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Book of Abstracts

Taming molecular collisions

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The study of molecular collisions with the highest possible detail has been an important research theme in physical chemistry for decades. Over the last years we have developed methods to get improved control over molecules in a molecular beam. With a Stark or Zeeman 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. 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 discuss our most recent results on the combination of Stark or Zeeman deceleration and velocity map imaging. The narrow velocity spread of 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[1,2], the observation of scattering resonances[3,4] at temperatures below 1 K revealing the influence of individual partial waves to the scattering dynamics, and product-pair correlations for bimolecular scattering processes.[5]

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Probing the collision mechanism via the scattering stereodynamics

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This talk will present new experimental results on the stereodynamics of the inelastic scattering of NO(X) by the rare gases, in which the NO(X) molecule is fully quantum state-selected both before and after collision. Experimental results will be presented concerning the state-to-state differential cross-sections (DCSs) and collision-induced angular momentum polarizations observed following the fully Λ-doublet resolved inelastic scattering of NO($X^2\Pi_{1/2}$, v=0, j=1/2,f) with the rare gases, and compared with the results state-of-the-art theoretical calculations.

New experimental results will be shown in which the scattering process is investigated as a function of arbitrary orientation of the NO molecule.[1] This is achieved by orienting the quantum state selected NO molecule using a static electric field. A particular focus of the talk will be a discussion of the quantum mechanical origin of the steric effect, and how complete measurements of the stereodynamics help to sheds light on the collision mechanism.

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Quantum control of rotationally inelastic cold scattering near 1 K

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The amount of dynamical information that can be extracted from a scattering experiment depends on how precisely the input and output quantum states are defined. In particular, because of the anisotropic nature of molecular forces, the result of a scattering experiment strongly depends on the collision geometry, which is defined by the orientation of the molecular axis relative to the collision velocity. To understand the effect of collision geometry at the quantum level we studied the rotationally inelastic scattering of oriented HD molecules in a supersonic beam co-expanded with its collision partners He, H_2 or, D_2.[1-2] Co-expanding the partners in a single molecular beam not only defines the direction of their relative velocity, it brings the collision energy down to a few Kelvin, thereby restricting the number of incoming orbital angular momentum states l.

To gain control over the internal quantum states we have devised a coherent optical technique known as the Stark induced adiabatic Raman passage or SARP. Using a pair of time-delayed coherent laser pulses with appropriate fluence SARP prepared a large population of HD in a single vibrational (v) rotational (j) and orientational (m)-quantum state within its electronic ground state. By selecting a single or coherent superposition of m-states SARP aligns the molecular bond axis with respect to the collision velocity. With a precise control over the internal quantum states we were able to extract detailed stereodynamical information using a partial wave analysis of the measured angular distribution. In this talk I will present our recent rotationally inelastic HD ($v = 1, j = 2$) → HD ($v = 1, j = 0$) scattering by ground state He atoms, where we observed the dominance of a single $l = 2$ input orbital wave, suggesting a scattering resonance. The partial wave analysis showed a striking four-fold preference for the $m = 0$ input state in the $\Delta j = 2$ rotational relaxation of HD.

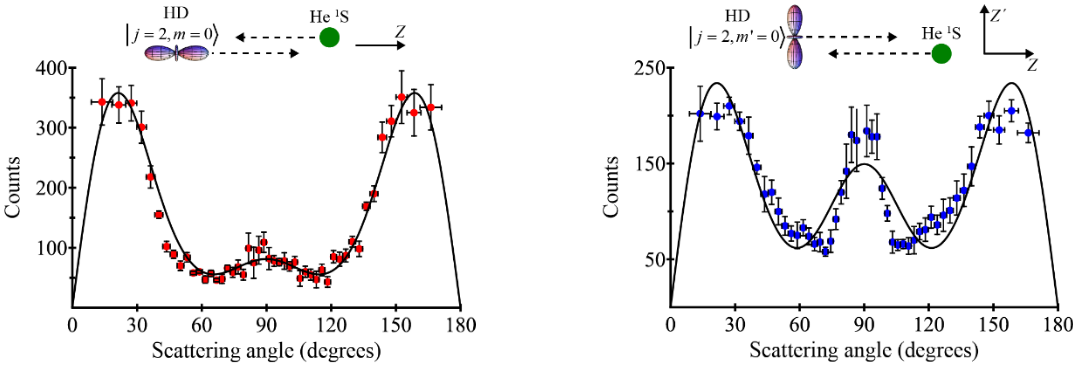

Figure 1: Rotationally inelastic scattering of HD (v=1, j=2, m) → HD (v=1, j=0) by He atom.

Acknowledgments: This work is supported by the U.S. Army Research Office.

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Imaging molecular dynamics by ultrafast X-ray scattering

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Rapid developments of new x-ray and electron scattering experiments provide exciting opportunities for the study of ultrafast photochemical and photophysical processes.[1–3] The focus of this talk is on the intersection of theory, simulations, and experiments.[4–6] In particular, we will discuss new types of experiments that might transgress the distinction between structural dynamics and spectroscopy.[6] Using comprehensive simulations of non-resonant ultrafast x-ray scattering from a molecular wavepacket, we examine the components that contribute to the total scattering signal. The simulations demonstrate how the elastic component, which can be used to determine the spatio-temporal structural dynamics of the molecule, also carries an imprint of the electronic structure, and how the inelastic component depends on the geometry of the molecule. Most interestingly, mixed coherent contributions to the scattering directly probe transient electronic coherences in the molecule.

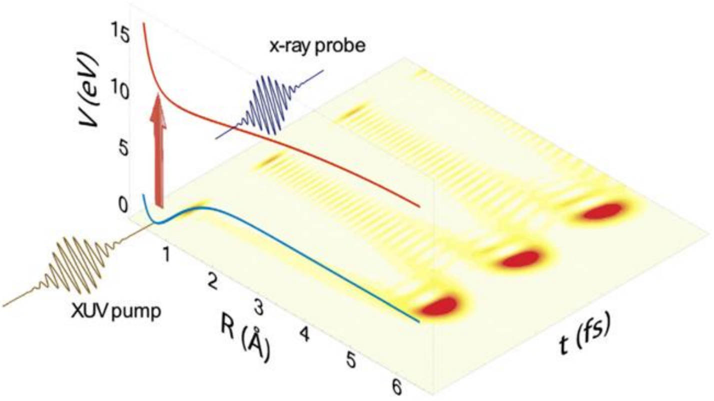

Figure 1: An XUV pump pulse excites a wave packet from the ground state of H_2 onto an excited state. After excitation, an x-ray pulse probes the system by non-resonant ultrafast scattering.[6]

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Probing geometric effects in chemical reaction

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It was long predicted theoretically that geometric phase effect could have a significant effect in the dynamics of chemical reactions with conical intersections. However, experimental observation of such effect proves to be extremely difficult and fruitless. Recently, we have developed a new crossed beams imaging machine and observed the geometric phase effect in the $H+HD\rightarrow H_2+D$ reaction at collision energy above the conical intersection of this reaction using the high resolution threshold ionization - imaging technique. In addition, we have also detected experimental evidence of geometric phase effect, through quantum interference between topological pathways, at collision energies significantly lower than the conical intersection energy using high resolution H-atom Rydberg tagging technique. These new experiments in combination with accurate quantum dynamics calculations allows us to probe and understand this interesting dynamics effect in chemical reaction at the most fundamental level.

HOT TOPIC: Indirect dynamics dominate base induced elimination (E2) for reactions of fluorine anions with tert-butyl halides

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Base induced elimination (E2) and bimolecular nucleophilic substitution (S_N2) are two important reaction mechanisms in organic synthesis and often appear in competition. The steric hindrance at the central carbon centre suppresses the S_N2 reaction and thereby enhances the abundance of E2 products.[1,2]

We investigated the reaction dynamics of the E2 reaction using the combination of crossed beams with velocity map imaging for the reactions $F^- + (CH_3)_3CX$ (X = Cl, I). By recording energy and angle differential cross sections, we could deduce atomistic reaction mechanisms for elimination reactions at a tertiary carbon centre. We found signatures for several atomistic reaction channels.[3] At low collision energy, the differential scattering cross section shows forward-backward symmetry, but with increasing collision energy the symmetry is reduced and forward scattering replaces this feature. However, the dominant scattering feature at all collision energies is rather isotropic scattering into high product ion velocities. We found that an increase of the collision energy is almost completely transferred into internal excitation of the molecular products. Thus, indirect dynamics dominate in the reaction of F^- with *tert*-butyl halides. We speculate on the origin of this dynamic signature with respect to the followed elimination pathways.[4] These results will be used to better understand the competition between S_N2 and E2 at primary and secondary carbon centres.

Our studies on ion-molecule dynamics[4] have been extended to metal organic chemistry, specifically to the reaction of transition metal ions with small organic molecules such as methane. We aim at recording differential cross sections in order to study the dynamics of catalytically relevant elementary reactions. Therefore, a new experiment is being set up and we will give an update on the progress on imaging the reactions of tantalum cations Ta^+ with methane. Specifically, we will show first results for the reaction of Ta^+ with CH_4 and present 3D velocity map images for the $TaCH_2^+$ product.

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Keep on growing: IR action spectroscopy probing peptide aggregation

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The biological function of peptides and proteins is determined by their structure and structural changes. An example of such a change is the misfolding of proteins into fibrillar structures: long aggregates of proteins stacked in a cross-β sheet structure. These β sheet structures, so-called amyloids, are associated with a wide variety of neurodegenerative diseases such as Parkinson's and Alzheimer's disease. It is generally thought that the actual malefactor in these diseases are not the fibrils itself, but rather the early oligomeric stages of the aggregation process. However, these early structures are not well understood β-sheet. One way to visualize these intermediate oligomers is by using infrared action spectroscopy. A number of very interesting papers combining infrared spectroscopy with mass spectrometry and for example ion mobility methods were published in the last decade. However, complementary studies on aggregates of neutral peptides remain elusive.

The main reason for this gap is that it is experimentally challenging to form and to measure these large neutral peptide aggregate clusters. Only a handful of publications show results on neutral gas phase peptide clusters, however they are limited to dimers only. Here, we show that by advancing current technology we are able to make large peptide aggregates using laser desorption with molecular beam cooling.[1] Moreover, we discuss here the mechanism of aggregation, including the competition between intramolecular interaction and intermolecular interaction, by probing their formation by a combination of infrared spectroscopy using the free electron laser FELIX and quantum chemical calculations.[2]

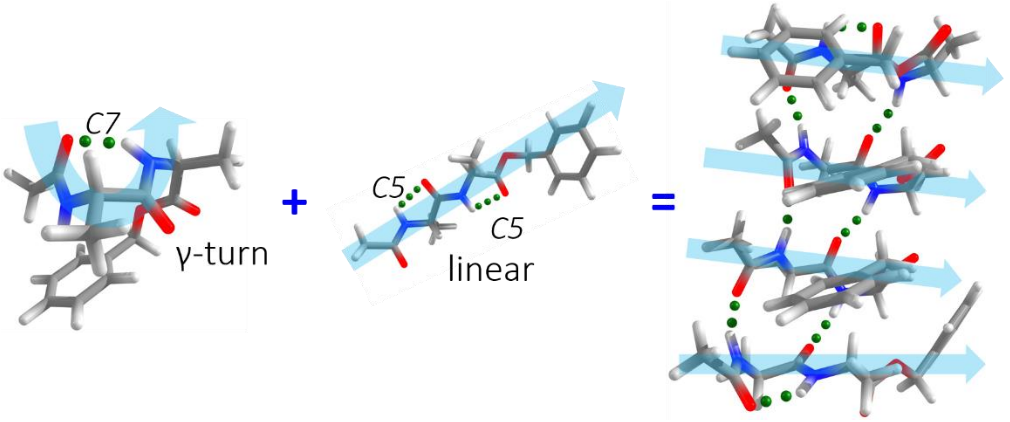

Figure 1: The mechanism of peptide aggregation and hydrogen bond patterns visualized by mass- and conformer selective IR action spectroscopy.

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A novel view of roaming in H_2CO from the H_2 perspective: Dividing surfaces, exit channel effects and phase space effects

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H_2CO is the prototypical system for the study of roaming reaction dynamics. Extensive theoretical and experimental work has gone into establishing and characterizing roaming as a genuine alternate pathway to molecular products. Experimental work to date has focused predominantly on the CO ($v = 0, 1$) photofragments, which gives a picture of the product state distributions of the corresponding H_2 co-fragment. Currently there are no data on higher vibrational states of CO and no direct observation of the H_2 photoproducts from this reaction.

In this work we fill in this gap using Velocity Map Ion Imaging (VMI) to measure the KE distributions of state selected H_2 photofragments. The results are surprising – the roaming channel, at threshold, produces CO excited up to $v = 3$, with some degree of vector correlation previously thought not to exist in roaming pathways. There are also two components in the angular momentum (J) distribution of the CO fragment. Quasi-classical trajectories run on a high-level potential energy surface suggest a roaming dividing surface and rotational dynamics dominated by the H_2 + CO exit channel. The two components to the rotational distribution are broadly understood in a Franck-Condon picture of where the HCO + H PES very rapidly evolves into the H_2 + CO PES. This results in two dominant impact parameters, leading to two rotational components. The comparison of molecular beam experiments and QCT calculation reveal a complexity to roaming dynamics that was unknown previously (and is still evolving).

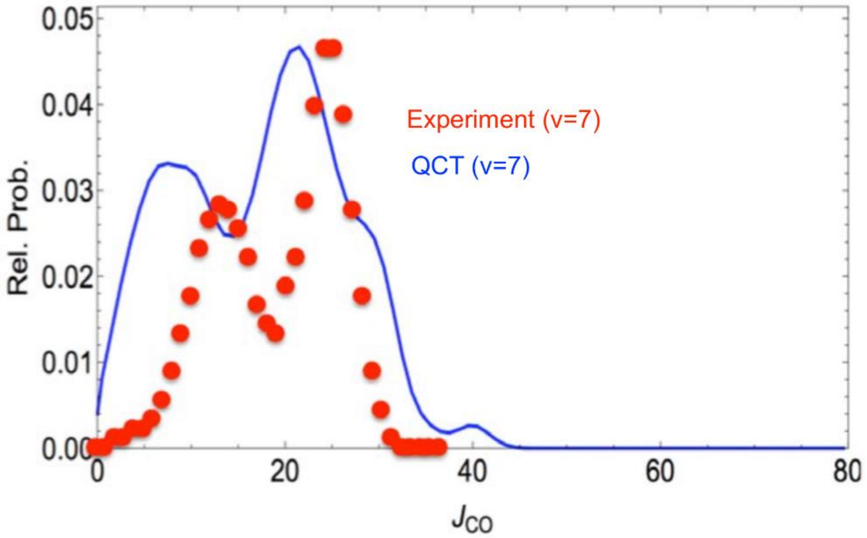

Figure 1: Rotational distributions for H_2 ($v = 7$, $J = 4$, expt.) and ($v = 7$, $J = 5$-7, QCT) following dissociation of H_2CO excited to the $2^1 4^3$ (S_1) state showing bimodal rotational distributions for CO co-fragment.

Accurate spectroscopic characterization of molecular complexes as a first step toward understanding intermolecular interactions

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Noncovalent interactions play a key role in several biological and technological processes, yet their characterization and interpretation are still far from being satisfactory. Integrated experimental and computational investigations of molecular complexes can play an invaluable to understand the properties of intermolecular interactions.

In the past decade, many gas-phase spectroscopic investigations have focused on the understanding of the nature of weak interactions in model systems, and a great effort has been devoted – for example – to studies dealing with complexes formed by small biomolecules with either water or other solvents. In this connection, molecular complexes involving hydrogen bonding between nitrogen-containing systems can be considered as prototypes for studying the (N-H...N) interaction in biological systems.[1]

Along with the well-established hydrogen bonds, emerging classes of noncovalent interactions are attracting increasing attention, such as those involving a pnicogen or chalcogen atom[2-3] because of the fundamental role they play in different fields such as catalysis, drug design, self-assembly processes, and crystal packing. Understanding the mechanisms at the basis of these technological processes requires the characterization of the directionality, strength, and nature of such interactions as well as a comprehensive analysis of their competition with other noncovalent bonds, also taking into account the tuning of these properties by different environments.

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Non-covalent interactions in odorants

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Our sense of smell is usually referred to as the least known among all our senses. Detailed information on the structures of some classes of odorants and on the interactions between odorants and olfactory receptors at the atomic level is lacking. To achieve a better understanding on the molecular mechanisms involved in olfaction, we are investigating odorants and their complexes with water and mimics of amino acid residues using chirped pulsed Fourier transform microwave spectroscopy and computational methods.[1-4] In this talk we will present recent results, focussing on the intra- and intermolecular non-covalent interactions driving the configurations of odorants and their complexes. The interplay between primary and secondary hydrogen bonds and/or dispersion forces will be discussed, as well as the performance of several theoretical methods in view of the experimental data.

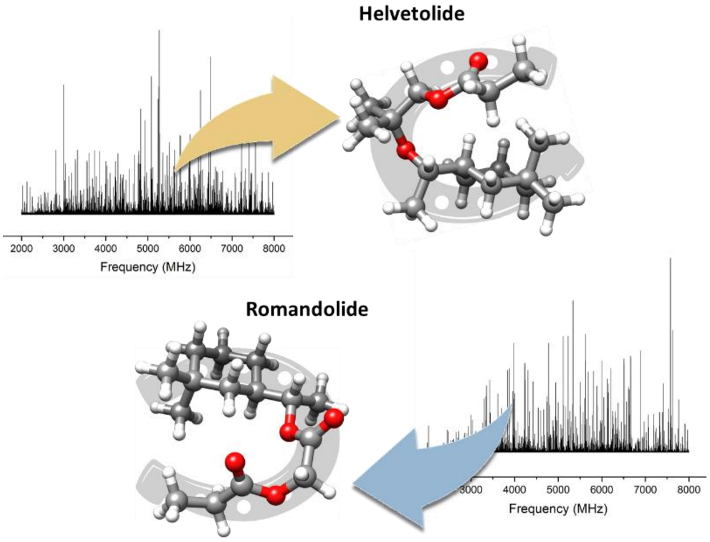

Figure 1: Horseshoe conformations adopted by alicyclic musks.

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HOT TOPIC: Two-dimensional electronic spectroscopy of molecules in helium nanodroplet isolation

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We present the first two-dimensional electronic spectroscopy (2DES) study of cold molecules (sub Kelvin internal temperature) prepared by helium nanodroplet isolation (HENDI).[1] In contrast to conventional pump-probe spectroscopy, 2DES reveals coherent and incoherent dynamics in molecular systems, giving detailed insight into system-bath interactions, charge/energy transfer and structural changes.[2] Until now, most 2DES studies were conducted with liquid/solid phase samples, due to their high target density. However, with the recent development of highly sensitive methods, gas phase samples like molecular and cluster beams have become accessible. The HENDI technique is of special interest, since it provides internally cold molecules and thereby strongly simplifies 2D spectra, leading to less ambiguous interpretations and an easier comparison to theory.

As a first benchmark system, we studied weakly bound Rb molecules attached to helium nanodroplets. Our results, including dynamics due to molecule-matrix interaction, show the applicability of 2DES to samples with extreme low target densities ($\leq 10^7$ cm^{-3}).

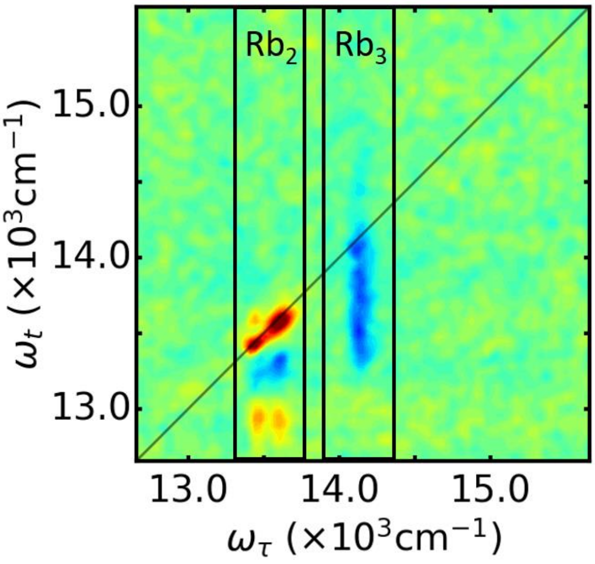

Figure 1: 2D-spectrum of Rb_2 and Rb_3 attached to helium nanodroplets at a pump probe delay of 200 fs. ω_τ and ω_t are the pump and probe frequency respectively. The Rb_2/Rb_3 features are assigned by comparison of the spectral profile along the pump axis to high-resolution absorption spectra.

Acknowledgments: This work has the support of the European Research Council (ERC) Advanced Grant “COCONIS” and Deutsche Forschungsgemeinschaft (DFG), program IRTG 2079

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Binding energies of solvated electrons and retrieval of true photoelectron spectra of liquids

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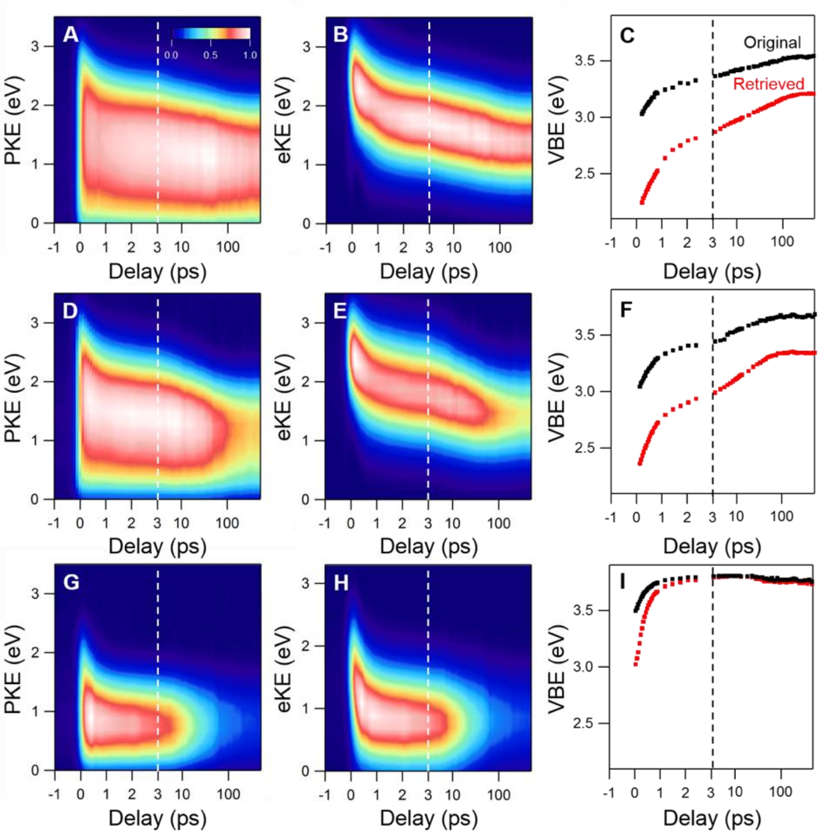
Here we present the electron binding energy distributions of solvated electrons in liquid water, methanol and ethanol accurately measured using extreme ultraviolet (EUV) photoelectron spectroscopy of liquids with a single-order high harmonic. Using the EUV and UV photoelectron spectra of solvated electrons, we succeeded in retrieving sharp electron kinetic energy distributions from the spectra broadened and energy-shifted by inelastic scattering in liquids, overcoming an obstacle in ultrafast UV photoelectron spectroscopy of liquids. The method is demonstrated for the benchmark systems of charge transfer to solvent (CTTS) reaction and ultrafast internal conversion of hydrated electron from the first excited state.



Ultrafast UV photoelectron spectra of CTTS reaction from I^- to polar protic solvents. *PKE time-energy map measured for (**A**) ethanol, (**D**) methanol and (**G**) water using 226-nm pump and 260-nm probe pulses. (**B, E, H**) The eKE time-energy map retrieved from **A**, **D** and **G**, respectively. (**C, F, I**) Time evolution of VBE obtained from **A**, **D** and **G** (Black), and **B**, **E** and **H** (Red), respectively. The time axes are in linear scale from -1 to 3 ps and in log scale from 3 to 500 ps. Broken lines indicate the boundary of the two scales.*

Accurate real-time determination of enantiomeric and isomeric content

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Baptiste Fabre,[†] Stéphane Petit,[†] Jason B. Greenwood,[‡] Valérie Blanchet,[†]
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It is now well-established that ionization of a randomly aligned sample of chiral molecules by a circularly polarized radiation leads to a forward/backward asymmetry in the emitted photoelectron distribution.[1,2] This effect, called photoelectron Circular Dischroism (PECD), originally demonstrated by the synchrotron community, is now routinely measured using table-top femtosecond lasers in the multiphoton ionization regime. Thus, PECD, combined with mass-spectrum spectroscopy, has been recently used to perform enantioselective analysis of a mixture of chiral samples. But, due to the limited ion-electron coincidence rate, this technique does not seem suitable for real-time applications.[3,4]

In this work, we propose and demonstrate a new enantioselective analysis where a randomly aligned sample of chiral molecules is ionized by intense femtosecond laser pulses whose ellipticity is continuously and periodically modified[5]. Experimentally, photoionization is achieved by the second harmonic of an industrial Yb fiber laser with a tunable repetition rate from 166 kHz to 2 MHz delivering 130 fs pulses at 1030 nm. The rotation of a quarter waveplate at a constant speed allows us to record continuously the photoelectron elliptical dischroism (PEELD) as a function of the third Stokes parameter S_3. A further analysis of the S_3 evolution, based on Fourier decomposition and called c-PEELD ("c" standing for continuous), for a set of enantiopure systems, allows us to generate a basis of molecular fingerprints. As a proof-of-concept, we have realized a mixture of enantiopure sample of camphor and fenchone, evolving as a function of time, and we have recovered the fast evolutions of both the proportion and the enantomeric excess using c-PEELD technique with an accuracy of a few % in few seconds.

In parallel, these experimental measurements have been analyzed using a Convolutional Neural Network (CNN). The Network has been first trained using random linear combination of symmetric and asymmetric part evolution of the photoelectron angular distribution coming from enantiopure samples. At the end of the learning stage, CNN is able to retrieve in real-time the relative proportion and enantiomeric excess of the mixture of enantiopure samples.

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Self-trapping relaxation decay investigated by time-resolved photoelectron spectroscopy

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The present work[1] combines time-resolved photoelectron spectroscopy on isolated species with high-level data processing to address an issue, which usually pertains to material science: the electronic relaxation dynamics towards the formation of a Self-Trapped Exciton (STE). Such excitons are common excited states in ionic crystals, silica and rare gas matrices. They are associated with a strong local deformation of the matrix. Argon clusters were taken as a model. They are excited initially to a Wannier exciton at 14 eV and their evolution towards the formation of a STE has showed an unusual type of vibronic relaxation where the electronic excitation of the cluster decreases linearly as a function of time with a 0.59 ± 0.06 eV ps^{-1} rate. The decay was followed for 3.0 ps, and the STE formation occurred in 5.1 ± 0.7 ps.

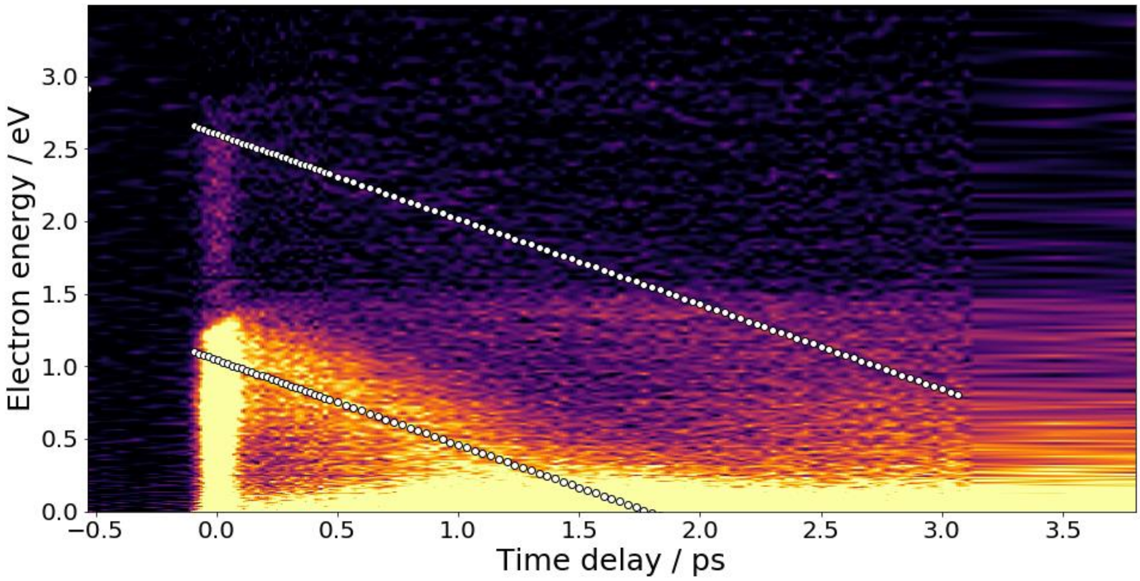

Figure 1: Time-resolved photoelectron spectrum as the function of the pump/probe delay after the excitation of a Wannier exciton in argon cluster.

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Probing electronic processes in large molecules

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Attosecond science is nowadays a well-established research field, which offers formidable tools for the realtime investigation of electronic processes.[1] In this context, we have recently demonstrated that attosecond pulses can initiate charge migration in aromatic amino-acids.[2] Still, there is a long path towards attochemistry and the full control of the molecule via electronic coherences.

In this talk I will first present a time-resolved study of photo-fragmentation following ionization by an isolated XUV attosecond pulse (20–35 eV) of the nucleobase adenine, one of the building blocks of DNA. The most intriguing experimental finding is that doubly ionized adenine can be stabilized by a NIR pulse delayed by 2–3 fs from the XUV. Without the properly timed NIR pulse, the singly or doubly photoionized adenine mainly undergoes fragmentation, as confirmed by theoretical simulations based on Time-Dependent Density Functional Theory combined with Ehrenfest dynamics investigations. We explain the need for a delay between NIR and XUV pulses as the time it takes for electronic correlation to bring the molecule into a state where the NIR pulse is able to remove excess energy through photoionization and hence stabilize the molecule. We identify the relevant mechanism as a shake-up process to an excited state with a delocalised electronic distribution, leading to charge inflation and therefore enhancement of the cross section for NIR photoionization.

In the second part of the talk I will show the results obtained in the C60 molecule. Here we have investigated delays in photoemission after exciting the Giant surface Plasmonic Resonance (GPR) around 20 eV.[3] To this end, we used attosecond streaking spectroscopy.[4] Two identical streaking measurements were acquired in C60 and Ne. The relative delay (attosecond streaking delay) between the spectrograms acquired in C60 and Ne was extracted in a range of photoelectron energies between 9 and 20 eV. This relative delay exhibits a clear trend from positive to negative with a zero-crossing around the plasmonic resonance (20 eV). Simulations allow to extract from the measured delay the interplay between the NIR- and the XUV-induced plasmonic response of the molecule.

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2D photoelectron imaging of anions as a probe of electron-driven chemistry

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Electron spectroscopy of neutrals has been used form many decades to probe resonances and electron-driven chemistry. Here, it will be shown how anion photoelectron (PE) spectroscopy and, specifically, 2D PE imaging can offer new insights into such processes. I will discuss how 2D PE imaging is complementary to 2D electron energy loss spectroscopy and will highlight some of the important advantages and the new information that can be gained. For example, the PE spectra reveal dynamics of the resonances, the PE angular distributions provide information on the electronic structure of the resonances, time-resolved PE spectroscopy offers a route to monitoring the dynamics of the resonances in real-time, and mass-selection allows the study of micro-solvation. I will exemplify these advantages using a few example systems.

