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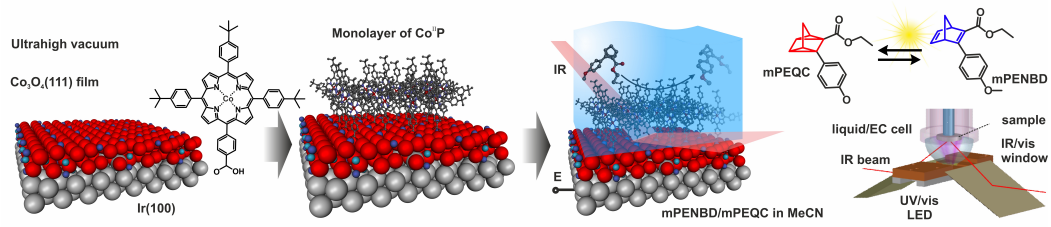
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# Catalysis for molecular solar thermal systems: From surface science to the solid/liquid interface

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In this presentation, we review recent work that aims at the development of tailored catalysts for controlled energy release in molecular solar thermal (MOST) systems. MOST systems utilize photoswitchable molecules to convert solar energy into chemical energy through simple unimolecular reactions. Thus, they provide a sustainable and efficient alternative for solar energy storage.[1] However, a persistent challenge lies in the effective triggering of the back-conversion reaction to release the stored energy on demand. In our studies, we combine surface science studies and in-situ methods at the solid/liquid interface to study catalytically, electrocatalytically and electrochemically triggered energy release strategies.[1-4]. For norbornadiene/quadricyclane based MOST systems, we demonstrate that Au interfaces are among the most active and selective catalysts known so far. Using photoelectrochemical infrared spectroscopy, we show that Au(111) surfaces can remain active over 1,000 storage cycles, retaining their structural integrity and losing less than 0.1% catalytic activity per cycle. More advanced "electro-switchable" catalysts allow us to control the rate of energy release via the applied electrode potential, enabling dynamic regulation of the energy release. We show that for Au-based catalysts, the energy release rate is indeed potential-dependent and can be adjusted over at least two orders of magnitude.[2]




Finally, we discuss the development of electroswitchable, noble metal-free hybrid catalysts based on immobilized organometallic complexes. Such hybrid catalysts combine the advantages of heterogeneous and homogeneous catalysis and provide systems that are easy to separate, highly selective and free of noble metals. For a functionalized Co(II) porphyrin anchored to an atomically defined cobalt oxide electrode, we demonstrate high catalytic activity and stability during repeated energy storage and release cycles, while the activity can be reversibly switched off by reduction to the Co(I) state.

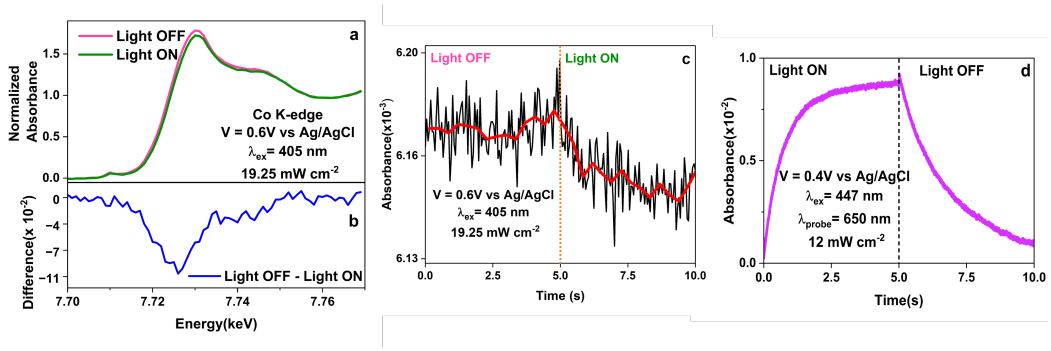
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# Time-Resolved X-ray Absorption Spectroscopy to Probe Cobalt Dynamics in Fe□O□-CoPi Photoanodes During Photoelectrochemical Oxygen Evolution

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**Hematite (α-Fe□O□)** is a promising photoanode for solar water splitting due to its chemical stability and suitable bandgap. However, its performance is limited by poor charge transport and sluggish oxygen evolution reaction (OER) kinetics. **Cobalt phosphate (CoPi)** has been used as a co-catalyst to improve Fe□O□ activity, but the exact role of cobalt remains unclear. Three main functions have been proposed: (1) acting as a hole accumulator to enhance charge separation [1], (2) directly participating in OER via Co(IV) intermediates at the cobalt oxyhydroxide surface [2], and (3) enhancing light absorption through its oxides, which absorb visible light and serve as catalytic sites [3].To investigate these roles, we employ **time-resolved X-ray absorption spectroscopy (XAS)** at the Co K-edge (Fig. 1a–c) to probe the electronic and structural dynamics of Fe□O□-CoPi photoanodes under operating conditions. A large set of XAS spectra was analyzed following established methods [4]. Additionally, we recorded optical absorption changes under light modulation (Fig. 1d) and correlated these with photocurrent measurements using the approach in [5] to assess hole accumulation. **Steady-state Co K-edge XAS** shows a shift toward higher cobalt oxidation states near OER potentials, indicating the formation of Co(III) species. Under modulated light, **time-resolved XAS difference spectra** suggests reversible oxidation from Co(II) to Co(III), consistent with hole accumulation (Fig. 1b). Kinetic data (Fig. 1c) for selected edge energies (7.70–7.77 keV) highlight hole recombination dynamics at Co sites. Comparing XAS and optical data clarifies the contribution of Co centers to hole accumulation. To further probe their catalytic role, time-resolved XAS was also performed at two applied potentials corresponding to redox peaks in the cyclic voltammogram.Our findings provide a deeper understanding of the cooperative interactions between Fe□O□ and CoPi, potentially guiding the rational design of more efficient photoelectrodes for solar-driven water splitting.




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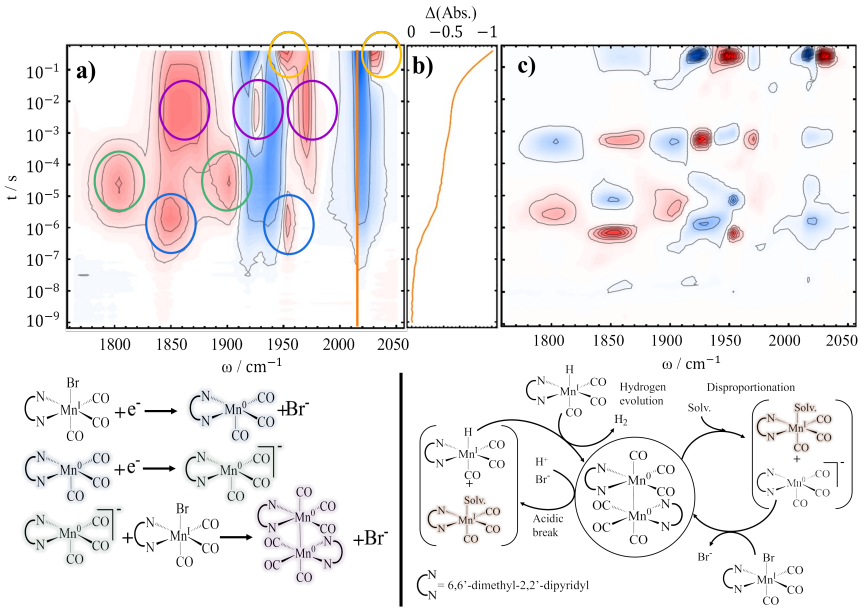
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# Transient IR spectroscopy - an ultimate tool for mechanistic studies - applied to catalytic $CO_2$ reduction by transition metal complexes

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Catalytic $CO_2$ reduction is a cornerstone of sustainable energy strategies. Since the 1980s, transition metal complexes have garnered significant attention for this application due to their multiple accessible redox states, which make them ideal platforms for multi-electron transfer processes. Extensive research has been devoted to elucidating catalytic mechanisms through electrochemical studies. However, such studies lack precise control over the number of electrons transferred and often fail to provide sufficient temporal resolution to capture key intermediates essential for a complete understanding of catalytic pathways. This information is crucial for designing more efficient catalysts suitable for large-scale, real world applications. To address these limitations, we have employed time-resolved infrared (TRIR) spectroscopy to investigate pathways towards catalytically active states of Mn-based transition metal complexes, which are used as pre-catalysts [1-3]. These complexes contain metal carbonyl ligands, allowing us to monitor electron density changes on the metal center through frequency shifts in the CO stretch region, which is characterized by a strong IR absorption cross-section.




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# In The Heart of CH: Spectroscopic Insights into Proper C−H Hydrogen Bonds

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Hydrogen bond (HB) is typically identified by two defining spectroscopic features: downfield shift of the bound proton in NMR, and a redshift in the X−H (X is a donor atom) stretching frequency compared to the free species. A red shift suggests an X−H bond elongation and is characteristic for classical O−H or N−H HB donors (proper HBs). On the other hand, in rare cases when C−H bonds engage in hydrogen bonding they contract and their frequency blue-shifts (improper HBs). But are all C−H hydrogen bonds improper?

Here, we present a comprehensive study of a model system featuring a hydrogen-bonding terminal alkyne proton, investigated using a broad array of spectroscopic techniques – including NMR, IR, and THz spectroscopy – complemented by ab initio molecular dynamics simulations, across more than 50 solvation environments. We observe that this molecule not only forms C−H hydrogen bonds with all electron-donating solvents (including C−H…π HBs with aromatic compounds) but also displays a strikingly prominent red-shift (exceeding 200 $cm^{-1}$) in the C−H stretching frequency upon hydrogen bonding, contrary to the typical blue-shifting improper C−H hydrogen bonds. By experimentally disentangling contributions of solvent-induced electric fields (Stark effect) from non-electrostatic (e.g., bond polarization, charge transfer components), we dissect key physical factors that determine this intermolecular interaction. Furthermore, we were able to directly interrogate its vibrational signature in the THz region – bending and stretching of H…A (A is an H-bond acceptor atom) bond – as well as establish details of its spatial arrangements. Remarkably, we also demonstrate that this system undergoes rapid spontaneous proton exchange in the absence of any acidic or basic catalysts similar to conventional O−H and N−H protic solvents.

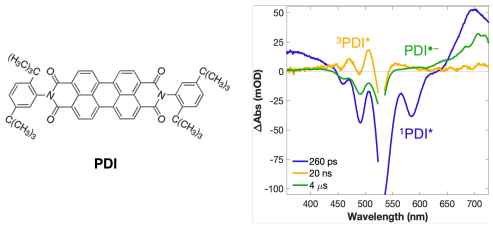
Our findings not only provide a rare spectroscopic insight into a strongly hydrogen-bonding C−H system but also highlight the intricate interplay of forces governing intermolecular C−H interactions, as well as invite a reassessment of common assumptions about hydrogen bonding.

# Excited Radical Ions in Organic Photocatalysis: A Photophysical Perspective

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The use of excited organic radical ions as photocatalysts for thermodynamically challenging synthetic reactions has been a topic of intense research in the past few years. Since the first report on the use of the excited radical anion of a perylene diimide derivative ($^2PDI^{\bullet-}$*) as a photocatalyst for the reduction of aryl halides in what came to be known as consecutive photoinduced electron transfer (conPET) mechanism,[1] many questions have been raised as the mechanism is constantly under scrutiny. This process is based on the excitation of PDI in the presence of a sacrificial electron donor, reductively quenching $^1PDI$* to generate its radical anion form. From there, a second photon excites $^2PDI^{\bullet-}$ and produces the species that is claimed to be the photocatalyst in the synthetic reaction. One of the main points of scrutiny in this mechanism is the very short lifetime of the $D_1$ excited state of $^2PDI^{\bullet-}$* (145 ps),[2] making it highly unlikely for this species to engage in any diffusion-driven electron transfer process with a substrate. Previous studies have attributed the observed photocatalytic activity to photoproducts of the decomposition of $^2PDI^{\bullet-}$*,[2] or even considered a pre-association between the excited radical anion and the substrate,[3] but a full description of the mechanism involving this elusive species is still missing. Our photophysical approach to this problem consists in photochemically generating the radical ion species and later probing its excited state properties via ultrafast optical absorption spectroscopy by using a double pump excitation strategy. Starting from a neutral ground state PDI derivative (Figure 1, left panel), we take an unusual pathway for the generation of the elusive $^2PDI^{\bullet-}$ in high concentration. We first induce the population of the excited triplet state of the dye ($^3PDI$*) by using halogenated electron donors (D1),[4] resulting in a high yield of $^3PDI$* that peaks at 20 ns with characteristic absorption bands at 470, 505, and 555 nm (Figure 1, right panel).




Once populated, $^3PDI$* can be efficiently quenched by a second electron donor (D2) to yield the free $^2PDI^{\bullet-}$ species whose maximal concentration is observed 4 µs after excitation as evidenced by its intense absorption features above 600 nm (Figure 1, right panel). From there, a second actinic pump can be used to selectively populate the excited state of the photogenerated radical anion, probing its ultrafast dynamics in the presence and absence of aryl halide substrates, therefore shining some light on the photocatalytic mechanism for the full photochemical scheme.

