

# State-to-state cross sections and rate coefficients for the rotational excitation of polyatomic hydrides in astrophysical environments

## Content

Recent astronomical observations have been showed that interstellar molecular clouds exhibit a very rich and complex chemistry [1]. In order to understand in details the chemical composition in such environments, a non-LTE analysis of the emission spectra is necessary. This requires reliable determination of collisional rate coefficients for the transitions between rotational levels of the target molecular species.

Both the isoelectronic hydronium cation ( $\text{H}_3\text{O}^+$ ) [2] and ammonia molecule ( $\text{NH}_3$ ) [3] have been detected in different regions of the interstellar medium (ISM). While  $\text{H}_3\text{O}^+$  plays a crucial role in oxygen and water chemistry in the ISM,  $\text{NH}_3$  has been widely used as a probe of physical conditions in interstellar environments. Thus, studying their collisional excitation is of high importance for the proper interpretation of astrophysical observations.

The rotational excitation of  $\text{H}_3\text{O}^+$  in collision with  $\text{H}_2$  molecule is studied for the first time [4]. State-to-state rotational de-excitation cross sections were computed using the close-coupling method, based on a highly accurate 5D potential energy surface [5]. The thermal rate coefficients were then derived up to 300 K kinetic temperatures.

We also present collisional data obtained for the excitation of  $\text{NH}_3$  by  $\text{H}_2$ . We have noticeably extended the range of collision energies (up to  $4500 \text{ cm}^{-1}$ ) and kinetic temperatures (up to 500 K), compared to previous studies by Bouhafs et al. [6] for this system. A comparative analysis of cross sections and rate coefficients is provided for the  $\text{H}_3\text{O}^+$  and  $\text{NH}_3$  target molecules. The calculated rate coefficients are used for modeling the collisional excitation of these species in interstellar molecular clouds.

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**Contribution Type:** Hot topic contribution

# Few- and many-body physics with ultracold dipolar quantum gases

## Content

Since the first realization of a Bose-Einstein condensate in 1995, the research field of ultracold atomic gases rapidly progressed and has proven to be an ideal testbed for e.g. the investigation of various few- and many-body phenomena, the realization of new and exotic quantum phases, and the implementation of quantum simulation protocols. In recent years, the emergence of magnetic atoms - in particular from the lanthanide series - opened up new and novel opportunities due to the complexity of their electronic structure and their large magnetic moment, realizing long-range interacting quantum matter. Here, we will present our results on the investigation of few- and many-body physics using ultracold dipolar quantum gases made of erbium and dysprosium. Starting with the scattering properties of single species and mixtures [1,2,3,4,5], we will continue to discuss the excitation spectrum and its rotonization [6,7]. Finally we show that beyond-mean-field effects allow to prepare liquid-like self-bound droplets and explore the phase diagram where the long-sought supersolid state - featuring superfluidity and a spatially periodic structure at the same time - connects those independent droplet phase with the regular BEC phase [8,9,10,11].

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**Contribution Type:** Invited talk

# Conformationally-selected ions for reactions with conformationally-selected molecules

## Content

The different effective dipole moment of conformational isomers allows for their spatial separation by means of electrostatic deflection, enabling their individual reactivity to be investigated [1]. Recently, the conformer-specific polar cycloaddition of dibromobutadiene (DBB) with trapped propene ions has shown that both gauche and s-trans DBB conformers display capture-limited reaction rates [2]. The reaction was found to occur through both a concerted and a stepwise reaction mechanism, despite the spatial rearrangement of atoms necessary in s-trans DBB for the latter to take place. These results were obtained by selectively aiming the molecular beam containing either one of the two conformers at a static target of propene ions embedded within a laser-cooled Coulomb crystal of calcium ions. In order to gain further control over the reaction partners, we now wish to also select the conformational isomer of the ionic reactant. Here, we discuss the generation of conformationally-selected ionic targets of 3-aminostyrene to enable the study of fully-conformationally-selected ion–molecule reactions. Following the detailed study of the isomer-selective ionisation of the two different 3-aminostyrene conformers, we aim to individually load them into a Coulomb crystal to determine their stability to such environment.

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# The mechanism of high harmonic generation in liquids and its application for electron scattering spectroscopy

## Content

High harmonic generation (HHG) takes place in all phases of matter. In gases it has been extensively studied and is well-understood. In solids research is ongoing, but a consensus is forming for the dominant HHG mechanisms. In liquids however, no established theoretical model exists yet, and approaches developed for gases and solids are generally inapplicable. Here there are many open questions such as cutoff scaling laws, the dominant HHG mechanisms, and more. Advancement on this front may lead to novel light sources, and are especially appealing for ultrafast spectroscopy of chemistry in solutions. In particular, the great success of high harmonic spectroscopy in both gas and solid phases motivates extending this technique to the liquid phase, but this is hindered by the lack of a microscopic understanding of the underlying light-driven electron dynamics. In this talk, I will present our recent collaborative effort in tackling this problem by combining HHG experiments from thin liquid flat jets, and theory based on a novel ab-initio approach that relies on clusters we have developed. We have employed these techniques to study HHG in different liquids and laser conditions, focusing on the microscopic mechanism and the cutoff scaling. Surprisingly, and opposed to the established cutoff scaling in gases and solids, we found that the liquid HHG cutoff does not scale with the driving wavelength, and scales very weakly with the driving power. We propose an extended semi-classical model which takes into account the electron-ion scattering processes in the liquid to explain our findings. The simple model qualitatively describes the main structure of the HHG spectra, and identifies the electron mean free paths as a principal factor in the HHG process in liquids. Our work thus paves the way to the utilization of HHG spectroscopy for probing electron mean free paths in liquids in the low energy regime ( $<10\text{eV}$ ), and has potential for probing ultrafast chemistry in solutions.

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**Contribution Type:** Hot topic contribution

**Status:** ACCEPTED

# Cold and controlled collisions using tamed molecular beams

## Content

The study of molecular collisions with the highest possible detail has been an important research theme in physical chemistry for decades. Experimentally, the level of detail obtained in these studies depends on the quality of preparation of the collision partners before the collision, and on how accurately the products are analyzed afterward.

Over the last years, methods have been developed to get improved control over molecules in a molecular beam. With the Stark decelerator, a part of a molecular beam can be selected to produce bunches of molecules with a computer-controlled velocity and with longitudinal temperatures as low as a few mK [1]. The molecular packets that emerge from the decelerator have small spatial and angular spreads, and have almost perfect quantum state purity. These tamed molecular beams are excellent starting points for high-resolution crossed beam scattering experiments.

I will illustrate the possibilities this new technology offers to study molecular collisions with unprecedented precision and at low collision energies. I will discuss our most recent results on the combination of Stark deceleration and velocity map imaging. The narrow velocity spread of Stark-decelerated beams results in scattering images with an unprecedented sharpness and angular resolution. This has facilitated the observation of diffraction oscillations in the state-to-state differential cross sections for collisions of NO with rare gas atoms [2,3], the observation of scattering resonances in low-energy inelastic [4-6] collisions that reveal the influence of individual partial waves to the scattering dynamics, and product-pair correlations for bimolecular scattering processes [7]. Finally, I will present recent results on collisions between NO and ND<sub>3</sub> molecules at collision energies down to 0.1 cm<sup>-1</sup> obtained using merged beam configurations.

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**Contribution Type:** Invited talk

# Time-resolved photoelectron imaging with a vacuum-integrated hollow capillary fiber light source

## Content

We exploit the phenomenon of resonant dispersive wave emission in gas-filled hollow capillary fibers (HCFs) to realize time-resolved photoelectron imaging measurements with an extremely short temporal resolution. By integrating the output end of an HCF directly into a vacuum chamber assembly we demonstrate two-color deep ultraviolet (DUV)-infrared instrument response functions of just 10 and 11 fs at pump wavelengths of 250 and 280 nm, respectively. This result represents a notable advance in the state of the art of ultrafast photoelectron spectroscopy. We then present a preliminary proof-of-capability measurement investigating the excited state photochemical dynamics operating in the *N*-methylpyrrolidine molecule. Given the substantial interest in generating extremely short and highly tunable DUV pulses for many advanced spectroscopic applications, we anticipate our initial setup will stimulate wider uptake of this approach – particularly given the relatively compact and cost-effective nature of the HCF source.