HOT TOPIC: Ultrafast molecular spectroscopy using a hollow-core photonic crystal fiber light source

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We demonstrate, for the first time, the application of rare-gas filled hollow-core photonic crystal fibers (HC-PCFs) as tuneable ultraviolet light sources in femtosecond pump-probe spectroscopy.[1] A critical requirement here is excellent output stability over extended periods of data acquisition, and we show this can be readily achieved. The time-resolved photoelectron imaging (TRPEI) technique reveals non-adiabatic dynamical processes operating on three distinct timescales in the styrene molecule following excitation over the 242-258 nm region. These include ultrafast (<100 fs) internal conversion between the $S_2(\pi\pi^*)$ and $S_1(\pi\pi^*)$ electronic states and subsequent intramolecular vibrational energy redistribution within $S_1(\pi\pi^*)$. Compact, cost-effective and highly efficient bench-top HC-PCF sources (see Fig. 1) have huge potential to open up many exciting new avenues for ultrafast spectroscopy in the ultraviolet and vacuum ultraviolet spectral regions. We anticipate that our initial validation of this approach will generate important impetus in this area.

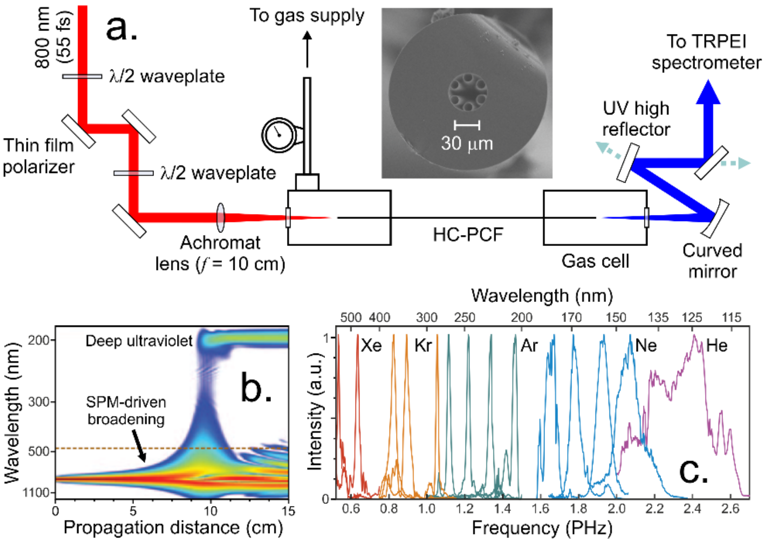

Figure 1: (a) Experimental setup - a short (15-20 cm) length of HC-PCF connects two high-pressure gas cells, each with a built-in window. A scanning electron micrograph showing the cross section of the fiber used in the present work is also included. (b) Numerical simulation illustrating key features of deep-ultraviolet generation in a HC-PCF. (c) Demonstration of the broad tuning range possible by varying the gas and associated pressure.

Acknowledgements: This work was supported by EPSRC Grants EP/R030448/1 and EP/P001459/1 and by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program: Starting Grant agreement HISOL, No. 679649.

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Liquid-liquid phase separation in nanoscale particles

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The phase and morphology of aerosol particles impacts their optical properties, reactive chemistry, water uptake behaviour, and fate. My research group has focused on studies of aerosol particles of atmospheric relevance that undergo liquid-liquid phase separation due to salting out of the organic component. We discovered that phase separation is inhibited in particles less than approximately 50 nm because particles of this size cannot overcome the activation energy needed to form a new phase.[1-3] In this talk, I will share our newest results in this area. Namely, ref. 1) we have extended our initial systems to ones that better mimic atmospheric particles, containing several to hundreds of organic compounds mixed with ammonium sulphate. We show that the size dependence of morphology is observed for all systems, though more complex phase separated morphologies are observed as well. 2) We have developed a chamber to flash freeze particles as a function of relative humidity to determine the water content of the particles at the point of phase separation. 3) We have explored the role of viscosity in the phase separation behaviour of these systems. I will conclude the talk by discussing the implications of our results for atmospheric chemistry and climate.

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Time-resolved dynamics of nucleobases in gas phase clusters and liquid water microjets

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The dynamics of nucleic acid constituents are investigated with time-resolved photoelectron spectroscopy (TRPES) in two complementary environments: gas phase clusters and liquid water microjets. In the gas phase work,[1] iodide-nucleobase clusters are excited with an ultraviolet pump pulse that either transfers an electron to the nucleobase or excites the $\pi\pi^*$ transition on the nucleobase. The ensuing dynamics are monitored via photodetachment with a femtosecond probe pulse and measurement of the resulting photoelectron spectrum. In the liquid jet experiments, adenine, thymine, and their corresponding nucleosides and nucleotides are excited at energies as high as 6 eV. The resulting relaxation dynamics are followed by TRPES. This instrument is currently being outfitted with a femtosecond XUV source and preliminary results will be presented.

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Photoemission from charged droplets

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Photoelectron velocity-map-imaging (VMI) studies on submicrometer-sized droplets have gained increasing importance for elucidating the properties of low-energy electrons in the condensed phase. An often neglected aspect of droplet VMI is the droplet charge. The presence of an additional electrostatic potential can modify electron transport and lead to a Coulomb barrier to electron escape. To explore and characterize the effects of positive and negative charges on low-energy electron transport we have performed a combined experimental and modelling study. To this end, photoelectron VMI spectra of size-selected droplets were recorded while varying the charge distribution in a controlled way. A probabilistic scattering model has been extended to include both classical and quantum effects of the electrostatic potential on the electron escape process. Good agreement between the experimental results and the extended scattering model is obtained.

Stories encoded in vibrational spectra: Obtaining insights into the spectroscopy of water from studies of ion-water complexes

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In this talk, I will discuss recent work in our group in which we made connections between proton transfer processes and hydrogen bonding and vibrational frequencies and intensities. Due to the large amplitude motions associated with proton transfer along a hydrogen bond, the vibrational spectra of these systems contain features that cannot be understood by the usual harmonic description of molecular vibrations, and even the widths of anticipated features encode information about these anharmonic couplings. The breakdown of the harmonic treatment of molecular vibrations reflects both the anharmonicity along this coordinate and coupling between this mode and other low frequency modes in these systems. It also reflects changes in the electronic structure as molecules vibrate. The presentation will draw from reported vibrational spectra for systems either containing intra- or intermolecular hydrogen bonds. The focus will of the talk will be on the methods used, including harmonic treatments, vibrational perturbation theory in internal coordinates and Diffusion Monte Carlo approaches, and insights gained by studying the spectra of these molecular systems. Implications of these studies of ion-water complexes to insights into the condensed phase dynamics and spectroscopy will also be discussed.

HOT TOPIC: Molecular activation and reactivity on small metal clusters

Alice E. Green,† Jasmin P. Justin,‡ Alexander S. Gentleman,† Ethan M. Cunningham,† Gabriele Meizyte,† Wieland Schöllkopf,‡ André Fielicke,‡ and Stuart R. Mackenzie†

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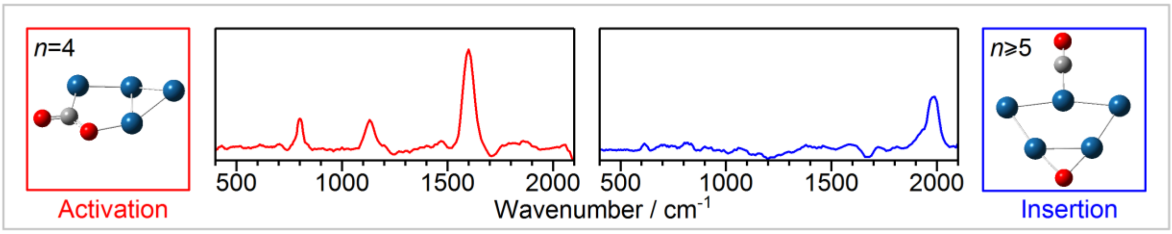
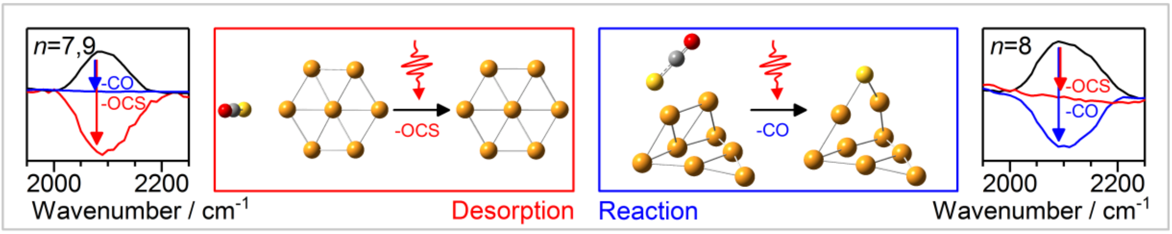
Using infrared free electron laser photodissociation spectroscopy we can investigate details of potential energy surfaces for a range of important catalytic reactions. In particular, we explore the extent of molecular activation upon interaction with a metal, and consequently identify some key features to aim for in catalytic processes. With this in mind, we demonstrate the ability to tune the degree of molecular activation induced in molecules such as i) CO_2 and ii) OCS adsorbed on small gas-phase transition metal clusters, by means of altering the cluster size.

i) Here we report the nature of carbon dioxide binding on isolated platinum cluster anions, Pt_n^- (n=4-7).[1] The CO_2 binding motifs observed illustrate clear size-dependence, indicative of a change from molecular to dissociative (*i.e.* completely activated) adsorption. Of potential practical significance in terms of further reactivity, CO_2 is observed to be molecularly-bound, but highly activated, on the Pt_4^- tetramer cluster anion. The bound CO_2 molecule is trapped behind a significant barrier to dissociation on the potential energy surface, preventing access to the global minimum, dissociated structure.



ii) Infrared studies of carbonyl sulfide adsorbed to cationic gold clusters, Au_n^+ (n=3-9), not only probe their structure and activation, but present evidence of the infrared light itself driving chemistry on size-specific cluster surfaces. In a different way to $Pt_4^-CO_2$, this system demonstrates the ability to size-selectively tune the degree of molecular activation.



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Strong-field physics in the molecular frame toward recording the ‘quantum molecular movie’

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The interaction of strong laser fields with matter intrinsically provides powerful tools, such as laser-induced electron diffraction, to image transient dynamics with an extremely high spatiotemporal resolution. In strong-field physics, the initial conditions of this interaction are generally considered a weak perturbation. We investigated strong-field ionization of state-selected and strongly laser-aligned molecules and showed, for the first time, a full real-time picture of the photoelectron dynamics in the presence of the laser field and the molecular interaction. We demonstrated that the molecular potential defines the initial conditions of the photoelectron at birth and has a dramatic impact on the overall strong-field recollision dynamics: it sets the clock for the emission of electrons with a given rescattering kinetic energy. This result represents a new benchmark for the seminal statements of molecular-frame strong-field physics. Our findings have strong impact on the interpretation of self-diffraction experiments, where the photoelectron momentum distribution is used to retrieve molecular structures. Furthermore, the resulting encoding of the time-energy relation in molecular-frame photoelectron distributions shows the way of accessing a deeper understanding of electron transport during strong-field interactions and probing the molecular potential in real-time.

References

https://www.controlled-molecule-imaging.org/publication/scientific

Generating a controllable beam of radicals for reaction studies

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Generating a controllable and pure source of molecular free-radicals or open-shell atoms has been one of the primary barriers hindering the detailed study of radical processes in the laboratory. A novel magnetic guide is described, for the generation of a pure beam of velocity-selected radicals. This magnetic guide will enable the study of radical interactions with exceptional control over the properties of the radical species. Only radicals with a selected velocity are transmitted through the guide; all other components of the incoming beam (radical species travelling at other velocities, precursor molecules and seed gas) are removed. The guide is composed of four Halbach arrays – hexapolar focusing elements – and two skimming blades. The relative positions of these components can be adjusted to tune the properties of the resulting beam and to optimise transmission for a given velocity. Experimental measurements of Zeeman-decelerated H atoms transmitted through the guide, combined with extensive simulations, show that the magnetic guide removes 99% of H-atoms travelling outside the narrow target velocity range.[1-2]

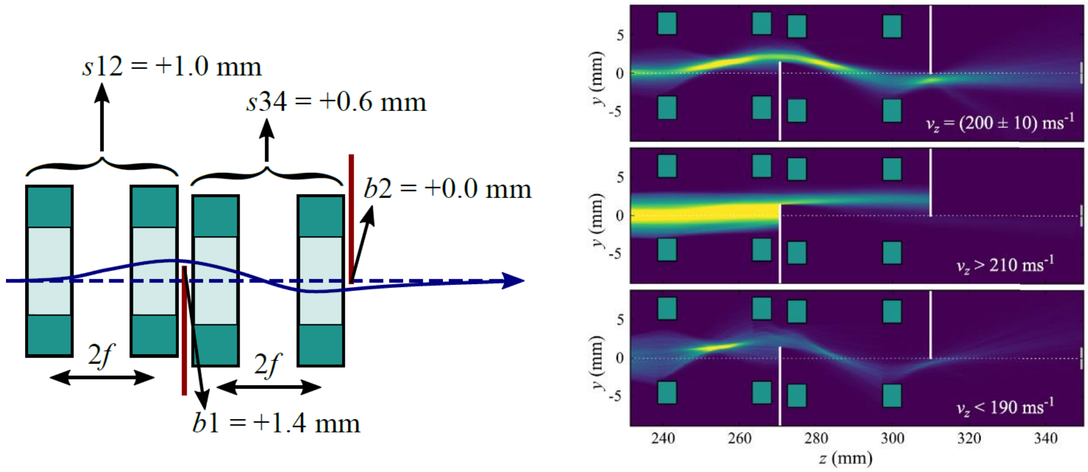

Figure 1: (Left) Schematic illustration of the magnetic guide, which is composed of four Halbach arrays (green, shown in side view) and two skimming blades (red). The passage of target particles through the guide is indicated by the solid blue arrow, with the dashed blue line indicating the initial beam axis. (Right) Three-dimensional particle trajectory simulations showing the passage of a beam of radicals through the magnetic guide. Only H atoms travelling with the target velocity (top panel) are transmitted to the detection region; faster particles are blocked by the blades and slower particles are deflected away from the detection region.

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Laser-induced alignment and imaging of molecules embedded in helium nanodroplets

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I will show how laser pulses can align molecules in helium nanodroplets and how the ability to place molecules in advantageous spatial orientations allows structural determination of molecular complexes. The talk will focus on the following topics:

1. Alignment of molecules with pulses much shorter than the molecular rotational periods.

The experimental results show rotational dynamics that differs completely from that of isolated molecules.[1] Notably, pronounced oscillations in the time-dependent molecular alignment, with no counterpart in gas phase molecules, are observed. Angulon theory identifies the oscillations to originate from the unique rotational structure of molecules in He droplets and transfer of rotational angular moment to the many-body He environment on picosecond timescales.[2]

2. Alignment induced by pulses that are turned-on (quasi) adiabatically.

It will be shown how the 0.4 K temperature of the molecules inside the droplets enables unprecedented high degrees of alignment, in either one or three dimensions. The method applies to large, complex molecules and the alignment can be made field-free by rapidly switching off the alignment pulse.[3]

3. Femtosecond-laser-induced Coulomb explosion imaging of the structure of molecular dimers and trimers created inside He droplets.

Results for both small linear molecules, including CS_2 [4] and OCS, and the larger molecule tetracene, are presented. Perspectives for time-resolved imaging of bimolecular reactions and interactions are discussed.

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Controlled ion-radical chemistry

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Reactions between ions and radical molecules play an important role in the chemistry that drives dynamics in the interstellar medium and during combustion of hydrocarbons. Unfortunately, experimental measurements of these reactions are very challenging, and thus very rare. We use tools borrowed from the cold atom community to measure ion-molecule reactions in a well-controlled environment. Here, we can study reactions between atoms and molecules in single quantum states at low temperatures. Our high sensitivity allows us to study reactions where the reaction rate can be as low as one reaction per minute. I will present the capabilities of this cold ion-molecule reaction apparatus and some example reactions we have been able to study using this new system.

Cold stereodynamics in merged beams

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We recently combined the merged beam technique with methods to orient reactants[1,2] and studied, for the first time, sub-Kelvin stereodynamics in a prototypical energy transfer reaction, namely between metastable Ne($^3P_2$) and ground state Ar atoms[3] or N_2 molecules.[1] This reaction can proceed along two pathways, one producing Ne(^1S)+Ar^+ (or N_2^+)+e^- (called Penning ionization), the other one producing $NeAr^+$ (or NeN_2^+)+e^- (associative ionization). At high energies the branching ratio between these channels can be controlled through the orientation of the Ne($^3P_2$) atom, but this ability is lost at low energies due to a reorientation of the reactants. The N2 case is particularly interesting because the vibrational structure of N_2^+ can be seen in the AI channel as a new channel wherein The NeN_2^+ predissociates by transfer of vibrational energy from N_2^+ to the Ne-N_2^+ bond.

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HOT TOPIC: Control and mapping of molecular states for long coherence spin state readout at the quantum projection noise limit

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Precise control and detection of internal states of molecules is crucial for a variety of scientific applications ranging from cold quantum chemistry to searches for physics beyond the Standard Model. However, the complexity of molecules often limits efficient quantum state preparation and detection. While molecules can be detected with high quantum efficiency by action spectroscopy methods, such as state selective photodissociation, these methods often suffer from technical noises common in nanosecond pulsed lasers. This excess noise dominates over quantum projection noise (QPN) in our experiment, since we internally cool our molecules, concentrating thousands of them in two targeted quantum states. By spatially separating the photofragments arising from different molecular orientations we differentially suppress the technical noise, reaching the QPN limit. Our state preparation and detection schemes are demonstrated for both HfF+ and ThF+, which are highly sensitive to the electron's permanent electric dipole moment (eEDM) and will be used in our upcoming measurement of the eEDM with projected state-of-the-art statistical sensitivity.

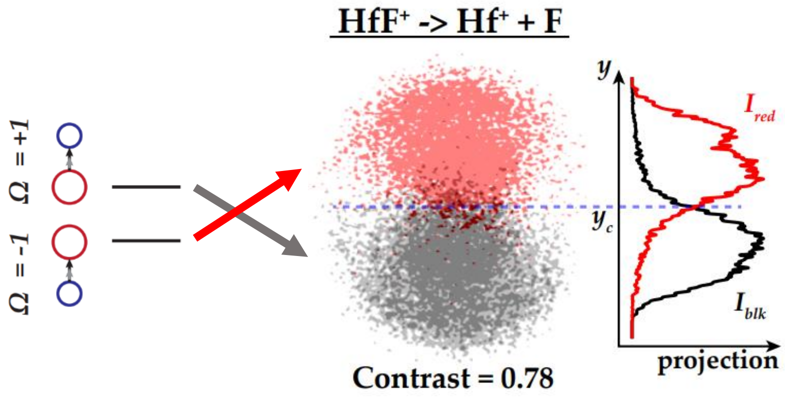

Figure 1: The Hf^+ photodissociation fragments of oriented HfF^+ molecules are imaged on separate sides of the detector enabling the simultaneous measurement of both quantum states. The resulting Ramsey fringes are quantum projection noise limited, drastically improving the precision of measurement of the electron's electric dipole moment.

Reactive-atom scattering dynamics and liquid-vacuum interfacial structure

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Duncan W. Bruce,[3] Matthew L. Costen,[2] Kenneth G. McKendrick,[2]
and Timothy K. Minton[1]

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Experiments to characterize reactive and nonreactive gas-liquid scattering dynamics were carried out with the use of a crossed molecular beams apparatus configured for beam-surface scattering. The identities of the gas and liquid were strategically selected to reveal fundamental insights on the relationship between scattering observables and liquid-vacuum interfacial structure. This work is important for the experimental advancement of liquid surface science and has the potential to impact our understanding of the chemical role of gas-liquid interfaces in various environments. Prior work has suggested that the inherent chemical specificity of reactive-atom scattering makes it a promising probe of composition at the liquid-vacuum interface. We expand on what has been demonstrated previously by exploring F-atom scattering from the liquid-vacuum interface of deuterium labeled variants of the common ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][Tf_2N]$). The experimental data and complementary molecular dynamics simulations provide evidence for the extreme surface specificity of reactive scattering and help to quantify the relative populations of C_4mim^+ conformations at the liquid-vacuum interface. A study on the liquid-vacuum interfacial structure of a solution of $RuCl_2(p\text{-cymene})P(C_8H_{17})_3$ in perdeuterated 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($d_6\text{-}[C_2mim][Tf_2N]$) will also be presented. The experimental data suggest that $RuCl(p\text{-cymene})P(C_8H_{17})_3^+$ is enriched at the liquid-vacuum interface at the expense of $d_6\text{-}C_2mim^+$ and the hydrocarbon chains of the Ru-complex protrude into the vacuum. The demonstration that such a transition metal complex can be designed to populate the liquid-vacuum interface suggests the possibility of exploring catalytic behavior by delivering reactants to the interface with a molecular beam and monitoring the scattering dynamics of reaction products to obtain detailed information on the reaction mechanism.

Diffraction of CH_4 from a metal surface

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Diffraction with matter waves has been reported since the beginning of quantum mechanics. In free space, diffraction effects have been observed even with objects as large as C_{60} molecules.[1] However, in scattering from a solid surface, pure elastic diffraction features have never been observed with molecules larger than D_2.[2] Here we report the first observation of pure molecular diffraction for CH_4 scattered off of an Ir(111) surface.[3] These results prove that quantum coherence is preserved, despite the small separation between rotational levels and the interaction with surface phonons. Density functional theory calculations of the potential energy surface provide some clues to understand the larger corrugation sampled by CH_4 molecules in comparison to Ne atoms. Measurements of similar data for other polyatomic molecules will allow characterization of the multidimensional PES with unprecedented precision. Our results show that isotope separation of polyatomic molecules may be possible using gas-surface diffraction.

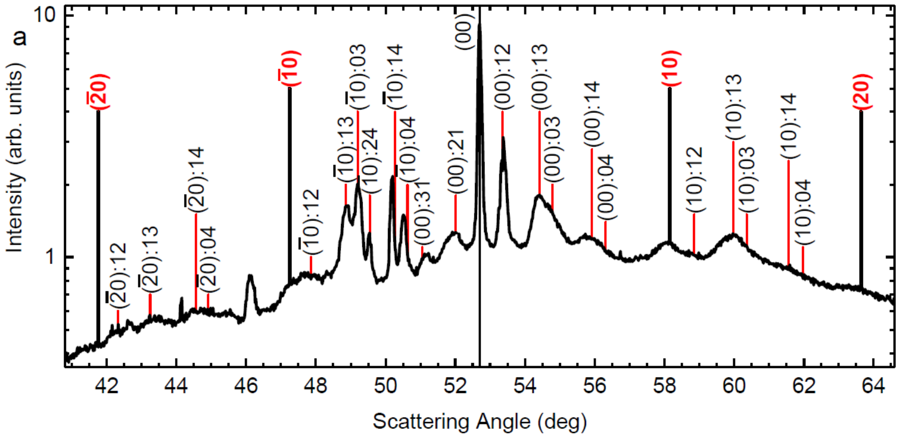

Figure 1: Angular distributions of CH_4 scattered from Ir(111) along the ΓM direction of the surface unit cell. The surface temperature is 110 K, and the incident energy 81 meV. The most intense RID peaks are labelled. Vertical lines indicate the expected position according to the Bragg condition.[3]

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Quantum state-resolved studies of methane chemisorption and surface scattering by vibrational spectroscopies

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Methane dissociation is the rate limiting step in the steam reforming process used by the chemical industry to convert natural gas into a mixture of H_2 and CO known as synthesis gas. To better understand the microscopic mechanism and reaction dynamics of methane chemisorption, we use vibrational spectroscopies and infrared lasers for quantum state-resolved studies of methane dissociation and state-to-state scattering on Ni and Pt surfaces.[1] Our experiments prepare surface incident methane molecules in specific ro-vibrational quantum states by state-selective infrared laser excitation via rapid adiabatic passage in a molecular beam. The state prepared molecules then collide with a clean single crystal transition metal surface in ultrahigh vacuum and both reactive and non-reactive processes are monitored by infrared spectroscopic techniques.

Surface bound methyl species as products of the dissociative chemisorption of methane are detected on the platinum surface by Reflection Absorption Infrared Spectroscopy (RAIRS). RAIRS allows for real-time and in-situ monitoring of the uptake of chemisorbed methyl species enabling quantum state-resolved measurements of reactive sticking coefficients. RAIRS is also used to study the vibrationally bond selective dissociation of partially deuterated methanes demonstrating that a single quantum of C-H stretch excitation of the incident methane is sufficient to achieve bond-selective chemisorption. Furthermore, RAIRS allows for site specific detection of reaction products used to measure separately the dissociation probability of methane on steps and terraces sites on Pt(211).[2-3]

Non-reactive, inelastic energy transfer is probed by combining infrared laser tagging of scattered molecules with bolometric detection. These first methane state-to-state scattering experiments yield state-resolved information about rotation and vibrational energy transfer between the incident molecule and the solid surface.[4]

Our state-resolved experiments provide clear evidence for mode- and bond-specificity as well as steric effects in chemisorption reactions and show that methane dissociation cannot be described by statistical rate theory but requires a dynamical treatment including all internal vibrational and rotational degrees of freedom of the dissociating molecule. The detailed reactivity and state-to-state scattering data from our measurements are used as stringent tests in the development of a predictive understanding by first principles theory[5-6] of these industrially important gas/surface reactions.

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Exploring surface landscape with molecules: Diffraction under fast grazing incidence conditions

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Since 2007, when first experimental measurement of diffraction of atoms and molecules under fast grazing incidence condition were published[1,2], quite a lot of effort has been invested to develop this very promising surface analysis tool.[3] To date, most of the fast grazing incidence diffraction, experimental and theoretical, studies have been focussed on atomic projectiles (GIFAD). However, the use of molecular projectiles (GIFMD) may open new interesting perspectives. The internal degrees of freedom of the molecule allow one for a more in depth examination of the surface properties, such as its anisotropy or its reactivity.[4]

Accurate theoretical description of GIFMD is truly challenging, which may explains the lack of studies focusing on it, but such description is pivotal to extract as much as possible meaningful information from experimental measurements. We have recently carried out a full dimension molecular dynamics studies of H_2 diffraction from LiF(001) under GIFMD conditions.[5,6] From these studies, we inferred first that diffraction is predominantly rotationally elastic, and second that initial rotational excitation leads to and increase in diffraction intensity of high-order peaks at incidence direction that satisfy precise symmetry constraints, which may provide more details on the surface properties than that obtained from low-order GIFAD peaks. More recently, theoretical results for H_2/KCl(001) reveal that an accurate theoretical description of GIFMD may be key to infer the characteristics (rovibrational states distribution) of the experimental molecular beam.

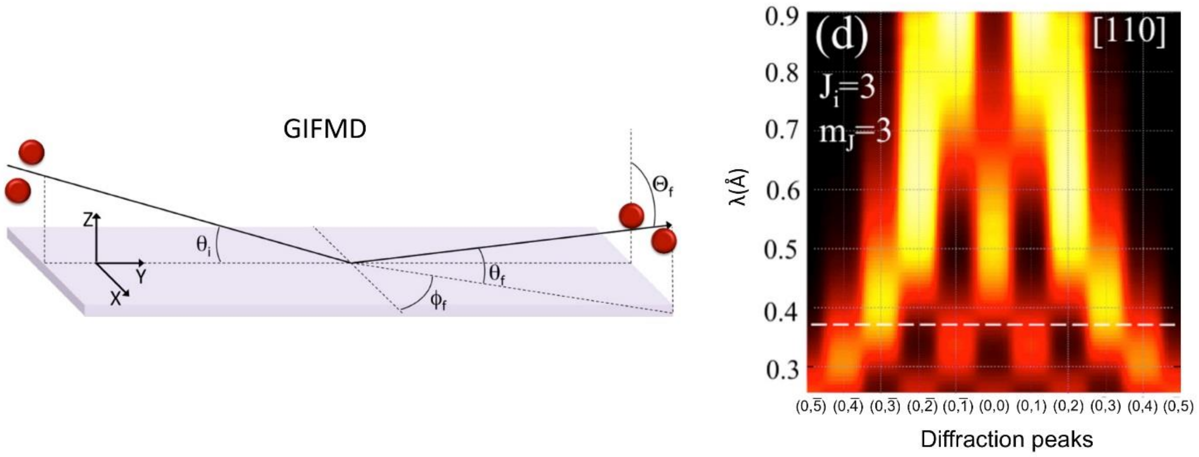

Figure 1: Left: Schematic representation of GIFMD. Right: Example of 6D theoretical simulated spectrum for H_2/LiF(0002).

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Pump-probe experiments using pulsed molecular beams

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Knowledge of the rates of elementary gas phase reactions has contributed decisively to our understanding of important societal problems, for example stratospheric ozone chemistry. Growing our knowledge of rates of elementary chemical reactions at surfaces is crucially important to improving heterogeneous catalysis. In comparison to gas phase reactions, there are surprisingly few known activation energies of elementary surface reactions, nor knowledge of the energies and entropies of the reactions' transition states. This situation is a result of limitations on our methods for measuring rate constants of elementary surface reactions. Furthermore, first principles theories to predict surface reaction rates remain largely un-validated. In this talk, I will present recent experimental advances yielding the rates of elementary reactions at surfaces, which rely on a stroboscopic pump-probe concept designed for neutral matter. This method is also capable of revealing surface-site-specific kinetics information. Not only is site specific reactivity an essential aspect of surface reaction mechanisms, it is essential to provide benchmarks for testing first principles methods for calculating reaction rates, another potentially powerful tool with which to investigate heterogeneous catalysis. Further improvements ride on future advances in pulsed molecular beams methods.

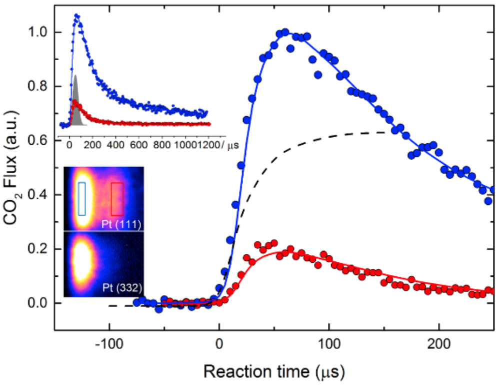

Figure 1: Kinetic Traces for CO$_2$ product obtained from velocity resolved kinetics. The inset labelled Pt(111) shows an ion image with velocity space integration windows for the hyperthermal (red, 1280-1610 m/s) and the thermal (blue, 420-590 m/s) channels. The black dashed curve represents the measured CO dosing function. The grey solid area indicates the temporal resolution in the detection of the thermal channel. For the hyperthermal channel this temporal spread is negligible. The two traces are normalized to reflect the experimental time-integrated branching ratio between the two channels (8.6:1 in favour of the thermal channel) at this temperature and O-coverage. The step density was 0.0025 ML, the O-coverage is O_a= 0.04 ML and the dose of a single CO pulse is 2 x 10^{-5} ML. The surface temperature was T_S =593 K. The experimental conditions for the (332) image (inset lower left) are similar but the step density, 0.167 ML, is much higher. Here O atoms are expected to be entirely at step sites. Here, the hyperthermal channel is absent.

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HOT TOPIC: Pyruvic acid on nanoices: Photon and electron driven chemistry

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Pyruvic acid is one of molecules that can form *inter*- and *intra*molecular hydrogen bonds. Moreover, it is abundant in various natural environments including the atmosphere. Its atmospheric chemistry both in the gas phase and in aerosol particles is of particular interest, because it can lead to CO_2 formation and to the generation of secondary atmospheric aerosols.[1] Therefore, studies with pyruvic acid clusters can be valuable not only to chemical community, but they can also contribute to a better understanding of atmospheric processes.