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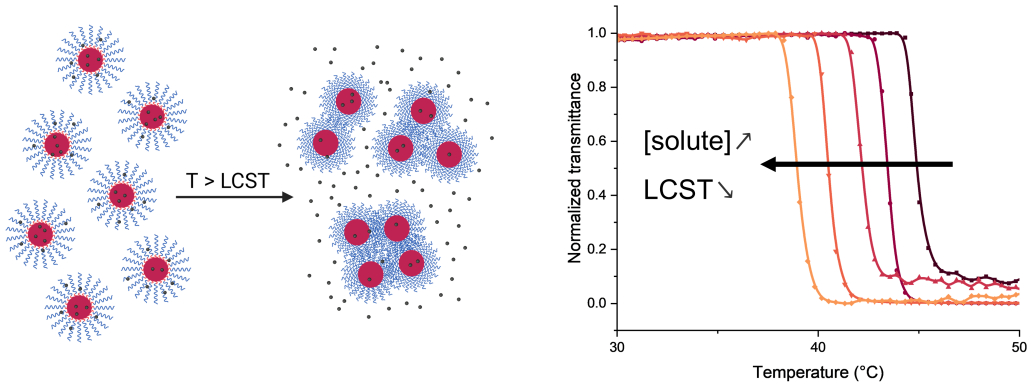
# Thermoresponsive polymers in biological environments: Impact of ions, small molecules and macromolecules on critical temperature

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Stimuli-responsive polymeric self-assemblies are promising drug delivery platforms offering on-demand release with dose and spatiotemporal control over delivery. Thermoresponsive polymers are widely explored as building blocks for such drug delivery systems. Polymers with a lower critical solution temperature (LCST) have hydrated polymer chains below the critical temperature (cloud point), but once heated beyond the LCST, they undergo entropy-driven hydrophobic collapse and aggregation.[1,2] However, their behavior is most often studied in pure water or PBS, which poorly mimics the complex biological environment. This overlooks the potential influence of biologically relevant ions, small molecules and macromolecules present at high concentrations *in vivo*.[3]

Herein, we systematically investigate how various ions, small molecules and macromolecules modulate the LCST of thermoresponsive polymers. We present the synthesis of novel thermoresponsive amphiphilic block copolymers based on poly(butyl acrylate) (PBA) and poly(di(ethylene glycol) methyl ether acrylate) (PDEGA). We synthesized a library of new PBA-*b*-PDEGA copolymers with varying end-groups and block lengths while maintaining precise control over polymer molecular weight and polydispersity. We tested the thermoresponsive behavior of PDEGA homopolymers and PBA-*b*-PDEGA copolymers in the presence of biologically relevant solutes. It was observed that ions, small molecules and macromolecules can significantly alter the critical temperature, reducing it up to 10 °C. This highlights the importance of testing thermoresponsive polymers in complex media to better predict their behavior in physiological environments.




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# Dynamic Studies of Au-doped $Ag_{29}$ Nanocluster

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Nuclear Magnetic Resonance (NMR) spectroscopy[1] is a powerful tool to study the structure and dynamics of all sorts of chemical compounds including atomically precise gold[2-3] and silver nanoclusters.[4,5] For example, some of us have recently studied the intracluster ligand dynamics for the $Ag_{25}$ and single atom doped $Ag_{24}Au$ nanoclusters using NMR spectroscopy.[4,5] In this poster presentation, I will discuss the structure and properties of $Ag_{29}(BDT)_{12}(TPP)_4$ and $Ag_{29-x}$ $Au_x$ $(BDT)_{12}(TPP)_4$ NCs (BDT = 1,3-benzenedithiol, TPP = Triphenyl phosphine).[6] I will focus explicitly on the dynamic properties of the metal core and the ligand shell using by NMR spectroscopy ($^1H$, $^{31}P$ and $^{109}Ag$) at different temperatures (Figure 1). The phosphine ligands are very dynamic at room temperature, desorbing from and re-adsorbing onto the cluster rapidly. At low temperatures the appearance of different $^{31}P$ NMR signals indicates a lowering of the cluster symmetry. Electronic structure calculations indicate that the origin of this symmetry breaking is a pseudo Jahn-Teller effect, which could influence the photophysical properties of these nanoclusters, such as photoinduced electron transfer (PET) processes.[7]

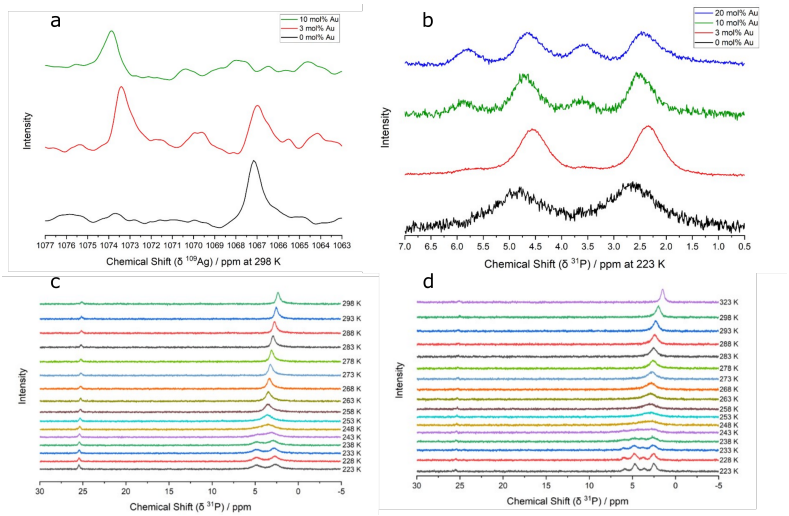



Figure 1. $^{109}Ag$ (a) and $^{31}P$ (b) NMR of Au doped (0 to 20%) and undoped $Ag_{29}$ nanoclusters at 298 (a) and 223 K (b). $^{31}P$ VT NMR of undoped $Ag_{29}$ (c) and 10 % Au doped $Ag_{29}$ (d) nanoclusters: 223 K to 298 K.

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# Ultrafast Fragment Screening with a Benchtop NMR Spectrometer and Fluorine NMR using Photoinduced Hyperpolarization

G. R. Stadler[1], M. Stricker[1]*, S. Rüdiger[1]*, T. F. Segawa[1]*, M. Bütikofer[2,1]*, V. Decker[3]*, S. Loss[3]*, B. Czarniecki[3]*, S. Rüdisser[1]*, A. D. Gossert[1]*, F. Torres[2,1]*, R. Riek[1]*

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Nuclear magnetic resonance (NMR) spectroscopy is a gold standard for fragment-based screening and drug design. Photochemically induced dynamic nuclear polarization (photo-CIDNP) enables to overcome sensitivity limitations of non-hyperpolarized NMR, enabling fragment screening at low micromolar concentrations in single-scan experiments of a few seconds. For $^{1}$H NMR, we established a 212-compound photo-CIDNP fragment library and screened it against cancer target Pin1 in a proof-of-concept study[1]. Combined with a fully automated NMR platform, the library can be screened in only half a day on a high-field (600 MHz) NMR spectrometer[2].

Benchtop NMR spectrometers provide a significantly cheaper, low-maintenance, cryogen-free platform for screening experiments since they operate with permanent low-field instead of superconducting high-field magnets[3]. We show that photo-CIDNP fragment screening can be performed on a benchtop NMR (80 MHz) with a measurement time of only 3 minutes per sample in a screening of 30 compounds against target Pin1 at 500 μM fragment and 10 μM protein[4]. Binding could still be observed at 50 μM fragment and 1 μM protein. Obtaining signal enhancements up to 3200-fold, the detection limit was pushed to 250 nM for a 3-minute experiment. Photo-CIDNP provides a higher binding contrast at low magnetic field due to higher ligand polarization. This reduces the amount of protein required for the screening.

Further optimization of protein consumption and screening throughput can be achieved with $^{19}$F photo-CIDNP. Fluorine NMR is the gold standard for NMR screenings at high field and allows screening in larger compound mixtures due to its broad chemical shift dispersion. Our first dedicated $^{19}$F photo-CIDNP library comprises 70 fragments that can be screened in mixtures of up to 10 compounds. The library was screened at 600 MHz against the two cancer targets Kras and Pin1 at 20 μM fragment and 10 μM protein in single-scan experiments, resulting in a total screening time of only 40 minutes in fully automated fashion[5]. Due to the high binding contrast of Fluorine photo-CIDNP, nanomolar protein concentrations can be used when screening in multi-scan experiments at high field. In the future, $^{19}$F-photo-CIDNP will also enable screenings in low micromolar fragment mixtures on the benchtop NMR in only a few hours.

In conclusion, photo-CIDNP presents a tremendous boost to NMR fragment screening by overcoming sensitivity and cost limitations. The use of benchtop NMR will facilitate the accessibility of NMR for a diverse life science community. Fluorine photo-CIDNP will allow to screen several thousand compounds per day by pooling fragments and will facilitate measurements in complex samples due to elimination of background signals. The high binding contrast will also enable photo-CIDNP NMR to tackle challenging screening targets like membrane proteins and intrinsically disordered proteins.

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# Analysis of the High Resolution Infrared Spectrum of Monodeutero-oxirane

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Monodeutero-oxirane (*c*-$C_2H_3DO$) is of fundamental interest in the context of the concept of isotopic chirality, which introduces a completely new isotope effect arising from the parity violating weak nuclear force [1−3]. It is also of astrophysical interest because of its recent detection towards IRAS 16293-2422B, based on our high resolution spectroscopic results [4, 5]. We have previously reported the analysis of GHz and THz *c*-$C_2H_3DO$ [4, 6] and *trans*-*c*-CHD-CHDO [7] spectra, and have provided a first high resolution analysis of the infrared spectra of the two *c*-$C_2H_3DO$ fundamentals at 896.025 $cm^{-1}$ and 837.36 $cm^{-1}$ [6]. Here we report new measurements of the infrared spectrum of improved newly synthesized samples of *c*-$C_2H_3DO$ (room temperature, Doppler-limited resolution), making possible the extension of our analysis towards the two lowest frequency fundamentals, as well as further stronger fundamentals, combination and overtone bands throughout the mid- to near-infrared range, using our Bruker IFS 125 HR ETH-SLS 2009 Prototype (MOPD=11.7m) [4, 8, 9]. We have used our improved molecular parameters for the ground state of *c*-$C_2H_3DO$ [6] to carry out the rovibrational analysis in several regions of interest and shall report on the current status of our analysis, including a discussion of the tetrad of the lowest four fundamentals with possible rovibrational interactions. The results will also be discussed as they pertain to ab initio calculations [6, 10] isotopic chirality, molecular parity violation, and the evolution of biomolecular homochirality [1, 9, 11]. We thank G. Matmon for his help with the experiments, F. Merkt for his continued support, and the SNF and the EU for financial support (COST COSY, ERC advanced grant).

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# Quantum-logic spectroscopy of forbidden rovibrational transitions in single molecular ions

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Ultranarrow, electric-dipole forbidden transitions between rovibrational states in molecules and molecular ions with expected natural linewidths on the Hz level present intriguing opportunities for the development of highly precise mid-infrared frequency standards and for the exploration of fundamental physical problems such as possible time variations of fundamental constants [1]. The molecular nitrogen ion $N_2^+$ has been proposed as an attractive system for precision molecular spectroscopy because, as an apolar diatomic ion, it features small systematic shifts and transitions with low sensitivity to magnetic fields in its electronic ground state [2,3]. However, the experimental detection of pure rovibrational transitions in systems like $N_2^+$ [4] and their precision spectroscopy is challenging on several levels. Besides the weak line strengths, which require highly sensitive detection methods, the positions of the lines are usually known only with substantial uncertainties based on spectroscopic constants determined through indirect methods. Moreover, theoretical predictions of the line strengths are also affected by significant uncertainties.

Here, we report the first observation of electric-quadrupole rovibrational transitions in single molecular ions using a highly sensitive quantum-logic detection protocol [5]. We studied individual hyperfine-Zeeman components of the $|v=1, N=2\rangle \leftarrow |v=0, N=0\rangle$ rovibrational transition in the $X^2\Sigma_g^+$ electronic ground state of single $N_2^+$ ions confined in a radiofrequency ion trap with a co-trapped $Ca^+$ ion used for sympathetic laser cooling and quantum-logic state detection. The transitions were directly driven by rapid adiabatic passage using a frequency-chirped laser pulse from a mid-infrared quantum cascade laser. This approach enabled the effective, fully reversible transfer of the rovibrational populations even without precise knowledge of the transition frequencies and at the same time allowed the recycling of the same single molecule in sequential spectroscopic experiments. Thus, line positions could be detected with a 2 MHz uncertainty limited by the frequency sweep of the laser pulse. The present approach represents a powerful methodology for coherently manipulating single molecules on ultranarrow spectroscopic transitions for precision measurements and quantum technologies applications. It can readily be adapted for other diatomic and polyatomic species, provided suitable laser sources for excitation and quantum-logic detection of transitions are available.

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# Beauty and complexity of calcium carbonate precipitation: optical microscopy and in situ Raman microspectroscopy characterization

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The formation of biogenic $CaCO_3$ has fascinated scientists over decades. A specific polymorph can be selected by living organisms and used to assemble complex morphology for biological functions, as seen in corals, coccoliths, bivalves and others. Many studies focus on how organic matter scaffolds or selects polymorphism, while others recreate in vitro these morphologies by using organic additives. Nevertheless, complex morphologies similar to biominerals can be obtained within inorganic matrix. These "biomorphs" trigger the question of how much we should trust complex morphology to be the trace of organic matter or even living organisms [1]. Crystal nucleation is a critical remaining question in $CaCO_3$ crystallization to understand its crystal growth and design. Several crystallization pathways, classical and non-classical nucleation [2], have been proposed, but no consensus has been reached due to the complexity of the system. Its low solubility and sensitivity to pH can lead to different observations and pathways. Furthermore, precipitation protocols and analytical techniques vary widely across literature. In situ Transmission Electron Microscopy (TEM) provides nano-scale details of crystal formation, though with a limited field of view. Spectroscopic means (FT-IR, Raman, SAXS, WAXS, neutron scattering etc.) could capture the signatures of various precipitation stages, but a spectrum is typically an average of ensemble. Surprisingly, bright field optical microscopy is not used for key insights, despite being well-suited to bridging the length scale gap between TEM and ensemble spectroscopy approaches. This may be due to the limited spatial resolution and difficulty in assigning polymorphs without a characterization technique. In our study, we combined optical microscopy with in *situ* Raman microspectroscopy as a mesoscale technique [3]. Using this method, we conducted unstirred precipitation experiments over a wide range of supersaturations, varying initial pH and concentrations of $CaCl_2$ and $Na_2CO_3$, and observed the evolution of mixed solutions up to 24 hours. This allowed us to obtain a landscape of crystallization processes and categorize precipitates formed at specific supersaturations. At high supersaturation, a gel formed whilst at low supersaturation, calcite crystals appeared first, followed by amorphous calcium carbonate (ACC). Morphologies reported in literature with additives, such as calcitic spherulites, aragonite and biomorphic vaterite, were observed without additives in our study. We highlight the coexistence, evolution of phases, and formation of a gel, as a metastable precursor to ACC. Its Raman signature and morphology differ from ACC, while the inversion test supports its classification as a gel. Our contribution will emphasize the importance of studying the system at the mesoscale scale as well as that of initial conditions so that the debates can converge in near future [3].