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**Contribution Type:** Hot topic contribution

# How heteromolecular clusters promote the condensation of volatile components in multicomponent vapors

## Content

Nucleation is the first step of a phase transition, in which a metastable parent phase spontaneously transforms into a thermodynamically stable daughter phase. This process lies at the heart of new particle formation and thus plays a key role in atmospheric science and many industrial processes. However, the underlying mechanisms and pathways of nucleation are in many cases not well understood. In our experiments we investigate gas-phase nucleation on the microsecond time scale, to gain insight into the processes accompanying this transition on the molecular level. We let molecular aggregates form in a pulsed Laval-expansion under constant temperature and pressure and probe them via soft ionization with vacuum ultraviolet light, coupled to time of flight mass spectrometry. From this, we retrieve time-resolved absolute cluster number concentrations, which enable us to calculate experimental nucleation rates and association rate coefficients for cluster growth. In a previous publication [1] we used this data together with a simple kinetic model to unravel how gas-phase nucleation can be significantly enhanced by the addition of a volatile substance. We found evidence that transient, mixed clusters play a crucial role in facilitating nucleation. Here [2] we investigate how clusters formed in this process can act as seeds for further particle growth. We demonstrate that the enhanced nucleation of low vapor pressure substances can promote the condensation of highly abundant, more volatile vapor components. Such processes involving CO<sub>2</sub> or other volatile components are relevant for natural gas separation and extraterrestrial cloud formation.

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**Contribution Type:** Hot topic contribution

# State-to-state chemistry of ultracold molecules

## Content

Ultracold molecules can be used to probe chemical reactions with an unprecedented control at the quantum level. All the fragments of an ultracold chemical reaction, from reactants to products, including intermediate complexes, can now be observed by ionization spectroscopy and velocity-map imaging [1] and the state-to-state rotational distribution of the products can be measured [2]. Molecules possess electronic, vibrational, rotational and spins degrees of freedom and the way they end up in a chemical reaction via the re-arrangement of the atoms is complex. While a full quantum treatment of all degrees of freedom for heavy barrierless systems is for the moment not yet achieved, one can investigate, as a first step, up to which point the nuclear spin degrees of freedom [3] are linked to the remaining ones in a chemical reaction.

A recent study [4] showed that experimental data are consistent with a theoretical model based on the condition that the nuclear spin degrees of freedom mainly act as spectators in chemical reactions of ultracold bi-alkali molecules in magnetic fields. This leads to the possibility to control the rotation parities of the molecular products (even/odd rotational quantum numbers) with a magnetic field. We further extend this theoretical model and propose a more analytical and general expression for the relative nuclear spin state-to-state distribution of an ultracold chemical reaction in a magnetic field [5].

We apply our formalism to the  $\text{KRb} + \text{KRb} \rightarrow \text{K}_2 + \text{Rb}_2$  ultracold reaction. We present the relative nuclear spin state-to-state distribution probabilities of the products given an initial quantum state of the reactants as a function of the magnetic field. The magnetic field trend of the summed probabilities is in very good agreement with recent experimental results [4].

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**Contribution Type:** Invited talk



# Strong light matter phenomena in molecules and low dimensional systems: from first principles

## Content

Strong-field effects and time-resolved spectroscopy can be used to expose dynamical, structural, and electronic properties of molecules. Here we present work that investigates these effects with different flavors of first-principles calculations. We will provide an overview of how well-established concepts in the fields of quantum chemistry and materials have to be adapted when the quantum nature of light becomes important. We will pursue the question whether it is possible to create these new states of materials as ground states of the system. To this end we will show how the emerging (vacuum) dressed states resembles Floquet states in driven systems. A particular appeal of light dressing is the possibility to engineer symmetry breaking which can lead to novel properties of materials. Strong light-matter coupling in cavities provides a pathway to break fundamental materials symmetries, like time-reversal symmetry in chiral cavities. We will discuss the potential to realize non-equilibrium states of matter that have so far been only accessible in ultrafast and ultrastrong laser-driven materials. We will briefly introduce our newly developed quantum electrodynamics density-functional formalism (QEDFT) as a first principles framework to predict, characterize and control the spontaneous appearance of ordered phases of strongly interacting light-matter hybrids.

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**Contribution Type:** Invited talk

# Stopping molecular rotation using coherent ultra-low-energy magnetic manipulations.

## Content

The most detailed insights into collisions at a molecular level are provided by quantum state resolved experiments, as they remove the averaging over the many degrees of freedom that can influence the outcome of the collision. One quantum state that was particularly difficult to control for ground state molecules is the rotational orientation projection ( $m_J$ ) state. This limitation has recently been overcome, with the development of a magnetic manipulation technique [1] which has made it possible to coherently control the  $m_J$  (and nuclear spin projection,  $m_I$ ) states of small ground state molecules. Here, the unique methodology will be presented using a recent study of the rotationally inelastic scattering of  $D_2$  from a Cu(111) surface [2] as an example. In these experiments, the  $m_J$  state of the incoming  $D_2$  molecule in the rotational state  $J = 2$  was controlled and manipulated and was shown to change the probability that the  $D_2$  molecule inelastically scattered into the  $J = 0$  rotational state, which effectively means that an energy perturbation on the order of peV changed the probability the molecule lost 22 meV of rotational energy in the collision. The results from state of the art calculations predict that only molecules in the  $m_J = 0$  state of  $J = 2$  undergo this rotationally inelastic transition when  $D_2$  scatters from Cu(111), but this does not reproduce the experimental data. Therefore, these, and similar [3], measurements provide an extremely stringent benchmark for the development of accurate theoretical models, potentially for the scattering of a range of small molecules both in the gas-phase and at the gas-surface interface.

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**Contribution Type:** Hot topic contribution

# Attosecond dynamics measured in the C state of molecular nitrogen

## Content

Due to the large number of accessible overlapping states, the ultrafast photoionization dynamics in molecules is rich and complex. In order to access the ultrafast evolution of the system experimentally, it is advantageous to detect all the charged products in coincidence. For such experiments an attosecond beamline driven by a 100 kHz noncollinear optical parametric chirped pulse amplification (NOPCPA) system was developed [1]. The beamline incorporates a reaction microscope (REMI) for performing electron-ion coincidence detection measurements. The NOPCPA delivers few-cycle laser pulses with approximately 7 fs duration at 800 nm central wavelength. Using these pulses, relatively short attosecond pulse trains (APTs) are obtained through high-order harmonic generation (HHG) [2]. The APTs are combined with synchronized near infrared (NIR) pulses in a pump-probe configuration.

Here we report on a series of RABBITT (Reconstruction of Attosecond Beating By Interference of Two photon Transitions) experiments performed in gas mixtures of  $N_2$  with argon or helium. In these experiments the photoionization dynamics associated with the photoinduced transitions to the predissociating  $C^2\Sigma_u^+$  state of  $N_2^+$  was investigated. Using the electron-ion coincidence capability of the REMI, the photoelectrons accompanying the formation of different vibrational states ( $v = 3-7$ ) of the C state were identified. Photoionization delays corresponding to the formation of the  $C^2\Sigma_u^+$  state were extracted from the acquired RABBITT spectrograms and compared with a noble gas reference. Theoretical calculations required for a better understanding of the observed non-trivial photoionization delay energy dependence have been performed and show a very encouraging agreement with the experiment.

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**Contribution Type:** Hot topic contribution

# Controlling the Electrons in Excited State Chemistry: Studies using the Quantum Ehrenfest Method (QuEh).

## Content

Attosecond spectroscopy has opened up the possibility of observing electron dynamics on timescale of a few attoseconds. We have been studying such electron dynamics together with the coupled nuclear motion, using our implementation of the Ehrenfest method with quantized nuclear motion (Quantum Ehrenfest QuEh method) (1) The initial electronic wavepacket is chosen as a superposition of eigenstates. If this superposition is chosen appropriately, it can be used to steer the coupled nuclear motion, and thus leads to attochemistry

We will review our methodology (1) for the combination of the Ehrenfest method with both classical and quantum dynamics (2) We will then focus on some model molecular systems (eg GLY+ see below) where the course of the nuclear motion is driven by the nature of the electron dynamics.

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**Contribution Type:** Invited talk

# Realtime tracking of plasmon dephasing in a sub-nm system

## Content

Research on nanoplasmonics has enabled multidisciplinary applications in the fields of solar energy harvesting, ultrafine sensor technology, controlled photocatalysis, etc. [1-3]. While the plasmonic response of particles with diameters exceeding 10 nm is generally well characterized by classical Mie-type models, the collective dynamics below this size limit acquires a predominantly quantum character that is only poorly understood. In particular, the exact origin of plasmon dephasing in this regime is still unknown.

Here, we report on the time-resolved study of the plasmonic dynamics for the sub-nm fullerene C60 [4]. In this system, the coherent dynamics among  $\pi$  and  $\sigma$  band states resulting from photoexcitation give rise to an ultrabroad giant plasmon resonance (GPR) in the continuum, with excitation energy around 20 eV (ionisation potential IP = 7.6 eV) and a bandwidth exceeding 10 eV. By employing attosecond streaking spectroscopy, we measured the photoelectron emission delay around the GPR, while ab-initio linear-response time-dependent density functional theory (LR-TDDFT) and classical trajectory Monte-Carlo (CTMC) calculations were used to simulate the plasmonic response of C60.