In this work,[2] we used a cluster beam apparatus in Prague to generate two different systems: a) pyruvic acid clusters $(PA)_N$, and b) pyruvic acid molecules adsorbed on a surface of water nanoices, $(PA)_N(H_2O)_M$ with $\bar{M} = 390$. These model clusters were then ionized by electrons (EI) or photons (PI), and mass spectra of the generated ions were recorded. The experimental observations are accompanied by theoretical calculations.

The mass spectra show large differences between EI and PI in PA molecules on nanoices (Fig. 1), but no such differences are found in $(PA)_N$ clusters. According to the calculations, upon the ionization of a PA molecule, a reaction cascade with several $H^+/H^\bullet$ transfers between PA molecules can take place. This is not the case once a water molecule is ionized instead. In water nanoices where much more water than PA molecules are present, water molecules are more probably ionized by EI, which is not selective. On the other hand in PI, pyruvic acid acts as a chromophore and is preferred for photoionization. Analogical processes can play a role in the atmosphere.

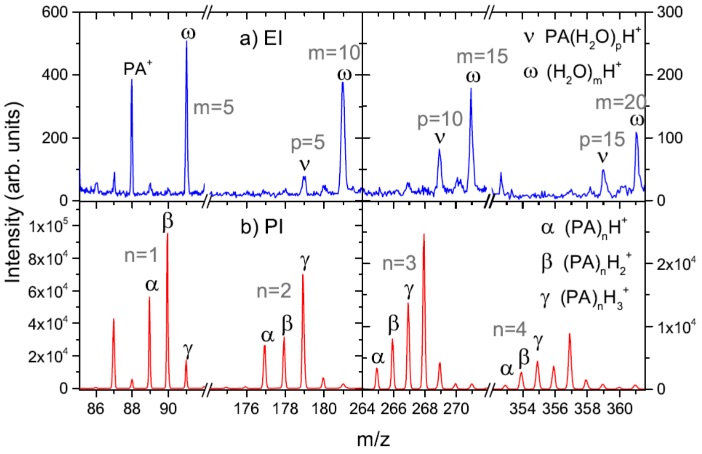

Figure 1: Mass spectra after electron ionization a), and photoionization b) of small pyruvic acid clusters deposited on large water clusters. Only regions with molecular cluster peaks are shown.

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Scattering of aligned molecules by nonresonant optical standing waves

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We study the effect of the rotational state-dependent alignment imparted by optical fields to molecular translation. CS_2 molecules in their lowest few rotational states are transversely accelerated by a nonresonant optical standing wave. The state-dependent alignment effect becomes manifest because of the strong acceleration and the state selection by the steep gradient of the standing wave potential as well as by the low rotational temperature of the molecules. Dramatic changes of measured velocity distribution caused by the optical standing wave are well reproduced by numerical simulations based on the rotational-state-dependent alignment.[1] Moreover, the molecular scattering by an off-resonant optical field amounts to manipulating the translational motion of molecules in a rotational-state-specific way. Conversely, such scattering can be used to state-select the rotational state of the scattered molecules.

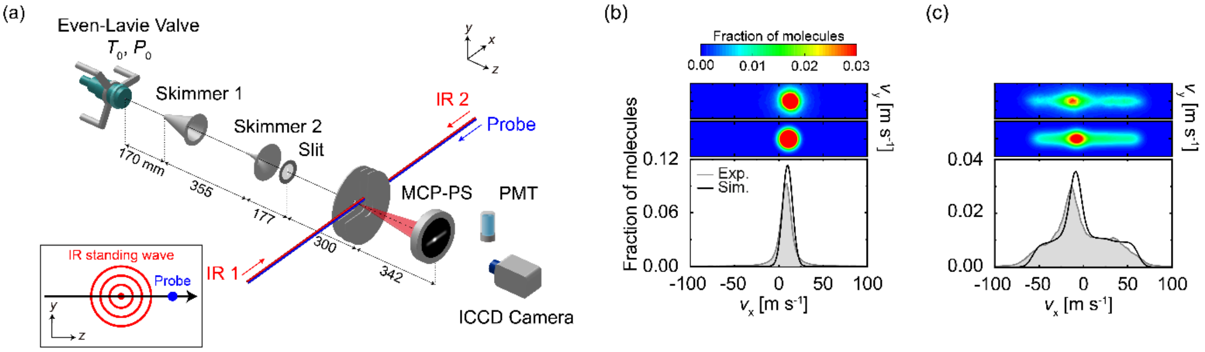

Figure 1: ***(a) Schematic diagram of the experimental setup.*** *A rotationally cold molecular beam of CS_2 is produced by supersonic expansion from an Even–Lavie valve.[2] The cold beam is collimated by two skimmers and a vertical slit and then interacts with the optical standing wave formed by two counter-propagating laser beams (IR1 and IR2) whose peak intensities are I_0. Molecules that pass through the center of the standing wave are ionized by a probe dye laser beam (Probe). An ion lens system consisting of three electrodes performs velocity map imaging, namely, ions with the same initial velocity are mapped onto the same position at the two-dimensional ion detector.[3]* ***Two sets of the measured (first panel) and simulated (second panel) velocity distributions and their profiles (third panel) along the v_x axis for (b) $I_0 = 0 \times 10^{10}$ W/cm^2 and (c) 3.2×10^{10} W/cm^2.*** *The accumulation time for the measured images is 1,200 s, which corresponds to 12,000 laser shots. The images are normalized by the total signal intensity of each image. Gray profiles with shading and solid black curves correspond to the profiles of the measured and simulated images, respectively.*

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Gas phase resonance Raman spectroscopy of huge biomolecule by IR-ablation of droplet beam: Local structure in isolated heme protein

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Gas phase spectroscopy is a powerful tool for structural identification of isolated biomolecules, which are separated from the aqueous environment. However the conventional gas-phase IR spectroscopy combined with supersonic-jet techniques has a difficulty towards the structural analyses of huge biomolecules like protein and DNA. This problem attributes to their extremely large vibrational freedoms, which gives low resolution (board) peaks in the IR spectroscopy. Therefore, we developed a gas-phase resonance Raman spectroscopy apparatus based on the IR-laser ablation of droplet beam.[1] This spectroscopic technique has a great advantage for the structural analyses of huge biomolecules because it focuses on the local site of a target molecule.

In this work, the gas-phase resonance Raman spectroscopy was applied to the structural analysis of heme structure of myoglobin (Mb, 17858 *m*/*z*). Droplets of 100 μM Mb aqueous solution were produced by a droplet nozzle driven at 10 Hz. The droplet stream was directly introduced into a vacuum chamber and transported into a trap/acceleration electrode of an ion-trap time-of-flight mass spectrometer. An IR laser (3591 cm^{-1}, 5.5 mJ/pulse) shined the droplet at the acceleration electrode and generated isolated Mb ions. By using an RF voltage (125 kHz, 1.08 $kV_{p\text{-}p}$), Mb^{2+} ion was trapped in the trap electrode. After 70 ms, a UV laser (395 nm, 3.5 mJ/pulse) was shined to the trapped ion for observation of resonance Raman scattering light. The obtained scattering light was collected by a lens and transported to a monochrometer through an optical fiber. Finally, the obtained Raman signals were detected by a photomultiplier. Compared with the gas-phase spectrum, we also measured a liquid-phase resonance Raman spectrum of the same sample solution by using the same monochrometer and photomultiplier.

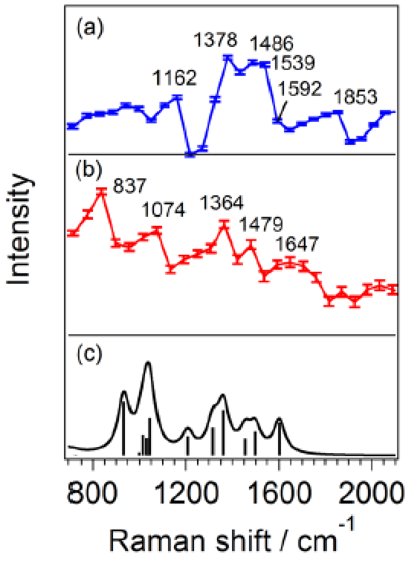

Figure 1: Resonance Raman spectra of Mb in the aqueous solution (a) and the gas phase (b). The calculated spectrum (c) of ferrous-heme structure was obtained at the B3LYP/ccpVDZ level.

As shown in Fig. 1a, the most intense peak (1378 cm^{-1}) was observed in the liquid-phase resonance Raman spectrum. This spectral feature corresponds to that of met-Mb[2], in which a ferric atom exists in the heme structure. However, the obtained gas-phase resonance Raman spectrum (Fig. 1b) were different from the liquid-phase one. Compared with quantum chemical calculation (Fig. 1c), the spectral feature was close to a low spin state (S=0) of ferrous-heme structure. This result suggests that reduction of Mb heme proceeds during desolvation process induced by IR-laser ablation.

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Unravelling the ultrafast dynamics in indole-water

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Atomic and molecular properties strongly depend on the environment. For a protein in an aqueous environment, for instance, hydrogen bonds between the protein and surrounding water molecules strongly affect its folding and thereby also its function. When hydrogen bonds between a protein and surrounding water molecules break, for instance *via* absorption of UV radiation, the protein structure changes and inactivation of the protein can occur. The amino acid tryptophan plays an important role in the UV inactivation of proteins, since it is the most strongly near-UV absorbing common amino acid.

We investigated the ultrafast dynamics of the hydrogen-bond formation and breaking between proteins and water in a bottom-up approach by studying the indole molecule – the chromophore of tryptophan – and the indole-water complex, which serves as a model system for the interaction between proteins and water in the gas phase. To study this in a controlled, high-precision approach, we first produce pure samples of indole and the indole-water complex using a molecular beam and an electrostatic deflector, with which we can spatially separate molecular species.[1] For some of the experiments, we also align the species in space so that we can study processes directly in the molecular frame.[2] These pure and controlled samples can be used to study the ultrafast hydrogen-bond dynamics upon UV absorption. In a pump-probe experiment, the molecule or complex is excited using UV light and subsequently ionized with mid-infrared light. After UV excitation, various electronically excited states are reached, and complex excited state dynamics can occur. The molecule or complex can dissociate and we record velocity-map images of the resulting molecular fragments and electrons as function of the pump-probe delay. Comparing the dynamics of indole and indole-water gives insights into the effect of the presence of the water molecule on the excited-state dynamics and fragmentation processes that occur. The mid-infrared probe also allows us to perform laser-induced electron diffraction experiments. Using this technique, we aim at recording a molecular movie with atomic resolution of the hydrogen-bond breaking in indole-water.

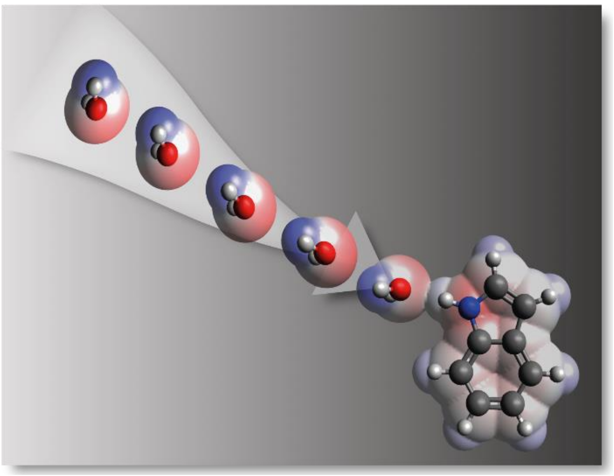

Figure 1: Illustration of the hydrogen-bond formation in the indole-water complex.

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International Symposium on Molecular Beams: Velocity map imaging

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Velocity map imaging, VMI[1], is a high resolution variant of the ion imaging method[2] invented by David Chandler and Paul Houston in 1987. The improved resolution of VMI was critical and VMI / ion imaging has evolved over the years into the premier research tool in the atomic and molecular dynamics community.[3] One example of this is the >2500 citations of the original VMI article. Part of the appeal of VMI is in the beauty of imaging (Fig. 1).

This talk will outline the development of VMI and its partner method spatial map imaging with highlights of recent applications in the molecular collisions field and then focus on the most recent work from our group on combining VMI with laser desorption on cold molecular ice surfaces. Using a new approach that we call atom fragment imaging mass spectrometry, we can now measure both the kinetic and internal energy of mass-selected species ejected by laser desorption from different ices held at 20K, free of the effects of fragmentation. Many surprising aspects of photochemistry at ice surfaces are revealed by this approach.

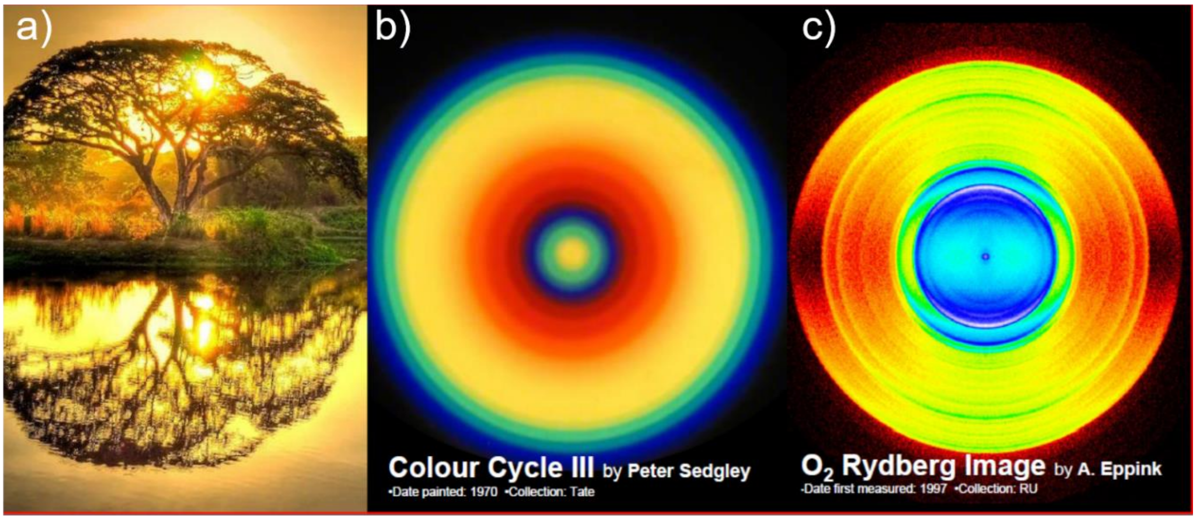

Figure 1: Spheres are inherently beautiful whether they arise a) in nature, b) in op-art paintings from the '70's, or c) from molecular dynamics processes such as the photodissociation/ionization of O_2[1].

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Spectroscopic and dynamical probes of atmospheric reaction pathways

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Alkene ozonolysis is a primary oxidation pathway for alkenes, the most abundant organic compounds in the Earth's troposphere after methane, and also an important source of atmospheric hydroxyl (OH) radicals. Alkene ozonolysis takes place through a complicated reaction pathway with multiple intermediates and barriers on the way to OH radicals and other products. A carbonyl oxide species, known as the Criegee intermediate (RR′COO), represents a critical branching point on the pathway that controls the products formed in this important class of reactions. In this laboratory, the simplest Criegee intermediate CH_2OO and methyl-, dimethyl-, ethyl-, and vinyl-substituted Criegee intermediates are generated by alternative synthetic schemes, cooled in a supersonic expansion, and isolated under collision-free conditions. Recent studies have focused on characterizing the Criegee intermediates utilizing infrared and ultraviolet spectroscopic methods, and examining the resultant dynamics. Infrared 'fingerprint' and electronic spectra reflecting π-conjugation of the Criegee intermediates are obtained,[1,2] along with time- and energy-resolved studies of their unimolecular decay to OH radical products.[3] Remarkably, the conformation and nature of the substituents (R, R′) of the Criegee intermediates are found to have a profound effect on their reaction dynamics. Extension to thermal conditions via theoretical modeling provides insight on the impact of Criegee intermediates in the atmosphere.

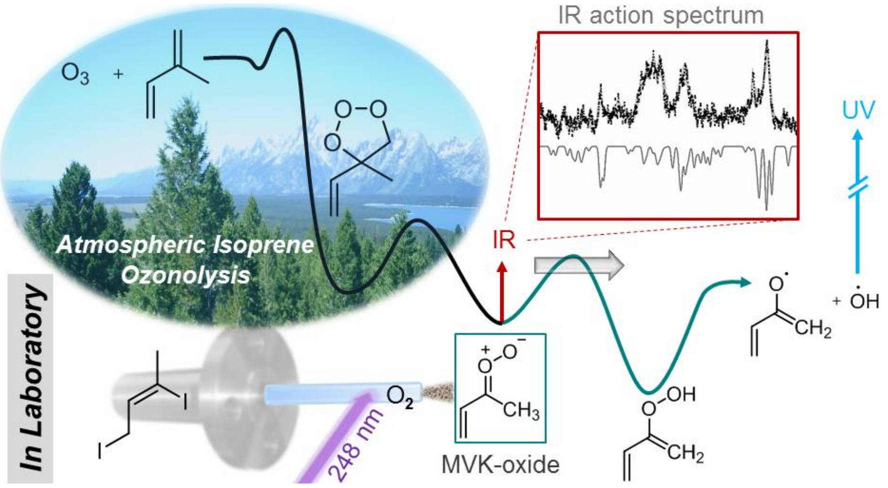

Figure 1: Direct synthesis and infrared action spectra of methyl vinyl ketone oxide, an unsaturated four-carbon Criegee intermediate from isoprene ozonolysis.[1]

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Quantum stereodynamics control of inelastic and reactive collisions

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One of the main goals of reaction dynamics is to provide means that allows experimentalists to control the outcome of a chemical event. To achieve that task, one should be able to imagine an experiment where the relative geometry and energy of the incoming atoms can be selected in such a way that maximizes the cross-section of the specific reaction channel. For bimolecular reactions in gas phase, it is possible to carry out sophisticated experiments by selecting, with extremely high resolution, the relative energy, the initial quantum state, and to detect the products with angular resolution. Moreover, it is also possible to polarize the reactants bond-axis and/or rotational angular momentum[1-4] so it can be achieved some control into the relative geometry of the colliding partners before their interactions. We will illustrate several cases of inelastic and reactive collisions in which the integral and differential cross section (DCS) can be exquisitely changed by a suitable and in all cases experimentally achievable preparation. By means of exact quantum mechanical calculations, we will examine the effect of an arbitrary orientation of internuclear axes in collisions of Rg+NO($X^2\Pi$) that has been subject of recent experiments.[2] We will also examine the effect of the polarisation of the HD rotational angular momentum in collisions with H_2 at cold and ultra-cold translational energies, as done in recent experiments.[3,4] As it will be shown, resonances can be dramatically switched off by the appropriate choice of the alignment of the HD rotational angular momentum. The effect will be also examined for reactive collisions of O(^{3}P)+H_2 below and above the reaction barrier.

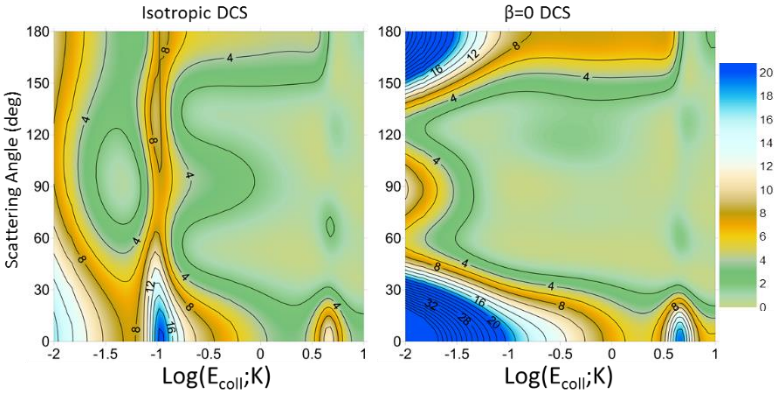

Figure 1: DCS of HD(v=1,j=2) + H_2(v=0,j=0)→ HD(v=1, j=1) + H_2(v=0, j=0) collisions as a function of the collision energy and scattering angle. The resonance at 0.1 K can be clearly appreciated in the absence of HD rotational angular momentum preparation. However, by polarising ***j***$_{\boldsymbol{HD}}$ *perpendicularly to the incoming velocity the resonance vanishes.*

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Cold collisions of hot molecules in nearly co-propagating beams

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State-to-state differential cross sections for rotationally inelastic collisions of highly vibrationally excited NO with Ar have been measured in a near co-propagating crossed beam experiment at collision energies from above room temperature to near 1 K. Stimulated emission pumping (SEP) to prepare NO in specific rovibrational levels is coupled with direct-current slice velocity map imaging to obtain a direct measurement of the state-to-state differential cross sections. The use of nearly co-propagating beams to achieve low NO-Ar collision energies and broad collision energy tuning capability are also demonstrated.

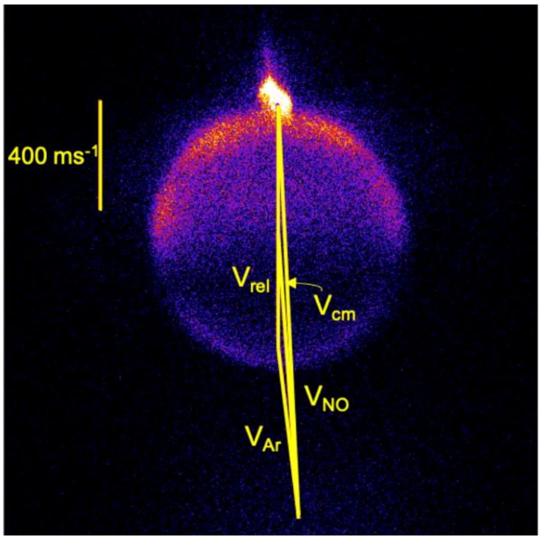

Figure 1: Raw experimental image for NO $X^2\Pi_{1/2}$ (v = 10, j = 9.5, +f) from scattering of NO $X^2\Pi_{1/2}$ (v = 10, j = 0.5, +e) with Ar at a collision energy of 530 cm^{-1} with nominal Newton diagram superimposed.

Velocity map imaging of inelastic and reactive scattering dynamics

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Crossed molecular beam and velocity map imaging techniques have been used to study the inelastic and reactive scattering of polyatomic molecules and radicals. Analysis of the images gives quantum-state resolved differential cross sections for scattering of the collision products which are sensitive to the shape of the multi-dimensional intermolecular potential energy surface. Results will be presented for methyl radical scattering with a variety of collision partners (He, Ar, H_2 and N_2) and compared with quantum scattering calculations on *ab initio* computed potential energy surfaces.[1-3] Very recent experimental results for NO scattering from CH_4 will be contrasted with the much-studied scattering of NO by Ar. Further developments in our experimental and computational studies of reactive scattering dynamics will also be presented.[4-6]

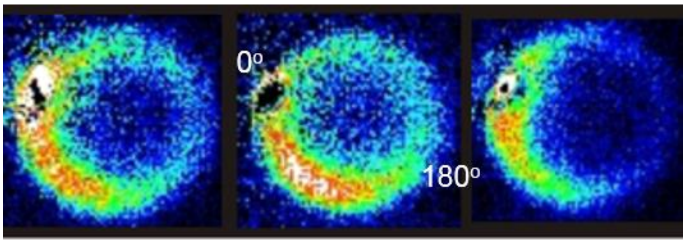

Figure 1: Selected velocity map images of CD_3 inelastically scattered by D_2 at a collision energy of 640 ±60 cm^{-1}. The images were all obtained for CD_3 in the N = 5 rotational level but using S (left), O (centre) and R (right) branch transitions in the (2+1) REMPI detection scheme, with different degrees of unresolved K level structure. Forward (0°) and backward (180°) directions with respect to the initial CD_3 radical velocity are indicated in the central image.

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Benchmarking the polyatomic reaction dynamics of X + methane

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With recent developments of sophisticated experimental techniques and advanced theoretical methods/computations, the fields of chemical reaction dynamics have reached to the point that theory–experiment comparisons can be made at a quantitative level for a prototypical A + BC system. As the system becomes larger, more degrees of freedom are involved and thus many new chemistry and novel phenomena await to be discovered—a land of opportunities. Over the past 15 years my laboratory has delved to the reaction dynamics of methane + X (X: F, Cl, O(^{3}P), and OH). This effort shifts the paradigm, making the title reaction a benchmark polyatomic system. In this talk, I shall highlight some of the key concepts introduced and unexpected phenomena uncovered. Those findings not only enrich our understanding of the studied reactions at the most fundamental level and inspire the theoretical developments, but also shape our thinking and lay the foundation for future explorations of different aspects of the multifaceted nature of polyatomic reactivity.

Covariance-map imaging: A new tool for chemical dynamics studies

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Over the past twenty years or so, velocity-map imaging[1,2] has revolutionised experimental work in the field of chemical reaction dynamics by allowing the complete scattering distribution for a chosen reaction product to be imaged directly in a single measurement. The development of universal ionization methods and ultrafast time-of-flight imaging sensors such as the PImMS[3] and TimePix[4] cameras has ushered in the era of multi-mass velocity-map imaging, in which multiple reaction products can be imaged in a single experiment. One key advantage of this approach is a vast reduction in the time required to acquire images for complex reaction systems leading to multiple different products. However, the power of multi-mass imaging is increased further using a statistical data processing technique known as covariance analysis or covariance mapping.

As well as containing the velocity distribution of each detected fragment, a multimass VMI data set recorded under conditions of sufficiently high ion detection probability also contains information about correlations between the velocity distributions of different fragments. Performing a statistical covariance analysis on the data allows these correlations to be revealed. Transforming the 'raw' velocity-map images into covariance images allows the velocity distribution of one product relative to one or more partner fragments to be determined and visualised. Importantly, a covariance signal is only observed when two products are formed in the same event. This makes the approach extremely useful for untangling contributions to the signal from multiple competing reaction pathways.

Covariance mapping has found an increasing number of applications over the past few years.[5,6,7] In recent work in our group, as part of a wider collaboration, covariance mapping has been used to disentangle multiple competing fragmentation pathways for singly and doubly charged PAH cations. We have also demonstrated 3D-sliced covariance-map imaging for the first time, measuring the three-dimensional recoil distributions of the laser-induced Coulomb explosion products of CF_3I. An example data set is shown in Fig. 1.

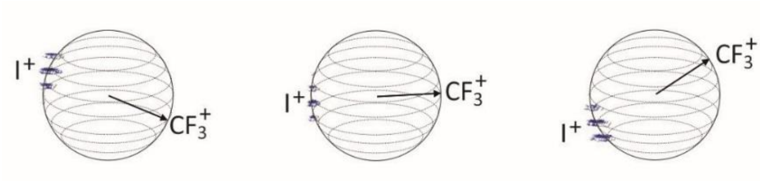

Figure 1: 3D-sliced covariance-map images of the CF_3^+ and I^+ fragments formed in the ultrafast-laser-induced Coulomb explosion of CF_3I. CF_3^+ has been chosen as the reference ion, and the images show the velocity distribution of the I^+ co-fragments relative to the CF_3^+ velocity vector (designated by the black arrow).

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

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Ion-molecule reactions at low temperatures (<100 K) involving the helium ion play an important role in the synthesis of organic molecules in interstellar gas clouds.[1] Studying such reactions at temperatures below 10 K is challenging because of ion heating caused by stray electric fields and Coulomb repulsion at high densities.

Here we present the results of experiments in which the $He^+ + N_2$ and $He^+ + CH_4$ reactions are probed at collision energies in the $E_{coll}/k_B = 0 – 40$ K range. To avoid heating of the ions by stray electric fields, we excite the He atoms to high Rydberg states and study the reaction within the orbit of the Rydberg electron.[2] The Rydberg electron acts as a spectator and does not significantly affect the outcome of the reaction. We use the large dipole moments of the He Rydberg states to deflect a He-Rydberg-atom beam with a curved 50-electrode chip device and merge it with a ground-state beam of either N_2 or CH_4.

The helium atoms are produced in a pulsed supersonic valve that is temperature-stabilized in the 35 – 100 K range. A dc electric discharge at the valve orifice populates the metastable (1s)(2s) $^3S_1$ state of helium, from which the atoms are excited to Rydberg-Stark states with principal quantum number $n = 30$. The velocity of the He-Rydberg-atom beam can be set to a value in the 600 – 1200 m/s range. After the He-Rydberg-atom beam is merged with the ground-state beam of either N_2 or CH_4, the two beams traverse a reaction zone and the product ions are detected with a microchannel-plate detector. By integrating the product ion yield as a function of the collision energy, it is possible to determine the energy dependence of the relative reaction rate at collision energies below $k_B \cdot 1$ K.

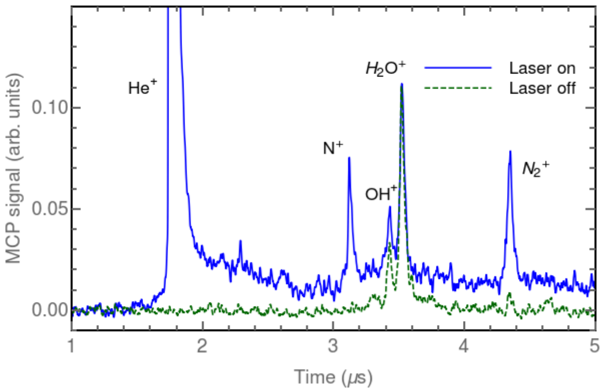

Figure1: TOF mass spectrum of the He^++N_2 reaction measured at $E_{coll}/k_B = 6.5$ K.