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# Using Spectro-Electrochemistry to Study Structure-Property Relationships in Organic Mixed Ionic-Electronic Conductors

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Organic mixed ionic-electronic conductors (OMIECs) are materials used in fields such as bioelectronics, ion-sensors and neuromorphic computing. Thanks to their unique ability to translate between ionic and electronic signals, OMIECs are well suited for directly interfacing biological systems with electronics [1]. One of the big advantages of such organic systems, often conjugated polymers, is the large variability in chemical design. While this allows for great tunability of material properties, it also makes OMIECs very complex systems that are hard to fully understand. In order to use the full potential of OMIECs and thus drive forward the development of applications, it is therefore needed to find ways to systematically study them.

Since the ionic-electronic translation involves ion migration, redox processes linked to electronic transitions in π-systems and the thereby incurred modulation of electrical conductivity, many employed measurement techniques involve electrochemistry and spectroscopy [1]. We use a home-built tabletop setup to combine vis-NIR spectroscopy and electrochemistry with device characterization methods. Through deconvolution of the spectral data and comparing to the electrochemical data we access information about the chemical species present in the material, which can be linked to the modulation of device properties. Like this, we are able to systematically characterize various OMIECs, eventually making the development of better materials more efficient.

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# Near-Unity Single-Photon Chiral Transduction from a Single Gold Helicoid to a Perovskite Quantum Dot

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Precise manipulation of light-matter interactions is essential for the development of quantum technologies. The Purcell effect, a key mechanism for enhancing the efficiency of quantum light emission[1], has been instrumental in generating photons with high indistinguishability, thereby pushing forward applications in photonic quantum computing[2]. A promising frontier in this field lies in the use of chiral photon modes to achieve quantum-level control over light polarization[3]. Using a single perovskite quantum dot (PQD) as a point emitter enables direct probing of the precisely engineered nanoscale optical helicity (*h*) of the gold helicoid, overcoming the averaging effects typically imposed by the optical diffraction limit. Serving as a localized signal transducer, the excitons in the PQD couple strongly with the chiral electromagnetic hot spots of the helicoid structure. This interaction leads to the emission of single photons carrying spin angular momentum (SAM), with their generation rate deterministically controlled by the helicoid's handedness-selective excitation. By fine-tuning the near-field coupling and the excitonic and plasmonic spectral resonances, we achieved single-photon chirality as high as 80% and an excitation dissymmetry factor reaching 90%, achieving a full optical chirality (excitation-emission) with a near-unity efficiency. These results are accompanied by rapid radiative decay (~300 ps) and a Purcell enhancement factor of approximately 3. Through numerical simulations of the electromagnetic field, we also demonstrate dual-mode circular dichroism behavior, where the chirality of excitation can be modulated via the excitation wavelength. This highly efficient chiral transduction paves the way for novel quantum light sources, with potential applications spanning integrated quantum photonic circuits and nanoscale chiroptical sensors.

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# Towards on-chip chemical computing: The oscillating Belousov-Zhabotinsky reaction in silicon micro-chips

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The pursuit of more energy-efficient computational architectures is an ongoing research topic. The necessity of such platforms is even enhanced by recent developments in artificial intelligence (AI) and the subsequent increase in power consumption. Brain-inspired neuromorphic computing has emerged as a promising solution to tackle the computation bottlenecks in AI applications. Most approaches rely on well understood CMOS (complementary metal-oxide semiconductor) technology [1]. Our approach is to rethink the current paradigm of a neuromorphic computer and use an oscillating chemical reaction network (CRN), the Belousov-Zhabotinsky (BZ) reaction [2], to emulate neurons.

This reaction features autocatalytic chemical reactions which lead to periodic spikes in activator concentration, causing an oscillatory chemical reaction. The spikes and their self-amplified propagation through the BZ medium resemble spiking and signal transport in neurons. Here we use these properties to enable signal transmission and thresholding in computing devices.

To approach energy efficient computation, a miniaturization of the reaction volumes is required. We use a compartmentalization of the oscillating solution into reactors on a Si chip (volume ~5 pL) interconnected with nano-channels (cross-section 0.75 $\mu m^2$). This enables us to encode the connectivity of chemical neurons by fabrication. Signals propagate between reactors by reaction-diffusion waves which may/may not cause a spike (phase-shift of the oscillation) in a connected reactor depending on the channel cross-sections, number of arriving signals, geometric pattern of the system and state of the local oscillation. For fluorescent imaging and to reset the reactors in-situ we use a 490 nm LED for global illumination, thus photo-chemically producing the inhibitor and quenching the oscillations.

A first proof of concept is depicted in the Figure in the form of freely oscillating chemical reactors. Our work is a first step towards energy efficient chemical computers fully operated by molecules. Information can be en- and decoded in the rate or the phase of designated reactors and the pattern.

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# Mechanistic Insights into SCN□ as an IR Probe in the Homogeneous Catalyst Ni(bpet)(SCN)□ for CO□ Reduction

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In the field of catalytic organometallic chemistry, complexes such as Ni(bpet)X□ [1] have shown promising activity as reductants for CO□ and H□. However, mechanistic studies often overlook the important role of labile ligands, despite their potential to significantly influence reactivity and the nature of catalytic intermediates. To address this gap, we investigated an analogue featuring SCN□ ligands [2] in place of MeCN, selected for their enhanced infrared absorption properties.

Time-resolved infrared spectroscopy was employed to probe short-lived intermediates and dynamic processes occurring during catalysis. Notably, we emphasize the importance of thoroughly characterizing the initial state of the catalyst upon dissolution—an aspect that remains underreported in much of the existing literature. Ligand lability and solvent coordination strongly influence solution speciation, which in turn directly affects the interpretation of transient spectroscopic data. Given the potential for side reactions to impact the photoreduction behavior of Ni(II), we employed a combination of FTIR, UV-vis, and electrochemical measurements (see Fig.1) to study the steady-state species.

To further explore whether hydride formation is a general intermediate in H□ evolution from CO□ reduction, or instead a pathway-specific feature, we introduced the non-nucleophilic base di-tert-butylpyridine. This approach helped suppress competing reactions while preserving the core integrity of the catalytic system. (see Fig.2)

Taken together, our findings highlight the critical importance of comprehensive initial-state characterization for the accurate interpretation of time-resolved studies and for distinguishing between parallel pathways in complex catalytic systems.

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# Surface hopping for open-quantum systems

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We propose an extension to the mapping approach to surface hopping (MASH)[1], integrating the open quantum dynamics of secular Redfield theory with the semi-classical framework of surface hopping. Unlike conventional trajectory-based surface hopping methods that solve the time-dependent Schrödinger equation along each trajectory, our approach employs stochastic quantum dynamics governed by a Lindblad master equation derived from secular Redfield theory. This enables the simulation of Markovian quantum baths—both bosonic and fermionic—coupled to two-level quantum-classical systems. Applications to the spin-boson model and to molecules interacting with metal surfaces show excellent agreement with exact quantum dynamics.

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# Characterizing volatile Po species formed in liquid-metal-cooled nuclear reactors

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With nuclear power being one of the main pillars of future low carbon energy supply, innovative nuclear technologies such as the Gen IV type nuclear reactors have received growing attention. The MYRRHA reactor (Multi-purpose hYbrid Research Reactor for High-tech Applications) is a so-called accelerator driven system (ADS) with a subcritical core where additionally needed neutrons are generated by nuclear spallation. In MYRRHA, lead-bismuth eutectic (LBE) alloy is used as primary coolant as well as spallation target material. Through proton-induced nuclear reactions, highly radiotoxic $^{208\text{-}210}$Po will form during reactor operation in non-negligible amounts. Therefore, evaluating the potential Po release under various conditions is needed.

Previous work on this topic has shown that water and oxygen impurities in the carrier gas as well as the formation of oxide layers on LBE have a large influence on the formation and release of volatile Po species from LBE. Hence, we aim to conduct experiments on the kinetics of Po release as a function of carefully controlled water and oxygen concentration in the carrier gas as well as $O_2$ in liquid LBE.

For this purpose, we present here the development of a gas purification loop for inert gases to remove all residual impurities down to ppb levels, to then selectively increase different contaminants (i.e., predominantly $H_2O$ and $O_2$) to the targeted concentrations. The thus prepared carrier gas will be used to perform transpiration experiments on irradiated LBE and to evaluate the influence of different $H_2O$ and $O_2$ concentrations on the release behavior of Po from liquid LBE. At the same time, the oxygen concentration in the liquid metal alloy will be monitored *in situ* by a dedicated electrochemical oxygen sensor that was developed for this purpose at SCK CEN in Belgium.

# A high-purity para-$H_2$ source for the study of cold ion-molecule chemistry

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The ability to control the translational motion of Rydberg atoms and molecules by Rydberg-Stark deceleration has enabled the study of several ion-molecule reactions at a broad range of low collision energies between $k_B \cdot 0$ K and $k_B \cdot 50$ K [1]. In these studies, a molecule or atom in a Rydberg state of large principal quantum number, that is $n \approx 30$, is employed in place of the ion. The Rydberg electron takes a "spectator role" [2] and at the same time shields the ion from stray electric fields, which allows one to precisely control the collision energies. An ion-molecule reaction of special interest is the para-$H_2^+(v^+ = 0, N^+ = 0)$ + para-$H_2(v = 0, N = 0) \rightarrow H_3^+ + H$ reaction because it is a good candidate to study quantum effects caused by the wave character of the collision system at low temperatures. In particular, owing to its low reduced mass and strong exothermicity, it is an ideal reaction to verify the theoretical prediction of a twofold reaction-rate enhancement over the classical Langevin rate, arising from s-wave scattering in the pure charge–induced-dipole interaction potential of the collision partners [3]. This reaction-rate enhancement cannot be explained by classical capture models and is a signature of "quantum capture". For the effects of quantum capture to become apparent in the $H_2^+ + H_2 \rightarrow H_3^+ + H$ reaction, the (para-)$H_2$ molecules need to be prepared in their rotational ground states where $N = 0$ because all states where $N \geq 1$ give rise to additional charge-quadrupole interactions.

The observation of quantum capture in an ion-molecule reaction was the main objective of a recent experimental study of the $H_2^+ + H_2 \rightarrow H_3^+ + H$ reaction by Höveler *et al.* [4]. However, an observation of the full twofold rate enhancement was hampered by the collision-energy resolution of their experiment and by the para:ortho ratio of about 80 %:20 % of their para-$H_2$ source. Here, we present a high-purity and continuous-flow para-$H_2$ source and its spectroscopic characterisation by laser-induced-fluorescence spectroscopy of $B \leftarrow X$ transitions in $H_2$ using a vacuum-ultraviolet laser system. Our characterisation demonstrates that we can realise a molecular beam of $H_2$ in which the para-$H_2$ population fraction is larger than 99 %. Moreover, by cooling the reservoir of the $H_2$ valve to about 55 K, the population fractions in $N \geq 2$ rotational levels are suppressed to less than 1 %. This paves the way for a quantitative study of quantum capture in an ion-molecule reaction.

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# Mind the spectral gap: Extending ultrafast spectroscopy to the deep ultraviolet with stretched hollow core fiber technology

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Ultrafast spectroscopy in the ultraviolet (UV) is an attractive tool to probe the dynamics of (bio)molecules via important UV-chromophores, such as peptide bonds, amino acids, nucleotides, and many organic ligands [1]. However, despite recent progress in photonic technology [2], the deep-UV region below 300 nm has remained largely unexplored, with only few reports of broadband ultrafast spectroscopy setups and studies in this spectral region [3].

To extend the spectral range of ultrafast spectroscopy, we now employ a novel source of intense, broadband deep-UV pulses: soliton dynamics in gas-filled hollow capillary fibers (HCF) [4,5]. Here we present the implementation of a HCF-based transient absorption setup with broadband coverage of the deep-UV window (200-450 nm) to study photochemical dynamics in solution. We demonstrate the capabilities of our novel approach with benchmark experiments on well-studied Fe(II)-complexes that display ultrafast dynamics encoded in the deep-UV. The results highlight the unique potential of HCF technology to extend ultrafast molecular spectroscopy to the deep-UV and expand its scope to study (bio)molecular dynamics in solution.

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# Surface Functionalities, Speciation and Strength of Brønsted Acid Sites Revealed by a Combined $^{31}P$–$^{109}Ag$ Molecular NMR Probe

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Understanding the atomic structure, speciation, and reactivity of surface sites is critical for establishing structure–activity relationships in heterogeneous catalysis.[1] A longstanding objective in this field is to identify the type and strength of Brønsted acid sites (BAS), which often govern the overall reactivity of catalysts and specific support effects, including bifunctionality. Among analytical methods, probe molecule-based solid-state NMR (SSNMR) spectroscopy stands out for its ability to characterize both the nature and acid strength of BAS.[2] While small organic molecules have traditionally served as probes, organometallic complexes (e.g. N-Heterocyclic Carbene (NHC) group 11 metal complexes),[3] have recently emerged as advanced alternatives, reacting (protonolysis) with surface functionalities (e.g. OH groups) and enabling their metal centers to act as spectroscopic and microscopic markers. However, acquiring corresponding informative metal NMR signatures remains challenging due to low sensitivity, which results in limited resolution.