By comparing experimental data and computations, we demonstrate that the GPR dephasing time maps directly to the energy-dependent intrinsic time delay of the electron photoemission. In particular, we identified the contribution originating exclusively from the large-scale correlation-induced collective excitation of the GPR to be the fastest route of dephasing, with a characteristic time between 50 and 200 as (See Fig.1). Our study sets a benchmark for a deeper understanding of the dynamics in nano- or sub-nanomaterials. Given the importance of plasmonics in many fields of science, the study can inspire investigations of rapid decoherence and control of plasmon phenomena on their natural time scale. This knowledge can be particularly important for the development of novel technology involving quantum plasmonics.

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**Contribution Type:** Hot topic contribution

# Disentangling the competition of elimination and nucleophilic substitution dynamics

## Content

Base induced elimination (E2) and nucleophilic substitution ( $S_N2$ ) reactions often appear in competition. We chose to study the reaction of  $F^-$  with  $CH_3CH_2Cl$ , as it represents one of the smallest model systems in which both pathways compete. In this reaction they lead to the same  $Cl^-$  product, which makes experimental approaches purely based on product mass very challenging.

Here we present a study combining angle- and energy-differential cross sections, obtained in a crossed-beam velocity map imaging experiment, with quasi-classical trajectory (QCT) calculations on an accurate 21-dimensional hypersurface [1]. The close agreement of the calculations with the experimental total cross sections allows us to disentangle the individual contributions and extract detailed information of the underlying atomistic reaction mechanisms.

We find that the anti-E2 pathway dominates over the whole investigated collision energy range with increasing contributions of  $S_N2$  towards higher energies. The identified reaction mechanisms also match previously identified “dynamic fingerprints” of the two pathways [2].

Additionally we present recent experimental results on steering this reaction by fully substituting the beta-hydrogens with fluorine atoms to suppress the E2 pathway.

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[2] E. Carrascosa, et al., “Imaging dynamic fingerprints of competing E2 and  $S_N2$  reactions” *Nature Communications*, 8:25 (2017)

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**Contribution Type:** Hot topic contribution

# Excited state electronic structure and ultrafast relaxation dynamics in aqueous pyrazine probed using liquid-jet time-resolved photoelectron spectroscopy

## Content

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Energy and charge transfer processes in aqueous solution play important roles in biochemical processes, material science, and environmental and energy science, where the mechanisms of such phenomena are affected, and even driven, by reactant-water interactions in an aqueous environment. Pyrazine exhibits rich photophysicochemical properties and has been studied extensively in isolated form [1,2]. Due to its high photoabsorption cross-section, vapor pressure, and aqueous solubility, it can be readily studied in the gas and aqueous phases, allowing water-induced electronic structure modifications and its solvent-perturbed photoexcited state dynamics to be studied, through comparison to gas-phase studies.

Here we report liquid-jet-(LJ)-based, fs-time-resolved, UV-EUV photoelectron spectroscopy (TRPES) experiments in aqueous pyrazine. The solute was resonantly-excited to the short-lived S<sub>2</sub> excited state at 267 nm, and the ground and excited states were simultaneously probed with 65-fs time-resolution using 32.1 nm probe pulses, generated via high harmonic generation (HHG). Pump-pulse-intensity studies revealed laser-intensity-dependent system energetics and dynamics. A corresponding mitigation of multi-pump-photon-induced space charge effects, under conditions that still permitted significant photoexcitation, allowed the nascent photoexcited-state dynamics to be interrogated. Global fit analyses to the resulting TRPES data revealed an initial relaxation via internal conversion (IC) in  $50 \pm 8$  fs, with subsequent population transfer to lower-lying states occurring on  $560 \pm 150$  fs,  $9 \pm 3$  ps and  $90 \pm 50$  ps timescales. Comparing our results to those from related gas-phase studies, slower relaxation behaviours are confirmed on  $>100$  fs timescales. These observations will be discussed in the context of the electronic structure of pyrazine and its known dynamic behaviors following photoexcitation in the gas-phase.

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**Contribution Type:** Hot topic contribution



# Unusual chemistry involving rearrangement and roaming following strong-field ionization of CH<sub>3</sub>NCS

## Content

We report on the reaction dynamics of CH<sub>3</sub>NCS following strong-field ionization. We track multiple different reaction pathways, among them the intramolecular rearrangement that yields the ion CH<sub>3</sub>S<sup>+</sup> which exhibits coherent oscillations in as a function of pump-probe delay. We also follow the roaming reaction that leads to the formation of H<sub>3</sub><sup>+</sup>.

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**Contribution Type:** Hot topic contribution

# Chiral control of spin-crossover dynamics in Fe(II) complexes

## Content

Iron(II)-based spin-crossover (SCO) complexes hold tremendous promise as multifunctional switches in molecular devices due to a low-spin (LS) to high-spin (HS) state transition that can be triggered by light, pressure and temperature [1]. However, whilst ultrafast spectroscopy studies have achieved a detailed understanding of the photoinduced forward-SCO to the HS state, the backward-SCO mechanism has remained unresolved – despite its crucial role in governing the technologically relevant lifetime of the HS state. Through ultrafast circular dichroism experiments on a prototypical chiral Fe<sup>II</sup> complex, we now show that the backward-SCO is governed by a symmetry-breaking torsional twist in addition to the well-known symmetric stretch mode of the metal-ligand bonds [2].

To this end, we characterize the backward-SCO dynamics of the tris-chelate Fe<sup>II</sup>(4,4'-dimethyl-2,2'-bipyridine)<sub>3</sub> in solution, associated for stereocontrol with enantiopure Δ- or Λ-TRISPHAT anions [3]. Combining ultrafast circular dichroism [4] with transient absorption and anisotropy measurements, we find that the HS state decay is accompanied by ultrafast changes of its optical activity, reflecting the coupling to an asymmetric torsional twisting mode known as the Ray-Dutt twist. Quite remarkably, the diastereoselective ion-pairing suppresses the vibrational population of the newly identified reaction coordinate, thereby trapping the HS state in the potential of the Ray-Dutt twist and achieving a four-fold extension of the HS state's lifetime.

More generally, our results finally provide a complete reaction mechanism for the Fe<sup>II</sup> backward-SCO, which motivates the synthetic control of the involved torsional modes as a complementary route to manipulate the SCO dynamics of Fe<sup>II</sup> complexes.

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**Contribution Type:** Hot topic contribution

# Time-resolved chiral X-Ray photoelectron spectroscopy of fenchone with transiently enhanced atomic site-selectivity

## Content

Chirality plays a fundamental role across the physical and biological sciences. A chiral molecule lacks both a plane of symmetry and a center of symmetry and thus can occur in two non-superimposable mirror-image forms called enantiomers. Despite having the same chemical structure, most enantiomers exhibit different properties when interacting with other chiral objects, such as other chiral reagents or circularly polarized light. While chirality has been a subject of deep investigation in biology and chemistry, its ultrafast dynamics are mostly unexplored. One of the most promising time-dependent investigation techniques of chiral dynamics is Time-Resolved Photo-Electron Circular Dichroism (TR-PECD), which provides a sensitive probe of the structural relaxation of the molecule on the femtosecond time scale [1]. In standard TR-PECD, an ultrashort circular pulse ionizes the molecule from a photo-excited state of the system, and the transient dichroism emerges from the forward-backward asymmetry of the photoelectron emission along the propagation axis of the pulse. However, the non-local character of this approach makes the interpretation of TR-PECD experiments challenging. In this respect, time-resolved X-ray Photoelectron Spectroscopy (TR-XPS) from the core level of a molecule would permit accessing the local relaxation dynamics of electronically excited states in a chemical- and site-selective way, through their transient excited-state chemical shifts (ESCS) [2].

We combined the chemical- and site-specificity of TR-XPS with the enantio-sensitivity of TR-PECD, studying the relaxation dynamics of photoexcited fenchone molecule at the carbon K-edge [3]. With this experiment, we demonstrate that femtosecond chiral dynamics can be probed using core level spectroscopy with circularly polarized XUV light provided by the FERMI free-electron laser. In addition, we demonstrate that core-level PECD spectroscopy of transient excited states allows us to isolate different carbon atoms inside the molecule through their different ESCS. This permit enhancing the site-specificity of the technique allowing to further separate and identify the PECD from different sites in the molecule that otherwise would not be accessible.

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**Contribution Type:** Hot topic contribution

# X-ray induced Coulomb explosion imaging of complex molecules

## Content

Recording images of individual molecules with ultrashort "exposure times" has been a long-standing dream in molecular physics, chemistry, and biology, because this would allow one to follow the motion of atoms on their inherent timescale. While X-ray and electron diffraction have been successfully used to retrieve the structure of large biomolecules, both are very challenging to apply to small molecules in the gas phase. Moreover, these techniques are insensitive to hydrogen atoms, which are key to many chemical reactions.

