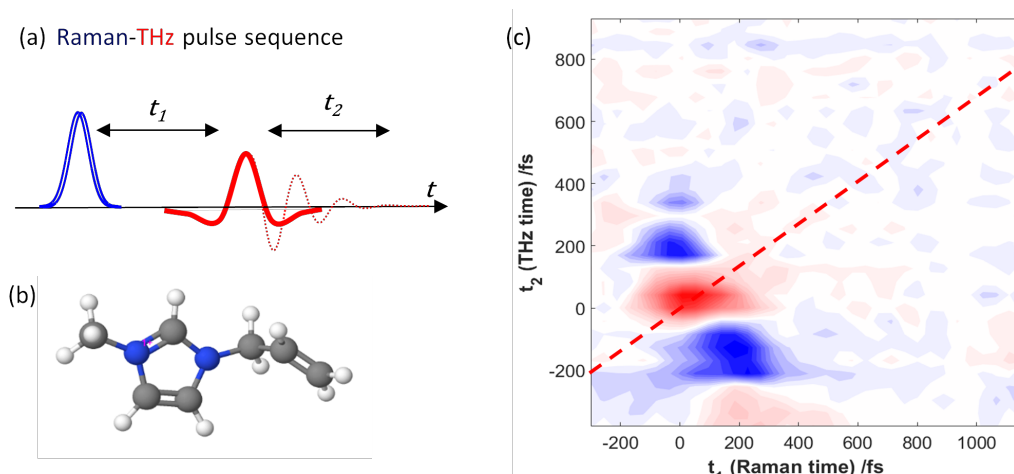


Fig.1 (a) Raman-THz pulse sequence (b) AMI molecular structure (c) 2D Raman-THz response of 1-Allyl-3-methylimidazolium dicyanamide

We are currently analyzing the data with respect to the possibility of seeing an echo along this diagonal.

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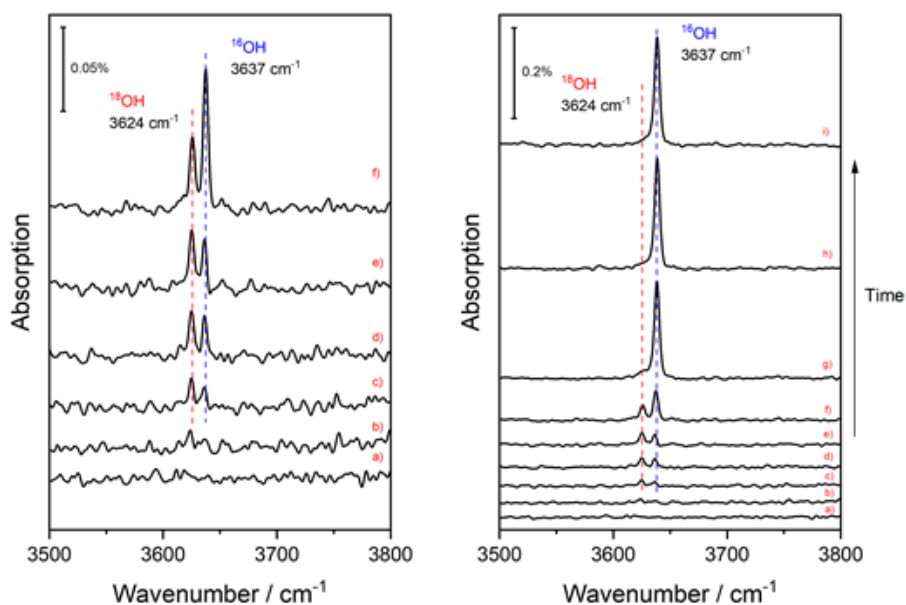
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Probing the mechanism of facile water dissociation on oxygen covered Cu(111) by Reflection Absorption Infrared Spectroscopy (RAIRS)