Here, we utilized a readily accessible probe molecule containing naturally abundant $^{109}Ag(I)$ and $^{31}P$, to selectively investigate surface BAS across various functional materials. Leveraging the Dynamic Nuclear Polarization (DNP) enhanced techniques and advanced NMR methodology, the sensitivity of $^{1}$□□Ag SSNMR measurements is significantly boosted, while simultaneously enabling direct correlation with $^{31}P$ NMR signatures through chemical bonding, thereby establishing a sensitive dual-probe approach for enhanced resolution of surface structures and properties. Notably, we demonstrated that these complementary NMR signatures serve as effective indicators of acidity, as supported by Density Functional Theory (DFT) calculations. Overall, this approach provides molecular-level characterization of surface sites and quantitative assessment of surface acidity, advancing our understanding of surface chemistry.

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# Optical Electrometer: Measuring the charge of a single optically-trapped particle

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## Introduction

Aerosol particles influence climate and atmospheric chemistry through light scattering, cloud formation and surface reactions [1]. Their electric charge, originating from ion-induced nucleation [2], contact electrification [3], or electrospray, can significantly affect their growth and reactivity [4]. However, precise charge measurements at the single-particle level remain limited. Electrodynamic Balances (EDBs) are restricted to charge measurements of highly charged particles ($q > 2 \cdot 10^{\square}$ e) [5].

## Methods

We developed a novel optical electrometer, which uses counter-propagating optical tweezers to immobilize a single particle in air and an oscillating electric field to induce harmonic oscillations in the particle position. The particle's motion was tracked via lock-in detection and modeled as a damped harmonic oscillator. Broadband light scattering (BLS) spectroscopy [7] was used to determine particle size, enabling simultaneous mass and charge determination.

## Results

Electric field simulations and analytical models confirmed a field homogeneity within 2 % in the trapping region. The electrometer allows charge measurements from ~ ± 20 e to ~ ± $10^4$ e. Charge measurements across voltages from 10 to 80 V yielded consistent results with uncertainties below 2 %. The method allows precise determination of both mass and charge, with improved accuracy at higher voltages due to enhanced signal-to-noise ratios.

## Conclusion and Outlook

This optical electrometer enables accurate measurements of the electric charge state of a single particle in an optical trap. Future work will explore charge dynamics under UV light and varying humidity and integrate complementary techniques such as Raman and photoacoustic spectroscopy [6].

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**Sampling rare non-adiabatic reactions with Transition Path Sampling and MASH.**

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Rare events are ubiquitous phenomena in nature [1]. Prototypes of these events can be identified in a plethora of chemical reactions where the transition takes an exponentially long time to occur compared to the more frequent thermal fluctuations of the system. Precisely due to the disparity in timescales, it is exceptionally difficult to capture such reactions with (plain-) molecular dynamics (MD) methods. Indeed, computational approaches under the term enhanced sampling methods, such as Transition path sampling (TPS) [2] and Umbrella sampling [3], were developed to facilitate MD in the study of rare events. Here, TPS, in contrast to Umbrella Sampling, is particularly praised for its ability to remain system-agnostic while it can considerably increase the rate of sampling transitions. Despite its simplicity of approach, it has proven difficult to incorporate the TPS approach with the famous Surface Hopping (SH) method to simulate non-adiabatic dynamics without any modification to the latter's equations of motion [4].

On the other hand, Mapping Approach to Surface Hopping (MASH) [5] was recently developed to improve on the SH's inconsistencies between the electronic population and active surface, and to remedy its violation of microscopic reversibility. Given that the latter is a crucial requirement for the application of the TPS approach, MASH provides an ideal avenue to apply and test the advantage of incorporating TPS for the study of non-adiabatic rare chemical reactions, e.g, photoexcitation. I will present our application of TPS with MASH to the N-H dissociation reaction of $CH_3NH_2$, and demonstrate our results in the poster.

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**Investigating phase transition of chiral liquids under high pressure - study of α and β pinene**

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The aim of this research is to elucidate the influence of chirality during phase transition processes and obtain a deeper understanding of the molecular dynamics under extreme conditions such high pressure. By using a Diamond Anvil Cell (DAC), a pressure regime of tens of GPa can be achieved easily, allowing the exploration of a large range of pressure. Chirality is a fundamental geometrical property exhibited in some molecular systems which significantly influences chemical behaviour, biological activity and material properties [1,2]. Small chiral molecules, such as pinene, might be considered as key models for studying the role of chirality during phase-transition phenomena. For this research, the two enantiomers of α-pinene and β-pinene were selected as ideal candidates. These chemical systems are liquid at standard atmospheric temperature and pressure. Phase-transition sensitive techniques, such as Raman scattering, crossed-polarized light microscopy, and X-ray powder diffraction, were used to monitor the behaviour of enantiopure and racemic liquids before and after the pressure induced phase-transition. Quantum chemistry simulations were conducted to support the experimental findings. The investigated mixtures of pinene show drastic differences during pressure-induces phase transition processes depending on their enantiomeric composition. The process of crystallization was observed for enantiopure liquids, whereas racemic mixtures resulted in liquid to amorphous solid phase-transitions. The obtained results show the influence of chirality during phase-transition processes, discriminating between obtaining a crystalline or amorphous phase. The absence of hydrogen bonds between pinene molecules results in only weak electrostatic interactions such as Keesom forces, and the comparable energies between enantiopure and racemic dimers open the discussion for geometrical frustrated driven phase-transitions. These results show an intricate picture of the complex relationships between the geometrical properties of chiral molecules and their behaviour when subjected to high-pressure.

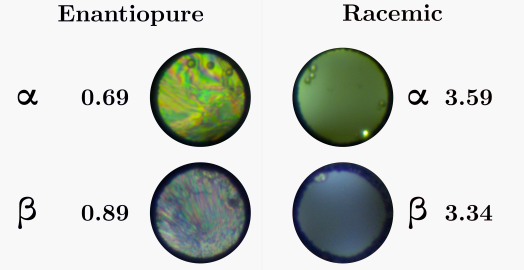



Figure 1: Crossed-polarized light microscopy images of enantiopure and racemic mixtures of α and β-pinene. Enantiopure liquids show the appearance of birefringence after crystallizations (0.69 GPa for α and 0.89 GPa for β). Racemic mixtures of α and β-pinene do not show birefringence even at ΔP=3.59 GPa for α and ΔP=3.34 GPa for β.

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# Acceleration of low temperature water nucleation in the presence of $CO_2$

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In planetary atmospheres like those of Earth and Mars, clouds often form from species present in only small amounts. We have recently shown, that intermolecular interactions with a second gas species may facilitate gas-phase nucleation [1][2]. Here, we demonstrate this behaviour for the binary $CO_2$ / $H_2O$ system at temperatures of 57 K and 75 K. The nucleation behaviour was measured for different $CO_2$ / $H_2O$ concentrations in a carrier gas in the uniform post-nozzle flow of a de Laval nozzle. Our results indicate, that the addition of $CO_2$ significantly increases the nucleation rate of water.

In our experiment [1] , a gas mixture containing $H_2O$, $CO_2$ and carrier gas was expanded through a Laval nozzle. The pressure in the vacuum chamber was adjusted to match the gas pressure in the uniform post-nozzle flow, ensuring constant temperature, pressure, and supersaturation in the post-nozzle flow. The post-nozzle flow acts as a wall-less flow reactor, allowing us to control the nucleation time by adjusting the nozzle position relative to the detection system. The clusters that form in the post-nozzle flow were softly ionized using single-photon ionization with a photon energy close to the lowest ionization threshold and detected with a homebuilt time-of-flight mass spectrometer.

Our setup provides information about the cluster composition and absolute cluster concentrations, allowing us to apply a kinetic model for nucleation and the initial stages of cluster growth. The model suggests that nucleation is accelerated through the formation of short-lived, transient heteromolecular $H_2O$ – $CO_2$ dimers, which we refer to as a chaperone cluster.

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# Determining the Gas-Phase Förster Radius Using the Constrained Peptide Linaclotide

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Förster Resonance Energy Transfer (FRET) is a cutting-edge technique used to explore the structures of labeled biomolecules. By measuring fluorescence lifetimes, the distances between fluorescence donors and quenchers in biomolecules can be accurately determined. Recently, FRET was integrated with mass spectrometry, enabling gas-phase FRET experiments on isolated biomolecules generated by electrospray ionization.[1] However, converting the measured lifetimes into precise distances is challenging because the Förster radius $R_0$, a crucial linking factor, is not easily determined in the gas phase (1). Current estimates of $R_0$, based on its value in aqueous solution but adjusted for the vacuum environment of a mass spectrometer, are likely inaccurate. The aim of this work is to precisely determine the gas-phase Förster radius $R_0$ using highly constrained peptides. This advancement is essential for a deeper understanding of biomolecular structures and interactions, with far-reaching implications.

To achieve this challenging goal, a dual experimental and theoretical approach was employed. Experimentally, the highly constrained cyclic peptide linaclotide was labeled with a fluorescence donor, while the transition metal ion $Cu^{2+}$ was used as quencher. After liquid chromatographic purification and confirmation of the labeling sites with tandem mass spectrometry, FRET experiments were conducted to measure quenched and non-quenched fluorescence lifetimes. Additionally, quantum chemical calculations were performed to model the peptide structures and determine the donor-quencher distances. This computational process involved sampling different conformations using empirical methods, followed by density functional theory calculations to obtain accurate energy values to identify the most stable structure.

By integrating experimental quenched and non-quenched fluorescence lifetimes ($t_{DA}$ and $t_D$) and computed donor-quencher distances ($r_{DA}$) into the Förster equation (1), the gas-phase Förster radius $R_0$ can be determined. This process will be repeated for various cyclic peptides to assess the consistency of the Förster radius across various peptides and its dependence on the peptides' microenvironment. The expected outcome of this research is a precise determination of the gas-phase $R_0$ value, which will significantly advance the field of gas-phase FRET. First results suggest that the value of $R_0$ for the donor-quencher pair carboxy-rhodamine 6G and $Cu^{2+}$ is in the range of 7–12 Å, contrasting previously approximations based on the solution-phase $R_0$ (26.0 and 19.5 Å, depending on the $Cu^{2+}$ binding motif).[2] Exact determination of $R_0$ will enable more accurate structural analyses of biomolecules, paving the way for the development of innovative therapeutic agents and diagnostic tools.

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# Exploring Transport Mechanisms of In-plane Oriented Organic Semiconductors

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Organic mixed ionic-electronic conductors (OMIECs) show promising advantages such as their versatile processing conditions, synthetic tuneability and their flexible nature. Additionally, the ability of this materials to enable both ionic and electronic transport makes it well-suited to interface biology and electronic devices. [1] So far, the field of bioelectronics has largely focused on device fabrication and performance. However, a comprehensive understanding of OMIEC charge transport mechanisms is still lacking. The electronic charge transport primarily occurs along the π-conjugated backbone, while ions penetrate the bulk material, interacting with the polymer matrix. [2,3]

In this study we investigate PBTTT-$^{8}$O films the PBTTT backbone shows a very high charge-carrier mobility, the insertion of an ether group onto the side chains enables easier ion uptake, which is further improving the performance. [4] The polymer films were oriented by high-temperature rubbing to gain a deeper insight into the fundamental processes of both ionic and electronic transport. Combining electrochemical and chemical doping with in-situ terahertz spectroscopy, spectro-electrochemistry, and chronoamperometry, we investigate the materials oxidation behavior and intrinsic charge transport properties. Terahertz spectroscopy measures the intrinsic nanoscale conductivity and gives access to short-range mobility, which is not affected by grain boundaries or electrodes.

Our findings reveal high conductivities exceeding 1000 S/cm for electrochemically doped PBTTT-$^{8}$O films, and over 2000 S/cm for chemically doped films. In addition, using temperature-dependent THz measurements, we unravel the transport mechanism in oriented PBTTT-$^{8}$O, which follows a metal-like transport behavior instead of thermally activated hopping behavior seen in lower conductive polymers, confirming the significant effect of in-plane orientation on OMIEC charge transport.

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**Stimuli-Responsive Prototissues via DNA-Mediated Self-Assembly of Polymer Giant Unilamellar Vesicles**

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Gaining insight into the complex functions of tissues, which involve communicating cell types, by utilizing materials that mimic the properties of real tissue, is an important step in developing advanced biomedical applications. However, building 3D networks of interconnected protocells capable of chemical information processing and collective output remains a challenge. Herein, the construction of a prototissue based on the DNA-mediated assembly of polymeric giant unilamellar vesicles (pGUVs) are presented with differential sensitivity, forming a multicompartment communicating system. One set of pGUVs hosts microgels as artificial $Mg^{2+}$ storage organelles, which can be triggered to release their $Mg^{2+}$ by pH changes in the environment. The downstream linked set of protocells contains a $Mg^{2+}$ sensitive dye that responds to the $Mg^{2+}$ signal. The density of complementary DNA strands on the surface of the respective pGUVs determines not only the size of the pGUV ensemble but also modulates sensitivity toward magnesium. Moreover, $Mg^{2+}$ signaling to downstream protocells loaded with monomeric actin induces the in situ formation of an artificial cytoskeleton. Overall, through the clustering of protocells hosting distinct artificial organelles with controlled architecture, such unique prototissues that mimic intratissue communication generate new prospects in using advanced functional materials for multi-step catalysis and biomedicine.

**Controlling spin lifetimes in lead-free halide perovskite semiconductors**

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Control over the electron's spin (up or down) within the field of spintronics introduces an additional degree of freedom compared to traditional electronics, opening up new opportunities for energy-efficient quantum information technologies. Such applications require a spin-polarized population on timescales ranging from nano- to microseconds. Recent studies on solution-processable lead-halide perovskite (HPs) semiconductors demonstrated spin lifetimes on the order of a few picoseconds at room temperature, too short for most spintronics applications, with spin depolarization mechanisms remaining poorly understood. Moreover, the use of lead-based materials is widely forbidden due to toxicity concerns.