We could recently demonstrate that snapshot images of the complete structure of a molecule with eleven atoms, including all hydrogens, can be recorded by Coulomb explosion imaging (CEI) when using very intense, femtosecond soft X-ray pulses from the European XFEL [1]. Up to now, it was generally expected that, in order to image polyatomic molecules via CEI, it would be necessary to record essentially all charged fragments in coincidence – a requirement that is currently impossible to fulfill for more than a few atoms within a reasonable measurement time. However, we show that, while it was possible to record up to six-fold ion coincidences in the experiment, even three-fold ion coincidences can be sufficient to image the full structure of a molecule. The X-ray intensity in the reaction microscope at the Small Quantum Systems (SQS) instrument is high enough (up to  $10^{13}$  photons/ $\mu\text{m}^2$ ) to produce extreme charge states in heavy atoms (e.g. up to 42+ in xenon atoms), and to Coulomb-explode molecules into individual atoms very quickly, such that the initial molecular structure is well preserved in the recorded momenta of all ions. The intriguingly clear momentum images allow us to identify each atom's position in the molecule unambiguously.

The sensitivity of the fragmentation pattern to the molecular structure at the instant of ionization, in combination with the femtosecond pulse duration opens the door to monitoring the temporal evolution of the molecular structure with this method in a time-resolved experiment [2]. In two recent follow-up beamtimes, we could obtain first delay-dependent, three-dimensional ion momenta. Together with the prospect of even higher repetition rates at upcoming FELs, this brings the dream of recording molecular movies of photochemical reactions very close to realization.

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**Contribution Type:** Hot topic contribution

# Chiral steering of free-induction decay

## Content

Chiral recognition is an vital task in chemistry, whose origin dates back to the birth of the discipline with the discovery of the optical activity of biomolecules in solution. However, for dilute media and in gas phase, this effect is severely challenging to implement, since it relies on rather weak optical magnetic interactions. This creates a strong demand for an optical chiral discrimination method which relies purely on dipole-interaction physics.

In this work we propose an experiment allowing chiral recognition on an ultrafast timescale using non-destructive weak fields based on pure electric-dipole interactions. Our scheme builds on recent advances on chiral synthetic light [1] to induce a controllable enantiosensitive quantum phase in the medium, which is then translated into easily measurable macroscopic observables. Specifically, we adapt the ability to steer bright and coherent free-induction decay (FID) radiation via its quantum phase manipulation in atomic gases [2] to chirally-sensitive drivers interacting with chiral media, thereby introducing an enantiosensitive Stark shift which gives rise to FID labelling of enantiomers (FIDLE).

We model a chiral molecule promoted from its ground state into a FID-active excited state and which re-emits this photon energy by decaying back to the ground state. The direction of this emission is defined by the quantum phase of the FID-active state. The simplest way to introduce the chiral Stark shift is to consider the interaction of the FID-active state with two other excited states induced by a

tricolour chiral (TRICC) field with noncollinear polarisations forming a chiral triplet. We create this chiral triplet macroscopically using tightly-focused Gaussian beams to provide a longitudinal polarisation component, resulting in a chiral time evolution of the electric field at every point.

We present TRICC FIDLE simulations of the enantiosensitive quantum phase (a) and far-field FID beam (b) for the methyloxirane molecule, showing a clearly visible enantiosensitive steering of the FID emission [3].

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**Contribution Type:** Hot topic contribution

# Probing Electron Dynamics with Ultrafast X-Ray Scattering

## Content

In the past decade, the advent of x-ray free-electron lasers has enabled ultrafast non-resonant x-ray scattering experiments to track photochemical reactions in real time [1] and to measure the change of the molecular electronic density upon photoexcitation [2]. These experiments offer information complementary to spectroscopic techniques with particular sensitivity to molecular structure. The recent increase in repetition rate of facilities such as the European XFEL and LCLS-II and the anticipated further decrease in pulse duration will make it possible not only to track the nuclear but also the electronic motion on the femto- and eventually attosecond time scale. [3,4] Here, we will present simulations of ultrafast x-ray scattering from a molecular electronic wave packet, demonstrate that the signal can probe electronic coherence, and discuss the underlying theory. [5–7] We will explain how these signals can be calculated from ab-initio electronic structure theory and quantum dynamics simulations. We will furthermore address important aspects of experiments such as rotational averaging and energy-integrating detectors that have to be considered to reliably predict the observable signal and to guide the prospective first observation of electron dynamics with ultrafast x-ray scattering.

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**Contribution Type:** Hot topic contribution

# Ultrafast Proton Transfer in Aqueous Urea Dimers Probed by X-ray Absorption Spectroscopy

## Content

Photo-ionization of most systems induces coupled electronic and structural dynamics [1]. Distinguishing between the nuclear and electronic dynamics remains challenging. In this contribution we present femtosecond time-resolved X-ray absorption spectroscopy (trXAS) of aqueous urea ( $\text{CH}_4\text{N}_2\text{O}$ ) solutions utilizing a high-harmonic-generation (HHG) source covering the carbon and nitrogen K-edges. We use this technique to investigate ultrafast proton-transfer dynamics in aqueous urea induced by ionization, as illustrated in Fig 1. The inherently broad HHG spectrum allows us to probe both K-edges simultaneously and is therefore ideal for trXAS [3]. Here, we demonstrate the remarkable properties of trXAS as an element and site-specific method in revealing coupled electronic and nuclear dynamics of matter including intermolecular proton transfer dynamics in a liquid environment. The inherent synchronization of laser-based experimental setup, where pump and probe pulses are derived from the same light source, allow for timing-jitter-free measurements. We utilize a sub- $\mu\text{m}$ -thin flat jet to record artefact-free XAS in transmission mode [3,4]. Our experimental results show spectral features appearing after  $\sim 100$  fs and increasing in absorbance up to around 700 fs before they reach a constant level. These bands are assigned to ionization-induced ultrafast proton transfer in urea dimers through comparison with calculations. The experimental findings are supported by nonadiabatic quantum-mechanical and molecular dynamics (QM/MM) calculations of several urea-dimer and urea-water geometries and can reproduce the main spectral features. They show that the shift of the absorption band highlighted by a black line in panels C and E traces the transfer of the charged proton, whereas the gradually increasing intensity traces the increasing amplitude of the valence hole at the carbon atom with site selectivity. Our results reveal an ultrafast proton transfer between urea molecules caused by valence ionization elucidating the electronic and nuclear dynamics driving proton transfer in a solvated biomolecule. They also reveal the remarkable capability of trXAS to distinguish electronic-structure rearrangements, manifested in the absorption strength, from the structural dynamics manifested in the resonance positions.

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**Contribution Type:** Hot topic contribution



# Conformational landscape in floppy chiral systems explored by one-photon Photoelectron Circular Dichroism (PECD)

## Content

Chirality plays a fundamental role in molecular recognition processes. Molecular flexibility is also crucial in molecular recognition, allowing the interacting molecules to adjust their structures and hence optimize the interaction. Methods probing simultaneously chirality and molecular conformation are therefore crucially needed.

This is the case of a newly introduced chiroptical effect called Photoelectron Circular Dichroism (PECD) leading to very intense (up to 35 %) forward/backward asymmetries, with respect to the photon axis, in the angular distribution of photoelectrons produced by circularly-polarized light ionization of gas phase pure enantiomers. PECD happens to be an orbital-specific, photon energy dependent chiroptical effect and is a subtle probe of the molecular potential being very sensitive to static molecular structures such as conformers, isomers, clusters, as well as to vibrational motion, much more so than other observables in photoionization such as the cross section (Photoelectron Spectrum-PES) or the usual (achiral) asymmetry parameter (for a reviews see [1] [2]).

After an introduction to PECD stressing the universality of the effect in terms of chirality type as well as in terms of targets, ranging from free chiral molecules to clusters and complexes, up to nanoparticles [3], several recent results regarding one VUV-photon valence-shell PECD on various floppy systems will be presented:

- Alanine, for which a Boltzmann-averaged global PECD response could be measured.[4, 5]
- Proline, for which owing to a large binding energy difference between two types of conformers, we could observed directly and rationalize with the help of theoretical calculation a conformer-specific PECD.[6]
- 1-Indanol, for which by changing the carrier gas of the molecular beam we could control the conformer distribution and observe a dramatic conformer inversion of PECD, while the PES and asymmetry parameters are completely insensitive to conformational isomerism.[7]

Such a sensitivity to conformation is both an asset and a challenge for the ongoing developments of laser-based PECD techniques as a sensitive chiral (bio)chemical analytical tool in the gas phase.