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Posters

Poster Titles

1 **Emily Warne** *(University of Southampton)*
Using UV and XUV time-resolved photoelectron spectroscopy to probe the dissociation dynamics of methyl iodide

2 **Marc Briant** *(CNRS, Université Paris-Saclay)*
Investigation of the weak hydrogen bond of some propyne complexes

3 **Michal Fárník** *(Czech Academy of Sciences)*
Electron and photon-triggered reactions between molecules adsorbed on clusters

4 **Ivo Vinklárek** *(Czech Academy of Sciences)*
Vibrationally mediated photodissociation dynamics of pyrrole

5 **Susanne Ullrich** *(University of Georgia)*
Thionated uracils under UV irradiation: Intramolecular micro-environmental effects on the intersystem crossing dynamics

6 **Stuart Crane** *(University of Bristol)*
Coulomb explosion imaging: A tool for molecular structure determination

7 **Aude Lietard** *(Durham University)*
Localisation of the excess electron in water clusters and anthracene-water clusters

8 **Gabriel Karras** *(STFC Rutherford Appleton Laboratory)*
Following macroscopic effects in gas phase experiments using XUV–UV spectroscopy

9 **Matija Zesko** *(ETH Zürich)*
Fluorescence-lifetime-limited trapping of Rydberg helium atoms on a chip

10 **Daniel Strasser** *(Hebrew University of Jerusalem)*
Ultrafast H_3^+ formation on the methanol dication: Competition of proton & electron transfer dynamics

11 **Akira Terasaki** *(Kyushu University)*
Evaporative cooling processes of liquid droplet in vacuum

12 **Piergiorgio Casavecchia** *(University of Perugia)*
Reaction dynamics of O(^{3}P) with 1-butene and 1,2-butadiene

13 **Gábor Czakó** *(University of Szeged)*
Dynamics of bimolecular chemical reactions on ab initio potential energy surfaces

14 **Alexandr Bogomolov** *(Novosibirsk State University)*
The formation of chemically bonded argon via photoexcitation of Ar-I_2 van der Waals complex

15 **Iakov Medvedkov** *(Samara National Research University)*
Design of a new molecular beams machine

16 **Bum Suk Zhao** *(Ulsan National Institute of Science and Technology)*
Matter-wave diffraction from a periodic array of half planes

17 **Eckart Wrede** *(Durham University)*
Absolute density measurements of trace amounts of OH radicals

18 **Klaudia Gawlas** *(University College London)*
Rydberg state electric field ionisation dynamics for quantum state-selective detection of resonant energy transfer in cold He* + NH_3 collisions

19 **Donatella Loru** *(DESY)*
Unravelling the formation of substituted polycyclic aromatic hydrocarbons in the interstellar medium by plasma sources

20 **Thomas Luxford** *(Czech Academy of Sciences)*
Dissociative electron attachment of hydrated biomolecules

21 **Björn Bastian** *(Universität Innsbruck)*
Imaging anion-neutral reactions: Carbon chain growth and single solvent effects

22 **Julia Bieniewska** *(Imperial College London)*
Mid-infrared spectroscopy of polyatomic molecules in a cryogenic buffer gas cell and progress towards a molecular beam of cold complex molecules

23 **Bruno Credidio** *(École Polytechnique Fédérale de Lausanne)*
Gas-liquid scattering dynamics in crossed beams

24 **Adam Deller** *(University College London)*
Long-lived high Rydberg states of NO for Stark deceleration and trapping

25 **Liam Duffy** *(UNC Greensboro)*
Sub-THz cavity enhanced absorption and dispersion effects in molecular beams

26 **Gerard Meijer** *(Fritz-Haber-Institut der Max-Planck-Gesellschaft)*
Spectroscopic characterization of AlF with relevance to laser cooling and trapping

27 **Roland Wester** *(Universität Innsbruck)*
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Posters

28 **Ozan Lacinbala** *(Institut des Sciences Moléculaires d'Orsay)*
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29 **Ondrej Votava** *(Czech Academy of Sciences)*
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30 **Theofanis Kitsopoulos** *(Georg August University and University of Crete)*
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31 **Felix Allum** *(University of Oxford)*
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32 **Christian Mangeng** *(University of Basel)*
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33 **Tobias Sixt** *(University of Freiburg)*
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34 **Lisa Saalbach** *(Heriot-Watt University)*
Time-resolved photoelectron imaging studies of steric effects in nitrobenzene derivatives

35 **Viktor Tajti** *(University of Szeged)*
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36 **Pedro Recio** *(University of Perugia)*
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37 **Thomas Giesen** *(University of Kassel)*
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38 **Paul Lane** *(Heriot-Watt University)*
Scattering dynamics at the gas-liquid interface

39 **Marco Flock** *(University of Wuerzburg)*
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40 **Tibor Győri** *(University of Szeged)*
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41 **Florian Hirsch** *(University of Wuerzburg)*
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42 **Jochen Küpper** *(DESY and Universität Hamburg)*
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43 **Simon Hofsäss** *(Fritz Haber Insitute)*
Towards laser cooling and trapping of AlF molecules

44 **Ardita Kilaj** *(University of Basel)*
Reaction kinetics of trapped molecular ions with conformer- and isomer-selected neutral molecules

45 **Domonkos Tasi** *(University of Szeged)*
Rethinking fundamental S_N2 reactions

46 **Siwen Wang** *(University of Science and Technology of China)*
A new crossed molecular beams apparatus

47 **Clément Soulié** *(Heriot-Watt University)*
Theoretical studies of electronic quenching via molecular collisions

48 **Charlotte Jansen** *(Leiden University)*
Unravelling the contribution of steps to D2 dissociation on Ni(711)

49 **Dóra Papp** *(University of Szeged)*
Benchmark *ab initio* study of the $X + C_2H_6$ [X = F, Cl, Br, I] systems, dynamics of the $X + C_2H_6$ [X = F, Cl] reactions, and PESs for spectroscopy

50 **Patrik Straňák** *(University of Basel)*
Investigating conformational and state-specific effects in chemical reactions

51 **Akihiro Kitazaki** *(Gakushuin University)*
Gas phase CD spectroscopy of albumin ion in DUV region by using IR-laser ablation of droplet beam: Analysis of secondary structure

52 **Jolijn Onvlee** *(DESY)*
Pure and aligned (bio)molecular samples

53 **Cornelia Heid** *(University of Oxford)*
Comparison of spin-orbit excitations in side-on collisions of Ar with NO

54 **Matin Kaufmann** *(University of Kassel)*
Building-up of a precision spectrometer using a REMPI detection scheme

Posters

55	**Maksymilian Roman** *(Heriot-Watt University)* Real-space imaging of OD collisions with liquid surfaces
56	**Thuy Dung Tran** *(Charles University)* Reaction of O^- with H_2, D_2 and HD at low temperature
57	**Aggeliki Afentaki / Peter Samartzis** *(Foundation for Research and Technology-Hellas)* Multiphoton Rydberg and valence dynamics of highly excited small molecules
58	**Tom Sharples** *(Heriot-Watt University)* A change of scene: Atom-diatom scattering in an electronically excited state
59	**David Chandler** *(Sandia National Laboratory)* Two-colour alignment and dissociation of molecular hydrogen when under intense laser fields
60	**Katharina Höveler** *(ETH Zürich)* Merged molecular beams to study ion-molecule reactions at temperatures down to 300 mK
61	**Joe Leng** *(Heriot-Watt University)* Stereodynamics of the inelastic collisions of NO(A) with molecules
62	**Floriane Grollau** *(CNRS, Université Paris-Saclay)* Spectroscopy of 4(5)-methylimidazole and its hydrates, hosted in helium droplets
63	**Stuart Greaves** *(Heriot-Watt University)* Studying gas-liquid surface reactions using velocity map imaging
64	**Arthur Suits** *(University of Missouri)* UF-CRDS: A pulsed uniform flow apparatus with cw-cavity ringdown spectroscopy
65	**Bernadette Broderick** *(University of Missouri)* Product branching and low temperature reaction kinetics by chirped-pulse Fourier transform mm-wave spectroscopy in a uniform supersonic flow
66	**Hendrik Nahler** *(Heriot-Watt University)* Absolute fluorescence quantum yield of acetone
67	**Jacqueline Arlt** *(Aarhus Universty)* Molecular frame photoelectron angular distributions of aniline obtained via weak-field ionization
68	**Katya Moncrieff** *(Heriot-Watt University)* Mid-infrared frequency modulated spectroscopy as a probe of scattering dynamics at the gas-liquid interface
69*	**Yuval Shagam** *(University of Colorado)* Control and mapping of molecular states for long coherence spin state readout at the quantum projection noise limit
70*	**Alice Green** *(University of Oxford)* Molecular activation and reactivity on small metal clusters
71*	**Kateryna Grygoryeva** *(Czech Academy of Sciences)* Pyruvic acid on nanoices: Photon and electron driven chemistry
72*	**Nikoleta Kotsina** *(Heriot-Watt University)* Ultrafast molecular spectroscopy using a hollow-core photonic crystal fiber light source
73*	**Bum Suk Zhao** *(Ulsan National Institute of Science and Technology)* Scattering of aligned molecules by nonresonant optical standing waves
74*	**Hiroya Asami** *(Gakushuin University)* Gas phase resonance Raman spectroscopy of huge biomolecule by IR-ablation of droplet beam: Local structure in isolated heme protein
75*	**Jolijn Onvlee** (DESY) Unravelling the ultrafast dynamics in indole-water
76*	**Ulrich Bangert** *(University of Freiburg)* Two-dimensional electronic spectroscopy of molecules in helium nanodroplet isolation
77*	**Jennifer Meyer** *(Universtiät Innsbruck)* Indirect dynamics dominate base induced elimination (E2) for reactions of fluorine anions with tert-butyl halides
78*	**Valentina Zhelyazkova** *(ETH Zürich)* Studying ion-molecule reactions at low temperatures with a merged-beam set-up

Posters denoted * also feature as either Hot Topic or Emerging Investigator talks.

1. Using UV and XUV time-resolved photoelectron spectroscopy to probe the dissociation dynamics of methyl iodide

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We combine the advantages of UV- and XUV-probe photoelectron spectroscopy in a study of the dissociation dynamics of methyl iodide at a range of pump wavelengths, Fig. 1. The UV probe provides high sensitivity and resolution to early time dynamics close to the Franck-Condon point, while the XUV probe provides measurements at all geometries, allowing us to follow the reaction to completion.

The pump wavelengths studied cover the red and blue sides of the absorption maximum, populating different parts of the excited state potentials. The dynamics on the red edge of the absorption maximum show rapid dissociation along the $^3Q_0$ potential energy surface as previously measured. This is seen in the XUV measurements as a shifting of the photoelectron bands that map the C-I bond length as the molecule dissociates, Fig. 2. At the blue edge, the spectral changes are more complex and show features associated with the rapid dissociation, but also band shifts to lower binding energies at later times, and excited state lifetimes that are over four times longer than those seen at the red edge. The measurements highlight how the advantages of various probe energies can be combined to obtain more complete information on the full dynamic process, the sensitivity of dynamics to initial conditions, and the complexity of dynamics in systems that are considered simple.

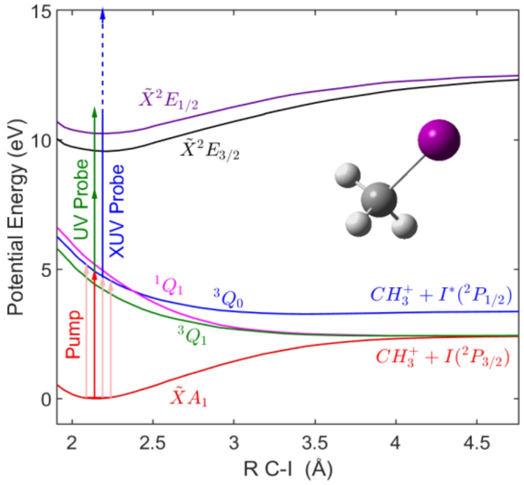

Figure 1: The potential energy surfaces of methyl iodide,[1,2] *with our pump and probe energies indicated by arrows.*

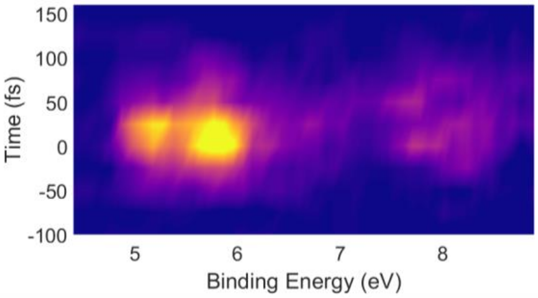

Figure 2: The time-resolved spectrum of methyl iodide with a pump energy at the red edge of the absorption band, and an XUV probe.

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2. Investigation of the weak hydrogen bond of some propyne complexes

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J.-M. Mestdagh,[†] B. Soep,[†] C. Crépin,[‡] and L. Poisson[†]

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The formation of molecular complexes depends on a subtle equilibrium between weak forces (van der Waals, hydrogen bonds, etc.). These forces make the systems very flexible and allow large amplitude deformations. Part of our activity focuses on situations where the molecular moieties can act as both hydrogen donor and acceptor. For example, an alkyne molecule has a triple bond (hydrogen acceptor) and a terminal acidic H atom.

In this context, the complexes of propyne (with a propyne[1] or a water molecule[2]) were studied on the Gouttelium setup. The "HElium NanoDroplet Isolation" (HENDI)[3] technique was used to record infrared spectra which inform on these floppy complexes in the region of the C-H vibration of the propyne molecule. Helium droplets are known indeed to be very convenient micro-reactors to form complexes whose stoichiometry is controlled at the molecular level. Furthermore, the helium droplets being superfluid essentially ($T_{goutte} \approx$ 0.4 K), the structure and the deformation of the complexes are expected to be weakly perturbed. The comparison between observed and simulated spectra inform both on structure and dynamics of large amplitude deformation.

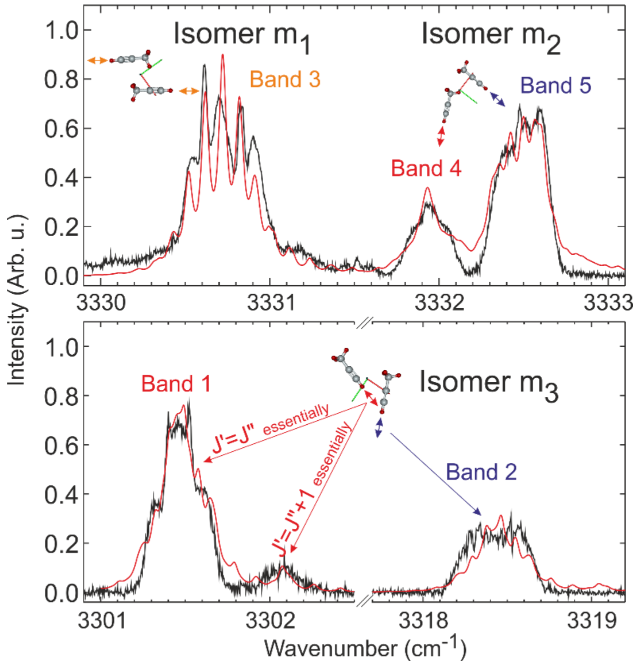

Figure 1: The propyne dimers observed in helium droplet

For the dimer, the central result is the existence of three isomers, reflecting the complexity of the weak CH…π H-bonding when several H-donors exist (Fig. 1). For the hydrate, the observed spectrum is consistent with a five member structure with two H-bonds between the water and propyne molecules, which was predicted by Lopes *et al.*[4]

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3. Electron and photon-triggered reactions between molecules adsorbed on clusters

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Molecular clusters represent a unique environment: the finite size of clusters allows for a detailed molecular level insight into the studied processes; while the inherent many-body nature of clusters provides a tool to investigate the solvent effects on studied processes.[1] Indeed, the interest in clusters as “a bridge between gas phase and bulk” has a long history,[2] however, there has been a recent revival of interest in connection with astrochemistry: synthesis of simple precursors adsorbed on ice grains in interstellar molecular clouds (ISMC) represents a pathway to more complex molecules in a very low density and cold environment of ISMC.[3] Another area, where clusters can provide an unprecedented, detailed insight, is aerosol chemistry which plays a crucial role in the atmosphere.[4] Such species as interstellar ice grains or atmospheric aerosol particles can be mimicked in laboratory studies by suitable clusters generated in molecular beams.

A versatile, universal, cluster beam apparatus (CLUB) in Prague, Fig. 1, allows for a large variety of different experiments with clusters:[5] pickup experiments,[6] mass spectrometry after photoionization, electron ionization[7] and electron attachment,[8,9] photodissociation and velocity map imaging including IR-UV pump-probe experiments,[10] etc. Here, we concentrate on different heterogeneous clusters and nanoparticles generated in coexpansion of different gases and/or by pickup of different molecules on clusters, and we observe reactions in the clusters triggered by photons and/or electrons of different energies in relevance to atmospheric chemistry and astrochemistry.

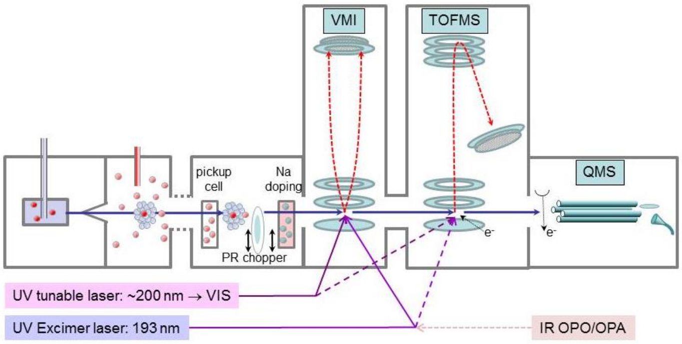

Figure 1: Schematic of CLUster Beam (CLUB) apparatus.

We will present several recent results: One particular example of atmospheric relevance is represented by mixed nitric acid–water clusters. Using our recently implemented method for pickup cross-section measurements,[6] we investigate an uptake of atmospherically relevant molecules (e.g. isoprene, pinene and their oxidation products) on acid $(HNO_3)_M(H_2O)_N$ clusters. The important result is that oxidation can increase the pickup cross sections for a molecule by more than an order of magnitude. This observation can explain the molecular level mechanism behind the secondary organic aerosol (SOA) generation by oxidative products of molecules like isoprene or pinene.

Besides, we investigate an electron attachment to these HNO_3/H_2O clusters[8] by far the major ion product of the dissociative electron attachment (DEA) of the gas phase HNO_3 molecule is NO_2^- ion. However, solvation of HNO_3 in clusters changes the major product to NO_3^-, which is one of the major atmospheric ions. Very recently, we have demonstrated that the kinetic energy of the attached electron in the DEA process has a pronounced effect on the ion-molecule chemistry in the clusters.[9]

In relevance to astrochemistry, we investigate deposition of different molecules on large clusters/nanoparticles in a pickup experiment, and subsequently observing their reactions triggered by photons and/or electrons, Fig. 2. One particular example represents reactions between formic acid and methanol on large argon clusters: an interesting channel is the proton transfer from methanol towards formic acid where the abstractions of protons from methyl and hydroxyl group of methanol compete. The experiments are accompanied by theoretical calculations detailing the corresponding reaction pathways.

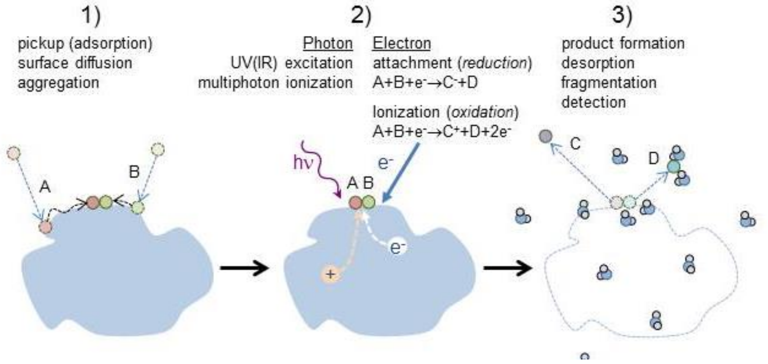

Figure 2: Photon and/or electron triggered chemistry on free nanoparticles.

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4. Vibrationally mediated photodissociation dynamics of pyrrole

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Photodissociation of pyrrole molecules with IR excited N-H bond stretching vibration ($v_1 = 1$, $v_{IR} = 3532\ cm^{-1}$) was investigated in a velocity map imaging experiment upon photodissociation at $\lambda_{UV} = 243$ nm. The velocity map images show the bimodal structure of fast and slow H-fragments. In the UV+IR experiment, the fast peak is shifted to 1.04eV compared to 0.81eV of the UV-only photodissociation, which means that approximately 53% of additional vibrational energy (0.44 eV) is deposited into H-fragment kinetic energy. The IR pre-excitation also exhibits enhanced H-fragment signal with respect to UV-only experiment due to a more favourable Franck-Condon factor of transition from the vibrationally excited pyrrole.[1] The UV+IR spectra were further compared with isoenergetic UV-only experiments. Upon excitation at $\lambda_{UV} = 224$ nm, the fast peak maximum shifts 0.15 eV towards lower energies and only 61 % of total available energy converts into H-fragment kinetic energy in respect to 72% of UV+IR photodissociation, which demonstrates efficient coupling of the excited N-H vibration to the bond dissociation and fragment kinetic energy. The observation corresponds to spectra of Cronin *et al*.[2] measured with excitation of $\lambda_{UV} = 220$ nm and $\lambda_{UV} = 228$ nm with similar lower conversion to fragment kinetic energy of 56% and 70%, respectively. Finally, we measured the time-resolved nanosecond experiment by pump-probe approach. The H-fragment signal shows similar intensification and kinetic energy distribution independently on the delay of IR pulse up to 150 ns, which illustrates preservation of the vibrational excitation in various degrees of freedom of pyrrole that enhances the UV photodissociation.[3]

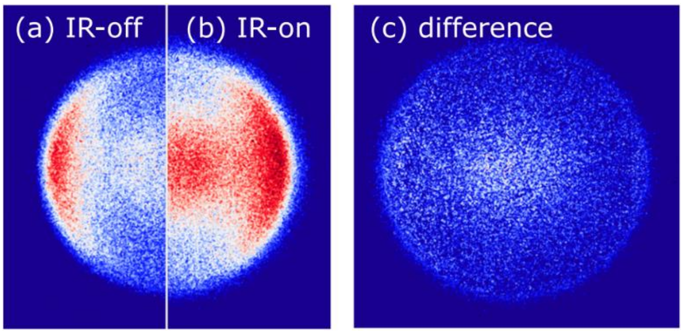

Figure 1: Hydrogen fragment raw images from pyrrole VMI experiment: (a) UV photodissociation and H-atom REMPI ionization at $\lambda_{UV} = 243$ nm; (b) IR vibrational excitation of N–H bond at $v_{IR} = 3532\ cm^{-1}$. The right image; (c) corresponds to the difference [(UV+IR)-(UV-only)].

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5. Thionated uracils under UV irradiation: Intramolecular micro-environmental effects on the intersystem crossing dynamics

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The canonical nucleobases, which form the building blocks of our genetic coding material, are known to protect themselves against photodamage through ultrafast internal conversion processes that dissipate potentially harmful UV energy into heat. However, seemingly minor changes such as single atom substitutions can profoundly alter the photophysics of the nucleobases. In thiobases, where an oxygen is replaced by sulfur, these internal conversion pathways are inaccessible and crossing onto the triplet manifold becomes highly efficient. While long-lived, reactive triplet states, as observed in some of the thiobases, negate their photoprotection, these properties are highly desirable for pharmacological applications, e.g. as photosensitizers in cancer treatments.

Using time-resolved photoelectron spectroscopy the response of a series of thiouracils to UV irradiation has been investigated to unravel the mechanistic details governing their unique ultrafast intersystem crossing dynamics. Remarkable differences are observed for 2-thiouracil[1-3], 4-thiouracil[4] and 2,4-dithiouracil when the degree of thionation and position of sulfur atom is altered.[5]

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6. Coulomb explosion imaging: A tool for molecular structure determination

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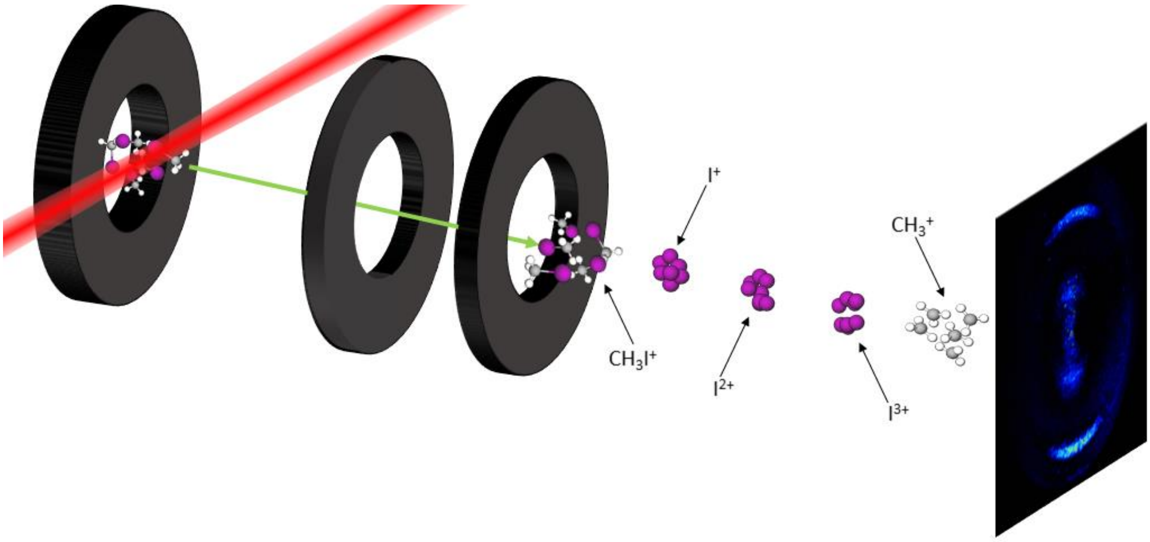
Gas-phase spectroscopic techniques provide a valuable insight into the fundamental dynamics of molecular systems, free of intermolecular and solvent effects. By applying an intense (fs) laser field over a species of interest, the system may be stripped of many electrons simultaneously inducing a Coulomb explosion.[1,2] Provided this ionisation process is shorter than the vibrational period of the molecule, the kinetic energy of the recoiling photofragments will be directly proportional to the net repulsion between fragments at the time of the explosion. When used in conjunction with newly established multi-mass imaging techniques and covariance analysis, it is possible to interrogate a species' molecular structure.[3] Furthermore, when employed as a time-resolved probe following ultraviolet (UV) photoexcitation, Coulomb explosion imaging provides an important insight into dynamically-evolving molecular structures,[4,5] such as photo-isomerisation and photo-induced ring-opening. Presented here is the current progress in developing a time-resolved Coulomb explosion imaging apparatus, intended for the study of excited structures, in addition to preliminary calculations and simulations of photofragment trajectories following Coulomb explosion.



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7. Localisation of the excess electron in water clusters and anthracene-water clusters

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Low energy electron driven processes are important drivers for chemistry in the interstellar medium and often occur on ice grains in which polycyclic aromatic hydrocarbons (PAHs) are also commonly found. Attachment to water leads to the formation of hydrated electrons, in which the excess electron is solvated much like an anion. In PAHs larger than naphthalene, the electron can be bound in a valence state leading to the stable anion, PAH^-. Here we investigated, using photoelectron (PE) imaging, the location of the excess electron to water clusters and anthracene-water clusters.

For water clusters, the results show that the binding site within a cluster depends sensitively on its nucleation stage, as measured by attaching electrons at various stages along a supersonic expansion.[1] Concerning anthracene-water cluster, it is known that for anthracene anion the surplus electron sits in the first LUMO π^* orbital of the neutral.[2] Here our results show that changing the environment around anthracene by adding water molecules or other anthracene molecules, the electron remains in this orbital. However, with increasing water clustering, new detachment channels are apparent at low electron kinetic energy. Such electrons imply the presence of an indirect detachment channel. We speculate on the nature of this channel.

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8. Following macroscopic effects in gas phase experiments using XUV–UV spectroscopy

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A novel experimental approach employing XUV and UV femtosecond pulses is presented and applied to the study of ultrafast physical processes in atomic targets in the gas phase. In particular, we report on the resonant pulse propagation of XUV pulses in He atoms employing photoelectron spectroscopy.

The propagation of light pulses with a spectrum containing frequencies that are resonant with the hosting medium has been studied extensively in the literature[1,2] and it has been shown that, when the pulse duration is shorter than the lifetime of the excited states, the pulse envelope can be significantly reshaped along its propagation. Here, we discuss the macroscopic propagation of a resonant XUV attosecond pulse train, APT, by performing photoelectron spectroscopy in He atoms. In particular, we show that the phase accumulated by the resonant propagation of the XUV pulse leads to a chirped electron wave-packet, EWP, with characteristic signatures both in the attosecond and the femtosecond timescales. The use of an APT provides a good compromise between time and spectral resolution, which is essential to explore quantum systems.[3] The use of the 2nd harmonic, which lies in the UV, instead of the often used fundamental frequency, which is in the IR here, has multiple benefits. Specifically, it avoids the spectral congestion, increases the energy range of the accessible bound states and projects the spectral properties of the emitted EWPs to the spatial coordinates.

Our results demonstrate the feasibility of studying real atomic and potentially molecular states with attosecond resolution, how the characteristics of matter in the frequency domain could be projected in the real space and how one could gain control on the directionality of electron wavepackets.

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9. Fluorescence-lifetime-limited trapping of Rydberg helium atoms on a chip

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The manipulation of highly excited atoms above surfaces is important for a wide range of applications in atomic and molecular physics, such as cavity QED,[1] studying chemical reactions with merged beams,[2] or as an initial step in building atom interferometers,[3] among others. In this work, we report on experiments in which metastable (1s)(2s) $^3S_1$ helium atoms produced in a supersonic beam were excited to Rydberg-Stark states in the n = 27-30 range, subsequently decelerated by, and trapped above, a surface-electrode decelerator in a cryogenic environment. The Rydberg atoms were decelerated to zero velocity in 75 μs over a distance of 33 mm and kept stationary for times in the 0-525 μs range, after which they were re-accelerated for detection by pulsed-field ionisation.

The long trapping times achieved in these experiments are attributed to: (i) using a home-built valve producing short-duration pulses of about 20 μs which enabled the reduction of losses from collisions with atoms in the trailing part of the gas pulse, and (ii) cooling the environment to cryogenic temperatures which supressed losses from blackbody-radiation-induced processes. At 4.7 K, the atom losses from the trap were found to come almost exclusively from the spontaneous fluorescence of the Rydberg-Stark states and the trapping lifetimes were found to correspond to the natural lifetimes of these excited states. Additionally, increasing the temperature of the environment to 100 K decreases the trap lifetime because of trap losses stimulated by blackbody radiation.

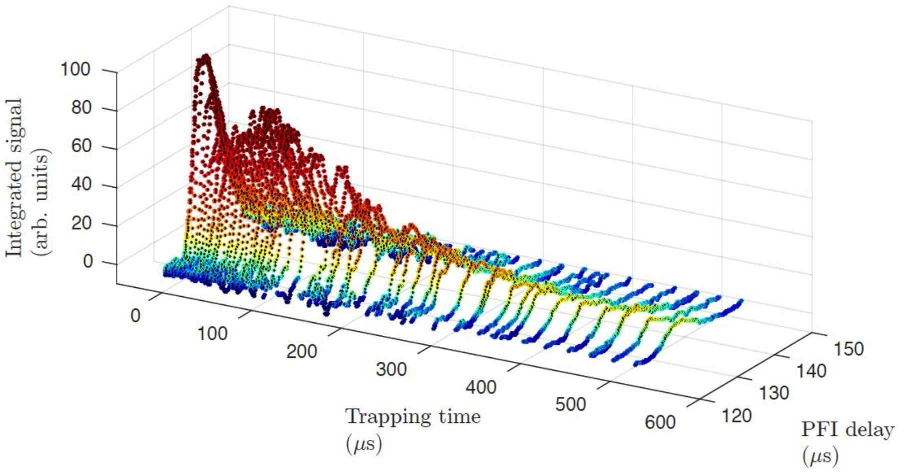

Figure 1: Recorded time-of-flight profiles of Rydberg helium atoms after their re-acceleration from the surface-electrode trap as a function of trapping time.

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10. Ultrafast H_3^+ formation on the methanol dication: Competition of proton & electron transfer dynamics

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Formation of the H_3^+ trihydrogen cation by significant structural rearrangement of ionized organic molecules has been ubiquitously reported for different systems and different ionization methods.[1-7] Experimental probing of such exotic molecular dynamics provides valuable challenges for state-of-the-art ab-initio theoretical modeling of the reaction mechanisms, revealing the underlying interplay between electronic and nuclear motion dynamics. Early theoretical modeling proposed a mechanism involving roaming neutral H_2 dynamics on a doubly ionized ground state potential surface, culminating in a proton transfer forming H_3^+.[2] Recent experimental studies using double-ionization of methanol by ultrafast strong-field laser pulses provided conflicting evidence as to the duration of these complex H_3^+ formation dynamics.[3-5]

We present time-resolved fragment imaging of Coulomb explosion events, initiated by single-photon double-ionization using an ultrafast EUV pulse, which removes the intrinsic uncertainties of previous strong-field laser experiments.[1] The low field of the high energy EUV photons allows detailed comparison with non-adiabatic ab-initio molecular dynamics simulations performed on field-free CASPT2 level potentials.[2] The combined time-resolved experimental and ab-initio theoretical study provides a detailed picture of the ultrafast dynamics that unravel on the methanol dication, involving competing electron and proton transfer mechanisms. The formation of H_3^+ via proton-transfer is in direct competition on ultrafast time scales with a long-range electron-transfer from the roaming H_2 to the dication and formation of H_2^+ in a mechanism termed "inverse harpooning".