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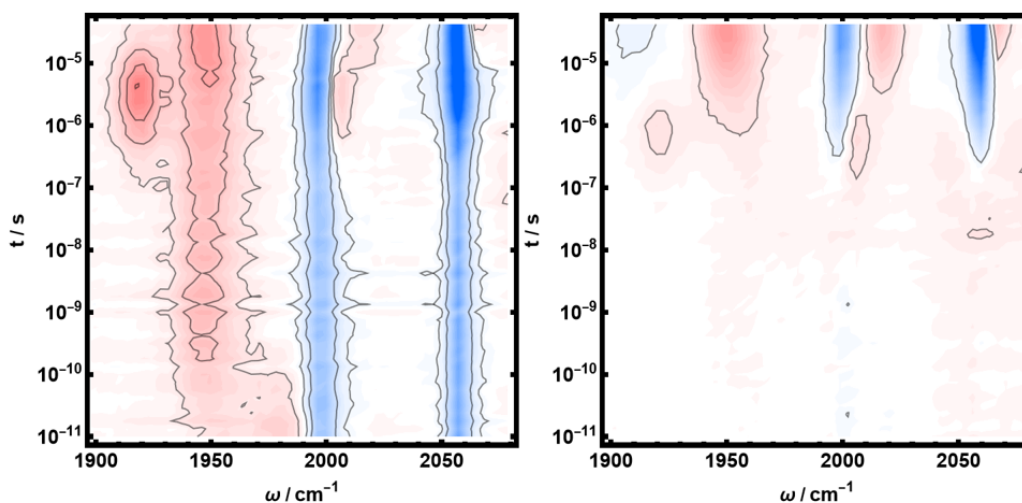
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The presence of oxygen atoms on a Cu(111) surface strongly reduces the activation barrier for water dissociation, as compared to bare Cu(111). In this work, we present a direct experimental observation of the hydrogen abstraction mechanism for H₂O dissociation on a O/Cu(111) surface using reflection absorption infrared spectroscopy (RAIRS). By dosing ¹⁸O₂(g) onto a Cu(111) single crystal, we create a partially oxidized ¹⁸O/Cu(111) surface, which is subsequently exposed to a flux of H₂¹⁶O molecules, resulting in the detection of two RAIRS peaks assigned to ¹⁸OH(ads) and ¹⁶OH(ads). With continued H₂¹⁶O exposure, the ¹⁸OH(ads) RAIRS signal decreases rapidly while the ¹⁶OH(ads) signal continues to increase, indicating a disproportionation reaction of the adsorbed hydroxyl species, resulting in net desorption of H₂¹⁸O(g) and replacement of ¹⁸O(ads) by ¹⁶O(ads).



Ligand exchange kinetics in the first reduction step of CO₂ reduction catalyst: trans-(Cl)-[Ru(5,5'-dimethyl-2,2'-bipyridine)(CO)₂Cl₂]L. Tatarashvili¹, S. Aranda¹, K. Oppelt¹, P. Hamm^{1*}¹Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

A significant amount of current research is dedicated to developing methods for reusing atmospheric CO₂ as a precursor in the production of valuable chemicals. Ruthenium mono- and bis(bipyridyl) dicarbonyl complexes are known as promising catalysts for electro/photo-chemical CO₂ reduction [1]. One such molecular catalyst is trans-(Cl)-[Ru(5,5'-dimethyl-2,2'-bipyridine)(CO)₂Cl₂]. To attain catalytic activity, this molecule undergoes a two-step reduction process (Ru(II) to Ru(0)). We used a simple photocatalytic system comprised of the catalyst, photosensitizer (Ru(bpy)₃Cl₂), and reductive quencher (1-Benzyl-1,4-dihydronicotinamide), and tracked the IR absorption by the carbonyls over picosecond to microsecond time range using time-resolved pump-probe spectroscopy. Since carbonyl ligands have excellent IR absorption cross-section and are sensitive to the variations of electron density on the metal, we could clearly monitor the system's evolution. Our results reveal the transient species related to the initial reduction of the catalyst and offer deeper insight into the processes leading to its activation and their associated timescales.



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High-resolution spectroscopy and multichannel quantum-defect-theory analysis of high Rydberg states of xenon.

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High-resolution spectra of high np and nf Rydberg states of Xe were measured by single - photon excitation from the metastable state of Xe $(5p)^5(6s)^1\ ^3P_2$ to the energy region located below the $Xe^+ (5p)^5\ ^2P_{3/2}$ ionization threshold. The experiments were carried out using a pulsed Fourier-transform-limited narrow-band UV laser and a supersonic-beam apparatus.