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**Contribution Type:** Invited talk

# Towards a Chemically Accurate Description of Reactions of Molecules with Transition Metal Surfaces

## Content

Heterogeneously catalyzed processes consist of several elementary reactions. Accurately calculating their rates requires the availability of accurate barriers for the rate controlling steps. However, currently no first principles methods can be relied upon to deliver the required accuracy. Aiming to solve this problem, in 2009 we came up with a novel implementation of the specific reaction parameter approach to density functional theory (SRP-DFT). While the original procedure was restricted to cases where the Born-Oppenheimer static surface (BOSS) model could be used (H<sub>2</sub> with surfaces), we can now also use it for heavier molecules interacting with metals. For this, we can combine SRP-DFT with Density Functional Molecular Dynamics (DFMD). Additionally, we are now able to develop potential energy surfaces also depending on the degrees of freedom associated with the surface phonons using a machine learning approach, for polyatomic molecules interacting with metals. The effects of electron-hole pair excitation can be modeled with the local density friction approximation (LDFA) and with orbital dependent friction (ODF). We are increasingly turning to systems for which DFT at the generalized gradient approximation (GGA) and even the meta-GGA level is insufficiently accurate. The example that will be discussed is O<sub>2</sub> + Al(111), which is infamous for how difficult it is to model with DFT. For systems like O<sub>2</sub> + Al(111), we have evidence to suggest that the accuracy for systems characterized by low values of (the work function of the metal surface minus the electron affinity of the molecule) can be described more accurately with screened hybrid than with GGA functionals. Also, for such systems (which are treated inaccurately with GGA-DFT) meta-GGA functionals already give results that are improved over GGA results. I will also discuss quantum Monte-Carlo results for H<sub>2</sub> + Al(110), that were obtained in a collaboration with Katharina Doblhoff-Dier. These results suggest that even GGA-DFT correctly describes the energetic corrugation of the barrier heights (how they vary with impact site and orientation of the molecule), although their absolute number may be wrong. They also suggest a way to obtain chemically accurate results for systems with (WF-EA) < 7 eV. Finally, I will briefly touch on efforts to develop an extended benchmark-database that may be used to test density functionals for their performance on dissociative chemisorption barriers on metal surfaces.

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**Presenter:** KROES, Geert-Jan (Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden )

**Contribution Type:** Invited talk

# Probing electronic coherences in chiral molecules

## Content

At the molecular level, chiral recognition manifests itself through the ability of a chiral entity to distinguish between the two non-superimposable mirror images of another chiral unit, resulting in different physical, chemical and biological properties. The manipulation of these properties requires a deeper understanding of the primary steps of chiral recognition, which is of interest for a wide variety of scientific fields. While signatures of transient molecular chirality have been observed with different chiroptical methods, the manifestation of chiral interactions at the ultrafast electron timescale has not been demonstrated.

Here we use a novel laser technology delivering few-femtosecond (fs) UV pulses [1] to photoexcite chiral methyl-lactate. The molecular relaxation is probed via time-resolved photoelectron circular dichroism (TR-PECD) [2,3] using a time-delayed circularly polarized near-infrared pulse, revealing an ultrafast chiroptical switching effect taking place on a sub-10 fs timescale. By modelling the experiment including both the UV photoexcitation and the photoionization by the circularly polarized probe, we show that the effect is driven by electronic coherences between Rydberg states.

With this experiment we achieve an important milestone of molecular spectroscopy that is to observe and manipulate electronic coherences in neutral molecules. The results demonstrate that TR-PECD provides a route to investigate transient chirality at the electronic timescale with high sensitivity, with numerous applications for a variety of chiral systems such as organometallic complexes and bio-relevant molecules.

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**Contribution Type:** Hot topic contribution

# Identification of the Low-energy Shape Resonances of a Nucleobase in Water

## Content

Low-energy electrons (<10 eV) have been shown to induce damage to DNA, where the degree of strand breakage increases at distinct electron energies.[1] Excited states of the nucleobases are believed to facilitate electron capture and subsequent breakage, but the responsible states remain to be precisely identified. Whilst many resonance state energies of isolated nucleobases have been measured,[2] these will be perturbed by the surrounding DNA environment.

We use two-dimensional photoelectron spectroscopy to probe the excited states of the uracil anion, selectively bound with a number of water molecules. Using clusters of up to 35 water molecules, detachment energies and resonance locations are extrapolated to the bulk. Both  $\pi_2$  and  $\pi_3$  resonances are observed to decay to the ground electronic state of the uracil anion. Upon extrapolation, the  $\pi_3$  resonance appears to become near-degenerate with the neutral ground state, but this is from the perspective of electron detachment from the anion. For electron attachment to the neutral, we account for the solvent reorganisation energy, which we measure to be  $\sim 1.0$  eV. Therefore, the vertical electron attachment energy to the  $\pi_3$  state becomes  $\sim 2$  eV. The lower  $\pi_2^*$  state may accept electrons too, but of much less energy, and it becomes a bound state in the bulk solvated anion. Both resonances therefore are likely to contribute to the electron accepting abilities of uracil at energies below 2 eV in water.

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**Primary authors:** CLARKE, Connor (Durham University); VERLET, Jan (Durham University)

**Presenter:** CLARKE, Connor (Durham University)

**Contribution Type:** Hot topic contribution

# Towards a molecular-level understanding of fluxional metal atomic clusters. Recent case studies.

## Content

The very recent development of highly selective techniques making possible the synthesis and experimental characterization of atomic metal clusters is pushing our understanding far beyond the present knowledge in materials science, driving these clusters as a new generation of quantum materials at the lower bounds of nanotechnology. When the size of the metal cluster is reduced to a small number of atoms, the d-band of the metal splits into a subnanometric d-type molecular orbitals network in which all metal atoms are inter-connected, with the inter-connections having the length of a chemical bond (1–2 Å). These molecular characteristics are at the very core of the high stability and novel properties of the smallest metal clusters, with their integration into colloidal materials interacting with the environment having the potential to further boost their performance in applications such as luminescence, sensing, bioimaging, theranostics, energy conversion, catalysis, and photocatalysis. Through the presentation of very recent case studies, my talk is aimed to illustrate how first-principles modelling, including methods beyond the state-of-the-art and an interplay with cutting-edge experiments, is helping to understand the special properties of these clusters at the most fundamental molecular-level. First, I will be shown how the application of first-principles methods have disclosed the fundamental reasons why Cu<sub>5</sub> clusters experience a reversible oxidation [1], including aggregation and support effects [2], and are capable of increasing and extending into the visible region the solar absorption of TiO<sub>2</sub>, of augmenting its efficiency for photo-catalysis beyond a factor of four, also considering the decomposition and photo-activation of CO<sub>2</sub> as a prototypical (photo-)catalytic reaction. Finally, I will discuss how the modification of the same material with subnanometric Ag<sub>5</sub> clusters has converted it into a “reporter” of a surface polaron property as well as a novel two-dimensional polaronic material.

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**Presenter:** LARA CASTELLS, MARIA PILAR DE (CSIC)

**Contribution Type:** Invited talk

# New avenues in laser-based photoelectron circular dichroism

## Content

Exploiting an electric dipole effect in ionization [1], photoelectron circular dichroism (PECD) is a highly sensitive enantioselective spectroscopy for studying chiral molecules in the gas phase using either single-photon ionization [2] or multiphoton ionization [3]. In the latter case resonance enhanced multiphoton ionization (REMPI) gives access to neutral electronic excited states. The PECD sensitivity opens the door to study control of the coupled electron and nuclear motion in enantiomers. A prerequisite is a detailed understanding of PECD in REMPI schemes. In this contribution I will report on our recent experiments devoted to unravel different aspects of this effect on the fenchone prototype by addressing the range from impulsive excitation on the femtosecond time scale to highly vibrational state selective excitation with the help of high resolution nanosecond laser techniques [4]. The reflection of the number of absorbed photons in the PECD will be discussed as well as subcycle effects in bichromatic fields [5].

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**Presenter:** BAUMERT, Thomas (Uni Kassel)

**Contribution Type:** Invited talk

# X-ray probing of nucleobase dynamics – comparing different x-ray observables

## Content

### Abstract:

The molecules in the center of this talk are nucleobases, which encode genetic information in life. Although possessing high UV absorption cross-sections, the associated damaging events are relatively rare. The ultrafast transfer of electronic energy into harmless vibrational energy plays a vital role as an internal photoprotection mechanism. This is accomplished via radiationless, ultrafast transitions from the initially excited  $\pi\pi^*$  state into lower lying electronic states. We present an experiment probing the nonadiabatic dynamics of the molecule by femtosecond resonant x-ray absorption spectroscopy at the oxygen K-edge. This scheme is particularly sensitive to holes in the oxygen lone pair orbitals ( $n$ ), which are induced in the  $\pi\pi^* \rightarrow n\pi$  relaxation. We find a  $\pi\pi^* \rightarrow n\pi$  transition, occurring via a conical intersection in less than 100 fs after excitation [1].