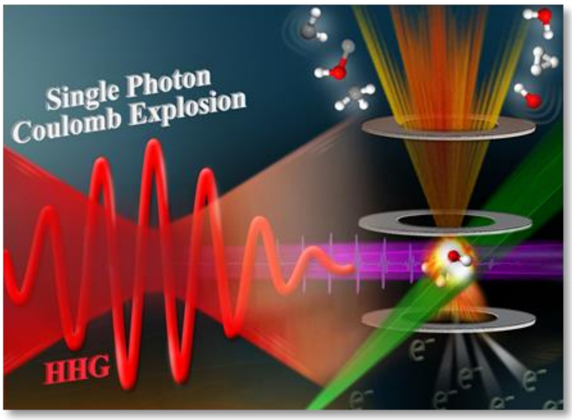

Figure 1, illustrating the experimental single-photon Coulomb explosion imaging setup. Ultrafast EUV pulses are produced by HHG and initiate the methanol dication dynamics, which are probed by time delayed near-IR pulses. 3D coincidence fragment imaging of the correlated cationic products allows experimental disentangling of the competing mechanisms of electron transfer, forming $CHOH^+$ + H_2^+ and proton transfer, forming COH^+ + H_3^+.

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11. Evaporative cooling processes of liquid droplet in vacuum

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We report evaporative cooling processes of liquids in a vacuum for droplets of ethylene glycol[1] and water[2] in the size range of 50−70 μm in diameter. These studies are based on our own technique enabling on-demand liquid-droplet formation directly in a vacuum. The droplets are characterized by optical microscope detection; the size is evaluated by a droplet image captured with strobe LED illumination, while liquid-to-solid phase transition is identified by depolarized laser scattering from a corrugated surface of frozen droplets.

For ethylene glycol, the droplet diameter was measured as a function of time, which kept decreasing linearly for more than 50 s (Fig. 1). This is an unexpected result because the droplet should be cooled down below the freezing temperature within several seconds even with the relatively low vapour pressure of ethylene glycol. Thermodynamic analysis of this result revealed that evaporative cooling competes with radiative heating from the surroundings at room temperature. The balance between the two competing effects allows the droplet to survive in the liquid phase much longer than naively anticipated.

For water droplets, a frozen fraction was measured as a function of time by examining 200 droplets at each time (a freezing curve in Fig. 2). They freeze very fast within 11 ms due to evaporative cooling accelerated by its high vapour pressure. Temporal evolution of droplet temperature (a cooling curve) was simulated, as superimposed in Fig. 2, by examining different sources of thermodynamic data such as heat capacity and homogeneous nucleation rate. The freezing was found to occur at temperatures between 233 and 236 K as indicated by the thick part of the cooling curve. This result shows in turn that water droplets can stay in liquid down to these deeply supercooled temperatures.

The present technique provides us with a novel method for manipulating liquids in a vacuum to combine gas-phase and liquid-phase chemistry.

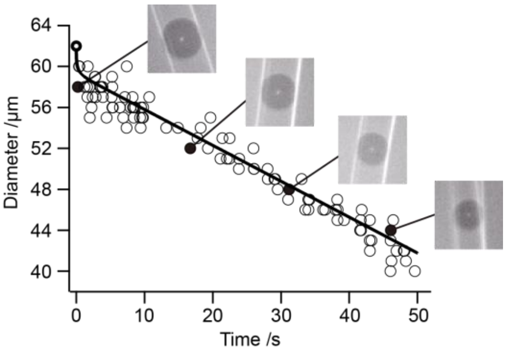

Figure 1: Diameter of ethylene glycol droplets as a function of time.

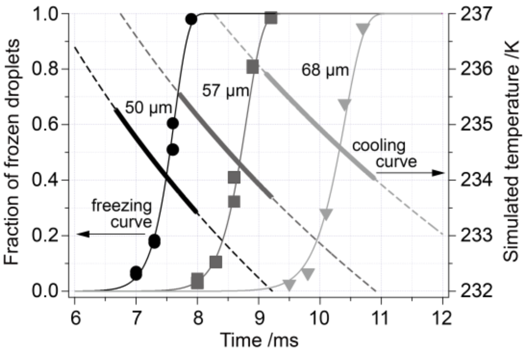

Figure 2: Freezing (experiment) and cooling (simulation) curves of water droplets.

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[PCCP Hot Article 2018]

12. Reaction dynamics of $O(^3P)$ with 1-butene and 1,2-butadiene

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The elementary reactions of $O(^3P)$ with unsaturated aliphatic (alkynes, alkenes, dienes) and aromatic (benzene, toluene) hydrocarbons play a central role in our understanding of hydrocarbon oxidation mechanisms in combustion processes. They exhibit a variety of product channels, some of which can only occur via intersystem crossing (ISC) from triplet to singlet potential energy surfaces (PESs).[1,2] Despite extensive studies of their kinetics, little is known about the identity of primary products and branching ratios (BRs) that are crucially needed to improve combustion models. Most suitable to determine these quantities is the crossed molecular beams (CMB) scattering technique with “universal” mass-spectrometric detection and time-of-flight analysis, empowered with soft-ionization by low energy electrons[1,2] or synchrotron radiation[3]. The power of this approach has been illustrated in combined experimental/theoretical studies of the $O(^3P)$ reactions with ethyne[4a], ethene[4b], propene[5], allene[6], and propyne[6b,7], for which product BRs and ISC extent were quantified. In this contribution, we highlight results of recent CMB studies extended to $O(^3P)$ reactions with a higher alkene (1-butene[8]) and diene (1,2-butadiene[9]) for which little information exists, to explore how product distributions, BRs and role of ISC vary with increasing molecular complexity, thus paving the way to an understanding of also more complex oxidation reactions of unsaturated hydrocarbons. The reaction dynamics are elucidated (7 and 9 product channels characterized for O+1-butene and O+1,2-butadiene, respectively) in the light of synergistic RRKM/Master equation non-adiabatic calculations on high-level *ab initio* triplet/singlet PESs, which are found to support the experimental BRs and extent of ISC. Similar studies have been very recently extended to also reactions with conjugated dienes (the particularly important 1,3-butadiene) and aromatics (benzene and toluene).

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13. Dynamics of bimolecular chemical reactions on *ab initio* potential energy surfaces

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We investigate the dynamics and mechanisms of chemical reactions using analytical *ab initio* potential energy surfaces (PESs) and quasi-classical trajectory and/or quantum methods. After many successful applications for atom + methane reactions, we have recently initiated an *ab initio* analytical PES-based approach for studying the dynamics of bimolecular nucleophilic substitution (S_N2) reactions (Fig. 1). Millions of trajectories obtained on the analytical PESs revealed a novel double-inversion mechanism for S_N2 reactions,[1] unexpected leaving-group effects,[2] non-traditional front-side complex formation,[3] and unprecedented agreement with experiments.[2,4] Besides the S_N2 studies, in 2017 our joint theoretical–experimental investigation uncovered the angle-dependent barrier for the Cl + CHD_3 reaction.[5] Moving beyond six-atom systems, we construct analytical *ab initio* PESs for the F/Cl + C_2H_6, OH^- + CH_3I, and F^- + CH_3CH_2Cl reactions using ROBOSURFER, our new automatic PES developer program package. These high-level PESs allow efficient dynamical investigations of the above reactions revealing the competitions between abstraction and substitution, inversion and retention, as well as S_N2 and elimination (E2) channels of F^- + CH_3CH_2Cl.

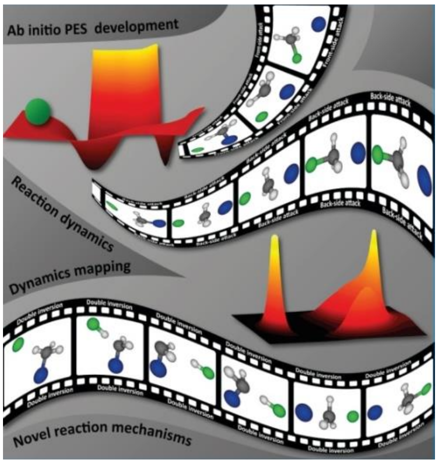

Figure 1: Different mechanisms of S_N2 reactions revealed on analytical potential energy surfaces.

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14. The formation of chemically bonded argon via photoexcitation of Ar-I_2 van der Waals complex

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Van der Waals complex Ar-I_2 is a model system for a study of the influence of weakly bonded molecular environment on the photochemistry and photophysics of molecules. Earlier studies of this complex reported in literature were focused only on processes including transition to the first excited states of iodine molecule. In the current work of the photo-induced processes following the excitation of the complex Ar-I_2 into high-lying Rydberg states and ion-pair states are investigated. The mechanism of the photodissociation of free iodine molecules excited to the high-lying Rydberg states (E≈9.2 eV) has been studied earlier with the use of velocity map imaging technique.[1] It was shown that excitation of I_2 into high-lying Rydberg states is followed by the formation of ion pair state $I_2(Ry) \rightarrow I^+ + I^-$ as well as of all energetically accessible Rydberg states of iodine atom $I_2(Ry) \rightarrow I + I(Ry)$. Femtosecond dynamics of these processes was also investigated.[2] In present work we have been focused on the processes of excitation of iodine in van der Waals complex Ar-I_2 in the same spectral range. Ar-I_2 van der Waals complex has been generated in supersonic molecular beam. Ions Ar^+ and ArI^+ were observed in a mass spectra at Ar-I_2 van der Waals complex photoexcitation by laser radiation with wavelength ~270 nm ($h\nu \approx 4.6$ eV). It should be noted that ionization potential of argon is 15.7 eV that requires four photons of radiation used. The four-photon ionization of free Ar atoms is not possible in our experimental condition (nanosecond laser with pulse energy about 1 mJ). Velocity map of Ar^+ (see Fig. 1) have rings as in case of diatomic molecule dissociation. It means that Ar^+ is formed from photodissociation of parent ArI^+ ion where argon ion is covalently bound. The photon energy dependence of the channels giving rise to Ar^+ ions with different kinetic energy has been also investigated. The mechanism of covalently bound Ar^+ ions formation is suggested.

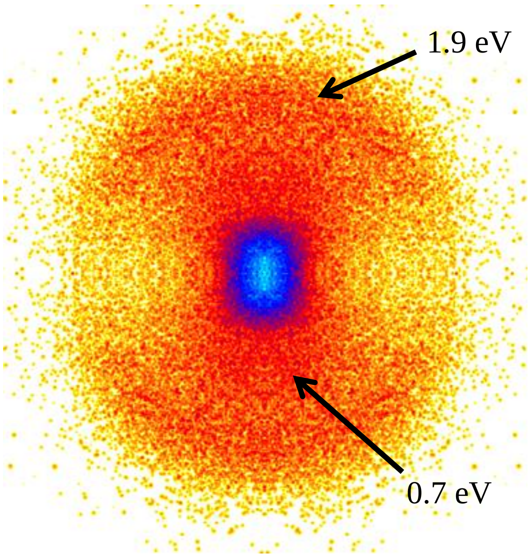

Figure 1: Velocity map image of Ar^+ arising from complex Ar-I_2.

Acknowledgements: This work has the support of Russian Science Foundation (Grant 16-13-10024).

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15. Design of a new molecular beams machine

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We present the design of a new molecular beams machine capable of elucidating the formation of carbon- and silicon-bearing molecules relevant to combustion and astrochemistry. The machine includes the following critical components:

1. **Main chamber** (MC) is a 304 stainless steel box (120 cm × 120 cm × 70 cm; 778 L) and pumped by 2400 L/s magnetically suspended turbo molecular pumps (Osaka TG2400M).[1]

2. Reflection Time-of-flight mass-spectrometer (**RETOF**) produced by Jordan TOF Products, Inc. RETOF is connected to the main chamber and interfaced to one turbo molecular pump (Osaka TG420M; 400 L/s).

3. **Source chamber** (SC) is located inside the MC so that the supersonic beam travels in the plane in between the repeller and an extraction grid of the RETOF. SC is evacuated by one maglev pump (Osaka TG2400M) backed by a dry roots pump (Leybold WS505; 140 L/s) roughed by one scroll pump (Edwards XDS35iC). A second chamber will be incorporated in the future for crossed beam studies.

4. **Pulse valve**. The piezo-electric valve is designed for generation of short gas impulses (80 µs) at high repetition rates up to 1 kHz and high gas flow. Mounted in the SC in front of a skimmer (1 mm) on the XYZ translation stage.

5. **Pyrolytic source**. Consists of a resistively heated SiC tube of 22 mm length, 1 mm inner diameter; the achievable highest temperature of the tube is 1300–1400 K. The electrical heating and mounting of this tube occurs through two silicon carbide electrode sleeves and two molybdenum electrode blocks.[2]

6. **The frequency tripling gas cell** (length 269 mm, diameter 35 mm), into which 355 nm pulsed, seeded Nd/YAG tripled laser radiation is focused, is used to generate the 118 nm (10.5 eV) radiation. The tripling cell contains a mixture of Xe and Ar gas (~1/10, 200 Torr).[3] This will be upgraded in the future to generate vacuum ultraviolet light via four-wave mixing.

The new machine will allow us to measure product distributions for various unimolecular (pyrolytic) and bimolecular reactions under combustion-like and circumstellar conditions.

Acknowledgements: This work was supported by Ministry of Education and Science of the Russian Federation under the Grant No. 14.Y26.31.0020 to Samara University.

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16. Matter-wave diffraction from a periodic array of half planes

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We report on reflection and diffraction of beams of He and D_2 from square-wave gratings of a 400-μm period and strip widths ranging from 10 to 200 μm at grazing-incidence conditions. In each case we observe fully resolved matter-wave diffraction patterns including the specular reflection and diffracted beams up to the second diffraction order. With decreasing strip width, the observed diffraction efficiencies exhibit a transformation from the known regime of quantum reflection from the grating strips[1,2] to the regime of edge diffraction from a half-plane array.[3] The latter is described by a single-parameter model[4] developed previously to describe phenomena as diverse as quantum billiards, scattering of radio waves in urban areas, and reflection of matter waves from microstructures. Our data provide experimental confirmation of the widespread model. Moreover, our results demonstrate that neither classical reflection nor quantum reflection are essential for reflective diffraction of matter waves from a structured solid, but it can result exclusively from half-plane edge diffraction. We apply diffractive reflection also to fragile He_2 and He_3 clusters. Unlike He atoms, the clusters's diffractive reflection probability is significantly increased as compared to quantum reflection.

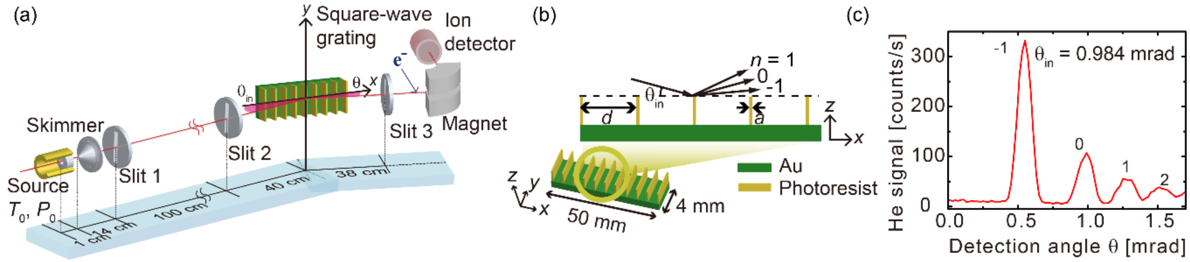

Figure 1: (a) Schematic of the experimental setup. The grating normal is chosen as the z axis of our coordinate system. Incidence θ_{in} and detection angle θ are measured with respect to the grating surface in the xz plane of incidence. (b) The reflection gratings are 50-mm-long microstructured arrays of 4-mm-long parallel strips made out of 1-µm-thick photoresist patterned on a commercial gold mirror. The center-to-center distance of the strips defines the period d = 400 µm identical for all gratings used. Four gratings with strip width a = 10, 30, 100, or 200 µm have been used. For all four gratings, the gold surface between the strips is completely shadowed by the strips for all incidence angles used in this work. A sketch of the a = 10 µm grating is shown in (b). (c) Representative diffraction pattern for a = 10 µm and θ_{in} = 0.984 mrad measured by rotating the detector around the y axis and integrating the signal for 8 s at each angular position.

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17. Absolute density measurements of trace amounts of OH radicals

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The knowledge of absolute densities of molecules is important for many disciplines, including atmospheric and astrochemistry, cold and ultracold molecules and molecular reaction dynamics. The OH radical plays an important role in many atmospheric and astrochemical reactions. Measurements of its absolute abundance will allow, e.g., the determination of product branching fractions and thus provide important inputs for atmospheric models.

We employ cavity-enhanced laser-induced fluorescence (CELIF) for absolute density measurements. CELIF directly combines laser-induced fluorescence (LIF) and cavity ring-down spectroscopy (CRDS) in a single laser beam (Fig. 1). CELIF is self-calibrating via a concurrent CRDS measurement at high densities and the combined technique achieves a lower limit of detection and a larger dynamic range than either standalone technique.[1]

We will report on absolute measurements of OH radicals produced via a pulsed electrical discharge in a molecular beam. Following our previous measurements of SD radicals,[2] we expect a CELIF limit of detection for OH in the order of 10^4 cm^{-3} with an accuracy of 10%.

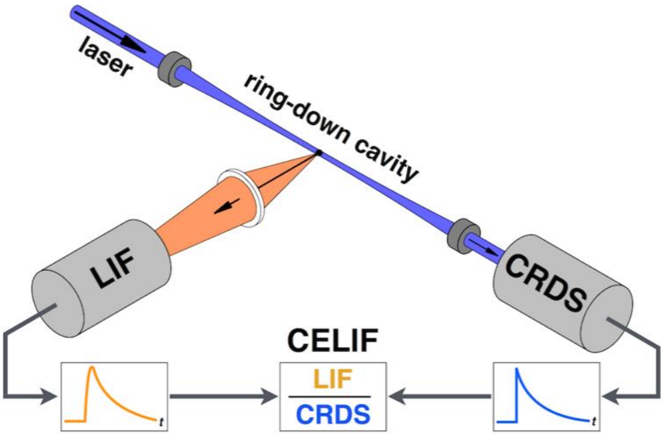

Figure 1: Schematic setup of a CELIF experiment.

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18. Rydberg state electric field ionisation dynamics for quantum state-selective detection of resonant energy transfer in cold He* + NH_3 collisions

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The large size of the Rydberg electron wavefunction, which scales as n^2 (n is the principal quantum number), means that Rydberg atoms and molecules can have almost macroscopic sizes. This feature not only makes samples in such states highly susceptible to perturbations by electric fields, but also extremely sensitive to collisions in many media. Collisions of Rydberg atoms with polar ground-state molecules, such as NH_3 and CO, have been studied experimentally.[1,2] In these studies, resonant energy transfer between the collisional partners was reported, which resulted in a change in the internal quantum states of both collisional partners. To optimise the detection process in these types of experiments it is important to implement reliable methods to selectively detect different Rydberg states following collisions with ground-state molecules. Rydberg states with principal quantum numbers above $n = 30$ can be ionised with electric fields less than 1 kV/cm.[3] In the laboratory, such fields can be controlled and manipulated with high precision, allowing studies of ionisation dynamics and therefore optimisation of Rydberg state-selective detection by electric field ionisation.

With this in mind we report here the results of experiments in which we have studied the electric field ionisation dynamics of triplet Rydberg states in helium with values of n close to 37.[4] The particular states studied were chosen because they are well suited for studies of resonant energy transfer in collisions with ground-state NH_3 molecules.[5,6] By laser photoexcitation of these states in electric fields close to the field ionisation threshold, we have probed ionisation dynamics and directly measured ionisation rates in the time domain using sequences of electric field pulses. We report on the observation of both adiabatic and non-adiabatic pathways to ionisation, and non-monotonic changes in the ionisation rates of individual quantum states in increasing electric fields. Progress towards the use of this new and detailed information for investigations of the effect of particle orientation and collision energy on resonant energy transfer in He* + NH_3 collisions at low translational temperatures will also be discussed.

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19. Unravelling the formation of substituted polycyclic aromatic hydrocarbons in the interstellar medium by plasma sources

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Detected through the unidentified infrared bands (UIR), polycyclic aromatic hydrocarbons (PAHs) are thought to be omnipresent in the interstellar medium and to play a key role in its physics and chemistry. In the extreme energetic conditions of the interstellar medium (ISM), PAHs are expected to undergo ionisation, fragmentation and dehydrogenation processes when interacting with the interstellar energy rich radiation. Therefore, depending on the interstellar environment, PAHs can potentially exist in different charge and dehydrogenation states. They can also contribute to the creation of a wide range of molecules, from small molecules, like H_2 and acetylene, to more complex organic molecules, such as oxygen and nitrogen containing molecules.

The reactivity of these molecules under extreme energetic conditions can be studied in the laboratory by means of electrical discharge sources combined with molecular beam cooling. In plasma conditions these molecules are expected to dissociate and to recombine to form new species. In this respect, we have coupled an electrical discharge nozzle with mass-resolved IR-UV ion dip spectroscopy using the free electron laser FELIX (550-1800 cm^{-1}) and chirped pulse broadband microwave spectroscopy, to give insight into the chemistry that can potentially take place when PAHs undergo the extreme energetic conditions of the ISM. The two techniques are complementary to each other. The combination of mass spectrometry with IR-UV spectroscopy exploits the advantage of probing and characterising the created species either via their mass as well as via their unique IR signature. Species that cannot be unambiguously characterised by IR-UV ion dip spectroscopy can be probed in depth via their microwave spectra, which are known to be fingerprints of the molecules.

In this work, we have investigated the products formed upon the discharge of PAHs with simple organic molecules that are prevalent in the ISM. We investigated the differences in PAHs such as sizes and degrees of aromaticity by choosing PAHs as naphthalene ($C_{10}H_8$), fluorene ($C_{13}H_{10}$), phenanthrene ($C_{14}H_{10}$), and pyrene ($C_{16}H_{10}$) to discharge with acetonitrile (CH_3CN), a nitrogen containing interstellar molecule. For all the investigated PAHs, addition of specific functional groups such as cyano (CN) methyl (CH_3) and ethynyl (CCH) groups as well as insertion of carbon atoms to form PAHs with additional and larger ring systems have been observed and their spectra in the mid-IR range have been characterised, thus providing us with relevant insight into the underlying processes. Proposed formation mechanisms are also presented.

20. Dissociative electron attachment of hydrated biomolecules

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Radiotherapy is a common cancer treatment, which utilises ionising radiation to damage cancerous tissue. As the radiation ionises a molecule, low energy (≤20 eV) secondary electrons are produced. A molecule can absorb one of these low energy electrons to produce a transient negative ion, which may then fragment into an anion and one or more neutral species. This process is known as dissociative electron attachment (DEA) and is as important as direct bond dissociation in radiotherapy.[1]

In the lab, DEA can be studied in the gas phase by crossing a molecular beam with a beam of low energy electrons, and recording the product anions with a mass spectrometer. While these gas phase measurements provide great insight into the dynamics of the DEA process, solvent effects remain a mystery.

Using a humidified buffer gas, our experiment generates a molecular beam containing neutral clusters of the target molecule with water. By controlling the hydration of the molecular beam, the effect of the solvent on the fragmentation can be investigated. In the gas phase, the nucleobases uracil and thymine undergo DEA to lose H to form $[\mathrm{Nuc{-}H}]^-$, while under microhydrated conditions, the hydrogen loss channel is supressed, and only the parent ion $(\mathrm{Nuc}\cdot(\mathrm{H_2O})_n)$ is observed.[2] We continued by studying the effect of microhydration on the DEA of amino acids. For valine, it was found that the hydrogen loss channel remained open at low levels of microhydration, but was blocked at higher levels of microhydration.

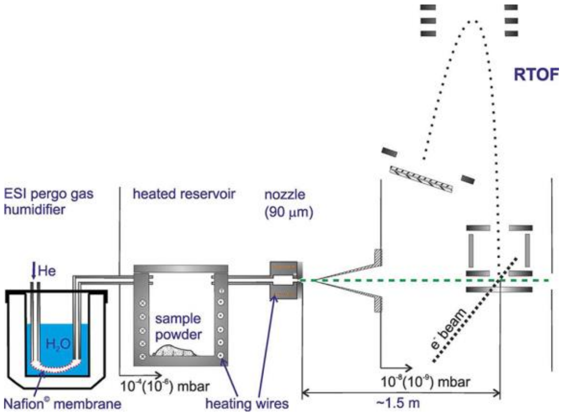

Figure 1: Schema of the experimental setup.

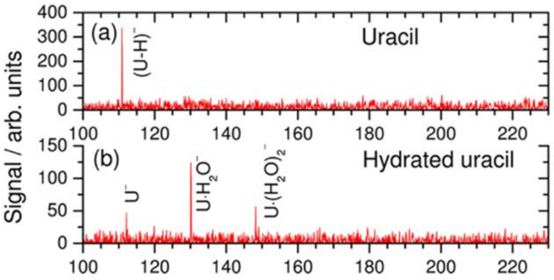

Figure 2: Cumulative negative ion mass spectra in the energy range from 0 to 3.5 eV for: (a) molecular beam of uracil without any humidification; (b) humidification of the molecular beam.

Acknowledgements: We acknowledge the support by Czech Science Foundation grant no 19-01159S

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21. Imaging anion-neutral reactions: Carbon chain growth and single solvent effects

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Mapping differential cross sections of reactive scattering sheds light on the dynamics of chemical reactions in the gas phase. The combination of crossed beams with three dimensional velocity map imaging for ion-neutral reactions[1] allows one to record different reaction products (revealing product branching ratios) and their differential cross sections at once. Here we present results on anionic chain elongation of C_{2n}^- and $C_{2n}H^-$ (n = 1, 2, 3) with C_2H_2 and on nucleophilic substitution (S_N2) and proton transfer reactions of $F^-(H_2O)$ with CH_3I. Furthermore, we discuss recent results for the chain growth reactions of C_2^-, CN^- and C_3N^- reacting with HC_3N.

Interstellar carbon chain anions have first been identified in 2006.[2] Neutral carbon chain growth with subsequent photodissociation and electron attachment to the radical is assumed to constitute the major route of their formation but the observed abundances are not yet fully understood. We have investigated the alternative route of anionic chain growth with the aim to clarify their possible relevance in interstellar environments.[3] The indirect reactions take place at collision energies ranging from 0.3 to 3 eV with $C_{2n+2}H^-$ as dominant products. On the other hand, reactions of C_2H^-, C_4H^- and C_6H^- with acetylene are slower than those with C_2^-, C_4^- and C_6^-, respectively. Consequently, chain growth tends to stop at the hydrogenated anions. Towards lower collision energies, the C_{2n+2}^- products become more important. If this trend continues down to the low temperatures in the interstellar medium, the anionic chain growth might play a role for the molecular abundances of the C_{2n}^- series.

The dynamics of a range of halide anion reactions with methyl halides, $X^- + CH_3Y$, have been investigated in both experiment and theory.[4] An unforeseen richness of reaction pathways has been unravelled, challenging the gas-phase dynamics paradigm of the S_N2 reaction. Microsolvation offers an experimental approach towards understanding the solvent effect on these mechanisms. Single solvent effects can be intricate as has been shown for the $OH^-(H_2O)_n + CH_3I$ reaction, for which only in the presence of a single water molecule the dominant pathway is the classical Walden inversion.[4] For the isoelectronic $F^-(H_2O)_n + CH_3I$ reaction, theory predicts (1) the suppression of solvated S_N2 products by avoiding the fully solvated potential energy barrier and (2) the inhibition of direct mechanisms already by a single water molecule.[5] This system is subject to ongoing theoretical efforts, asking for the comparison with experiments.[6] We present the first results of crossed beam studies of $F^-(H_2O) + CH_3I$ at 0.3 to 2.5 eV collision energy.

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22. Mid-infrared spectroscopy of polyatomic molecules in a cryogenic buffer gas cell and progress towards a molecular beam of cold complex molecules

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We are building a cryogenic source of polyatomic molecules, with the aim of performing precise tests of fundamental physics.[1,2] Molecules of interest are injected through a capillary into a copper cell cooled to 7 K. The molecules thermalize with a buffer gas of helium which flows through the cell. The molecules are probed inside the cell by wavelength-modulation absorption spectroscopy in the mid-infrared. Fig. 1 shows a portion of the spectrum of 1,3,5 trioxane cooled to 15 K and probed at around 10.2 µm.

We will present our measurements of the Q- and R-branches of the ν_5 vibrational band of this molecule, and a study of the temperature and density of the molecules in the cold cell.

Molecules flowing out of the cell produce a cold beam which we detect using a mass spectrometer. We will present a study of how the beam flux depends on the helium and trioxane flow through the cell, and discuss our efforts towards the state-selective detection of the cold, slow beam by absorption spectroscopy. We also present our plans to introduce a multi-pass optical assembly and cavity enhanced spectroscopy into this setup.

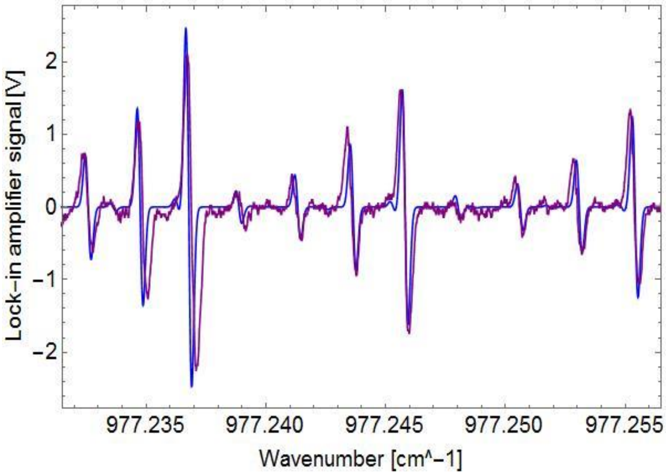

Figure 1: Trioxane spectrum at 15 K (purple) overlaid with the calculated spectrum (blue)

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23. Gas-liquid scattering dynamics in crossed beams

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

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

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

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

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24. Long-lived high Rydberg states of NO for Stark deceleration and trapping

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Rydberg-Stark deceleration, which exploits the large electric dipole moments of Rydberg states with high principal quantum number, *n*, has made possible studies of excited-state decay processes on previously inaccessible timescales[1] and inelastic molecular scattering at low temperature.[2,3] Previous experiments demonstrated trapping of H_2,[4] although the technique is applicable to any molecular species that can be excited to long-lived Rydberg states. Here, we demonstrate excitation of the NO radical to Rydberg states with lifetimes on the order of 100 µs.

NO molecules in a supersonic beam were excited by pulsed lasers to Rydberg states with $N^+ = 2$ and $n = 40 – 75$. The pre-dissociation lifetimes associated with the low-*l* states are less than 100 ns. Nevertheless, we observed that an appreciable number survived 120 µs after excitation. We utilised ramped-electric-field ionization for state-selective detection to examine the final distribution of Rydberg states over a broad range of *n*, and explored how this distribution is affected by weak electric fields.

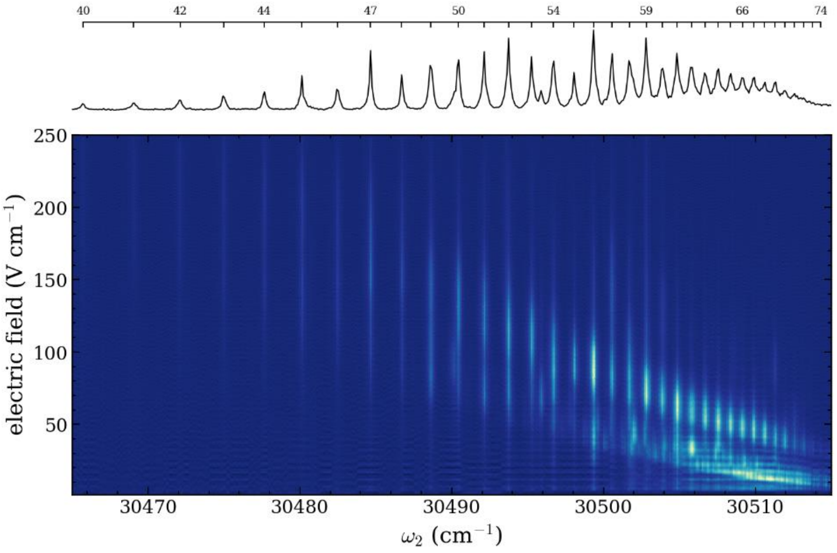

Figure 1: Ramped-electric-field ionization spectroscopy of Rydberg NO. The field-integrated signal and the expected transition wavenumbers to the nf states with $N^+ = 2$ are indicated along the top.