In this talk, I will discuss how the substitution of lead with lighter, less toxic elements with reduced spin-orbit coupling may be used to manipulate and potentially increase the spin lifetime in HP semiconductors using transient polarization-resolved optical spectroscopy. I will discuss the challenges faced when developing lead-free HP thin layers and demonstrate the influence of the crystal composition on the observed spin lifetime.

# Hydrogen Bond Cooperativity in Binary Liquids: A Spectroscopic and Molecular Dynamics Study of Formamide Mixtures

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Hydrogen bonds are invisible threads that organize the world of molecules, determining the structure and function of complex systems. The complex nature of hydrogen bond gives rise to its non-pairwise additivity, or , in other words, cooperativity.[1] Hydrogen bond cooperativity is a key phenomenon in many natural and artificial systems, especially in structures where molecules form complex ordered architectures. The well known examples are various protein secondary structures: alpha helix, beta sheets and polyproline II helix etc. Hydrogen bond cooperativity also plays a role in the formation of amyloids, the proteins suspected as responsible for Alzheimer disease. The strength and flexibility of natural silk are attributed to hydrogen bond cooperativity of beta sheets in nanocrystalline domains. Quantitative characterization of cooperativity will not only lead to further understanding of its underlaying mechanism in biological systems but also possibly enables one to tune materials with desired properties via hydrogen bond cooperativity. The signature of cooperativity has been mostly reported by computational works. On the other hand, experimental characterization has been limited to gas phase vibrational spectroscopy or nuclear magnetic resonance (NMR) spectroscopy. Analyzing and extracting information about hydrogen bond cooperativity from bulk vibrational spectra from liquid at ambient environment is rather challenging. A few reports trying to address this issue adopted a technique called excess infrared (IR) spectroscopy to probe these effects more selectively

Here, we experimentally characterized the hydrogen bond cooperativity of formamide and how it alters when it is mixed with other liquids (methanol, acetone and water) by means of Raman spectroscopy. Formamide is well known for its complex and cooperative hydrogen bond network[2]. It is structurally similar to animo acids, and therefore it can be regarded as a simplified yet important model for more complex biochemical systems. The high frequency region of Raman spectrum allows us to track local changes in vibration frequency due to hydrogen bonds. In addition, the low-frequency modes (<300 $cm^{-1}$) provides insight into collective vibrations of hydrogen bonding networks. Using these spectral ranges, we qualitatively proposed possible structures of the hydrogen bonding network in the studied binary liquids and how formamide networks are altered by mixing with another liquid. To evaluate the proposed structures, molecular dynamics (MD) simulations of liquids were performed. By analyzing trajectories, the most common hydrogen bond pairs and motifs for each system were obtained. The results establish fundamental knowledge of how Raman spectrum at both high and low frequency regions can be interpreted for understanding the solvent structures. By combining Raman spectra and MD simulation, the interpretation of solvent networks was further reinforced. The implication of this study is important for the fundamental understanding of intermolecular bonds and their role in physicochemical processes.

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# Disentangling the Excited State Behaviour of Single- and Multi-Branched Donor–Acceptor Systems with Multidimensional Spectroscopies

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We are investigating Donor–Acceptor (D–A) and Donor–Acceptor–Donor (D–A–D) systems linked via acetylene bridges. Starting from diphenylacetylene systems as models for single-branched D–A systems, we utilize time-resolved infrared spectroscopy (TRIR) as well as transient electronic absorption spectroscopy (TA) to understand their behaviour in the excited state. In this first stage, we evaluate the effect of both solvent polarity and the identities of the acceptor. To differentiate between the fundamental vibrations of the investigated species and potential Fermi resonances we further employ transient two-dimensional infrared (t2DIR) spectroscopy, as t2DIR is uniquely suited to study this phenomenon.[1]

In a second step, we expand the scope of D–A molecules by exchanging the acceptor moiety of the system for fluorenone.[2] We focus on the influence of the 4-N$R_2$-phenyl donor units, studying the effect of the alkyl chain length on the excited-state dynamics, resonance conditions and spectral properties, before extending the scope by substituting the fluorenone core a second time, thus creating symmetric D–A–D molecules. This approach enables us to directly compare the influence of the involved chromophore(s) on the excited state behaviour of single-branched D–A systems and the symmetry breaking observed in the symmetric D–A–D molecules.

We complete the survey by switching to a naphthyl-based donor group, introducing intrinsic asymmetry into the studied molecules. The presence of the acetylene bridges leads to a wide distribution of dihedral angles between the donor and acceptor planes in the ground state. In the excited state, however, the rotational barrier is significantly increased.[3] In the phenyl-substituted molecules, rotation around the C-C bond produces a symmetric modulation of the conjugation of the system, whilst in the novel naphthyl-substituted molecules this modulation is asymmetric. This in turn gives rise to increased differences in both the electronic absorption spectra and the observed dynamics as a function of the D–A torsion angle (θ). A combination of t2DIR spectroscopy and excitation wavelength dependence studies are uniquely suited to study this phenomenon, disentangling the complex excited-state dynamics observed in these systems.

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# Investigation on Fission Product Release Behavior for GEN-IV Reactor Designs

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Analyzing the potential dispersion of radioactive material into the environment is essential for reactor licensing. This project examines the release behavior of fission product radionuclides (FPs) in the cooling systems of two GEN-IV reactor types: lead-cooled fast reactors (LFR) and molten salt reactors (MSR). For LFR, Cs has been selected for detailed studies due to its significant radiological risk and volatility. The Henry's law constant for Cs in molten lead can be determined using the transpiration method, providing critical data on the behavior of Cs under reactor conditions. Cs-134 was produced at PSI-SINQ´s neutron irradiation facility and used as radioactive tracer during the transpiration experiments, allowing quantification of the evaporated Cs. Analogous methods will be applied to address the release from MSR, where FPs such as Zr-95 are of particular interest due to the expected high release amount of $ZrF_4$.

Additionally, electrochemical techniques, such as, e.g., electromotive force measurement will be employed to prepare homogeneous Pb-Cs samples and accurately determine the activity coefficient of Cs in Pb. The thermodynamic data measured by both transpiration and electrochemical methods will be evaluated and compared.

Besides, the PSI-SINQ Gasjet facility offers the potential to produce a wide spectrum of FPs extracted from a U-235 fission chamber via aerosol. These products can be incorporated into reference liquid lead or molten salt matrices, enabling the production of ‘universal’ samples for studying diverse FP release behaviors at carrier-free conditions, i.e., “zero” concentration. Preliminary tests have already been conducted on FP transport from the Gasjet chamber into molten lead.

Overall, this research will provide critical insights into the behavior of fission products in GEN-IV reactors, supporting the development of robust safety protocols and improved reactor designs.

# Solid-Supported Polymer Membranes: Deposition Method Influences Morphology and Properties

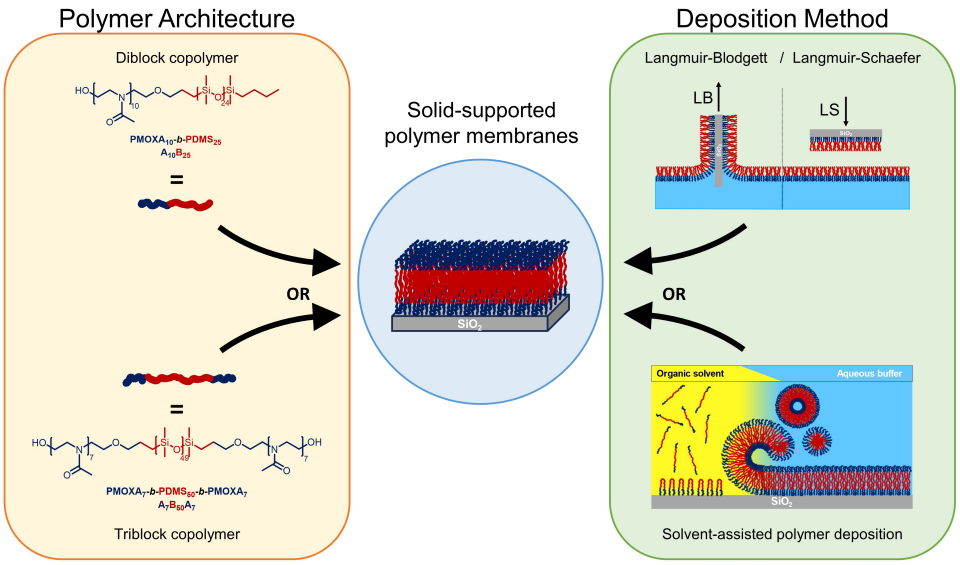
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Solid-supported polymer membranes (SSPMs) formed by the self-assembly of amphiphilic block copolymers offer enhanced stability and chemical versatility compared to lipid-based membranes. They can be used to modify the surface properties of underlying substrates or serve as stabilizing platforms for (bio)macromolecules, making them highly relevant for applications in materials and life sciences. Despite their broad potential, a systematic comparison of how different deposition methods influence their internal organization and physicochemical properties remains lacking.

In this study, we compare SSPMs prepared using two widely employed methods—Langmuir monolayer transfer and solvent-assisted polymer deposition—to assess their impact on membrane morphology, thickness, wettability, roughness, and elasticity. We investigate amphiphilic di- and triblock copolymers based on poly(dimethylsiloxane) (PDMS) and poly(2-methyl-2-oxazoline) (PMOXA) to understand how polymer architecture affects membrane formation and properties. Our findings reveal that the choice of deposition method significantly influences SSPM organization, with triblock-based membranes exhibiting more pronounced structural and property variations than diblock ones.

These insights demonstrate that the selection of an appropriate deposition technique is crucial for tailoring membrane characteristics to specific applications. By identifying key advantages and limitations of each method, this study provides a framework for the rational design of SSPMs, supporting their further development for functional surface modifications, (bio)sensing, and other advanced applications.




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# Illuminating Complexity: Photophysics in $Au_{25}$ atomically precise nanoclusters

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Metal nanoclusters (NCs) with ultra-small sizes (the metallic core <2 nm in diameter) provide an exciting opportunity to investigate the structure–property correlations at the atomic level owing to the monodisperse size and accurately characterized structures of nanoclusters. Thus far, more than 100 species of nanoclusters (mono-metallic Au or Ag nanoclusters, and bi- or tri-metallic alloy nanoclusters) with crystal structures have been reported [1]. Among these nanoclusters, $Au_{25}(PET)_{18}$, has been one of the most widely studied NCs, commonly found in three oxidation states ( −1, 0, and +1).

Our concern with the previously published results in the area regards the scarcity of systematic photophysical studies and accurate analysis of the measurements. For example, very often emission data are not collected in the full range of wavelengths due to the limited spectral coverage in the near infrared of the most common commercial fluorometers, or the excited state dynamics are oversimplified by the lack of sensitivity of the typical setups in this range [2]. This work intends to achieve such a level of understanding of the photophysical properties of $[Au_{25}(PET)_{18}]^{-1/0}$.

To this end, the absorption and fluorescence spectra (steady-state and time-resolved) were obtained by exciting samples at different energies. Unlike its "closed shell" anionic counterpart, the neutral $Au_{25}(PET)_{18}$ showed a series of deviations from conventional molecular photophysics such as 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 non- monoexponential behavior for the ns-µs emission decays. The interpretation of the time-resolved studies probably suggests that a continuous distribution of decay times best describes the observed phenomena. Our findings are compared with previous experimental results for these nanoclusters [3,4].

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# Formulation and characterization of functional microemulsions

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Microemulsions are mixtures of water, oil, surfactants, and sometimes co-surfactants that self-assemble into different structures depending on composition and conditions.[1] They are thermodynamically stable and can exist as oil-in-water (Winsor I), water-in-oil (Winsor II), or bicontinuous (Winsor III) systems. The Winsor systems have been studied for decades, mainly using temperature, the oil's alkane carbon number, or salt concentration as triggers.[2] The formation of responsive microemulsions that can switch between Winsor states has not yet been achieved.

This work demonstrates the formation and characterization of novel, stimuli-responsive microemulsions that can switch their structure with defined environmental changes.[3] These smart microemulsions are formulated with food-grade molecules. Spinning drop tensiometry is used to study the effect of composition on the interfacial tension between the microemulsion system with oil and water. Additionally, small-angle X-ray scattering studies the corresponding microemulsion nanostructure. Based on these findings, we will discuss the transition mechanisms between Winsor I, II, and III systems and their potential application as novel materials for nutrient extraction and drug delivery.

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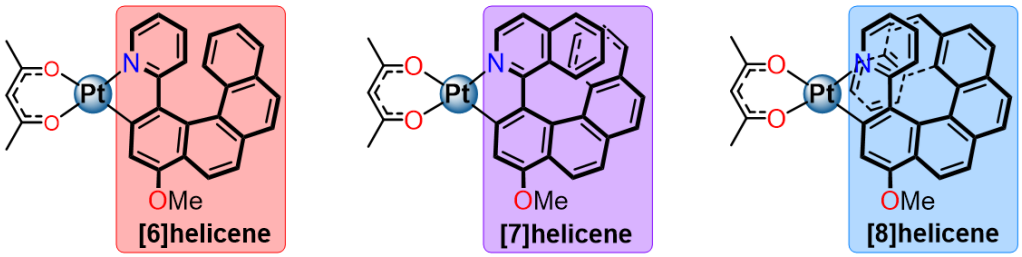
# One Ring to Rule Them All: Ultrafast Spectroscopy Study of Chiral Platina[n]helicenes with Circularly Polarized Emission

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Circularly polarized luminescence (CPL) from chiral luminescent materials has promising applications in high-efficiency displays, security inks, telecommunications and cryptography.[1] In this respect, chiral d-block complexes have emerged as attractive CPL emitters due to their high luminescence quantum yield, kinetic inertness and tunable emission wavelength covering the visible part of the electromagnetic spectrum.[2] In particular, platina[*n*]helicenes have achieved relatively high CPL emission enantiopurity, resulting from the chirality of the helicene ligand along its helical axis. However, a clear understanding of the coupling of the chiral molecular structure to the dynamics of the excited luminescent states, giving rise to the observed CPL, has not yet been achieved.