Thiolated nucleobases show an efficient and ultrafast relaxation into long-lived triplet states, contrasting with the ultrafast relaxation to the ground states observed in canonical nucleobases. The triplet channel gives rise to applications as photoinduced-cross linkers but also to problems related to its current use of thionucleobases as medication. We investigate the UV induced dynamics of 2-thiouracil via time resolved x-ray photoelectron spectroscopy (XPS) at the sulfur L-edge [2]. We find a direct connection between the charge moving within the molecule and the binding energy shifts observed in the photoelectron spectrum. The mechanism manifests itself into coherently modulated signals due to the oscillating electronic population. The XPS probing mechanism is sensitive to the local charge at the probed atom. Probing at multiple core levels allows to dynamically image molecular valence charge, moving over the molecule as a consequence of nonadiabatic dynamics.

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**Contribution Type:** Invited talk

# Water molecules in space: near-thresholds inelastic collisions of water isotopes.

## Content

Water is the third most abundant molecule in the interstellar medium (ISM) and has ubiquitously been observed by ground- and space-based telescopes since its first detection in 1969 in the Orion nebula [1-3]. Thus water is a key molecule for the understanding of the energy balance and the physical-chemical processes that occur in these environments. Its principal collision partner obviously is  $H_2$  because of its high abundance in ISM. Therefore, an accurate description of  $H_2O$ - $H_2$  collision dynamics is required at low temperature/energy, where the quantum nature of interaction may be revealed by the observation of resonances (Feshbach or shape/orbiting) [4].

The first rotational excitations of the water isotopologues by collisions with  $H_2$  were observed in the near-cold regime in a crossed-molecular beam apparatus (CMB). The experimental scattering cross-sections were compared with the theoretical calculations performed on the potential energy surface of Valiron et al. [5], both at the state-to-state level and at low collision energy (near rotational thresholds) [6-7]. The different dynamical behaviors of  $H_2O$ ,  $D_2O$  and  $HOD$ , colliding with *normal-* or *para-* $H_2$  will be presented.

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**Contribution Type:** Invited talk



# Probing Entrance and Exit Channel Dynamics in Hydroxyl Radical Reactions by Photodetachment

## Content

Studies using the photodetachment of precursor negative ions to examine the transition state dynamics of hydroxyl radical reactions will be reviewed. In cases where the anion has a geometry similar to the transition-state region for a bimolecular neutral reaction, dissociative photodetachment occurs, and a photoelectron-photofragment coincidence experiment can be used to kinematically characterize the resulting dissociation event, allowing a correlation of the electron kinetic energy distribution determined by Franck-Condon photodetachment with the final neutral product states determined by the kinetic energy release between the neutral atomic and molecular products. Examples will include a benchmark measurement of the dynamics of an elementary chemical reaction: using the  $F^-(H_2O)$  complex to study the  $F + H_2O \rightarrow OH + HF$  neutral reaction. This four-atom system has six internal degrees of freedom and represents a grand-challenge for accurate calculations of the Born-Oppenheimer potential energy surfaces and quantum dynamics of the system. Comparison of experiment with theoretical predictions shows that this system can be treated with near chemical accuracy, but there are still challenges in accounting for excited states and long-lived complexes.<sup>1</sup> Extension of this method to examining the effect of parent anion vibrational excitation on the dissociation dynamics on the neutral surface through overtone excitation of the F-H-O proton transfer coordinate in the anion will also be discussed,<sup>2</sup> as well as the prospects for further studies of the effects of vibrational excitation. This work has been supported in part by the US DOE under grant DE-FG03-98ER14879

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**Presenter:** Prof. CONTINETTI, Robert (University of California San Diego)

**Contribution Type:** Invited talk

# The primary steps of ion solvation

## Content

I will present recent experimental results that have enabled us to observe the solvation dynamics of a single alkali cation ion in liquid helium with atomic resolution and on the natural femtosecond time scale.

A single  $\text{Na}^+$  or  $\text{Li}^+$  ion is created instantly at the surface of a liquid He nanodroplet and we measured in real time the gradual attachment of individual He atoms to the ion. Our results show that both ions bind 8-9 He atoms during the first 6 ps. However, while the time-dependent number distribution of solvent atoms for  $\text{Na}^+$  are well-described by Poisson distributions,  $\text{Li}^+$  shows irregular distributions revealing the formation of particularly stable solvation-complexes. The experimental findings for  $\text{Na}^+$  are in agreement with numerical simulations based on time-dependent density-functional theory.

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**Contribution Type:** Invited talk

# Stereodynamics and Control in the cold-energy regime.

## Content

The last decade has witnessed extraordinary advances in the exploration of inelastic and reactive collisions at cold ( $<1$  K) and ultra-cold ( $< 1$  mK) energies, to the point that our understanding of these processes has experienced a stunning progress paving the way for applications in quantum control of chemical reaction dynamics. At these collision energies, scattering is contributed by few partial waves whose manifestation in the integral and differential cross sections can be singled out thus making possible to isolate and detect resonances, which are ubiquitous in most of the studied processes. One such elementary molecular process is a rotation–translation energy exchange in which a rotationally excited molecule undergoes relaxation (quenching) in collisions with an atom or another molecule and the energy released is transferred to the relative translation of the collision partners. Such processes have been extensively studied in the literature for many neutral and ionic molecular systems, including the simplest molecule  $H_2$ . In particular, the regime near 1 K has also been the focus of a series of experiments by Zare and coworkers [1-3] in which rotational quenching of HD and D<sub>2</sub> by He, D<sub>2</sub> and He has been reported. The experiment involves coexpansion of the molecular species in a supersonic beam combined with selection of the initial alignment of the molecular rotational angular momentum through Stark-induced adiabatic Raman Passage (SARP). The SARP method allows stereodynamical control of the collision process by selecting a given projection ( $m_j$ ) of the molecular rotational angular momentum  $j$  on the relative collision velocity vector or preparing a molecular state.

In our recent work we have applied theoretical methods to describe the stereodynamics of inelastic and reactive atom-molecule and molecule-molecule collisions in the cold energy regime. In my talk I will show some examples of how the stereodynamics of cold molecule-molecule collisions can be determined by a single partial wave shape resonance and how it can be used to achieve exquisite control of the collision outcome. Specifically, I will address the issue of how scattering resonances are affected by the polarization of the collision partners and the extent of control that can be achieved by a suitable preparation of internuclear axis/rotational angular momenta at cold collision energies and how the integral and differential cross sections are influenced. It will be shown that low energy resonances can be dramatically affected by some specific preparations and in some cases completely suppressed. In addition, I will present the simulation of the results of the SARP experiments [4-6] and it will be shown that the theoretical approach is necessary for a full interpretation of the experimental results. [6]

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**Contribution Type:** Invited talk

# Photoelectron elliptical dichroism spectroscopy of resonance enhanced multiphoton ionization

## Content

The resonance-enhanced multiphoton ionization of chiral molecules by elliptically polarized laser pulses produces photoelectron angular distributions that are forward/backward asymmetric with respect to the light propagation axis. We investigate this photoelectron elliptical dichroism (PEELD) in the (2+1)-photon ionization of fenchone molecules, using wavelength tunable femtosecond UV pulses. We show that the photoelectron elliptical asymmetry is extremely sensitive to the intermediate resonant states involved in the ionization process, and enables to reveal electronic couplings that do not show up so clearly when using circularly polarized light. Using elliptically polarized laser pulses in resonance-enhanced multiphoton ionization enables modifying the anisotropy of excitation as well as the multiphoton absorption probabilities. Scanning the ellipticity thus considerably enriches the photoelectron spectroscopy.

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*Phys. Chem. Chem. Phys.* 24 6415–27 (2022) - DOI:10.1039/D1CP05618B

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**Presenter:** BLANCHET, Valerie (CELIA)

**Contribution Type:** Invited talk

# Ion processes in space and planetary atmospheres

## Content

Among the multitude of molecules detected in space and in the atmospheres of planets, including our own, ions have been known to play an important role [1,2]. During the processes of star formation and evolution ion reactions have been invoked as intermediate steps in the build-up of complex organic molecules (COMs) [3], which can function as missing link in the formation of prebiotic molecules. Such biomolecule precursors can be delivered to planetary surfaces by accretion as well as comet and asteroid impacts and act as starting points for the formation of the building blocks of life. In addition, a multitude of ions including protonated nitriles and other nitrogen-containing compounds have been observed by the Cassini Plasma Spectrometer (CAPS) and the Ion and Neutral Mass Spectrometer (INMS) in the atmosphere of the Kronian satellite Titan [4]. It is therefore necessary to investigate possible formation and destruction pathways of these complex species in the interstellar medium and planetary atmospheres. With increasing complexity, also isomerism of ions gains importance and the different behaviour of isomers of ions upon chemical reactions has to be studied. During the last years, ion traps and guided beam devices have been successfully employed to investigate ion-neutral processes. We investigated the chemical reactions of isomers of nitrogen-containing ions using guided beam machines and their vibrational spectra using infrared photodissociation spectroscopy in a cold ion trap. The role of these species in the build-up of COMs in the interstellar medium and planetary ionospheres is discussed.