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25. Sub-THz cavity enhanced absorption and dispersion effects in molecular beams

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While molecular beam experiments are ideal for generating and studying transient species, low number densities and short pathlengths require highly sensitive spectroscopic methods. Unfortunately, in the THz / sub-THz region, the lack of strong sources combined with relatively insensitive detectors significantly impacts sensitivities. In the optical and Near-IR, fluorescent photon counting is possible, while in the longer microwave and RF regions, exquisitely sensitive heterodyne techniques are available. Not only are the sources and detectors better in these other electromagnetic regions, they may also be combined with cavities to dramatically increase the effective sample pathlengths, e.g., Cavity Enhanced Absorption Spectroscopy. Robustly coupling radiation in and out of cavities has proven to be problematic in the THz / sub-THz region due to the lack of high reflectivity / partially transmissive concave dichroic mirrors at these wavelengths. A partial solution has been to employ multipass or unconventional cavity geometries.[1,2] In this poster we demonstrate that it is possible to create a pass-through confocal Fabry-Perot resonator at sub-THz wavelengths; the novelty being the simple conventional layout. To do this we have created, the equivalent of dichroic mirrors with concave wire-grid polarizers on a supporting plastic substrate. The resulting signals are beautiful and dramatic (see Fig. 1). We obtain cavity Qs on the order of 100,000, a 70-fold sensitivity increase and use it to demonstrate the detection of ClO radicals and even the weak magnetic dipole allowed transitions of O_2 near 60 GHz. As the signals are coherent, we model the line shapes using a modified Flygare et al. solution to the Optical Bloch equations.[3]

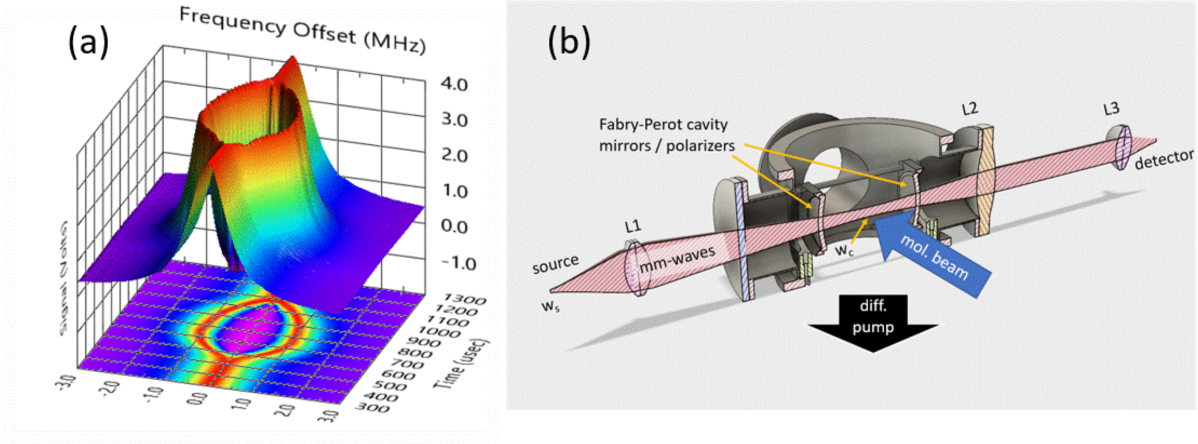

Figure 1: (a) Transient absorption and dispersion signal of N_2O crossing (b) a pass-thru confocal Fabry-Perot cavity tuned to be coincident with a rotational transition (N = 4 ← 3, ν_{ba} = 100491.76 MHz). Early and late molecule-free time signals, depicted in (a), show the cavity mode transmitted power spectrum. On line center, the cavity results in saturated absorption, while off-resonance, dispersion causes the cavity mode transmitted power to bifurcate as the molecules enter and then leave the cavity.

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26. Spectroscopic characterization of AlF with relevance to laser cooling and trapping

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During the last decades, there has been great progress in the cooling and trapping of neutral molecules in the gas-phase. Ultracold molecules can be used for studying collisions and chemistry at low temperature, for precision measurements to test fundamental symmetries and for quantum information and simulation. The molecules can be associated at ultralow temperatures from pre-cooled atoms or they can be produced in a molecular beam and subsequently cooled and trapped. Experimental techniques involve buffer gas cooling, Stark deceleration and Zeeman deceleration, Sisyphus cooling and laser cooling. Laser cooling has so far been demonstrated for four diatomic species SrF, YO, CaF, and YbF and one polyatomic species SrOH. Magneto-optical traps (MOTs) for SrF, CaF and YO have been demonstrated and sub-Doppler temperatures have been reached. Magnetic and optical trapping of laser cooled molecules has been demonstrated and sympathetic and evaporative cooling is being explored. The density of ultracold molecular samples that can be reached this way is typically four to five orders of magnitude lower compared to the association methods. New methods are steadily being developed to deliver more molecules at low speeds to the trapping region.

For all the molecules that have been laser cooled so far, a $^2\Pi_{1/2} \leftarrow {}^2\Sigma^+$ transition is used. In this case, rotational branching is suppressed on the P(1) line by angular momentum selection rules. The molecule must have an excited state that decays at a high rate to just one or a few vibrational levels in the ground state and there should be no accessible intermediate electronic state. Preferably, the hyperfine structure of the molecule should be simple. Molecules with a $^1\Sigma$ ground state and a $^1\Pi$ excited state are very attractive candidates for laser cooling. All Q-lines of a $^1\Pi \leftarrow {}^1\Sigma$ transition are rotationally closed, the hyperfine splitting in the $^1\Sigma$ state is typically within the natural linewidth of the optical transition, and molecules in $^1\Sigma$ states are intrinsically more stable.

The $A^1\Pi$, v'=0 $\leftarrow$ $X^1\Sigma^+$, v''=0 band of AlF around 227.5 nm has a Franck-Condon factor of 0.996 and is an excellent candidate for cooling with just a single laser. The photon scattering rate is very high with a calculated value of $\Gamma=1/\tau=5.3\text{x}10^8$ s^{-1}, where τ is the lifetime of the $A^1\Pi$, v'=0 state. The spin-forbidden $a^3\Pi$, v'=0 $\leftarrow$ $X^1\Sigma^+$, v''=0 band is highly diagonal as well; it has a Franck-Condon factor of 0.992. Furthermore, the $P_1(1)$ line and all Q-lines of the $a^3\Pi - X^1\Sigma^+$ transition are rotationally closed. These transitions can be used for laser cooling to final temperatures in the low μK range, after pre-cooling on the much stronger $A^1\Pi - X^1\Sigma^+$ band.

AlF is a promising candidate to reach high densities of ultracold molecular samples. It has a binding energy of almost 7 eV and forms as a stable constituent of aluminium-fluorine systems at high temperatures via the reaction: $2\text{Al(l)} + \text{AlF}_3\text{(g)} \rightarrow 3\ \text{AlF(g)}$. Vapour pressures of tens of mbar can be reached at temperatures around 1200-1350 °C. Therefore, a bright beam of AlF can be produced, either pulsed or cw. Because of the high photon scattering rate on the $A^1\Pi - X^1\Sigma^+$ band, the distance needed for laser slowing a beam to rest is only several centimeters and the capture velocity of a MOT will be exceptionally large. The bimolecular rearrangement channel in which two AlF molecules react to form a fluorine molecule and an aluminium dimer is strongly endothermic. This reaction channel will therefore not limit the lifetime of AlF molecules in dense, cold samples.

Prior to cooling and trapping experiments, it is necessary to measure the fine and hyperfine structure of the lowest rotational levels in the $X^1\Sigma^+$, $A^1\Pi$ and $a^3\Pi$ states. The degree of mixing of rotational levels due to hyperfine interactions determines in how far branching to other rotational levels, i.e. loss from the cycling transition, occurs. Molecules that decay on the spin-forbidden $A^1\Pi \rightarrow a^3\Pi$ transition are also lost from the laser cooling cycle and it is therefore important to measure the strength of this transition. The predicted high scattering rate on the $A^1\Pi - X^1\Sigma^+$ band needs to be experimentally verified. In addition, it is important to know how the hyperfine levels split and shift in external electric and magnetic fields. We have used a pulsed beam of jet-cooled AlF in combination with radio-frequency, microwave and optical fields to experimentally determine this data.

27. Spectator behavior, enhancement, and suppression of ion-molecule reactions by vibrational excitation

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Vibrational excitation constitutes a very specific way to transfer energy into a chemical reaction. Understanding vibrational mode-specific dynamics allows one to unravel details of the interaction potential and the coupling of different inter- and intramolecular degrees of freedom in the course of a chemical reaction.[1]

We have brought selective vibrational excitation to our crossed-beams experiment for studying ion-molecule reaction dynamics.[2] Studying the reaction of F^- with CH_3I, we have identified the CH symmetric stretching excitation as a spectator mode for the nucleophilic substitution pathway, while the proton transfer reaction path is strongly enhanced.[3] Quasi-classical trajectory simulations as well as results from the sudden vector projection (SVP) model agree very well with the experiment.[3]

Since our first results on the spectator mode effect, we have improved the fraction of vibrationally excited reactant molecules in the crossed-beam setup by a factor of more than two. This has allowed us to obtain a much more stringent test on the computational models as will be presented. In the differential scattering images we have also found that the reaction dynamics of the proton transfer channel changes upon vibrational excitation. At higher collision energies two new reaction pathways open up in the reaction that lead to dihalide formation.[5] The vibrational excitation is found to have an interesting suppression effect on the dihalide formation. Possible mechanisms for such a counter-intuitive effect will be discussed.

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28. Laboratory astrophysics: Towards a better understanding of the aromatic infrared emission features

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In several interstellar regions, Aromatic Infrared emission Bands (AIBs) are observed between 3 µm to 20 µm but until now, no molecules have been clearly assigned. Polycyclic Aromatic Hydrocarbon molecules (PAH) with more than about 50 carbon atoms are considered as the carriers of these bands by an IR fluorescence process after UV stellar photon excitation. In the aim to understand this mechanism and the competing relaxation channels, we need laboratory astrophysics experiments.

In our laboratory, we are developing a supersonic molecular beam seeded with a mixture of PAHs in **Nanograins**, an experimental setup which harbor a carbon-rich flat flame with an extracted Laval flow that operates at 50 K.[1] A mixture of PAHs should then be excited by an UV laser[2] and the subsequent IR fluorescence is detected with **FIREFLY**, a homemade IR spectrometer.[3,4] By combining these two experimental setups, we would like to better understand the IR emission bands of a mixture of PAHs in collision-free conditions and compare them to the AIBs spectra.

The **FIREFLY** infrared spectrometer can also be used separately by placing a gas cell in front of it. We can thereby study the photophysics and photochemistry after UV excitation of a specific PAH molecule by introducing it in the cell. In particular, we are studying the photoisomerisation process in competition with IR emission, focusing on the toluene to cycloheptatriene isomerization and exploiting deuterated molecules to trace the processes. Even if toluene is very unlikely present in ISM, ring opening is expected to occur in the ISM in larger PAHs, and understanding the IR emission of small aromatic molecules is a necessary step. This experimental study in cell is supported by a Monte-Carlo simulation of the time-dependent IR fluorescence of the PAH after UV-excitation.

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29. Gold-mining the molecular overtone spectra using supersonic beam techniques

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Molecular overtone spectroscopy targets high vibrational states sampling the nuclear dynamics far from equilibrium geometry. In the recent years, there has been a significant progress in computational methods that can predict such vibrational energy levels and transition probabilities for small polyatomic species with near spectroscopic accuracy. With improving level of theory there is increasing need for reliable experimental data in the overtone and combination band region for validation of theoretical approaches. Unfortunately the overtone bands typically exhibit complex an irregular rovibrational structure and their analysis is challenging. Indeed, the spectra measured by traditional techniques at room temperature are often too dense and irregular to be successfully assigned, which makes them virtually useless for rigorous comparison with the theory. We present alternative approach developed in our laboratory which is based on laser absorption spectroscopy at very low temperatures (~10K) in the supersonic molecular beams.[1,2] Instead of measuring large number of unassignable spectral transitions we focus on selected few spectral lines with reliably determined and cross-checked quantum assignments. In addition to the well-known simplification of the spectra at low temperatures we show that by controlling the expansion conditions the beam temperature can be varied over a wide range which provides valuable additional experimental information.

In this contribution we present this approach on high resolution overtone spectra of selected polyatomic molecules (NH_3, CH_3Cl, and HCOOH) in the near infrared spectral range. We will demonstrate the clear advantage provided by measurements in cold molecular beam environment and will discuss the unique approaches for spectral analysis, specifically the two-temperature analysis for experimental determination of lower state rotational energies. In addition we will show how this approach can be combined with assignment verification using extended ground state combination differences technique. This combination of unique measurement techniques and advanced approaches in analysis dramatically improves the usability of the data for direct comparison with the state-of-the-art calculations for critical evaluation of the computational approaches.

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30. Kinetics and dynamics of CO oxidation on atomically stepped Pd surfaces

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Our new experimental approach, velocity resolved kinetics, combines surface science techniques, such as ultra-high-vacuum and single crystal surfaces, with slice imaging[1] of reaction products to measure the reaction dynamics and kinetics of catalytic reactions at surfaces simultaneously. A well-chosen arrangement of the ion imaging detector[2] offers a straightforward way to map out the in plane velocity distribution, while velocity-resolved kinetics (product flux as a function of reaction time) is measured in a Pump-Probe type experiment. With this approach, we have recently determined the site-specific oxidation mechanism for CO on platinum surfaces, which could explain the results of 40 years of research on this system.[3] In this work we investigate the kinetics and dynamics of CO oxidation on Pd(111), which show similarities but marked differences from Pt(111). CO_2 shows two distinct channels: a hyperthermal CO_2 formed on terraces, showing large translational energies and an angular distribution peaked along the surface normal; a thermal CO2 channel formed at atomic steps of the crystal and has thermal speed distributions with cos(θ)-angular distributions. We show that the combination of reaction dynamics and kinetics can determine and quantify the underlying kinetic mechanism even though the adsorbates are exchanging between the active sites.

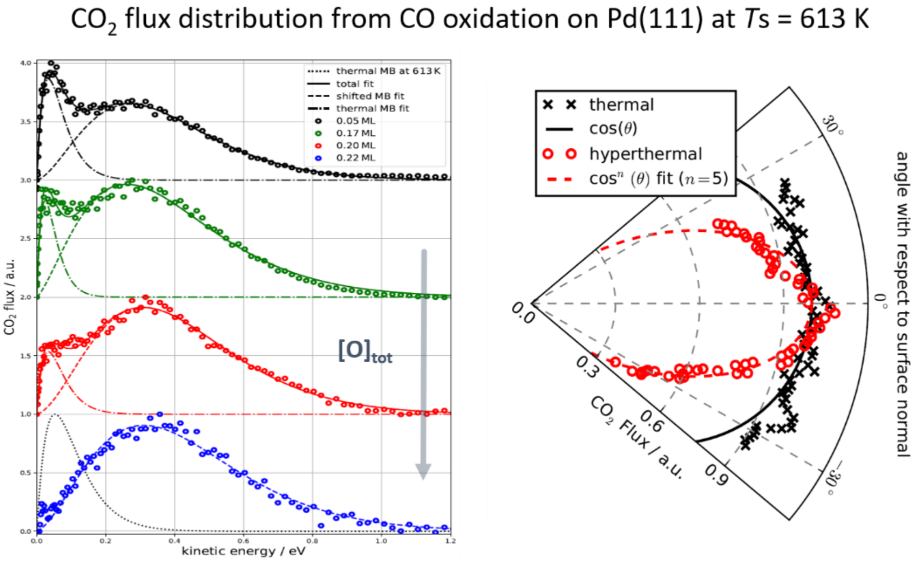
CO_2 flux distribution from CO oxidation on Pd(111) at *T*s = 613 K

Figure 1: Speed and angular distributions of CO_2 products from the oxidation of CO on Pd(111).

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31. High-resolution sliced velocity-map imaging following newton sphere inversion

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We apply the post-extraction differential acceleration technique[1] to velocity-map ion imaging,[2] greatly enhancing the obtainable velocity resolution along the time-of-flight axis. The method incorporates an additional electrode that is pulsed to invert the ion Newton sphere, resulting in elongation along the time-of-flight axis and a far greater spread of arrival times at the detector. Consequently, a very thin central slice of the ion sphere may be recorded through gating the detector, yielding a highly resolved central slice of the ion velocity distribution without the use of any reconstruction algorithms.[3] We demonstrate the technique by simultaneously imaging an entire three-dimensional Newton sphere[4] of CO^+ and S^+ ions following the UV photodissociation of OCS using the timestamping Pixel Imaging Mass Spectrometry (PImMS) camera.[5] An order of magnitude increase in the number of slices imaged through the Newton sphere relative to DC slicing[6] is demonstrated experimentally, as predicted *in silico*. We expect this technique could have a number of applications in velocity map imaging experiments in which it is desirable to directly record a full three-dimensional velocity distribution, such as studies of photofragment angular momentum polarization.[7]

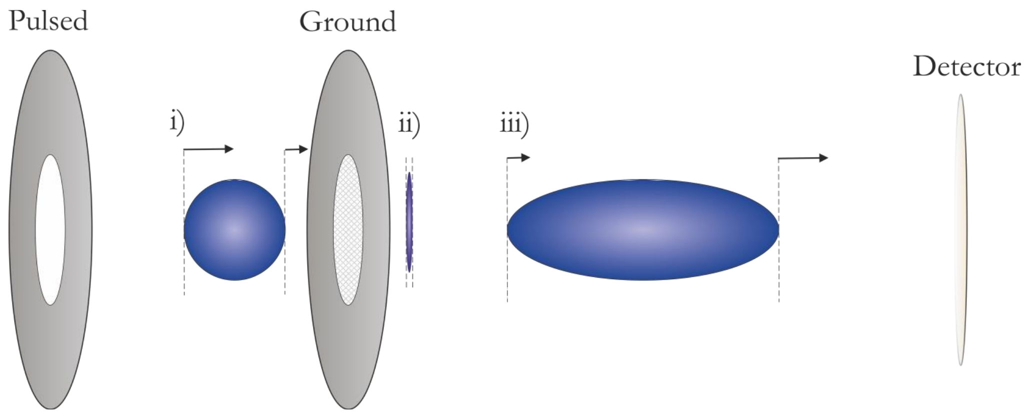

Figure 1: Schematic of the post-extraction region of the experiment, illustrating the i) differential acceleration between the 'front' and 'back' of the Newton sphere, ii) subsequent 'pancaking' and iii) inversion and stretching of the Newton sphere.

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32. Long-term trapping of Stark-decelerated polar molecules

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

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

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33. Quantum-state-controlled Penning collisions between lithium atoms and metastable helium atoms

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Our work is aimed at understanding the mechanistic details of reactive collisions and at controlling the outcome of chemical reactions. In our experiment, we study quantum-state-controlled Penning collisions between lithium atoms (Li) and metastable helium atoms (He*) at various collision energies, e.g., to study the influence of electron-spin polarization on the reaction rate. For this, we have combined a supersonic beam source for He* atoms with a magneto-optical trap (MOT) for Li atoms.[1] Our initial investigations have shown that the reaction rate dramatically depends on the initial electronic states of the reaction partners. In order to get full quantum-state control of the reaction partners, the Li atoms are optically pumped into selected electronic hyperfine and magnetic substates. Additionally, we produce a pure beam of He(2^3S_1) by the optical depletion of the He(2^1S_0) state using a novel excitation scheme.[2] In this contribution, I will give an overview over the different methods used to achieve quantum-state control of the reaction partners and I will discuss experimental results that show the dependence of the reaction rate on the initial electronic state of both He* and Li.

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34. Time-resolved photoelectron imaging studies of steric effects in nitrobenzene derivatives

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Nitroaromatic compounds are known harmful environmental pollutants which may release NO radicals upon interaction with ultraviolet (UV) light. However, this NO radical release channel also has the potential to be used in beneficial applications such as photodynamic therapy.[1,2] Investigating the excited state photochemistry of nitroaromatic systems is therefore of considerable interest.

In a study from 2005, Suzuki and co-workers suggested that the conformation of the nitro-group with respect to the aromatic ring influences the photoinduced NO-releasing activity in nitrobenzene derivatives.[2] Motivated by this finding, our present study employs the highly differential time-resolved photoelectron imaging (TRPEI) technique[3-5] to explore this effect systematically in gas-phase nitrobenzene and three of its methyl-substituted derivatives (2,6-, 2,4- and 3,5-dimethylnitrobenzene). The use of site-selective methylation varies the dihedral angle between the aromatic ring and the nitro-group. The influence this exerts over the UV relaxation dynamics – and the effect this subsequently has on the propensity for NO vs NO_2 release – may then be evaluated. In this study, 267 nm was employed as the pump and two photons of 400 nm as the probe.

Our observations lead us to conclude that the dihedral angle between the aromatic ring and the NO_2 group has little influence on the ultrafast molecular dynamics of the various nitrobenzenes studied (see Fig. 1). Although perhaps initially surprising, this is, however, in good agreement with recent theoretical work on nitrobenzene which attributes the ultrafast relaxation dynamics to motions along nuclear coordinates localised within the NO_2 group.[6,7]

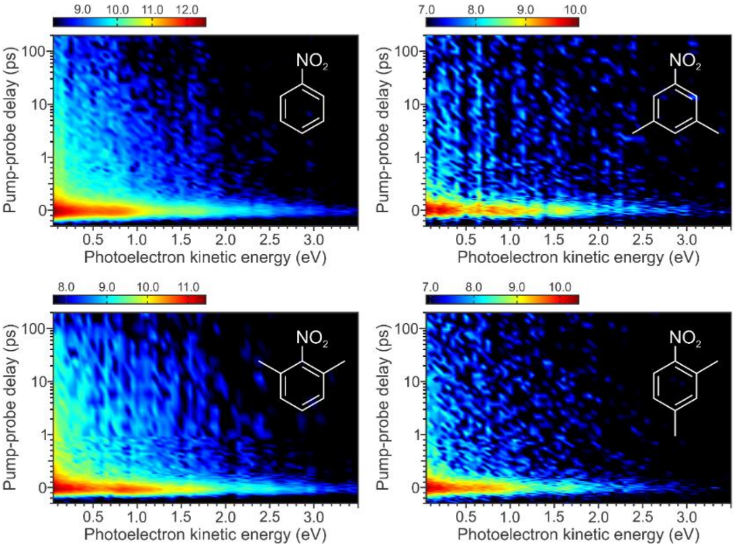

Figure 1: Time-resolved photoelectron spectra of nitrobenzene and three methyl-substituted derivatives using a 267/400 nm pump/probe scheme.

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35. Accurate *ab initio* thermochemistry, potential energy surface, and dynamics of the $F^- + CH_3CH_2Cl$ reaction

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Recently we have investigated the dynamics and mechanisms of the 9-atomic $F^- + CH_3CH_2Cl$ reaction. In this system the most common product channels are the bimolecular nucleophilic substitution (S_N2) and the bimolecular elimination (E2). In 2017 we characterized the most important stationary points of this reaction reporting benchmark structures, frequencies, and relative energies using explicitly correlated *ab initio* levels of theory.[1]

In order to better understand the mechanisms of the $F^- + CH_3CH_2Cl$ reaction we develop a full-dimensional, permutationally invariant analytical potential energy surface (PES). We use the Monomial Symmetrization Approach[2] (MSA) for fitting the *ab initio* energies and our in-house automatic PES developer program package called ROBOSURFER. This analytical PES allows using the quasi-classical trajectory (QCT) method to study the competition of the S_N2 and E2 channels of the title reaction and uncover possible retention pathways such as double inversion (di) and front-side attack (fs) as shown in Fig. 1.

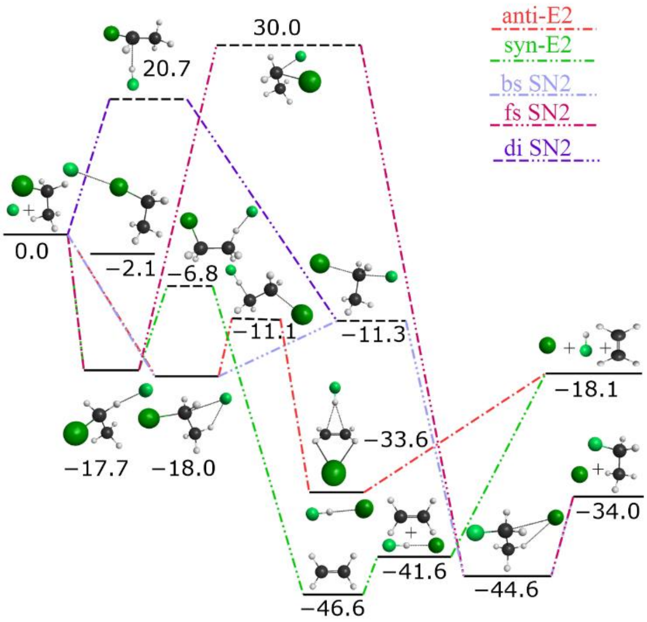

Figure 1: Schematic potential energy surface of the $F^- + CH_3CH_2Cl$ reaction showing the benchmark classical relative energies (kcal/mol) of the stationary points corresponding to the different reaction pathways.

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36. Crossed molecular beam studies of the reaction dynamics of O(^{3}P) with 1,3-Butadiene

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The combustion relevant reactions of O(^{3}P) with unsaturated hydrocarbons exhibit in general a large variety of competing product channels, some of which can only take place via intersystem crossing (ISC) from the entrance triplet to the underlying singlet potential energy surface (PES)[1]. While there have been extensive studies on the overall kinetics of many of these reactions, much less is known about the identity of the primary products and branching ratios (BRs), especially at combustion temperatures. The most suitable technique to unravel unambiguously the detailed dynamics of this class of reactions is the “crossed molecular beams” (CMB) scattering technique with *universal* mass-spectrometric detection and time-of-flight analysis, empowered with *soft* ionization by tunable low energy electrons.[1] The capabilities of the CMB technique with soft electron ionization detection have been demonstrated in other studies on the reactions O+ethyne[2], O+ethene[2], O+propene[3], O+allene[4], O+propyne[5] and, recently, studies were extended to the higher alkene O+1-butene[6] and diene O+1,2-butadiene[7], where the BRs and ISC have been quantified.

In the present contribution we report on a CMB study of the reaction O(^{3}P) + 1,3-butadiene. Since 1,3-butadiene is one of the most present molecules in combustion flames, the understanding of primary products and relative yields (BRs) of the title reaction is crucial for future improvements of flame modelling. Some kinetic[8] and theoretical[9] studies have been performed, but little is known about the above parameters. From product angular and velocity distribution measurements at different mass-to-charge ratios we have identified primary products attributable to the main (seven) channels leading to C_4H_5O+H, C_4H_4O+H_2, C_3H_6 (propene)+CO, C_3H_5+HCO, C_2H_3+CH_2CHO (vinoxy), C_2H_4+CH_2CO (ketene), C_3H_4+CH_2O (formaldehyde), and determined the BRs. Synergistic theoretical calculations of the underlying triplet/singlet PESs and related RRKM/Master Equation computations of the BRs are currently under way by C. Cavallotti (Polytechnic of Milan) to assist the interpretation of the experimental results.

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37. Infrared cavity ringdown spectroscopy of molecules in supersonic jets

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The surprising chemical diversity of molecules in space can be seen in a wide variety of regions. Atoms in the vicinity of old dying stars combine to form molecules and serve as seeds for dust production (example: silicon carbides). The interstellar molecules are, unlike here on earth, often unsaturated compounds that are highly reactive or even of an ionic nature. These species, which are difficult to produce on earth, are valuable probes to determine the local physical conditions in space. The recent availability of high-resolution infrared (IR) instruments on telescopes such as EXES/SOFIA and TEXES/N-Gemini has created a demand for IR spectroscopic data. Our aim is to perform spectrally highly resolved and extremely sensitive measurements on astrophysically relevant molecules in the mid-infrared region, *i.e.* the typical fingerprint region of molecules, utilizing the highly sensitive cavity ringdown (CRD) method. Suitable light sources are powerful quantum cascade lasers (QCLs) above 4.5 µm, as well as OPOs (Optical parametric oscillators) for the wavelength range 2 - 4.7µm. To achieve a high precision the lasers are stabilized by a frequency comb. This cavity enhanced IR spectrometer is combined with various molecular sources producing supersonic jets. Available sources are heating sources (e.g. for hydrogen peroxide), as well as laser ablation and electrical discharge sources to generate transient molecules *in situ*. We started investigations on hydrogen peroxide and silicon carbides. The experimental setup as well as first results will be presented.

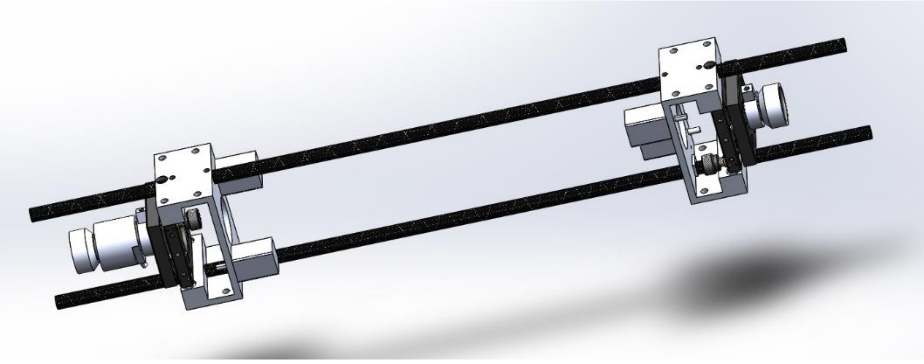

Figure 1: The CRD cavity of our CARMA (Comb Assisted iR Multipass Absorption) experimental setup.

38. Scattering dynamics at the gas-liquid interface

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The gas-liquid (G-L) interface is ubiquitous in nature, and important in industrial processes and atmospheric chemistry.[1] In recent years, new experimental methodologies have led to an increasing knowledgebase of inelastic and reactive dynamics at the G-L interface. One intriguing possibility is to use the G-L interface as a partially solvated environment, and thereby gain information on dynamics in solution. We have developed a new apparatus to study inelastic and reactive dynamics at gas-liquid interfaces using high-resolution cw-absorption spectroscopy. We are using this apparatus to study the inelastic and reactive scattering of CN radicals at inert and hydrocarbon surfaces. We generate a molecular beam of CN radicals from BrCN seeded in He via a pulsed electric discharge. The resulting rotationally cold supersonic beam of CN radicals is scattered from a continually refreshed liquid surface. Inelastically scattered CN radicals are probed with frequency-modulated (FM) transient absorption spectroscopy in the near infrared, using a multi-pass optical cell.[2] Reactive scattering, in which the CN radicals abstract a hydrogen, results in the production of HCN. To probe this HCN a FM mid-infrared (MIR) has been developed by performing difference frequency generation in a Periodically Polled Lithium Niobate crystal between two near-infrared lasers. We will report on the scattering of CN radicals from the surface of liquids, including the inelastic scattering of CN from the inert surface of per-fluoro poly-ether (PFPE) and a reactive hydrocarbon surface, squalane. We are able to compare the dynamics of the systems and determine the reactive uptake of CN at the squalane surface.