To address this gap, we investigate a series of three platina[*n*]helicenes (*n*=6,7,8) (Figure 1), which differ only in the number of benzene rings constituting their helical ligand.[3,4] To determine the underlying CPL mechanism and its structural dependence, we present a systematic study using transient absorption spectroscopy (TA) covering the spectral range from the deep-UV (250 nm) to the near-IR (900 nm) and spanning from the femtosecond up to the nanosecond time scales.




With this methodology in hand, a strong dependence of the dynamics following the formation of the Franck-Condon state on the pump-wavelength and the structure of the helical ligand was observed. This finding underlines the strong mixing between ligand- and metal-based states and, consequently, the challenge of decoupling both contributions to the CPL mechanism. In future studies, we intend to employ time-resolved circular dichroism spectroscopy to identify their chiral features as part of the CPL mechanism.[5]

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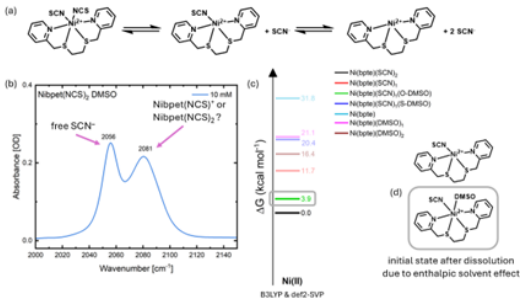
# Characterizing the ligand lability of a Nickel-based $CO_2$ & $H^+$ reduction catalyst.

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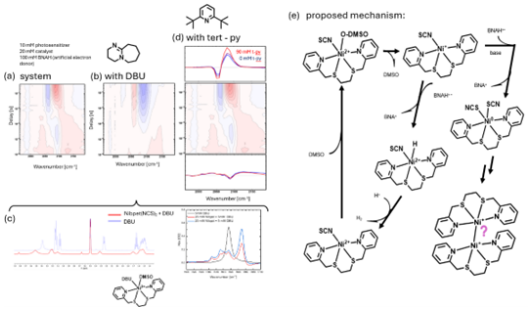
In the framework of catalytic organometallic chemistry, complexes such as Ni(bpet)X□ have demonstrated promising activity as reductants for CO□ and H□. However, mechanistic investigations often overlook the critical role played by labile ligands, despite their potential influence on reactivity and intermediate speciation. To address this gap, we have synthesized and investigated an analogue bearing SCN□ ligands [2] in place of MeCN, chosen for their enhanced infrared absorption characteristics.

Time-resolved infrared spectroscopy (TRIR) was employed to probe short-lived intermediates and dynamic processes during catalysis. Crucially, we underscore the need for thorough and precise characterization of the catalyst's initial state upon dissolution (Fig 1 a & 1 b) — an aspect largely underreported in previous literature. The solution speciation, influenced by ligand lability and solvent coordination (Fig 1 c), directly impacts the interpretation of transient data.




In order to disentangle if hydride formation is a common key step for $H_2$ evolution from $CO_2$ reduction or a selective pathway, we introduced the non-nucleophilic base DBU. This led to a distinct inversion in IR absorption features compared to experiments conducted without DBU (compare Fig 2 a & 2 b). Further FTIR and NMR studies confirmed that DBU coordinates to the nickel center, displacing one SCN□ ligand (Fig 2 c). These observations highlight the importance of selecting truly non-coordinating bases – such as di-tert-butylpyridine (Fig 2 d) – to suppress side reactions while preserving the integrity of the catalytic system (Fig 2 e).

Altogether, our work emphasizes that comprehensive initial-state characterization is essential for correctly interpreting time-resolved experiments and for disentangling parallel reaction pathways in complex catalytic systems (Fig 2 e).




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# Examining the Interaction Between Thiolate Protected Nanoclusters and Lipid Bilayers Using ATR Infrared Spectroscopy

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The understanding of the interactions of monolayer protected metal clusters with biological membranes is of fundamental importance for applications of these systems in medicine and for biosensing. At the same time, using metal clusters imposes some restrictions such as toxicity[1] and undesirable immunological responses. In fact, the chemical properties and biological effects of monolayer protected metal clusters can critically depend on the size of the clusters, the protecting ligand layer and chirality. Therefore, different kinds of coatings are used to reduce the negative impacts of metal clusters and increase the beneficial interaction with biological systems. Although thiol groups play an important role for biological systems and have been used as a ligand for the preparation of metal clusters in many areas, the effect of thiolate protected metal clusters on the cell membrane is not well understood.

In our study, lipid bilayers are used as a model of the cell membrane. Different methods have been reported to prepare lipid bilayers[2]. We use several methods to prepare lipid bilayers on solid substrates including Langmuir Blodgett/Schaefer combination and vesicle fusion. We study interaction between different types of thiolates protected clusters and bilayer membranes, by atomic force microscopy (AFM), ellipsometry, quartz crystal microbalance (QCM) and attenuated total reflection infrared (ATR-IR) spectroscopy in a microfluidic and temperature-controlled flow-through cell (Figure 1). We furthermore make use of polarized light to study the orientation of the phospholipid bilayer and their order in presence and absence of metal clusters.

For spectroscopic analysis suitable lipid bilayers have prepared by vesicle fusion were obtained and their interaction with clusters was studied. Two gold-based nanoclusters were synthesized and their interactions with three different phospholipid bilayers were systematically investigated. Our fındıngs shows that among them, DPPC bilayers exhibited the highest adsorption capacity for the clusters. In particular, $Au_{25}GSH)_{18}$ showed interactions with the polar head groups of DPPC, primarily through ionic interactions and hydrogen bonding between the carboxylate groups (R-COO-) of the cluster and the protonated amine groups ($H_3N^+$-R') of the phospholipid. Partial desorption of the clusters from the surface was observed and some phospholipid molecules were also observed to desorb from the bilayer together with the clusters, leading to a disruption of membrane integrity. The phase transition temperature (Tm) of phospholipids has been observed to influence the strength of these interactions. During these interactions, there was minimal disruption in the molecular orientation of the phospholipids.

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# Dynamic Stereochemical Analysis via Enhanced Vibrational Circular Dichroism

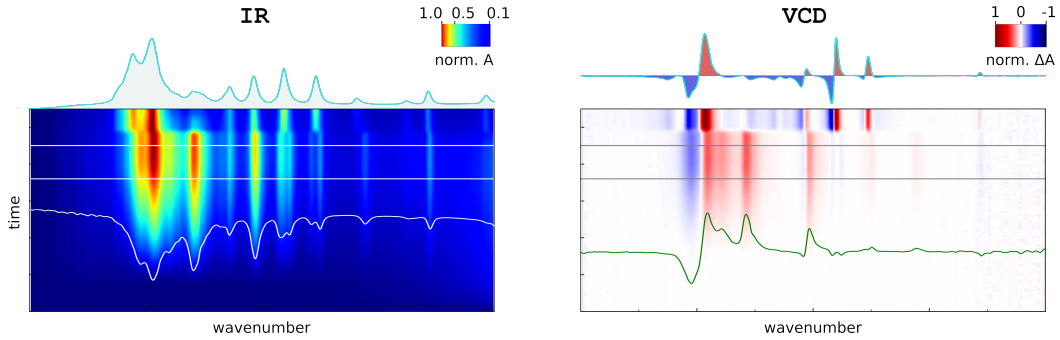
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Chirality is a fundamental property in the molecular sciences[1], describing entities that are non-superimposable on their mirror images, akin to left and right hands. This property is crucial in understanding the stereochemistry of organic molecules in biological systems[2]. Traditionally, determining the absolute configuration of chiral molecules has relied on techniques such as Vibrational Circular Dichroism (VCD)[3], which measures the differential absorption of circularly polarized light by chiral substances in solution. However, VCD's application has been limited by its need for prolonged data accumulation, typically requiring six to eight hours[4] to achieve a reliable signal due to the minimal absorption differences ($10^{-5}$ to $10^{-4}$).

In a significant advancement, our research group has developed an innovative method that drastically reduces the data accumulation time to approximately two minutes. Our approach exploits the enhanced VCD signals in crystalline materials, allowing for rapid and dynamic monitoring of molecular processes. This enhancement improves the efficiency of VCD and extends its practical applications beyond steady-state measurements, facilitating real-time insights into the dynamic stereochemical landscapes of organic molecules.

Using the method, we monitor the growth of crystalline alanine films produced by physical vapor deposition and their phase transition upon moisture exposure, as shown in the figure. We use ex-situ morphological techniques, including atomic force microscopy and surface X-ray powder diffraction, for further characterization.




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**Morphology by Design: Sustainable Hematite Nanoparticle Synthesis via Ionic Liquids**

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The performance of nanostructured materials is intricately linked to their composition, morphology, crystallinity, surface characteristics, and size. Among various nanomaterials, iron oxides—and hematite (α-Fe□O□) in particular—have gained significant interest due to their promising roles in catalysis, optics, and sensing. However, tailoring their nanoscale properties with precision remains a difficult synthetic challenge due to limitations of conventional synthesis methods like sol-gel processes, which often suffer from reproducibility issues and lengthy protocols.

In this contribution, we want to report a sustainable two-step synthesis strategy for hematite nanoparticles (NPs), leveraging room-temperature ionic liquids (ILs) as structure-directing and stabilizing agents. We developed a method capable of producing hematite nanoparticles with tunable morphologies by employing FeCl□ as the iron source and exploring a range of ILs based on ammonium and imidazolium cations. By tuning the synthetic parameters—including the variation of the type of IL, reaction temperature, and reaction duration—we achieved designed control over the formation and morphology of the nanoparticles.

Scanning electron microscopy (SEM) and complementary physicochemical characterization reveal that the structure of the IL cation plays a pivotal role in changing nanoparticle shape and size. Mechanistically, ILs modulate nanoparticle nucleation and growth through a combination of $Fe^{3}$□ coordination, supramolecular templating, and facet-selective stabilization. The IL's role could be defined as a dual reaction medium and shape-aided agent, enabling fine control over the morphology of the particle formation pathways, as depicted (Fig. 1). We can propose a tunable and eco-friendly experimental protocol for the hematite-based nanostructured materials by such an approach.

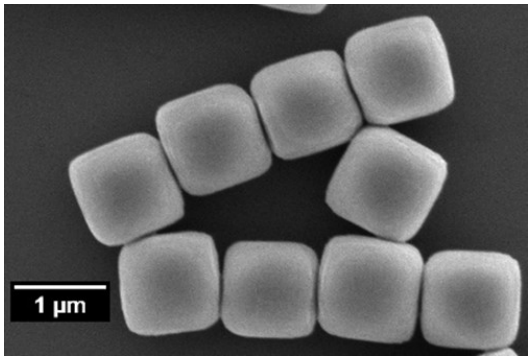



*Fig. 1: SEM image of α-Fe□O□ cubic particles synthesized with C12-trimethylammonium chloride*

# Controlled laboratory astrochemistry: Rotational-state-selected carbon reactions in space

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The relative abundance of $HOC^+$ and $HCO^+$ ions is observed to be higher in x-ray-dominated regions than in photon-dominated regions of space, which makes these isomers useful molecular tracers for distinguishing between these entangled regions of ionized gases and neutral molecules in interstellar molecular clouds [1]. The higher abundance of metastable HOC□ ions compared to their more stable isomer is primarily due to their formation by the reaction between carbon cations (C□) and water, where the branching ratio favors HOC□ over HCO□ [2].

It was recently shown that the two nuclear spin isomers of water, *para*-$H_2O$ and *ortho*-$H_2O$ with $j = 0$ and $j = 1$ as their lowest rotational energy state respectively, display different reactivities towards trapped diazenylium ($N_2H^+$) ions [3]. We aim to investigate whether *para*- and *ortho*-water react differently with $C^+$ ions and whether their relative abundances and individual reaction rates consequently affect the ratio of $HOC^+$ / $HCO^+$ isomer population in the interstellar medium. This will also let us determine if the two nuclear spin isomers of water should be treated as different chemical entities in astrochemical models [4].

Here, we report on the progress we made on the rotational-state-selected reaction of water with Carbon cations. $C^+$ ions produced by multiphoton dissociative ionization of a precursor were loaded and sympathetically cooled within a $Ca^+$ Coulomb crystal in a linear radiofrequency Paul trap. We can separate *para* and *ortho* water in a molecular beam using an electrostatic deflector due to their different effective dipole moments and, therefore distinct Stark energy shifts. We plan to collide the separated *para*- and *ortho*-water with the trapped $C^+$ ions and measure the rotational-state-dependent reaction rates and branching ratios by analyzing the ion peak signals following the ejection of the ion crystals as a function of reaction time.

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# High-resolution two-photon Doppler-free UV spectroscopy of Xe with direct measurement of the AC-Stark shift

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One of the main systematic uncertainties in Doppler-free two-photon laser spectroscopy, and more generally in multiphoton spectroscopy, arises from the AC-Stark shift induced by the laser intensities required to drive the transitions. Here, we present a technique for performing precision Doppler-free two-photon UV spectroscopy with direct measurement of the AC Stark shift. This was achieved using the frequency-upconverted output of long-pulse-length narrow-bandwidth (FWHM ~15 MHz) Ti:Sa bow-tie amplifiers [1], that exhibits large shot-to-shot pulse-energy fluctuations. A single-shot detection method was used to simultaneously but separately record spectra over the entire range of laser intensities. This method was demonstrated by performing (2+1) REMPI spectroscopy of the $(5p)^6\ ^1S_0 \rightarrow (5p)^5\ 6p\ [1/2]_0$ transition in Xe, with uncertainties of down to ~0.7 MHz achieved for transition wavenumbers around 80118.9 $cm^{-1}$. These measurements, when combined with recent precision [2-4] and historic [5-11] data, allowed for a new determination of the isotopic-abundance-weighted first ionisation wavenumber of Xe, which was found to be 97833.7644(14) $cm^{-1}$. This new value resolves the ~1 GHz discrepancy of recent measurements from the metastable $(5p)^5\ 6s\ [3/2]_2$ state with the previously determined ionisation limit [2].