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**Contribution Type:** Invited talk

# Study and control of chemi-ionization reactions

## Content

Ultracold mixtures of different atomic species are used to obtain dense samples of ultracold heteronuclear molecules which may feature long-range and anisotropic interactions. Such interactions allow for new physics and chemistry studies in a regime purely dominated by quantum effects. To achieve the co-trapping of ultracold atoms, reactive collisions must be efficiently suppressed.

As a first step towards co-trapping, we study the chemi-ionization of ultracold Li by metastable He (He). *For this, we combine a supersonic-beam source for He with a magneto-optical trap for Li [1]. To distinguish in between the contributions of He(23S1) and He(21S0) to the ionization rate, we deplete the He population in the 21S0 state using a novel laser-excitation scheme [2]. We also use laser-optical pumping to prepare both He(23S1) and Li(22S1/2) in selected magnetic sub-levels prior to the collision [3].*

*Here, we demonstrate the efficient control of He-Li chemi-ionization at thermal energies using spin- and quantum-state preparation. Our results imply a strong suppression (enhancement) of chemi-ionization for non-spin-conserving (spin-conserving) reaction channels [4]. These results are in good agreement with a model based on spin angular momentum coupling of the prepared atomic states to the molecular reaction channels. Small deviations from the model are indicative for a violation of spin-conservation rules. The ionization rate also decreases when Li is laser-excited to the 22P<sub>1/2,3/2</sub> states. This is due to the conservation of the projection of the total molecular orbital angular momentum along the internuclear axis [5].*

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# Molecular photophysics and photochemistry probed by ultrafast optical and X-ray spectroscopies

## Content

The past ten years have witnessed a revolution in science with the advent of new ultrafast optical and X-ray domain methodologies enabled by new instrumentation, such as X-ray free electron lasers (XFEL) and table-top HHG sources of Extreme UV pulses radiation. In this presentation, I will focus on developments in deep-UV (sub-300 nm) to X-ray spectroscopies. I will present some results of 2D deep-UV studies of biological systems, revealing hitherto unknown electron transfer processes, [1,2] and then proceed to presenting recent ultrafast deep-UV Circular dichroism studies of molecular systems. [3–5] I will then present the first results on the X-ray helical dichroism of molecular systems, [6] and move onto recent developments in ultrafast non-linear X-ray science, focusing on hard X-ray transient grating spectroscopy, [7,8] as well as subsequent developments.

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# Imaging the photodissociation dynamics of small hydrocarbon radicals

## Content

The photochemistry of small hydrocarbon radicals is of great importance in fundamental processes in Chemistry, such as atmospheric chemistry, hydrocarbon combustion, formation of complex hydrocarbons in the interstellar medium, troposphere chemistry or chemical vapour deposition for diamond growth. Recently we have studied the photodissociation dynamics of the methyl ( $\text{CH}_3$ ) radical from the  $3s$  and  $3p_z$  Rydberg states by one and two-photon excitation, respectively, using a combination of femtosecond [1] and nanosecond [2] laser pulses and the velocity map and slice ion imaging techniques. A great deal of details about the time-resolved predissociation dynamics of the  $3p_z$  state and of the photodissociation dynamics to the final photofragments  $\text{CH}_2 + \text{H}$  from the two excited states, have been obtained and the experimental results have been explained by high level ab initio calculations of the potential energy surfaces involved in the photodissociation process [1-3]. More recently, we have studied the photodissociation dynamics of hot and cold ethyl ( $\text{C}_2\text{H}_5$ ) radicals from Rydberg states by absorption of one-photon in the region of 200 nm [4] and at 193 nm [5]. Velocity map imaging of both the H-atoms (C-H bond cleavage) [4,5] and the methyl radicals (C-C bond cleavage) [6] have been measured. A novel mechanism governed by a conical intersection allowing prompt site-specific hydrogen-atom elimination is presented and discussed [4,5]. References

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**Contribution Type:** Invited talk

# Towards controlled reactive collisions

## Content

One of the important goals in physical chemistry is to get a complete understanding of chemical reactions and the underlying dynamics on the molecular level. We therefore investigate collisions and reactions between individual molecules and atoms in high detail, using the powerful combination of Zeeman deceleration and Velocity Map Imaging in a crossed molecular beam setup [1]. The decelerator allows for precise control over paramagnetic species, while Velocity Map Imaging in combination with near-threshold ionization enables us to accurately probe the velocity vectors of the scattered products. This powerful combination of techniques enables scattering experiments with extraordinary resolution, thereby unveiling intimate details of molecular collisions, such as diffraction oscillations and scattering resonances.

So far, we used this experimental approach to investigate inelastic collisions, for instance between carbon atoms and helium atoms [2] or hydrogen molecules. Recently, we started examining reactive scattering processes. We aim to measure the collision-energy dependence of state-to-state differential cross sections in order to provide an extremely sensitive test for potential energy surfaces and scattering calculations used to describe the molecular reaction dynamics.

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**Contribution Type:** Invited talk

# Exploiting electronic entanglement for steering bond dynamics in molecules pumped by ultrashort optical pulses

## Content

Photoexcitation or photoionization by short attosecond (as) or few femtoseconds (fs) pulses build a superposition of the electronic states that fall within the broad pulse energy bandwidth. By tuning the pulse parameters, one can engineer electronic coherences between selected electronic states and control the charge migration and the spatio-temporal beating of the electronic density on a purely electronic time scale[1]. As the nuclei begin to move, the electronic and nuclear motions are entangled and the engineered electronic coherences can be usefully exploited for steering the vibronic density through the network of non adiabatic interactions to specific products.[2,3] We discuss three recent dynamical computations for which we analyze the time evolution of the entanglement between nuclear and electronic degrees of freedom using singular valued decomposition (SVD) of the wave function.[4,5] At each time step, the wave function is thereby written as a superposition of singular states weighted by their corresponding singular values ordered by their decreasing magnitude. Each singular state is a product of a component that depends only on the nuclear degrees of freedom and a component depending on the electronic coordinates. This singular state is a separable wave function. When more than one singular state is necessary for describing the wave function, it is entangled. This analysis gives valuable insights on how the entanglement of the initial state governs its subsequent modulation by the nuclear motion on coupled electronic states. It is the initial entanglement that can be controlled by the excitation pulse. We first compare the entangled electron-nuclei dynamics in two diatomic molecules, LiH and N<sub>2</sub>, excited by short 2fs UV pulses. In LiH, the targeted electronic states are shallow and dissociative for the energy range span by the broad energy bandwidth of the 5 eV – 2fs pulse and the non adiabatic interactions (NAC) are rather weak. Our results show that a few singular states are necessary for accurately describing the time evolving wave function and that their number is modulated in time by the interplay between the gradients of the potential energy curves of the excited states and the NAC between them driven by the nuclear motion.[4] In N<sub>2</sub>,[6] we targeted with the pulse a superposition of the three lowest  $\Sigma$  states, two Rydberg states and a shallower valence state, strongly coupled by NAC at the exit of the Franck-Condon region. In that case, there is a strong modulation in time of the entanglement due to the NAC coupling.[5] If time permits, we will also report preliminary results on the time evolution of the entanglement in the ultrafast structural rearrangement of the methane cation ionized to a superposition of its three lowest electronic states.[2]

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**Contribution Type:** Invited talk

# Attosecond Interferometry

## Content

Attosecond science is a young field of research that has rapidly evolved over the past decade. One of the most important aspect of attosecond spectroscopy lies in its coherent nature. Resolving the internal coherence is a primary challenge in this field, serving as a key step in our ability to reconstruct the internal dynamics. As in many other branches in physics, coherence is resolved via interferometry. In this talk, I will describe advanced schemes for attosecond interferometry. The application of these schemes provides direct insights into a range of fundamental phenomena in nature, from tunneling and photoionization in atomic systems to ultrafast chiral phenomena and attosecond scale currents in solids.