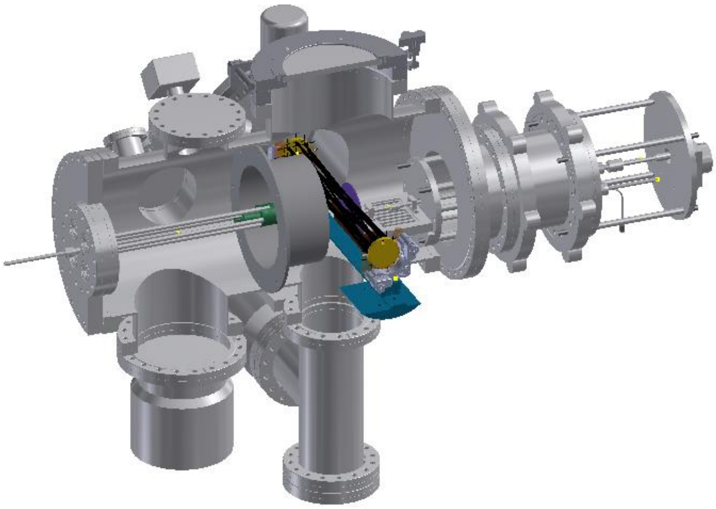

Figure 1: A cross-section of the experimental apparatus.

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39. A ps time-resolved photoelectron study on the photophysics of tolane

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Photoelectron spectra recorded via resonance-enhanced multiphoton ionization (REMPI-PES) contain information on the structure of excited neutral states, since the kinetic energy distribution of the photoelectrons is highly sensitive to the electronic character of the neutral molecule. Time-dependent changes in the spectra thus also yield information on relaxation dynamics after photoexcitation. The combination of small bandwidth ps laser pulses and supersonic jet expansion allows us to excite zero order vibronic states of cold molecules and to elucidate their dynamics.

The subject of our present study is tolane (diphenylacetylene, $C_{14}H_{10}$), a fundamental building block for conjugated polymers or dendrimers. The interest on the photophysical properties of tolane is based on its unusual fluorescence, which breaks down after exciting vibronic modes higher than 700 cm^{-1} above the origin of the first bright excited state ($^1B_{1u}$).[1, 2] The low-energy part of our S_1 ($^1B_{1u}$) ← S_0 REMPI spectrum is very similar to earlier recorded LIF spectra,[1, 2] however additional bands were observed at higher energies above the fluorescence cut-off. For a number of bands the dynamics were investigated via pump-probe photoionisation and photoelectron spectroscopy. Around the B_{1u} origin the lifetimes are in the ns range, but they drop to some 10 ps at higher excitation energies. For the short-lived bands at higher energies a sequential two-step relaxation to a long-lived electronic state was observed that proceeds via an intermediately populated state with a lifetime of 100-200 ps. By comparison with previous quantum chemical calculations we assign this state as the biradicalic *trans-bent* ^1A_u state that is ionised in a two-photon process via an intermediate 3p Rydberg state.

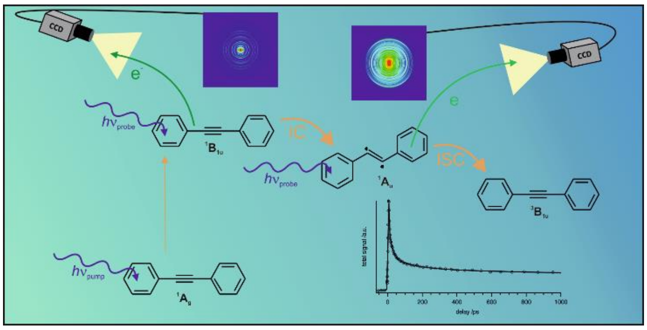

Figure 1: Relaxation scheme after exciting higher vibronic modes of the bright B_{1u} state in tolane. The first step is a fast internal conversion (IC) to an intermediate trans-bent *A_u state, followed by intersystem crossing (ISC) to a long-lived linear triplet state.*

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40. Automated potential energy surface development: Application to the F^- + CH_3Br system

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In the last few decades, molecular dynamics simulations have become an indispensable tool for the study of reaction dynamics. The advent of techniques for fitting accurate *ab-initio* data with high-dimensional potential energy surfaces (PESs) has enabled the detailed study of a vast array of new, larger systems. The construction of these global PESs, however, requires the selection of a suitable collection of geometries. So far, this has remained a mostly ad-hoc process, involving substantial human effort, thus limiting their proliferation.

We present an early preview and demonstration of the ROBOSURFER program system that aims to fully automate the construction and validation of high-dimensional PESs. The system is designed to be fitting procedure agnostic, highly modular, parallelizable and extendable.
The system relies on an iterative improvement approach (Fig. 1), where an initial set of geometries are fitted, new geometries are generated and filtered using the fit, quantum chemical calculations are run at the filtered geometries and geometries are selectively added to the fitted set. This iterative sampling of the configurational space is continued until the desired accuracy is reached. The procedure does not require *a priori* knowledge of reaction paths or stationary points, and can minimize the number of geometries used for fitting.
Using early development versions of the ROBOSURFER program system, we have constructed multiple global PESs for the F^- + CH_3Br system, and used them to perform QCT reaction dynamics simulations. The PESs provided sub-kcal/mol fitting errors at known stationary points in almost all cases, despite the lack of manual inclusion of nearby geometries.

The program system is currently being used in the construction of multiple new PESs.

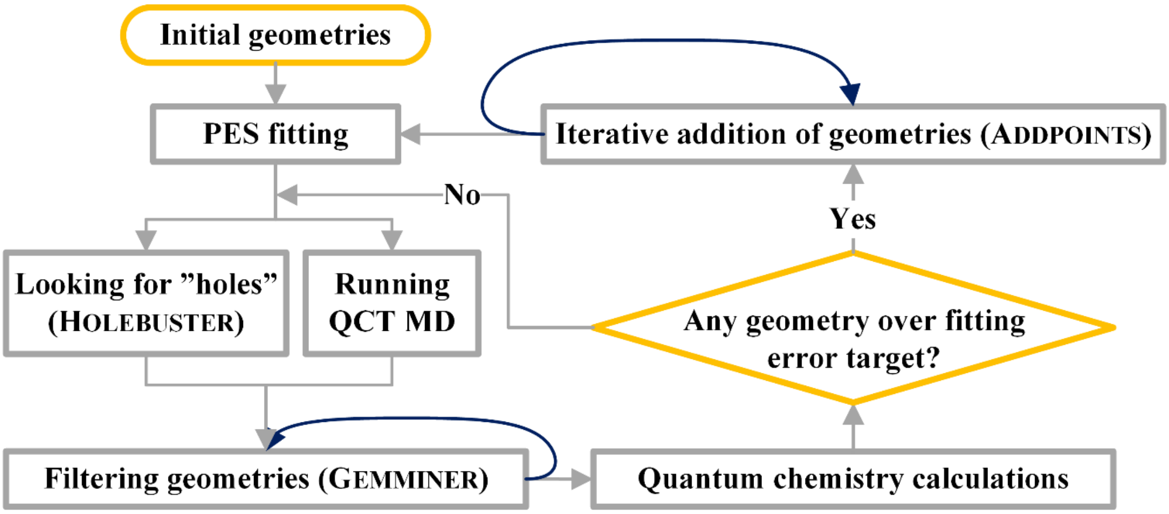

Figure 1: Simplified operational flowchart of the ROBOSURFER program system

41. The gas-phase IR spectra of xylyl radicals

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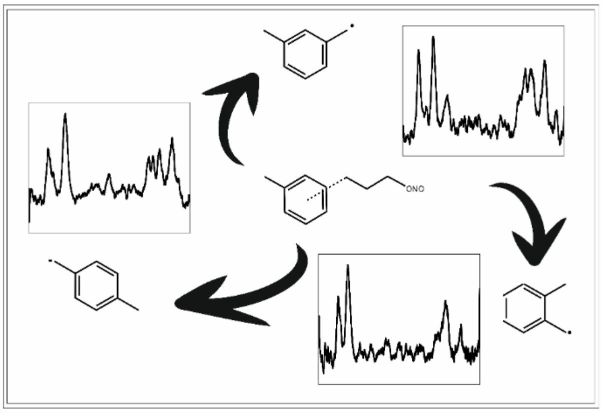
We employ IR/UV Ion-Dip-Spectroscopy for the analysis of gas-phase reactions and isolated reactive molecules, like radicals, carbenes and biradicals. This double-resonance spectroscopic method delivers mass selected IR spectra, which are used for characterization of structures, isomerization processes and further reactions. Due to the low concentrations in the gas phase, a high flux tunable IR source is required. Here, we use an IR Free Electron Laser (FELIX, Netherlands), which can be scanned over the typical IR fingerprint region and has enough power for sufficient IR excitation. Consequently, the IR data is compared to DFT-calculations for product identification and analyses of possible reaction pathways.

In this study we investigated the gas-phase IR spectra of xylyl radicals **2**. These molecules play an important role in the decomposition of xylene, which is a common fuel additive in modern gasoline blends, due to its anti-knock properties and high-octane rating.[1,2] The resulting radicals are resonance stabilized and hence long-lived. Therefore, they can accumulate in hot flames and be available for further reactions to form polycyclic aromatic hydrocarbons and soot. The radicals are generated pyrolytically from their respective nitrite precursor **1**, seeded in 1.5 bar He and consequently detected by IR/UV Ion-Dip-Spectroscopy. The resulting IR spectra are compared to DFT calculations on a B3LYP/6-311++G** level of theory for identification.



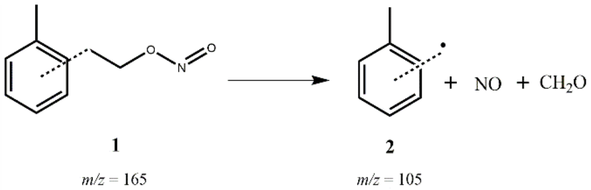


*Figure 1: The pyrolysis of methylphenyl ethyl nitrite **1** producing xylyl radicals **2**, as well as nitric oxide and formaldehyde as by-products. The radicals are identified by their IR/UV gas-phase spectrum in comparison to quantum chemical vibrational calculations.*

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42. Creating, imaging, and controlling chiral molecules with electric fields

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Chirality is one of the hot topics in the fields of physics, chemistry, and biology as well as pharmacology, with its importance emphasized by the fact that life on earth is based on chiral biomolecules all naturally selected with a single handedness. Chirality is a fundamental and important property of molecules and materials leading to very interesting optical-activity effects in linear and nonlinear optics. Accurate experimental characterisation of the enantiomeric excess and absolute handedness in mixtures of chiral molecules, efficient chiral purification and discrimination remain very challenging and highly demanding tasks for a broad scope of applications. Recently, a number of novel experiments have been developed for measuring the enantiomeric excess[1,2] or absolute handedness.[3,4]

We will present novel robust techniques devised in our group for (i) producing dynamic chirality from samples of statically achiral molecules[5], (ii) efficient spatial separation of chiral molecules, and (iii) detecting the enantiomeric excess.[6] The results are based on robust and highly accurate variational simulations of molecular ro-vibrational dynamics in the presence of electric fields.[7] We will also present challenges and perspectives for experimental realizations of the proposed techniques.

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43. Towards laser cooling and trapping of AlF molecules

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The aluminium monofluoride molecule (AlF) is an excellent candidate for laser cooling to ultracold temperatures and trapping at high densities. The favourable Franck-Condon factors of the A(v'=0) → X(v''=0,1) transitions (see Fig. 1) allow to scatter up to 10^5 photons with two lasers. The first excited singlet state ($A^1\Pi$) has a lifetime of 1.9 ns. This gives rise to a high photon scattering rate which results in a short stopping distance for a molecular beam. We estimate the stopping distance for a cryogenic buffer gas beam (150 m/s) to be 2 cm. The short excited state lifetime leads also to an exceptionally large capture velocity of a magneto optical trap of >40 m/s.

Prior to laser cooling experiments, it is essential to determine the detailed energy level structure in the $X^1\Sigma^+$ electronic ground state, in the $A^1\Pi$ state and in the metastable $a^3\Pi$ state as well as the strength of the transitions between these states. We here report the results of spectroscopic measurements with relevance to laser cooling[1] and the characterization of a cryogenic buffer gas source for AlF. We measure the molecular flux by laser induced fluorescence and absorption spectroscopy at different positions along the propagation axis. The velocity distribution in the beam is interrogated using the time of flight of the molecules in combination with optical pumping. This technique is not limited by the large Doppler width of the transition.

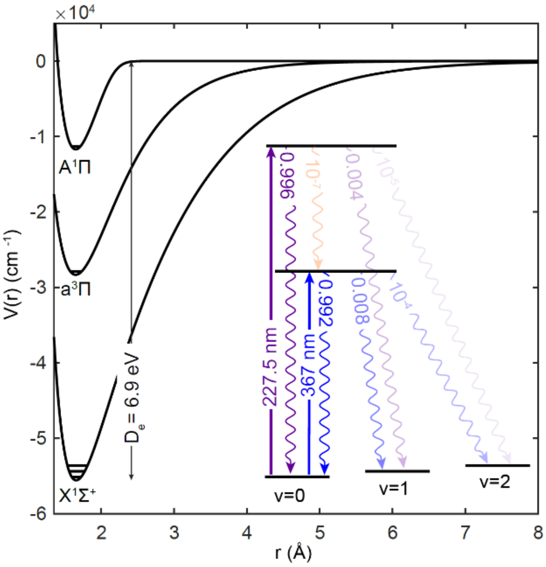

Figure 1: Potential energy curves of the three electronic states of AlF relevant for laser cooling. The inset on the right shows the transition wavelengths and calculated Franck-Condon factors.

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

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

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

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

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45. Rethinking fundamental S$_N$2 reactions

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We study the possible mechanisms for the S$_N$2 reactions of X^- + CH_3Y [X = OH, SH, CN, NH_2, PH_2; Y = F, Cl, Br, I], emphasising the Walden-inversion, front-side attack retention, and double-inversion[1] retention pathways.[2,3] By using the high-level explicitly-correlated CCSD(T)-F12b method with the aug-cc-pV*n*Z(-PP) [*n* = D, T] basis sets the energies, geometries, and harmonic vibrational frequencies of the stationary points are computed, utilizing the aug-cc-pVQZ(-PP) basis sets for the benchmark relative energies. For the OH^- + CH_3I reaction we develop an accurate analytical potential energy surface (PES) by fitting high-level *ab initio* energies using the permutationally invariant polynomial approach and the ROBOSURFER program package developed recently in our group. Applying this PES quasi-classical trajectory (QCT) computations are performed to investigate the dynamics of the OH^- + CH_3I S$_N$2 reaction.

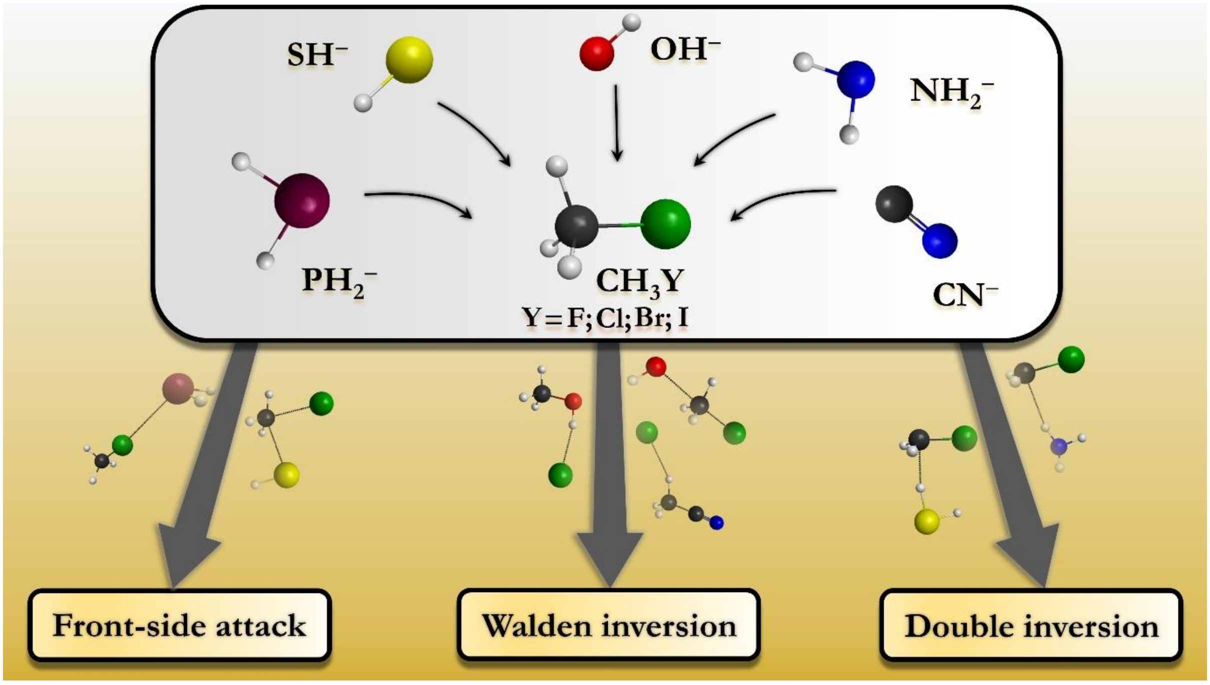

Figure 1: The possible mechanisms of the X^- + CH_3Y [X = OH, SH, CN, NH_2, PH_2; Y = F, Cl, Br, I] S$_N$2 reactions and the structures of some notable stationary points.

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46. A new crossed molecular beams apparatus

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Crossed molecular beams method has played an important role in the development of molecular reaction dynamics.[1,2] It has been a mature technique to study the reaction mechanism of elementary chemical reactions by using detection methods with high resolution and high sensitivity.

To achieve a high signal-to-noise ratio in crossed molecular beams experiments, it is beneficial to set the detection region away from the collision zone, particularly when reactants are highly photo sensitive. As a result, in our new crossed molecular beams apparatus (see Fig.1), we employ the universal quadruple mass spectrometry, and the spatial ion imaging technique. By using the vacuum ultraviolet free electron laser (VUV-FEL) as a detection light source, it is expected that the detection efficiency can be significantly improved in crossed molecular beam experiments.

Figure 1: The experimental setup of the crossed molecular beams apparatus.

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47. Theoretical studies of electronic quenching via molecular collisions

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In atmospheric chemistry, the concentration and photoinduced reactivity of trace species such as OH or NO radicals are responsible for most of the chemical transformations occurring in the gaseous envelope[1]. Understanding both the reactive and quenching photochemistry of these species is therefore of primary interest, both experimentally[2,3] and computationally.[4]

Here, we present a theoretical study to understand the quenching and scattering properties of the NO ($A^2\Sigma^+$) + O_2 ($X^3\Sigma_g^+$) system. The nature of the coupled potential energy surfaces is investigated at the CASSCF, MRCI and CASPT2 level, and we stress on the importance of the choice of the basis set to describe the long-range forces, because of the diffuse nature of the NO $A^2\Sigma^+$ state. Previous experimental work[3] proposed the existence of two non-reactive quenching pathways and cite the temperature dependence of the observed cross section. To understand this, we provide a comprehensive analysis of the orbital interactions, depending on the irreducible representation of the different point groups (C_s and C_{2v}) associated with different orientations to characterize the conical intersection seams between the component states. We also study the Van der Waals region where the last populated σ orbital of the NO $A^2\Sigma^+$ state seem to play a major role because of its Rydberg character.

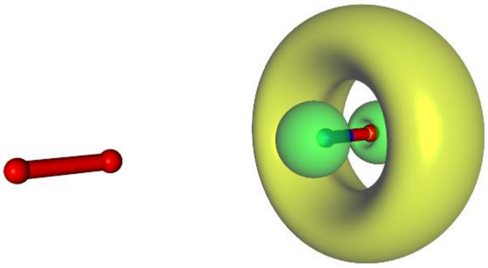

Figure 1: σ orbital of the excited electron in NO $A^2\Sigma^+$ in a linear geometry with O_2.

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48. Unravelling the contribution of steps to D_2 dissociation on Ni(711)

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We study the influence of steps on the dissociation of hydrogen (D_2) on Ni. The similarity of Ni and Pt for this reaction makes us expect that the dissociation probability may consist of several terms, each with different kinetic energy dependencies.[1,2] These different terms represent the different reaction mechanisms (direct and indirect) at terraces and steps. By measuring the sticking probability for different kinetic energies, varying surface and angle of incidence, and fitting the data to this model, we gain insight in the contribution of the steps to dissociation. Here, we use a Ni(711) surface and control the kinetic energy of the D_2 molecules using supersonic molecular beam techniques. We determine their energy with time of flight (TOF) measurements and their initial and coverage-dependent sticking probability using the King and Wells (KW) approach.

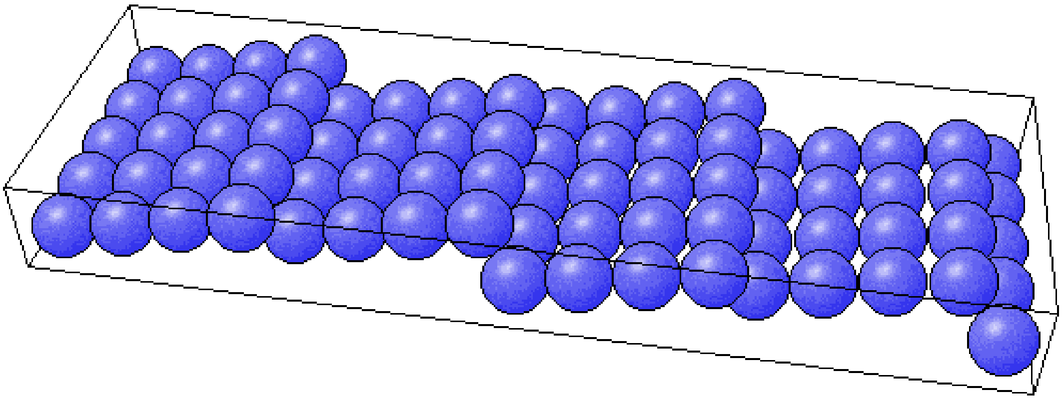

Figure 1: The (711) surface, consisting of and (111) steps and (100) planes of 4 atoms wide.

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49. Benchmark *ab initio* study of the X + C_2H_6 [X = F, Cl, Br, I] systems, dynamics of the X + C_2H_6 [X = F, Cl] reactions, and PESs for spectroscopy

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We investigate the thermochemistry of the X + C_2H_6 [X = F, Cl, Br, I] reactions using high-level *ab initio* methods, *i.e.* augmenting the CCSD(T)-F12b/aug-cc-pVQZ energies by core-correlation, post-CCSD(T) and spin–orbit corrections, focusing on three different reaction pathways: H-abstraction, methyl-substitution, and H-substitution, with the latter two proceeding via either Walden-inversion or front-side-attack mechanisms.[1] On the basis of this study we develop global analytical *ab initio* spin-orbit-corrected potential energy surfaces (PESs) for the Cl and F + C_2H_6 reactions using the permutationally invariant monomial symmetrization approach (MSA) and an in-house automatic-PES-developer program, called ROBOSURFER.[2] With the analytical PESs at hand we also investigate the dynamics of these two 9-atomic reactive systems using the quasi-classical trajectory (QCT) method. Besides studying the halogen atom + ethane reactions, we also develop analytical *ab initio* PESs for the $CH_4{\cdot}Ar$[3] and the $CH_4{\cdot}F^-$ weakly-bound complexes, which PESs are subjects of spectroscopic investigations.

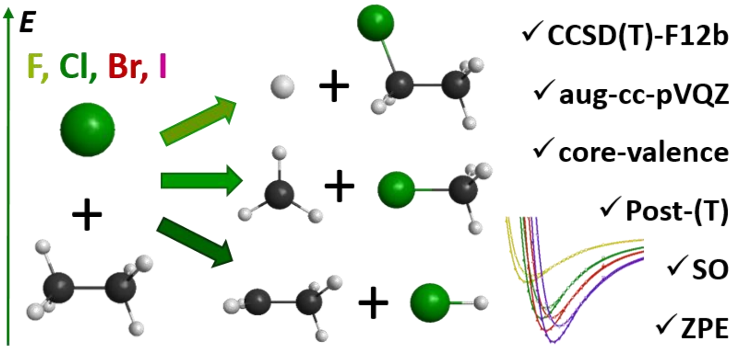

Figure 1: Schematics of the benchmark ab initio study of the X + C_2H_6 [X = F, Cl, Br, I] reactions.

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50. Investigating conformational and state-specific effects in chemical reactions

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Despite their great importance, the influence of molecular conformations and individual quantum states on the mechanisms and dynamics of reactions is still poorly understood. Due to thermal interconversion, the isolation and control of individual conformers was until now a major obstacle in their experimental investigation. Recently, the successful spatial separation of conformers and rotational states of molecules entrained in a beam was demonstrated using an electrostatic deflector by exploring the interaction of strong, inhomogeneous electric fields with their different effective dipole moments.[1,2] The resulting molecular beams of state- and conformationally selected species provide the starting point to perform controlled, state- and conformer-selective reaction experiments. In-depth study of the dynamics of conformation and state dependent reactions has already been successfully applied to the investigation of reactive collisions of 3-aminophenol with a Coulomb crystal of Ca^+ ions and more recently, nuclear-spin isomers of water with sympathetically cooled N_2H^+ ions .[3,4]

Here, we present progress towards a crossed-molecular beam machine in which a beam of spatially separated conformers is crossed with a beam of neutral molecules or free radicals. Product detection is performed by a combination of TOF-MS and velocity-map imaging[5] allowing us to obtain angle-, energy- and mass-resolved distributions of the reaction products. First target systems include the reactions of halogen radicals with rotationally state-selected molecules, such as OCS and H_2O. Development of the crossed-molecular beam machine along with the ion-trap setup will give us the experimental means to unravel the mechanistic details of conformationally and state selective reactions from the synergistic perspective of both, neutral-ionic and neutral-neutral reaction partners.

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51. Gas phase CD spectroscopy of albumin ion in DUV region by using IR-laser ablation of droplet beam: Analysis of secondary structure

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Circular dichroism (CD) is absorbance difference between clockwise and counter-clockwise circular polarized (CP) light, which is observed for chiral molecules. Biomolecules, such as proteins, have a lot of chiral moieties due to secondary structures of peptide chain, which has absorption in the deep ultraviolet (DUV) region. Therefore, the CD spectroscopy in the DUV region is a powerful tool for secondary structural analysis of protein. However the CD spectrum in the aqueous solution broadens by inhomogeneous hydration. In the gas phase, on the other hand, the spectrum is likely to be sharper than that in the liquid phase because desolvation reduces the inhomogeneity.

In this work, we measured a gas-phase CD spectrum of bovine serum albumin (BSA) in order to improve resolution.[1] BSA negative ions were produced in a vacuum chamber and isolated by an IR-laser ablation of a droplet beam of 100 μM BSA aqueous solution. The BSA ions which were generated in the vacuum chamber were shined by a DUV laser (192-208 nm, 0.4-2 mJ / pulse). Photoelectrons released from the BSA ions were detected by a time-of-flight mass spectrometer. Then, we measured the difference of the photoelectron detachment yield for the clockwise / counter-clockwise CP laser irradiation, which was regarded as the CD intensity of BSA ions.

Fig. 1 shows CD spectra of the isolated BSA, background signal from water cluster ($OH^-(H_2O)_n$, n=0-10), and BSA aqueous solution.[2] Three sharp and positive CD bands (192, 199 and 204 nm bands) are apparently observed in the CD spectrum of the gas-phase BSA ions, whereas no CD band is observed in that of $OH^-(H_2O)_n$. In the spectrum of the BSA aqueous solution, a broad positive CD band is observed at 195 nm. This band has been assigned to α-helix structure, which occupies 60 % of the peptide chain in a BSA molecule[2].Therefore, the 192 nm, band of the BSA ion, is assignable to the α-helix structure. On the other hand, the 199 and 204 nm bands are assignable to an antiparallel β-sheet structure, because (1) the β-sheet structure occupies 13 % of the peptide chain in a BSA molecule, and (2) the antiparallel β-sheets are known to show two positive CD bands at 195 and 202 nm.[3] Then, the gas-phase CD bands at 199, 204 nm are assigned to antiparallel β-sheet structure. In the presentation, we will show a gas-phase CD spectrum above 208 nm and the structural assignment.

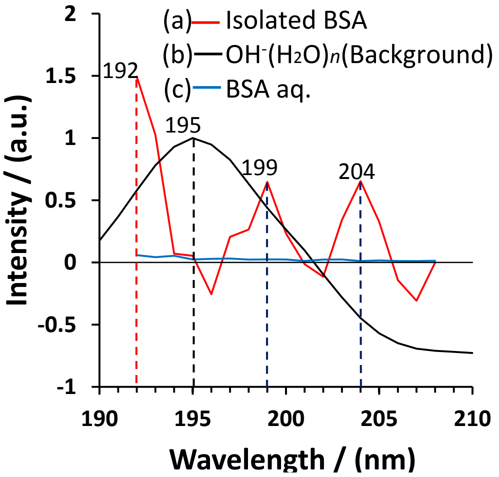

Figure 1: CD spectra of (a) isolated BSA ion (b) $OH^-(H_2O)_n$ and (c) BSA aq.[2]

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52. Pure and aligned (bio)molecular samples

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Supersonically expanded molecular beams are used for a large variety of experiments. In many cases, the molecular beam not only consists of the molecule of interest, but also contains a seed gas and other molecular species. It would often be an advantage to have a pure sample, for instance in the case of strong-field ionization or x-ray imaging techniques, which are not species-specific. We use the electrostatic deflector to spatially separate different species.[1] When the molecule of interest is deflected the most, experiments can be performed in the deflected part of the molecular beam to minimize the amount of signal originating from the seed gas or other species present in the beam. This technique for instance allowed us to create pure samples of indole-water, pyrrole-water, and water-dimer.[2-5]

In order to access the molecular frame, we not only need a pure sample, but we also need to align or orient the molecules of interest. Since the electrostatic deflector also disperses the rotational energy levels of polar molecules, we can use this technique to select molecules in the lowest-energy rotational states and use these as starting point for the molecular alignment and orientation using a non-resonant laser field.[6]

Here, we present how we were able to 3D align asymmetric top molecules such as indole and indole-water. For indole-water, we obtained a strong alignment with $< \cos^2\theta_{2D} > \geq 0.9$ using long-pulse quasi-adiabatic alignment.[7] Furthermore, we demonstrated laser-field-free three-dimensional alignment of indole using a truncated quasi-adiabatic elliptically polarized laser pulse. We could demonstrate how to detect and quantify the degree of alignment for such complicated molecules without good precursors for alignment or orientation detection.[8]

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53. Comparison of spin-orbit excitations in side-on collisions of Ar with NO

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We have investigated the scattering dynamics of side-on oriented NO molecules colliding with Ar, probing both spin-orbit conserving and spin-orbit changing final rotational states. Our crossed-beam experiments use a combination of hexapole state-selection, electric field orientation, and velocity-map ion imaging to obtain a detailed picture of the collision process, in which the initial bond orientation and the initial and final relative velocity vectors of the collision partners are well defined. By recording the outgoing relative velocity, we are able to distinguish between impacts on either side of the molecule, which result in clearly distinct scattering dynamics, irrespective of the spin-orbit manifold being probed. While the scattering distributions in the forward direction ($\theta < 90$) are nearly maximized for the side-on geometry in the spin-orbit conserving manifold, the trend is less clear for the spin-orbit changing transitions. Comparison with quantum calculations suggests a preference for end-on oriented molecules in the very forward scattered region for even changes in rotational quantum number (Δj), while for odd Δj, the trend for side-on preference remains similar to the one observed in the spin-orbit conserving manifold. The distinct characteristics for the two manifolds point to inherent differences in the underlying potential energy surfaces.

54. Building-up of a precision spectrometer using a REMPI detection scheme

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The molecular composition of diffuse interstellar matter is still an unsolved problem in astrophysics. For more than a hundred years, the carriers of the diffuse interstellar bands (DIBs) in the visible spectral range have been largely unknown. A first success was achieved in 2015 with the assignment of C_{60}^{+} as one of the carriers of some DIBs.[1] Despite this success, the majority of the bands remain unassigned due to the lack of laboratory data. Complex organic hydrocarbons such as polycyclic aromatic hydrocarbons, their ions, or radicals amongst others constitute potential carriers of the DIBs.