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# Development of single-photon Doppler-free VUV/XUV spectroscopy experiment

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The ionisation energies of many atoms and molecules lie in the vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) parts of the electromagnetic spectrum, which correspond to wavelengths (frequencies) of light of <200 nm (>$1.5\times10^{15}$ Hz) and <105 nm (>$2.9\times10^{15}$ Hz) respectively [1]. Laser radiation generated at these wavelengths can therefore be utilised to perform single-photon excitation from the ground electronic state of an atom or molecule to highly excited electronic states, including direct excitation to Rydberg states with a large value of the principal quantum number, $n$ [1]. However, although VUV/XUV laser sources with <250 MHz bandwidths have been achieved [2-6], large Doppler broadening of transitions at VUV/XUV wavelengths (with Doppler widths typically >100 MHz) often limit the achievable resolution of single-photon VUV/XUV spectroscopy. Additionally, large Doppler shifts can result in >100 MHz systematic shifts of measured transition frequencies in the VUV/XUV. Here we present the development of a new experimental apparatus for performing Doppler-free spectroscopy at VUV/XUV frequencies. This method is based on combining an imaging-assisted single-photon Doppler-free spectroscopic technique, recently developed for precision Rydberg-state spectroscopy [7], with a long-pulse-length (□100 ns) narrow-bandwidth VUV/XUV laser. The initial aim of such an experiment is to generate laser radiation with a wavelength of □80 nm, for use in precision single-photon XUV spectroscopy of $H_2$ molecules excited to high- ( > 30) Rydberg states from the ground $X\ ^2\Sigma_g^+$ state.

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# Branching ratios and their reduced mass and collision-energy dependence in ion-molecule reactions near 0 K: $H_2^+$, $HD^+$ and $D_2^+ + CH_3F$

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Ion-molecule reactions are essential steps of astrophysical and atmospheric chemical networks but are difficult to study in the laboratory at low energies ($<k_B\times 50$ K) because stray fields heat the ions up. We circumvent this difficulty by replacing the ion (here $H_2^+$, $HD^+$ and $D_2^+$) with a highly excited Rydberg state of these molecules [1,2]. The distant Rydberg electron shields the ion core from external fields without influencing the ion-molecule reaction taking place within its orbit. We use a Rydberg-Stark deflector [3] to merge a supersonic beam of hydrogen molecules in high Rydberg states with a supersonic beam of ground-state neutral $CH_3F$.

This deflector is also used to set the velocity of the Rydberg molecules ($v_{Ryd}$). By tuning $v_{Ryd}$ relative to the velocity of the ground-state molecules, we tune the collision energy $E_{coll}$ from $\sim k_B\times 500$ mK to $\sim k_B\times 50$ K. The product ions, the reaction rates and the branching ratios for the formation of $CH_3F^+$, $CH_2F^+$ and $CH_3^+$ product ions are measured as a function of $E_{coll}$. Short (~ 20 μs) gas pulses ensure a high collision-energy resolution.

We report here on the reactions of $H_2^+$, $HD^+$ and $D_2^+$ with $CH_3F$, which were studied following the same procedure as used for the $D_2^+ + NH_3$ reaction [4]. The rate coefficients of these reactions deviate strongly from Langevin rates and increase sharply below 2 K, as expected for reactions between ions and dipolar molecules. These observations are analysed using (I) a rotationally adiabatic capture model including the Stark effect of the rotational states of the symmetric-top $CH_3F$ in the electric field of the ion [5,6,7] and (II) classical trajectory calculations of a dipolar molecule approaching a point-like ion.

All reactive systems exhibit a competition between charge-transfer and short-range $F^-$-transfer and $H^-$-transfer processes. This competition results in a dependence of the reaction branching ratio on the collision energy and the degree of deuteration of hydrogen, particularly at the lowest collision energies. Theoretical modelling allows us to qualitatively describe the dependence of the branching ratio on the collision energy and the degree of deuteration of hydrogen.

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**From Kinetics to Molecular-Level Insights into Group 4 Metal Oxide Nanocrystal Synthesis**

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Kinetic control is a powerful tool for traversing the chemical landscape towards the intended product. For group 4 metal oxide nanocrystals, the development of complex multimetallic heterostructures is still a challenge, partly due to the lack of kinetic and mechanistic understanding. Here, we study the reaction kinetics of the nonaqueous synthesis of titanium, zirconium, and hafnium oxide nanocrystals, from the decomposition of metal isopropoxide and metal halide, in the presence of tri-n-octylphosphine oxide (TOPO). The reaction rate depends on the metal: Ti >> Zr > Hf. While titanium follows an $S_N1$ substitution mechanism, zirconium and hafnium follow an auto-catalyzed E1 elimination. In both cases, the reaction kinetics can be tuned by varying the amount of TOPO or the chloride content due to their impact on the electronic structure of the transition state of the rate-determining step. The proposed mechanism was shown to be consistent with kinetic modelling of the data for different metal concentrations. This deeper understanding of group 4 metal oxide nanocrystal formation will facilitate access to novel heterostructures, relevant for optical, catalytic, and electronic materials.

# Time resolved DLS microscopy : Acquisition of particle size distributions at high temporal resolution

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Dynamic Light Scattering (DLS**)** is a well-established technique used across scientific and industrial domains to determine in a non-destructive manner the size of particles in the nanometer to micrometer range[1]. Commercially available DLS devices typically need seconds to minutes for a measurement, by feeding photon counts to a hardware or software correlator that outputs the corresponding autocorrelation function from which the size distribution is extracted. This process requires measurements to be made under static conditions, thus limiting its applications with regards to dynamic systems[2].

To address this issue, we developed a DLS microscopy setup (micro-DLS) that is able to characterize accurately particle sizes from data obtained in sub-100 ms time windows, which corresponds to an improvement of several orders of magnitude[3]. The arrival time of the scattered photons is registered by a time-correlated single photon counting module, which allows post processing of the data and the ability to reconstruct autocorrelation functions over arbitrarily defined time windows. The setup is capable of resolving both monomodal and multimodal size distributions, successfully characterizing a range of particles including 3 nm gold nanoparticles, 10 nm silica particles, 60 and 220 nm polystyrene beads, as well as lysozyme proteins. It was also found that short time windows produced sharper size distributions, which was attributed to the resolution of sub-ensembles of the broader size distribution, as the accumulation of short time windows distributions could be used to reconstruct it. This improved temporal resolution allows the application of DLS to new systems with the ability to track the dynamic evolution of particle size in solution.

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# State-preparation and quantum control of polyatomic molecular ions

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Precise quantum control of isolated molecules has emerged as a key technology in a wide range of applications such as precision spectroscopy, quantum computing, tests of fundamental physics, and state-to-state chemistry [1,2,3]. The development of experimental techniques for the preparation, cooling, and coherent manipulation of molecular ions has made significant progress over the past years. However, due to the complex internal structure of molecules and the absence of closed-cycling transitions, these techniques are rather demanding and have been employed for only a limited number of molecules.

In recently developed quantum-logic schemes wherein single molecular ions are co-trapped with single atomic ions, the molecules were sympathetically cooled and their state was non-destructively detected [1,4,5]. The first and crucial step in such experiments is to prepare the molecules in a well-defined quantum state, and this can be carried out by utilizing the photoionization process - 2+1 resonance-enhanced multi-photon ionization (REMPI) [6].

The goal of this project is to adapt the existing quantum-logic techniques for diatomic molecules to polar, polyatomic molecular ions – specifically, $H_2O^+$ ions. Water is one of the important polyatomic molecules that is also of significant relevance in chemistry, biology, and astrophysics. We are currently building and characterizing a cryogenic experimental setup to trap single $H_2O^+$ ion and study its collision dynamics. I will present the current status of the project, with a focus on the state preparation of molecular ions. The quantum control of polyatomic molecules can open new prospects, including new applications in precision spectroscopy, as well as providing new sets of properties to investigate, like isomerism, chirality, parity doublets, etc. at single molecule level.

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# Long-Time Scale Molecular Dynamics of Large-Scale Simulations Enhanced by Machine Learning of Hydroxylated Tin Oxide with Mixed Additives for Solar Cell Devices

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data-pm-slice="1 1 []">Tin oxide ($SnO_2$) semiconductor is frequently used in solar cell devices as an electron transport layer (ETL).

However, due to its inherent highly reactive nature, interface passivation is required to ensure stability and prevent undesirable reactions with the active layer.

In this context, the use of self-assembled monolayers (SAMs) with organic additives have been explored to protect the surface of the ETL.

Notwithstanding, the molecular arrangement of these SAMs, as well as the reactive processes at the surface of $SnO_2$, present a high-dimensional problem that requires electronic structure methods with high accuracy and remains a challenge in the scientific community.

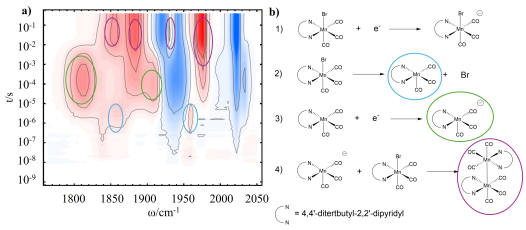
In this work, we constructed a machine learning force field (MLFF) based on first-principle method, to understand the reactive mechanisms involved in the hydroxylation process of $SnO_2$ as well as the interactions between hydroxylated $SnO_2$ and typical additives utilized in SAMs for surface passivation.

# Insights into Mn-based catalyst Activation in $CO_2$ Reduction using TRIR Spectroscopy in a 3-component system

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The catalytic reduction of $CO_2$ remains a central challenge in the development of sustainable energy systems. Transition metal complexes have been investigated for decades as potential solutions due to their ability to facilitate multi-electron reactions. Yet, conventional electrochemical analyses often fall short in providing precise control over electron transfer and typically overlook short-lived intermediates, which are essential to elucidating catalytic mechanisms and improving system design. In our work, we utilize time-resolved infrared spectroscopy (TRIR) to monitor reaction intermediates in real time. The presence of metal carbonyl groups in many such complexes affords strong, diagnostic IR signals, which sensitively reflect changes in electronic structure around the metal center. Our focus is on a photocatalytic system based on manganese, an earth-abundant and cost-effective metal. Specifically, the complex *fac*-MnBr($^t$Bu$_2$–bpy)(CO)$_3$ demonstrates effective $CO_2$ conversion with a lower overpotential compared to its rhenium-based counterpart, yet retains comparable catalytic efficiency.1–3 This study emphasizes the utility of TRIR in identifying transient species and provides valuable mechanistic insights that inform the rational development of next-generation $CO_2$ reduction catalysts.




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# Ground-State Structure and Excited-State Dynamics of a Donor-Acceptor Complex with Two Charge-Transfer Bands

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Electron donor-acceptor complexes (DACs) are increasingly used in many light-based applications such as molecular electronics[1] or photoredox catalysis[2]. Surprisingly, although DACs have been known for more than 70 years[3], little is known about their structure in liquids.

Here, we investigate the excited-state dynamics of the D = anisole / A = tetracyanoethylene DAC in different solvents at room temperature. This DAC exhibits two charge transfer (CT) absorption bands that are usually explained by invoking two distinct π-stacked isomers[4,5] of the complex, suggesting the possibility of photoselection of either isomer. Transient absorption spectroscopy upon excitation at either band maximum, however, reveals that the ensuing excited-state dynamics are largely independent of the initially excited CT transition. Moreover, the pure ground-state bleach dynamics, extracted from polarized transient absorption measurements, show no holeburning effect and remain independent of the excitation wavelength. Molecular dynamics simulations explain these findings and suggest that a broad ensemble of DAC structures contributes equally to both transitions, challenging the commonly accepted view.

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# High Resolution Spectroscopy of Vibrational Tunneling Doublets and Overtones of the Inversion in Aniline

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Extending our knowledge about the inversion at the nitrogen atom in aniline ($C_6H_5NH_2$) or in other aromatic amines is of interest because of the widespread occurrence of the -$NH_2$ substituent in aromatic biomolecular compounds, in particular nucleic acids. The inversion barrier in aniline is about 450+/- 80 $cm^{-1}$ [1,2] (much lower than for ammonia $NH_3$ with about 2000 $cm^{-1}$ [3]). Here, we report highest resolution results from our GHz measurement from 75 GHz to 500 GHz and from the THz (FIR) range measured with our 2009 ETH-Bruker prototype spectrometer at the SLS (Swiss Light Source). We observed the rotationally resolved spectrum and analysed the three vibrational-tunneling doublets ($I_0$, $I_1$), ($10b_1$, $10b_1I_1$), and ($T_1$, $T_1I_1$) and the overtones of the inversion $I_2$, $I_3$, and $I_4$ providing accurate rotational parameters. We firmly assigned the spectra, including also the nuclear spin statistics seen by the intensity patterns in the GHz range and in part also resolved the hyperfine structure. The results are also discussed in relation to transient chirality in aniline –NHD and ammonia NHDT [3] and in relation to our ongoing efforts on precision experiments concerning the electroweak force of the standard model of particle physics (SMPP) by measuring the parity violating energy difference between the two enantiomers of chiral molecules [4-6]. We discuss in particular the closely related spectroscopic challenges in the vibrational tunneling dynamics for 1,2-dithiine ($C_4H_4S_2$) as a prototype for measuring parity violation needing the analysis of parity states in the mid-IR range in very dense spectra with multiple overlapping rotation-vibration-tunneling structures (see reviews [5,6]).