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**Contribution Type:** Invited talk

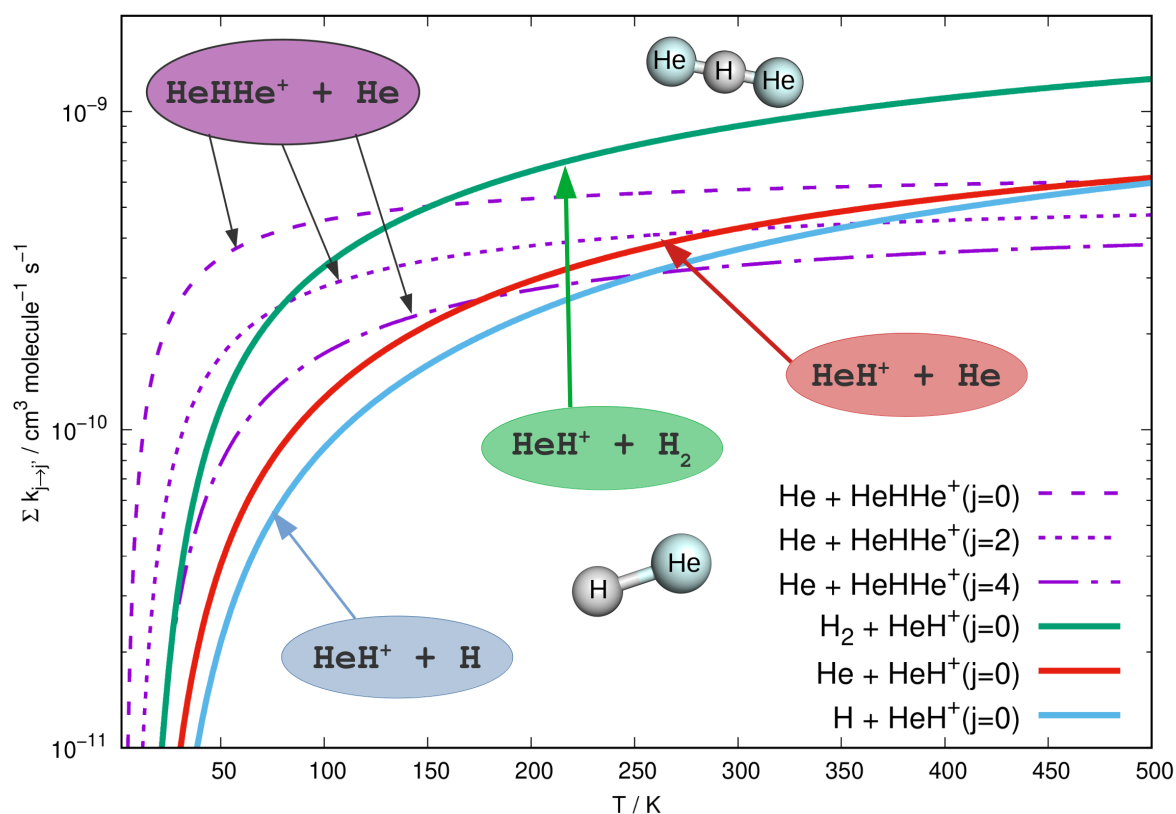
# Study of gas-phase reactions of small systems with relevance in astrochemistry

## Content

I will present a comparison of our studies on the collisions of HeH<sup>+</sup> molecules with He and H<sub>2</sub>, [1,2,3] and the collisions of HeHHe<sup>+</sup> molecules He [4]. New ab initio potential energy have been used in quantum close coupling calculations for different initial states of these molecules in their ground electronic states, over a range of collision energies.

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**Contribution Type:** Invited talk

# Molecular processes between the stars

## Content

The space between the stars is not empty but filled with a very dilute gas. In spite of the extremely low temperatures and densities, these clouds contain a surprisingly rich and interesting chemistry, as evidenced by the detection of more than 200 different molecules, from simple to complex.

These clouds are also the birthplaces of new stars and planets. New facilities such as the Atacama Large Millimeter Array and the James Webb Space Telescope allow us to zoom in on dense cloud cores and planetary system construction sites with unprecedented sharpness and sensitivity.

Spectral scans of young disks contain tens of thousands of rotational lines, revealing water and a surprisingly rich variety of organic materials, including simple sugars and high abundances of deuterated species.

How are these molecules formed and what molecular processes play a role? How common are they? How do abundances compare with those found in comets by the Rosetta mission to 67P? Can they be delivered to new planets and form the basis for life elsewhere in the Universe?

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**Contribution Type:** Invited talk

# Controlled molecules for ultrafast chemical dynamics studies

## Content

Imaging the temporal evolution of the valence electrons and the positions of the atoms during a chemical reaction allows for direct insight into fundamental chemical processes. State-selected, strongly-aligned, and oriented molecular ensembles allow for studies of ultrafast chemical dynamics directly in the molecular frame. Such dynamics can be extracted, for instance, from molecular-frame photoelectron angular distributions (MFPADs) or obtained via x-ray or electron diffraction. However, the properties of atoms and molecules strongly depend on their environment. In particular, solvation and hydrogen bonding plays an important role in chemistry and biochemistry. It is therefore of great interest to bridge the gap between single molecules and molecules in solvation. We have developed techniques to manipulate the motion of molecules and small clusters in cold supersonic beams using strong inhomogeneous electric and laser fields. State-selected molecules are aligned or oriented by the combined effect of a dc electric field and shaped laser pulses [1]. This allows for adiabatic, nonadiabatic, and laser-field-free three-dimensional alignment of complex molecules and molecular clusters. In the Controlled Molecule Imaging group, we focus on the experimental investigation of model-chromophore dynamics. Our studies include gaseous, one-to-one clusters of (bio)molecules with a single water molecule attached, as well as liquid-phase studies [2].

We have investigated indole-water [3] and pyrrole-water clusters, both of which are model systems for the photophysics of tryptophan, the most strongly near-UV absorbing amino acid. Here, we present results on the control of molecules and clusters as well as the UV-induced dynamics of these systems, probed by IR and x-ray laser sources, both in our lab and at larger facilities such as LCLS and the European XFEL.

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**Contribution Type:** Invited talk

# Plasmonic hybrid systems in external light fields: from high-resolution sensing to plasmonic catalysis

## Content

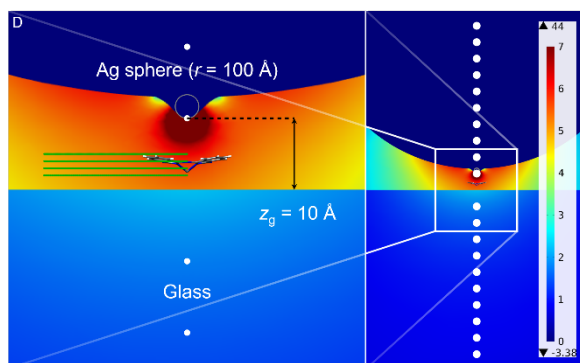
The excitation of collective electron dynamics inside the metallic nanoparticles induced by external light fields leads to strongly re-shaped electromagnetic nearfields with a complex spatial and temporal profile. The interaction of these modified and enhanced nearfields with systems located in close vicinity to the metallic nanoparticle is the origin of many astonishing physical and chemical phenomena, such as the formation of new quasi-particles, new mechanisms for chemical reactions or the ultra-high spatial resolution and selectivity in molecular detection.

Besides being of fundamental interest, this interplay between nearfields and molecules promises great potential on the application side, potentially enabling breakthrough in new emerging technologies in a broad range of research fields, such as nanophotonics, energy and environmental research, biophotonics, light-harvesting energy sources, highly sensitive nano-sensors etc. This necessitates a solid theoretical understanding and simulation of these hybrid systems.

For the theoretical description of such plasmonic hybrid systems in external light fields, it is necessary to describe both the electromagnetic interaction and the more chemical effects equally. In this talk, I will introduce our recent results on the theoretical description of these systems, with particular emphasis on spectroscopic applications, e.g., in the context of tip-enhanced Raman scattering spectroscopy: several recent experiments provide evidence for an extremely high spatial resolution of this setup on the nanometer or even sub-nanometer scale. Our calculations show pronounced changes of the Raman spectrum under non-resonant and resonant conditions and support the possibility of sub-nanometer spatial resolution.

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**Contribution Type:** Invited talk



# Quantum flows neural network for variational solutions of the Schrödinger equation

## Content

The computational technology of highly expressive parametric neural-network-functions has allowed machine learning to make a major foray into disciplines of natural sciences. The neural network functions may be effectively “fitted” to a loss function, given in the form of a variational principle or virial theorem, to provide solutions to quantum mechanical problems. Recently, a few deep neural network models for solving the electronic Schrödinger equation were developed [1-3], demonstrating both outstanding computing efficiency and accurate results.

Here, we present a new quantum-flow-neural-network approach for obtaining variational solutions of the Schrödinger equation. At the core of the method is an invertible neural network composed with the general basis of orthogonal functions [4], which provides a more stable framework for simultaneous optimization of the ground state and a lot of excited states. We apply our approach to calculations of the vibrational energy levels of polyatomic molecules as well as of electronic energies in a single-active-electron approximation. The results show a considerable improvement of variational convergence for the ground and the excited states.

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