The fine and hyperfine structures of np and nf Rydberg states of the nine most abundant isotopes of xenon have been analyzed in the range of the principal quantum number between 60 and 75 using multichannel quantum-defect-theory (MQDT). For the analysis of the fine structure of xenon, the formalism introduced by Lu and Lee [1] and Lu [2] was followed. This formalism was extended by Wörner et al. [3,4] and Schäfer et al. [5] to treat the hyperfine structure in Rydberg states of ^{129}Xe and ^{131}Xe . By using the eigenquantum defects and channel interaction parameters for the even-parity states of xenon from Schäfer et al. [5], improved values of the ionization energies and the isotopic shifts have been determined from the MQDT analysis.

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Investigating Bimolecular Symmetry Breaking Charge Separation in Highly Concentrated Perylene Solutions

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Symmetry breaking charge separation (SB-CS) enables the conversion of solar energy into charge carriers by photoinduced electron transfer between identical molecules (M).¹ Generally, SB-CS is studied in systems in which the two chromophoric moieties undergoing SB are covalently linked, $M^*-M \rightarrow M^+-M^-$.² Examples of bimolecular SB-CS, $M^* + M \rightarrow M^+ + M^-$, of organic chromophores yielding free ions, on the other hand, remain scarce due to solubility or aggregation issues of the dyes at high concentrations.

Here, we explore the excited state dynamics of Perylene (Pe) and its alkyl substituted derivatives³ in highly concentrated solutions using transient absorption spectroscopy. By mapping out the excited state dynamics from subpicosecond to microsecond timescales, we demonstrate that the locally excited (LE) state undergoes quenching through excimer formation⁴ in concentrated solutions. Moreover, we observe the characteristic bands of the perylene ions⁵ in polar solvents next to the excimer decay, highlighting the possibility of bimolecular SB-CS in these systems (see Figure 1).

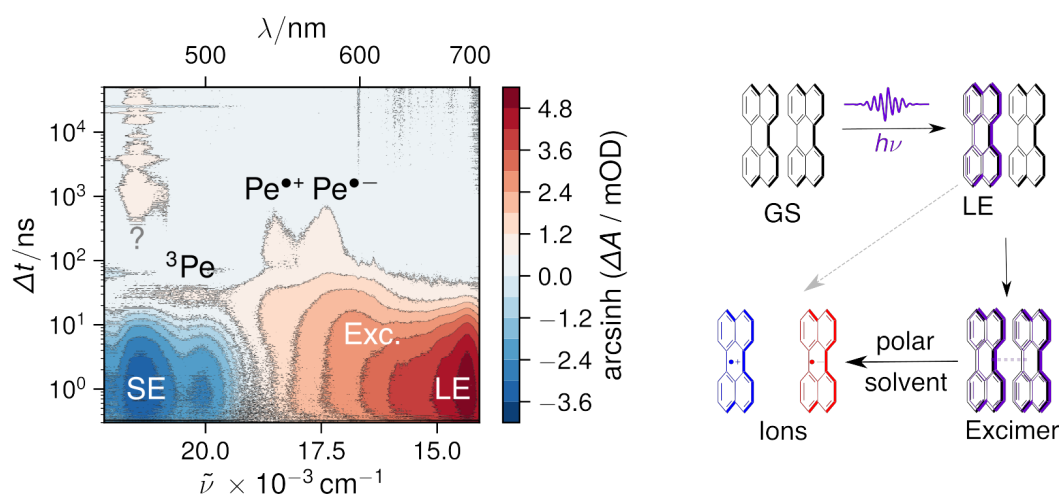


Figure 1: Nanosecond-microsecond visible transient absorption spectrum of Pe (1 mM) in acetonitrile showcasing bimolecular SB-CS as well as excimer formation.