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# Hydrogen bonding to build viscoelasticity with amino acid surfactants

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The design of self-assembled systems to deliver actives, build viscosity and tune texture is essential to replace current unsustainable commercial surfactants. Drug delivery, nanoscale engineering and personal care industries heavily rely on the interactions in these complex fluids to achieve their high performance, yet with tightening restrictions on functionality like ethoxylation, it is important to understand their behaviour and uncover ways to mimic their contributions sustainably [1]. In particular, commercial formulations of anionic:zwitterionic surfactants to build wormlike micelles are widely exploited [2], yet molecules such as sodium laureth sulfate are becoming less desirable to consumers and regulatory bodies, but are extremely effective in building viscosity.

Through small-angle neutron scattering and rheology, we demonstrate the enhanced viscoelasticity of amino acid surfactant sodium *N*-lauroyl L-serinate (R = $CH_3OH$) and laurylamidopropyl betaine mixtures, in efforts to replace sodium laureth sulfate as well as incorporate hydrogen bonding interactions. Through comparison to analogous surfactants that omit hydrogen bond donor and acceptor groups, such as sodium *N*-lauroyl L-alaninate (R = $CH_3$) and lauryl betaine, it is starkly apparent that hydrogen bonding between the hydroxyl side chain of the serinate surfactant and the amide linker of the betaine surfactant appear to be the key to forming wormlike micelles and building viscoelasticity. We attribute this transition from spherical to elongated micelles to an increase in micellar scission energy $E_{SC}$, increasing the time required for relaxation as shown with oscillatory rheology, as well as the mean contour length enhancing micelle entanglement and viscosity.

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# Precision Spectroscopy of the Fine-Structure in the a $^3\Sigma_u^+$ (v = 0) and c $^3\Sigma_g^+$ v = 4) States of the Helium Dimer

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The helium dimer ($He_2$), having only four electrons, no nuclear spin and being the prototypical example of a Rydberg molecule [1], serves as a benchmark system for testing *ab initio* calculations. In recent years, highly accurate calculations from first principles including relativistic and quantum-electrodynamical effects of molecular three- and four-electron systems have become feasible [2–5]. Accurate experimental data on the lowest-lying electronic states of $He_2$ are needed to validate the current level of theory, but are scarce in the literature. Especially the fine structure in the triplet manifold, arising from the spin-spin and spin-rotation interactions, has only been measured for a few rovibrational levels in the a $^3\Sigma_u^+$ state [7–12] and for only three rovibrational levels ($v = 4$, $N \in \{8, 10, 12\}$) in the c $^3\Sigma_g^+$ state [9].

We report on a high-resolution spectroscopic study of the fine structure of the a $^3\Sigma_u^+$ ($v = 0$) and c $^3\Sigma_g^+$ ($v = 4$) states of $He_2$ including all rotational levels of the c $^3\Sigma_g^+$ ($v = 4$) state up to N = 10. The experiments combined a dense cold supersonic beam of $He_2$ in the a $^3\Sigma_u^+$ metastable state generated by a cryogenic pulsed valve, and single-mode laser radiation in a geometric arrangement optimized to suppress Doppler shifts. Measurements were performed using a two-color resonant two-photon ionization scheme. A narrowband continuous-wave laser was used drive transitions from the fine-structure levels of the a $^3\Sigma_u^+$ ($v = 0$) to those of the c $^3\Sigma_g^+$ ($v = 4$) state. The c-state levels were then photoionized with a pulsed dye laser for background-free detection.

The absolute level positions of the a $^3\Sigma_u^+$ ($v = 0$) and c $^3\Sigma_g^+$ ($v = 4$) fine-structure levels could be determined to within 1 MHz and better in a linear-least squares fit including the transition frequencies of Ref. [9] and fine-structure intervals of Ref. [12].

The rotational, spin-spin and spin-rotation constants with their respective centrifugal distortions and the band origin were fitted in a global weighted nonlinear least-squares fit to the measured transition frequencies, again including the measurements of Refs. [9] and [12]. Significant improvements in the precision of the molecular constants were achieved compared to the previous measurements.

The c $^3\Sigma_g^+$ state is of particular interest also because its potential-energy curve exhibits a local maximum and its high vibrational levels ($v = 3$ and 4) undergo tunneling predissociation. The high spectral resolution enabled the characterization of the rotational-state-dependent tunneling dynamics through the observation of line broadening. The broadening was found to be in good agreement with calculated values, which were obtained by determining the energy dependence of the phase-shift of the scattering wavefunctions.

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# Universality of hydrogen-bonded linear networks formation in amino acids crystallization

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Crystallization is a key process in various disciplines at both fundamental and practical levels. Establishing the molecular level understanding of crystal nucleation is crucial in designing crystallization pathways and obtaining desired crystal polymorphs. One of the significant challenges to studying the mechanism of nucleation is its stochastic and heterogeneous nature. Single Crystal Nucleation Spectroscopy (SCNS) [1, 2] is a promising approach which combines optical trapping induced crystallization and *in situ* Raman microspectroscopy. SCNS measures the evolution of Raman spectrum during single crystal nucleation. Glycine crystallization in aqueous solution at room temperature was revealed that it follows a non-classical pathway with the appearance of prenucleation aggregates. Based on the Raman spectrum of aggregates compared with theoretical studies, the structure of the aggregates was proposed as linear networks connected via intermolecular hydrogen-bonding interactions between $-NH_3^+$ and $-COO^-$ group of the zwitterionic backbone.

The zwitterionic backbone is a common feature in all amino acids at neutral pH, which implies that the formation of hydrogen-bonded linear networks may be universal at the prenucleation step. In this work, Raman spectral feature of prenucleation aggregates and the nucleation process of eight amino acids (alanine, valine, phenylalanine, serine, threonine, glutamine, asparagine, and histidine) were studied. They were selected to compare between a wide range of the properties of the neutral sidechains. SCNS led to crystal nucleation of alanine, valine, phenylalanine and serine that revealed that they crystallize via nonclassical nucleation pathway. The Raman spectrum of prenucleation aggregates all showed NH---O hydrogen bonding feature, which proposes that the formation of hydrogen-bonded linear chains is a common feature. Although threonine, glutamine, asparagine, and histidine could not be crystallized by optical trapping, interestingly Raman spectrum evolved to the one with aggregate (NH---O broadband) feature. We could also observe the formation of sub-micron scale aggregates at the laser focus under bright-field microscope.

We hypothesized that the different outcomes of SCNS are related to the property of sidechains and their interaction with water. The sidechains of the amino acids that did not nucleate in SCNS are more hydrophilic in general. Dehydration process is an essential step upon forming anhydrous crystal nucleus. The stronger the interaction between sidechains and water, the more difficult the dehydration process may be. To test this hypothesis, we conducted multiple batch crystallization experiments to measure the induction time distribution of each amino acid. The histogram of the induction time can be used to extract information such as nucleation rate and critical nucleus size [3]. The result showed that the amino acids with more hydrophilic sidechains deviate further from the classical nucleation model. A two-step nucleation model which includes the rate of aggregate formation is needed to fit this result. While all the amino acids crystallize via nonclassical nucleation pathway by forming hydrogen-bonded prenucleation aggregates, the nature of sidechains strongly modulates the dehydration process of forming anhydrous nucleus. For amino acids with hydrophilic sidechains, the size of prenucleation aggregates may keep growing up to submicron scale due to the difficulty of dehydration and forming nucleus.

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# Chemi-ionization Dynamics of Carbonyl Sulfide (OCS) with Metastable Neon Investigated by Velocity Map Imaging

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Chemi-ionization (CI) reactions are fundamental in high-energy environments such as plasmas, planetary atmospheres, and interstellar space[1,2] and have become valuable tools for probing quantum effects in reactive collisions.[3] Here, we report a new velocity map imaging (VMI) crossed-molecular-beam experiment for studies of gas-phase CI reactions.[4,5] An electrostatic deflector is integrated into the setup to enable the spatial separation of different conformers or individual rotational states of molecules according to their different effective dipole moments, while the ionic products are probed using time-sliced VMI technique. As the pioneer application of this new method, we first studied rotational-state-dependent CI reaction of OCS with metastable neon atoms at collision energy of 0.3 eV via time-of-flight mass spectrometer (TOF-MS). OCS molecules in the rotational ground state (J = 0) were found to be 2.5 times more reactive in dissociative ionization (yielding S□) than in Penning ionization (producing OCS□), compared to those in J = 1.[4]

Here, time-sliced VMI technique is utilized to detect the products OCS+ and S+ . For OCS+, strong forward scattering and minor backward scattering were observed. The total kinetic energy distribution exhibited a peak around 0.16 eV and extended up to ~0.5 eV. These experimental results are reminiscent of the angle-energy distributions of Penning ions (Ar+) in the CI reaction of metastable helium with argon.[6] The product S+ exhibits a nearly isotropic angular distribution, and analysis of the total kinetic energy distribution suggests that the lowest dissociation channel S+(4S) + CO(X1Σ+) is formed. These findings are in agreement with previous comprehensive studies on photodissociation dynamics of OCS+ in its A2Π and B2Σ electronic states.[7] Further VMI experiments are currently underway to investigate potential rotational state-specific effects on the product branching ratios.

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# Speciation of Tellurium evaporated from Lead–Bismuth Eutectic

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Lead-bismuth eutectic (LBE) is a promising coolant for the next generation lead-alloy cooled fast reactors because of its favourable thermophysical properties. Safety assessments for these reactors require an understanding of the volatilisation behaviour of radioactive impurities such as tellurium (Te) dissolved in the liquid metal. The present work quantifies Te retention and volatility in support of assessments for lead-alloy fast reactors.

We investigated Te speciation over LBE by *thermosublimatography* and determined the saturated vapour pressure over dilute *solutions* of Te in LBE by the *transpiration* technique over 300-600 °C. Experiments were conducted using LBE doped with activated Te (atomic fraction $x = 1 \times 10^{-3}$), fused silica and stainless-steel columns, and helium (dry, water-saturated, and with addition of 10 vol. % $H_2$) as a carrier-gas; γ-spectrometry and SEM/EDX analysis methods were employed.

Thermosublimatography revealed two distinct depositions when Te is evaporated from LBE in fused silica columns: a high-temperature deposition (~500 °C) identified as PbTe, and a low-temperature deposition (~200 °C) identified as crystalline Te (Fig. 1). The formation of elemental Te is attributed to PbTe decomposition producing a volatile fraction. Water vapour significantly enhanced the PbTe decomposition. On the other hand, this process was inhibited in reducing atmospheres. In steel columns only PbTe deposition was observed; no Te was detected. The saturated vapour pressure study demonstrated that in both dry and humid atmospheres ($p(H_2O) = 3 \times 10^{\square\square}$ and $6 \times 10^{\square 3}$ bar, respectively) the Henry constant continues the previously reported high-T trend, confirming stronger Te retention than the ideal-solution model predicts.

Our findings demonstrate that Te primarily evaporates as PbTe from LBE, and its release to the cover-gas is lower by ≈ 3 orders of magnitude (at 350 °C) than if elemental Te evaporated directly. The PbTe decomposition on fused silica surface in the presence of humidity is concerning and highlights the importance of cover-gas conditioning and proper selection of filtering materials.

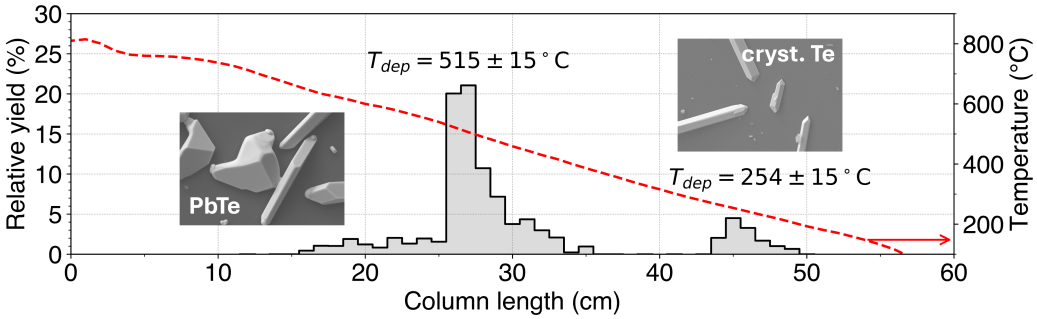



Figure 1. Tellurium distribution along the fused silica column in thermosublimatography experiment with dry helium carrier-gas and SEM scans of its deposits.

# Understanding the photoinduced electron-transfer quenching of PDI radical anion

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Due to its very high reducing potential, the lowest electronic excited state of the radical anion of the perylene diimide chromophore ($^2PDI^-$) has recently been proposed as an organic photocatalyst in the reduction of aryl halides such as 4-bromoacetophenone (4BAP). These reactions are reported to follow the so-called consecutive-photoinduced electron transfer mechanism (conPET), in which the successive absorption of two photons allows first the generation of the $^2PDI^-$ using a sacrificial electron donor, and second the population of the electronic excited state of $^2PDI^-$. However, this mechanism has been questioned by Ceroni1, who pointed out that, first, the very short excited state lifetime of $^2PDI^{-*}$ (145 ps) precludes its diffusion-controlled quenching by the reaction substrate, and, second, the absorption of this radical anion at the wavelength used in the original report (425 nm) is negligible. These authors attributed the photocatalytic activity to an unidentified radical species resulting from the photodegradation of $PDI^-$. More recently, Schanze et al. studied the quenching of $^2PDI^{-*}$ by aryl halides using transient absorption spectroscopy, and conclude that the quenching was entirely dynamic and diffusion controlled. We will present our reinvestigation of the quenching dynamics of $^2PDI^{-*}$ using transient electronic absorption spectroscopy in the visible and near IR regions. Our results show that, contrary to previous conclusion, static quenching is indeed operative, and becomes very efficient at high quencher concentration. However, the recombination of the ensuing quenching product is so fast that the proposed conPET mechanism is highly inefficient.

***Figure***: Left: PDI radical anion and 4-bromoacetophenone (4-BAP). Upper right: Evolution-associated difference spectra (EADS) of PDI with and without 4-BAP. Bottom right: Kinetic traces

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