The use of a time-of-flight mass spectrometer in combination with a frequency-selective multiphoton ionization scheme (REMPI) facilitates the sensitive measurement of optical spectra of possible DIB carriers under controlled laboratory conditions. Molecular radicals and ions are produced in an electrical discharge, where organic precursor molecules are ionised or fractionated and form new, highly reactive and short-lived species. Using helium as a buffer gas, these are then diluted into a molecular beam and probed by a pulsed, tunable dye laser. In a planned extension, ro-vibrational transitions of the molecules can be specifically excited by the use of a frequency comb-stabilized infrared optical parametric oscillator system before they are ionized using the dye laser. In this presentation, the design and operation of the spectrometer are presented and first mass-selected molecular spectra are shown.

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55. Real-space imaging of OD collisions with liquid surfaces

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The gas-liquid interface is a relatively understudied environment. Reactions and energy transfer occurring at the interface are some of the key components in processes such as respiration, distillation, combustion and atmospheric chemistry. Despite their importance, the mechanisms of gas-liquid interactions are much less established than the equivalent mechanisms for gas-phase and gas-solid interactions. This is due to problems with experimental approach and the complexity of characterising a dynamic system like a liquid surface. Nonetheless, in the past 30 years substantial progress has been made in studying the inelastic and reactive scattering of gas molecules from liquid surfaces.[1,2]

Presented here are proof-of-concept results from a new experimental approach for studying collisions at the gas-liquid interface. Planar laser-induced fluorescence was used to acquire real-space images of molecular beams of OD radicals impinging on surfaces of two atmospherically relevant reactive liquids (squalane and squalene) and an inert liquid (PFPE). Radicals that survive such collisions are found to scatter uniformly in a broad range of directions regardless of their initial angle of approach. The distribution of the scattered products resembled that stemming from a trapping-desorption mechanism. However, the peak final speeds of scattered OD were measured to be superthermal and depend systematically on the final angle of scattering. These results point towards a substantial component of the OD scattering off the studied surfaces in an impulsive manner, with relatively low energy transfer and without being thermally accommodated at the surface.

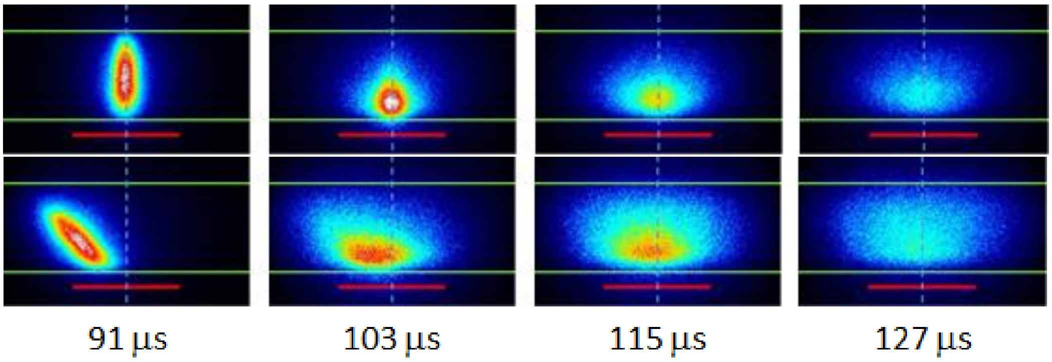

Figure 1: OD N = 4 scattering from a surface of PFPE after approaching it at normal incidence (top) and at 45° (bottom). Times represent delays between the pulsed HV discharge forming the OD packet and the firing of the probe laser sheet. The lines are guides only, indicating the positions of the edges of the laser sheet (green solid), the liquid surface (red solid) and the middle of the surface (blue dashed).

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56. Reaction of O⁻ with H_2, D_2 and HD at low temperature

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The study of the reaction of O^- with HD is a follow-up to the study of reactions of O^- with H_2 and with D_2.[1, 2] The reaction of O^- with HD has three exothermic channels, a dominant channel of a major associative detachment

$$O^- + HD \xrightarrow{k_{HDO}} HDO + e^-$$

and two minor channels of OH^- and OD^- production

$$O^- + HD \xrightarrow{k_{OH}} OH^- + D,$$

$$O^- + HD \xrightarrow{k_{OD}} OD^- + H.$$

The O^- with HD has been studied using a 22-pole ion trap apparatus.[3] The apparatus allows measuring of reaction rate coefficients in the temperature range 15 – 300 K. The systematic uncertainty of measurement is 20 %. During the measurement, the loss of O^- and the production of OH^- and OD^- were observed. From the decreasing of the primary ion O^-, the total reaction rate coefficient k_{tot}, which is the sum of the rate coefficients of all channels of the reaction $k_{tot} = k_{HDO} + k_{OH} + k_{OD}$, can be determined. From the increasing of the secondary ions OH^- and OD^-, we can determine the reaction rate coefficients k_{OH} and k_{OD}, respectively. k_{tot}, k_{OH} and k_{OD} have been measured as a function of the temperature. First results are shown in Fig. 1. Our measurements will be compared with theoretical calculations as in the case.[1,2]

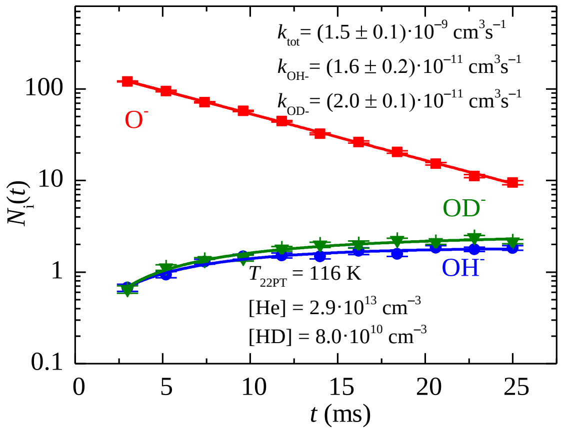

Figure 1: Example of time evolution of numbers of O^- (■), OH^- (●), and OD^- (▼) ions in the trap at 116 K.

Acknowledgments: We thank the Technical University of Chemnitz and the DFG for lending us the 22-pole ion trap instrument and professor Dieter Gerlich for the discussion. This work is partly supported by GACR Grant No. 17-19459S and 17-18067S, by GAUK Grant No. 1584217.

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57. Multiphoton Rydberg and valence dynamics of highly excited small molecules

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The family of reaction product imaging techniques such as Ion Imaging, Velocity Mapping, Slice Imaging and Photoelectron Imaging –to name a few- have provided valuable information over the past decades on the photodissociation dynamics of small molecules with quantum-state resolution, correlating kinetic energy release and internal energy of photoproducts with their angular distributions/differential cross sections. The effort to understand more complex systems and higher excited states in that level of detail continues and keeps the field alive and vibrant.

In this contribution we compare selected results from Velocity Map Imaging (VMI) and Slice Imaging experiments as well as photoelectron images following multiphoton excitation of HBr,[1,2] CH_3Br [3] and CH_3I close to their ionization limits. The kinetic energy release (KER) and angular distributions extracted from the ion and photoelectron images reveal dynamics that differ by molecule and excitation energy. The data are explained by the existence of multiple exit channels and molecular excitation and relaxation pathways as well as interesting interactions between Rydberg and valence states that depend on the excitation scheme used.

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58. A change of scene: Atom-diatom scattering in an electronically excited state

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Combined experimental and theoretical investigations of rotational energy transfer in the scattering of diatomic molecules with atoms have played a vital role in gaining understanding of molecular collisions and intermolecular interactions. State-specific spectroscopic methods of detection may be combined with methods of initial state preparation to measure the scattering on a fully state-to-state level. A very successful technique of realising this is the combination of crossed molecular beams with velocity map imaging (CMB-VMI). The simplicity of these systems makes possible a highly accurate theoretical treatment of the scattering dynamics using close-coupled quantum scattering calculations. The scattering of nitric oxide with rare gas atoms has been the most extensively studied system, due in part to this open-shell molecule's unusual stability.

We have undertaken the first systematic investigation of the stereodynamics of the collisions of NO in the A $^2\Sigma^+$ state with the rare gases, using optical absorption to access the A state. By preparing an electronically excited state we gain the opportunity to explore dynamics that are kinematically identical to those taking place on the well-studied ground state, but which traverse a very different potential energy landscape. We explore the dynamical differences between scattering on the X and A states, and the insight that these experiments and complementary scattering calculations have yielded into the intermolecular interactions in these systems. This includes evidence that the attractive interactions may be underestimated in the most recent *ab initio* potential energy surfaces. In addition to surveying our published work on scattering with He, Ne and Ar, we introduce our recent measurements of differential cross sections and collision-induced alignment for NO(A) + Kr, a system exhibiting stronger attractive interactions than the previously-studied members of the group.

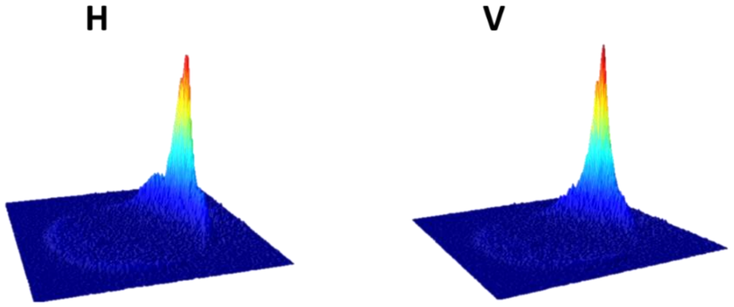

Figure 1: 3D Plots of example images for NO(A) + Kr scattering at a mean collision energy of 806 cm^{-1}, probing N' = 9. Images labelled H and V are measured with the probe light polarized parallel and perpendicular to the scattering plane, respectively, and the differences between them result from collision-induced alignment.

59. Two-colour alignment and dissociation of molecular hydrogen when under intense laser fields

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Dissociation followed by ionization of aligned, electronically excited H_2 (E, F) is analyzed by Velocity mapped imaging technique. H^+ photofragments images generated by 2-photon dissociation of H_2 forming H ($N = 0$) + H ($N = 3$) followed by 1-photon ionization of the H ($N = 3$) using a weak 532 nm beam of photons. The velocity (angle and speed) distribution of the H^+ atoms are recorded and analysed. A second laser beam, 1064 nm, is overlapped in time and space with the weak 532 nm beam and its intensity is increased while the H^+ angular distribution is monitored. The angular distribution of the H^+ is measured as a function of 1064 nm laser intensity. For prepared H_2 (E, F; $v = 0$, $J = 0$), at lower alignment laser field values, we observe an almost spherically symmetric angular distribution with a slight peak in intensity orthogonal to the polarization of the 532-nm laser beam. As the 1064 nm laser beam intensity is increased the angular distribution is seen to become peaked along the direction of the polarization axis of the 1064-nm laser beam. We model this alignment behaviour with a simple two state model involving the stark mixing the initially prepared $J = 0$ with $J = 2$ rotational state. This model is able to explain all of the observed angular distribution and permits us to extract from the fit the polarizability anisotropy of H_2 (E, F) electronic state (the difference in polarizability parallel to the bond axis versus perpendicular to the bond axis). We determine this value to be 5301 ± 714 A.U. As this value is extremely large in comparison to what one would expect from the pure H_2 (E, F) electronic state. We hypothesize that this value comes from the 1064 nm laser beam mixing nearby electronic states with the E, F state generating a mixed state that has extremely polarizability anisotropy

60. Merged molecular beams to study ion-molecule reactions at temperatures down to 300 mK

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Merged-beam experiments enable the study of chemical reactions a low temperatures. Ion-molecule reactions are important in low-density gaseous environments, such as cold (3 - 60 K) interstellar clouds. Quantum-mechanical effects start to influence the kinetics of bimolecular reactions when the collision energy approaches zero. The barrierless and strongly exothermic ion-molecule reaction $H_2 + H_2^+ \rightarrow H_3^+ + H$ provides the opportunity to observe quantum effects at collision energies below $k_B \cdot 1$ K. In past experiments, the cross section could be measured down to collision energies of $k_B \cdot 60$ K, limited by the presence of stray electric fields, which heat up the ions.[1] To avoid this effect, we substitute the H_2^+ reactant by the H_2^+ core of a hydrogen molecule excited to a high Rydberg state. The Rydberg electron does not influence the reaction for states with a principal quantum number $n \geq 20$ but provides electric neutrality. To reach very low collision energies, we exploit a curved Rydberg-Stark surface-electrode deflector to merge two supersonic beams, one containing the deflected Rydberg H_2 molecules, the other containing H_2 molecules in the ground vibronic state (Fig. 1). The collision energy is tuned by adjusting the temperature of the supersonic valve of the ground-state beam or by decelerating the H_2 Rydberg molecules during deflection. We measure the cross section at collision energies from $k_B \cdot 60$ K down to temperatures below $k_B \cdot 1$ K, where deviations from predictions based on the classical Langevin capture model are observed[2], primarily caused by the influence of the quadrupole moment of the quantized rotation of H_2.[3] The universal approach was also used to determine the ratio of the $H_2D^+ + D$ and $D_2H^+ + H$ channels of the reaction $D_2 + H_2^+$.

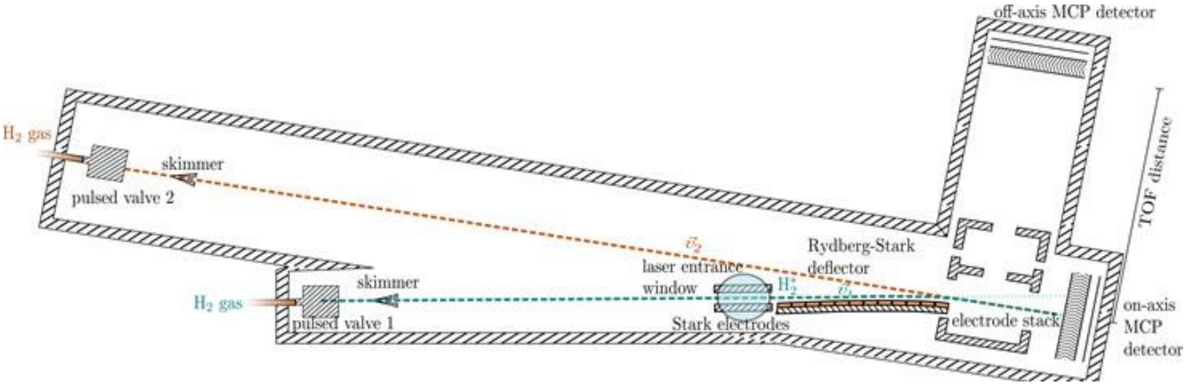

Figure 1: Experimental setup. The lower beam (blue) is deflected by Rydberg-Stark deceleration onto the axis of the other beam (brown) containing H_2 molecules in the ground vibronic state (75% ortho H_2 ($N = 1$) and 25% para H_2 ($N = 0$)). The relative rate constants are determined by monitoring the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

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61. Stereodynamics of the inelastic collisions of NO(A) with molecules

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We present the results of a crossed molecular beam – velocity map imaging (CMB-VMI) study of the stereodynamics of state-to-state rotational energy transfer (RET) of NO($A^2\Sigma^+$, v = 0, N = 0, j = 0.5) + various molecular colliders (CO, N_2, CO_2, O_2, and CH_4). We report state-to-state differential cross sections (DCSs) for NO(A) N'-rotational levels (N' = 5 – 12), as a function of the correlated internal (rotational) energy of the *unobserved* molecular collision partner. We discuss the dependence of the scattering dynamics on the degree of rotational excitation of the two colliders, inferring details of the currently unknown NO(A)-Mol (Mol = CO, N_2, CO_2, O_2, and CH_4) potential energy surfaces through detailed comparison with previous measurements and calculations of the scattering dynamics of NO(A) + rare gas RET.[1] Specifically, through comparison of the inelastic scattering dynamics of molecular colliders that quench NO(A) (e.g. O_2 & CO_2) and those that don't (e.g. N_2 and CH_4) we infer details of the collisions that lead to quenching.[2]

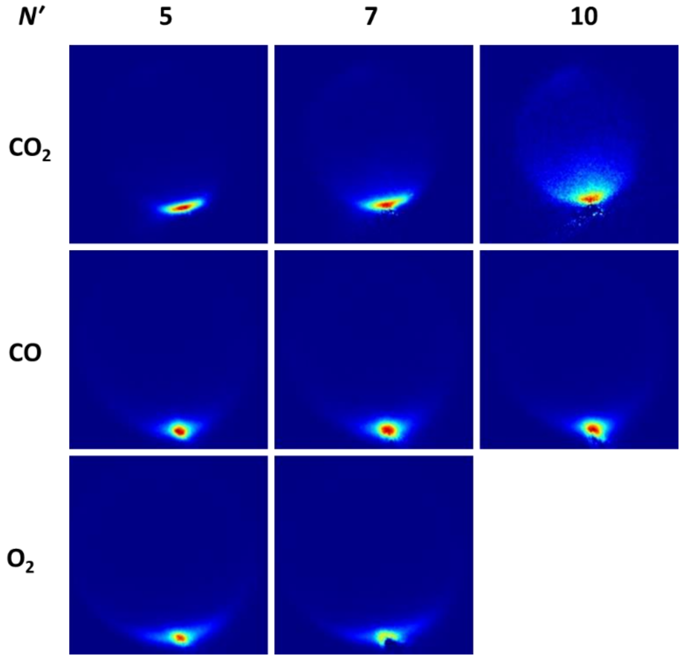

Figure 1: Top row: (V + H) scattering images of NO(A) + CO_2 for N′ = 5, 7 and 10. Middle row: (V + H) scattering images of NO(A) + CO for N′ = 5, 7 and 10. Bottom row: (V + H) scattering images of NO(A) with O_2 for N′ = 5 and 7.

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62. Spectroscopy of 4(5)-methylimidazole and its hydrates, hosted in helium droplets

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Histidine is a biological molecule that is one of the two amino acids exhibiting a tautomeric equilibrium. Moreover, this molecule has the specificity to be acceptor and donor of proton. This confers to the histidine molecule several roles as a proton transfer mediator in various proteins. These two properties are due by the imidazole cycle, which is a side chain of histidine. It appears important to understand how the tautomeric equilibrium and the proton transfer evolve according to its environment. Unfortunately, histidine is a complicate system and its size could be a problem for theoretical calculations and for helium droplets deposition. The 4(5)-methylimidazole molecules were chosen as simple model of histidine. These molecules and their hydrates were characterized by infrared (IR) spectroscopy in helium droplets.

The Gouttelium device[1] allowed recording IR spectra of the two tautomers by using the "Helium NanoDroplet Isolation" technique (HENDI).[2] The purpose was to characterize unambiguously the two tautomers via the tautomeric signature: the NH vibrational stretching. The recorded bands and DFT calculations allowed estimating the constant of tautomerization (K_T(43°C)=4.7), which was not accurately known. We also evaluate the rotational constants of the 4-methylimidazole in order to simulate its spectrum.

In a second step, the 4(5)-methylimidazole-water complexes were formed by the deposition of the two species on helium droplets. A search of the signal of the NH stretching of the methylimidazole and of the symmetric and asymmetric stretch of the OH of water was performed. The results constitute the first study of these complexes embedded on helium droplets.

The different spectra and preliminaries conclusions will be presented at the conference.

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63. Studying gas-liquid surface reactions using velocity map imaging

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We present the second generation of ion optics capable of Surface Scattering Velocity Map Imaging (SS-VMI) experiments. Building on the capabilities of the first generation[1] the new design provides significantly enhanced velocity resolution and a larger ionization region capable of VMI.[2] In SS-VMI the surface of interest is introduced into the ion optics, between the repeller and extractor, to minimise the surface to probe laser distance and thus capture a greater range of scattering angles from the surface. The electric field necessary for VMI is maintained by tuning the voltages on stabiliser electrodes on either side of the surface. While the surface and stabilising electrodes are flat and parallel to the ion optics our approach could be adapted to other gas-liquid scattering techniques, e.g. liquid micro-jets.[3]

The performance of the 2nd generation ion optics is shown in Figure 1 below, which compares the rings of NO^+ fragments from the photodissociation of NO_2 both with and without the surface present inside the ion optics. The SS-VMI image in Fig. 1 was taken with the surface 10 mm below the ionization laser axis, and is indistinguishable from the image taken under standard VMI conditions (could you tell the difference if the labels were not on the figure?). This technical development opens up the possibility of applying all the multiplexing and quantum state specific advantages of resonance enhanced multiphoton velocity map imaging (REMPI-VMI) to gas-liquid scattering systems.

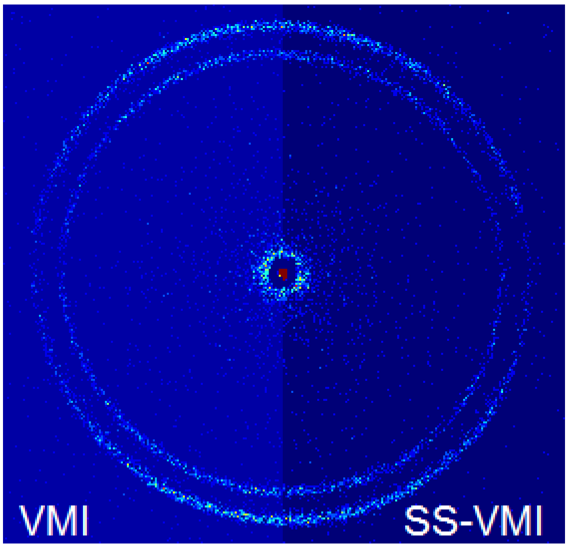

Figure 1: Side-by side comparison of experimental images of NO^+ from NO_2 photodissociation and subsequent ionization at 226.1 nm conducted under normal VMI conditions (left hand side) and SS-VMI conditions (right hand side). SS-VMI image taken with surface 10 mm below laser axis.

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64. UF-CRDS: A pulsed uniform flow apparatus with cw-cavity ringdown spectroscopy

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We introduce a new apparatus in which a high-performance pulsed supersonic uniform flow from a Laval nozzle is coupled with continuous wave cavity ringdown spectroscopy (*cw*-CRDS). This approach is related to the CRESU[1] technique developed in France to study reaction kinetics at low temperature. A related system developed in our group in which chirped-pulse microwave spectroscopy is coupled to a pulsed Laval flow has successfully demonstrated its investigative capability of isomer-specific product branching in reactions and photodissociation at temperatures as low as 22 K.[2]

The pulsed uniform flow is produced by means of a high throughput piezoelectric stack valve combined with a Laval nozzle[3]. At present, we employ two machined aluminum nozzles (for carrier gases He and Ar at temperatures around 25 K), and numerous in-house 3D printed nozzles. The 3D printed nozzles are designed using a Matlab program developed in-house, which allows us to create supersonic uniforms flows with different carrier gases and at various temperature and densities. These nozzles are validated experimentally as well as theoretically using a computational fluid dynamics program, OpenFOAM.

The current configuration can probe the pulsed uniform flow either by *cw*-CRDS, operated in the near infrared region, or laser-induced fluorescence as in the traditional CRESU approach. The *cw*-CRDS spectrometer consists of a high finesse optical cavity (F~200000) which is composed of two high reflective plano-concave mirrors (R~99.9988%) leading to an empty cavity decay constant of ~160 µs. The long uniform hydrodynamic flow time and ringdown decay together permit monitoring the reaction kinetics during the course of each ringdown, a technique termed SKaR (Simultaneous Kinetics and Ringdown). We will present our first low temperature kinetics experiments performed with this apparatus including reaction of CN (v=1) with alkenes probed by *cw*-CRDS.

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65. Product branching and low temperature reaction kinetics by chirped-pulse Fourier transform mm-wave spectroscopy in a uniform supersonic flow

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The CRESU technique[1] (French acronym for “reaction kinetics in uniform supersonic flows”) has been applied with great success in the past three decades to study the kinetics of reactions at low temperatures. In this approach, a pulsed uniform flow (which is equivalent to a wall-less reactor at constant temperature and pressure) is produced by expansion of a gas through a Laval nozzle. We have combined these low temperature Laval flows with broadband mm-wave detection (chirped-pulse/uniform flow or “CPUF”) to study product branching in photodissociation and reaction.[2] However, in these experiments, the high collision frequency in the uniform flow condition attenuates the mm-wave signal. Therefore, we have developed two approaches to address this challenge. In one approach, we use a modified “quasi-uniform” flow where the initial conditions are uniform and high density.[3] This is followed by a second expansion to a very cold, low density detection region optimal for the mm-wave detection. Aided by detailed characterization of this flow condition by experiments and fluid dynamic simulations, product branching as well as observation of product evolution as a function of reactant density. In a second approach, we have recently implemented airfoil sampling of a fully optimized flow. This allows us to study low temperature kinetics as in CRESU, but with the power of broadband mm-wave detection. Recent results for several systems relevant to photodissociation and low temperature reaction kinetics will be presented using both the quasi-uniform flow and airfoil sampling.

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66. Absolute fluorescence quantum yield of acetone

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We recently demonstrated the measurement of absolute number densities in molecular beams using cavity-enhanced laser-induced fluorescence (CELIF).[1,2] Here, we present that CELIF has been successfully used to determine absolute spectroscopic quantities under ambient conditions.

The strength of cavity-enhanced laser-induced fluorescence lies in the simultaneous absorption (cavity ring-down) and fluorescence measurement of the same sample using the same light source, eliminating common cross-calibration issues. An absolute calibration is achieved with the cavity ring-down measurement while the high sensitivity of laser-induced fluorescence opens up a dynamic range of up to six orders of magnitude.

In contrast to a molecular beam, the absolute concentration of a trace gas in a filled cell under ambient conditions can be obtained relatively easily. In this instance, we can use the simultaneous measurement of absorption and fluorescence to obtain an absolute fluorescence quantum yield of a trace gas. Acetone recently gained importance as a biomarker in breath analysis measurements. In addition, it serves as a trace-VOC in tropospheric monitoring. At acetone concentrations relevant in breath-gas analysis and tropospheric trace-gas monitoring we measured an absolute fluorescence quantum yield of $\sim 4 \cdot 10^{-4}$ following 266 nm laser excitation (Table 1). These values are in good agreement with the model proposed by Thurber *et al.*[3] We attribute small discrepancies to induced dipole interactions.

Bath gas	$\Gamma / 10^{-4}$
N_2	4.49 ± 0.12
Air	3.02 ± 0.15
He	3.91 ± 0.04
Ar	3.62 ± 0.16

Table 1: Absolute fluorescence quantum yield of 100 ppmv of acetone at 1 bar following laser excitation at 266 nm.

We have demonstrated that the initial application of CELIF in molecular beam spectroscopy can be extended to ambient environments. Further developments to apply CELIF in analytical measurements will focus on the replacement of the pulsed Nd:YAG laser with a broadband LED source.

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67. Molecular frame photoelectron angular distributions of aniline obtained via weak-field ionization

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Molecular frame photoelectron angular distributions (MFPADs) provide a means to investigate intramolecular processes.[1] Here we report MFPADs from the 0^0_0 transition of aligned aniline molecules, obtained with [1+1] photoionization with a picosecond UV pulse (293.85 nm, FWHM ~0.06 nm). Prior to ionization, the molecules have been aligned in the lab frame with a laser pulse that turns on slowly (~100 ps), but switches off quickly (<10 ps). The respective delay in between the two laser pulses was chosen so that the maximum of the probe pulse was coincided with the onset of the alignment pulse's truncation edge. At the truncation edge, the alignment is reasonably maintained, whereas the electric field is considerably smaller, reducing its impact on the ionization dynamics.[2]

Varying the polarization of the alignment pulse allows us to control how the molecules are fixed in space. Confinement can be one- or three-dimensional, with the major axis parallel or perpendicular to the detector plane. Molecules which are unaligned give an isotropic PAD, which is signicantly perturbed by both 1D alignment parallel to the detector, and 3D alignment. The analysis of the obtained data is challenging and ongoing, since the ionization occurs while a part of the alignment pulse is still present. The experimental data demonstrate sensitivity to the molecular frame and are compared with simulated MFPADs calculated with ePolyScat.[3,4]

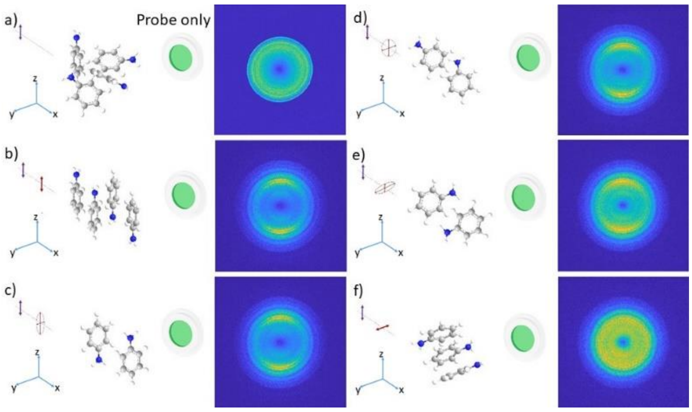

Figure 1: MFPADs obtained from the 0^0_0 transition of aligned aniline molecules, via [1+1] photoionization. a) probe only image, b) 1D aligned ‖ to the detector plane, c) 3D ‖ aligned, d) 2D aligned, e) 3D ⊥ aligned, f) 1D ⊥ aligned.

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68. Mid-infrared frequency modulated spectroscopy as a probe of scattering dynamics at the gas-liquid interface

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We are expanding our technical ability to study the inelastic and reactive scattering dynamics at the gas-liquid interface using a new narrowband continuous-wave (CW) frequency-modulation spectroscopy (FMS) probe. With two independent probes in the near-IR (NIR) and mid-IR (MIR) ranges, we will have the ability to detect both inelastically scattered open-shell species (e.g. CN) and reactively scattered closed-shell molecules (e.g. HCN) of the same system with quantum state resolution. Comparison with state-of-the art theory will unravel subtle dynamical aspects of the chemical systems studied.

We report the successful construction of a tuneable, narrowband, CW-FM-MIR detection system based on difference frequency generation (DFG) in periodically-poled lithium niobate (PPLN) using tuneable NIR and fixed-frequency 1064 nm lasers. We have characterized the MIR-generation dependence on PPLN temperature and input laser beam shape, focussing and power. We present the first spectroscopic measurements determining the system performance and sensitivity, using the v_3 asymmetric stretch to probe jet-cooled CH_4. As proof-of-concept, we report initial measurements of CH_4 inelastic scattering at a squalane surface, demonstrating the high spectroscopic resolution and sensitivity of the system. While this new detection system has been designed to probe HCN formed in reactions of CN at hydrocarbon surfaces, the PPLN based DFG system provides flexibility to probe a wide range of polyatomic species via CH, NH or OD stretches, enabling studies of a wide range of inelastic and reactive scattering processes of interest in atmospheric or combustion chemistry.

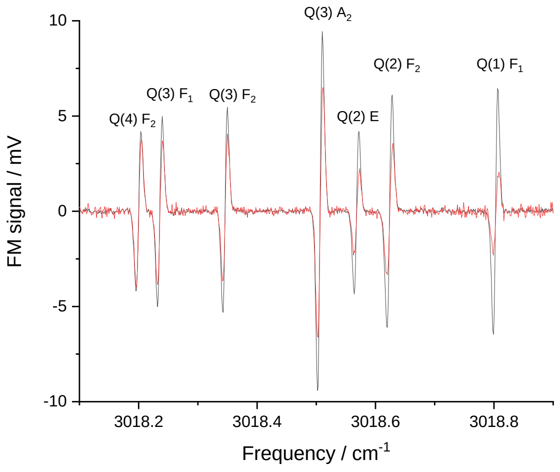

Figure 1: MIR-FM spectrum of the asymmetric stretch band of CH_4. Black line: Free-jet expansion of 2% CH_4 in He. Red line: partially thermalized CH_4 from background gas/wall collisions.

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