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Progress in the Zurich experiment on parity violation in chiral moleculesG. Wichmann¹, G. Seyfang¹, M. Quack^{1*}¹Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich

Because of the space inversion symmetry of the electromagnetic force, the ground state energies of the enantiomers of chiral molecules would be identical by symmetry in conventional quantum chemical theory. Including also the parity violating weak nuclear force, they are, however, predicted to be different by a very small parity violating energy difference $\Delta_{\text{pv}}E$ in the sub-feV and low feV range. This small effect from the 'electroweak quantum chemistry' has so far never been measured and such experiments constitute a major challenge of physical-chemical stereochemistry with possible importance both for the fundamental physics in the standard model of elementary particles and for the evolution of biomolecular homochirality in the origin of life as reviewed in [1, 2].

An important step in our approach following [3] has been the proof of concept for the experimental stability of parity states (tested with the achiral molecule NH_3 [4]) demonstrating the possibility to detect values of $\Delta_{\text{pv}}E$ as small as 100 aeV (or larger). Our current efforts concentrate on developing techniques to measure and analyze mid-IR vibration-rotation-tunneling spectra (around 3000 cm^{-1}) of one of our mid-sized chiral candidate molecules with low vapor pressure (listed e.g. in Tab. 2 of Ref. [2]). Here, we report improved cw-laser cavity ring-down spectroscopy [5, 6, 7] referenced to a frequency comb combined with a slit jet expansion and partial pressures below 1 mbar sufficient for highly resolved absorption spectra of aniline with our new setup. We report also the spectrum of benzene spanning ranges of more than 10 GHz in the mid-IR with complexity similar to the spectroscopy of our chiral candidate molecule, 1,2-dithiine.

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Trapping and sympathetic cooling of conformationally selected ions

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The different effective dipole moment of conformational isomers allows for their spatial separation by means of electrostatic deflection, enabling their individual reactivity to be investigated¹. Recently, the conformer-specific polar cycloaddition of dibromobutadiene (DBB) with trapped propene ions has shown that both *gauche* and *s-trans* DBB conformers display capture-limited reaction rates². The reaction was found to occur through both a concerted and a stepwise reaction mechanism, despite the spatial rearrangement of atoms necessary in *s-trans* DBB for the latter to take place. These results were obtained by selectively aiming the molecular beam containing either one of the two conformers at a static target of propene ions embedded within a laser-cooled Coulomb crystal of calcium ions. In order to gain further control over the reaction partners, we also wish to select the conformational isomer of the ionic reactant.

Here, we demonstrate for the first time the sympathetic cooling of different conformational isomers within a Coulomb crystal, setting the scene for fully conformationally selected ion-molecule reaction studies. Following the successful isomer-selective ionisation and loading of the two *m*-aminostyrene conformers into Coulomb crystals of trapped and laser-cooled calcium ions, we now aim to investigate their isomer-specific reactivity.

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Cold ion chemistry within a Rydberg electron orbit: the effect of the molecular structure at the lowest collision energies

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In the study of ion-molecule reactions, Rydberg atoms and molecules can be used as a proxy for the ions. The Rydberg electron shields the ion-core-molecule reaction from stray electric fields, making it possible to reach collision energies (E_{coll}) near zero Kelvin [1,2]. Rydberg atoms can possess high induced electric dipole moments which allows for the manipulation of their translational motion by modest electric-field gradients using surface-electrode devices [3]. We use such a device to merge a beam of Rydberg helium atoms [He(n)] with a molecular supersonic beam. We vary the relative velocity between the reactants by changing the velocity of the He(n) atoms, and thereby the collision energy. With this method, we can reach $E_{\text{coll}}/k_{\text{B}}$ from ~ 40 K all the way down to ~ 100 mK in the moving centre-of-mass reference frame.

In this contribution, we present an overview of the results of experimental studies of reactions between the He⁺ ion and several small molecules. We find that for molecules with a strong electric dipole moment (such as CH₃F [4] and NH₃ [5]) the reaction yield is strongly enhanced near 0 K, and the reaction rate coefficients reach more than ten times the typically assumed Langevin rate coefficient. For molecules with no dipole moment (e.g. N₂ [6]), the opposite effect is observed, *i.e.*, a *suppression* of the reaction yield near 0 K. We also investigate the reactions with molecules which have only a small dipole moment and find that the E_{coll} -dependence of the reaction yields in this case are determined by the character of the electronic ground state. For example, we measure strikingly different reaction yields for NO (² Π character [7]) and CO (¹ Σ^+ character [8]). Our experimental results are interpreted with the aid of a rotationally-adiabatic-capture model [5,6] inspired by earlier theoretical treatments [9,10].

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Evaporation of polonium from LBE-cooled reactors

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Liquid metal-cooled reactors are among the proposed designs for Generation IV nuclear reactors. These designs are distinguished from the current generation by their enhanced safety, increased energy efficiency, and reduced costs. The use of liquid metals, like lead-bismuth eutectic (LBE), as a substitute for the traditional coolant water, significantly bolsters the safety of these reactors, particularly in accident scenarios. Moreover, this coolant enables reactors to be employed for transmutation purposes, presenting a viable promising solution to reduce nuclear waste and thus facilitate its storage in deep-geological repositories.

LBE showcases an array of favorable properties, such as superior thermal capabilities, low vapor pressure, a high boiling point, a notable capacity for γ -radiation shielding and transparency to fast neutrons. To employ it as a coolant, it is crucial to understand the distribution and behavior of radionuclides within LBE, as this is paramount for assessing the safety aspects of such systems. For precise predictions, a comprehensive understanding of radionuclide release from the coolant is vital.

The HORIZON2020 project PATRICIA extends previous research on radionuclide volatilization from LBE, a topic of significant relevance to the licensing and safety of future accelerator-driven systems. A particular focus is given to the volatility of polonium in the presence of other impurities, generated in or transferred to the liquid metal during operation. This research is of utmost importance, as polonium is one of the most radiotoxic and volatile radionuclides produced during reactor operation.

Here, we present the most recent findings from our volatilization studies of polonium from LBE. Representative samples were retrieved from the prototype high-power spallation target, MEGAPIE, irradiated in 2006 at the Swiss Spallation Neutron Source SINQ at the Paul Scherrer Institute. The chemical environment in the MEGAPIE target closely represents that encountered within a reactor coolant. Hence, samples from MEGAPIE provide, for the first time, valuable insights into potential interactions of polonium and other impurities during reactor operation. These investigations were conducted using the transpiration method, which measures the amount of a volatile substance evaporated from a condensed phase.

Thermosublimatographic study of Te volatile species formed over LBE melts.

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Liquid metal cooled fast reactors (LFRs) are an important part of fourth-generation nuclear reactor technology. These reactors can "burn-down" long-lived actinides, significantly reducing the time required for spent fuel storage. To assess the safety of reactors of new designs, it is important to understand which radionuclides in the coolant can transfer into a gas phase, in which species, and what their vapor pressures are.

This work focuses on tellurium. Its isotopes are formed in the spallation zone of an accelerator-driven LFR system cooled with a lead-bismuth eutectic (LBE). Additionally, it is produced in fuel pellets as a fission product. Tellurium is also a polonium homologue, for which experiments are limited due to its radiotoxicity. These factors make tellurium an important element to study.

This work describes the thermosublimatography approach for studying the release of tellurium from lead-bismuth eutectic melts. The approach involves evaporating melt components and condensing them in a negative temperature gradient of a thermochromatographic tube. The different tellurium species condense at different temperatures, and their characterization is based on thermochemical parameters such as sublimation enthalpy and entropy (ΔH_{subl} and ΔS_{subl}). This allows the identification of volatile tellurium species that form in vapors over LBE melts using their corresponding deposition temperatures.

The study found that at 800 °C in a quartz glass tube the majority of tellurium evaporated in the form of lead telluride, which condensed at around 600 °C, followed by a tellurium peak at 300 °C, which likely corresponds to a ditellurium volatile form. A minor portion of tellurium evaporates in the form of bismuth telluride ($T_{\text{dep}} = 500 \pm 24$ °C). An experiment carried out in a humid helium atmosphere demonstrated that the tellurium deposition site at 300 °C becomes predominant with a minor presence of bismuth telluride, while lead telluride was not observed.

Experiments performed in stainless steel columns did not show any deposition at 300 °C. In both dry and humid helium flows only the peak around 600 °C was observed. This may indicate that the formation of ditellurium species in quartz columns is due to surface interactions.

The deposition sites were additionally characterized using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX).

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