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Book Of Abstracts

Part 1

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Probe the molecule-surface interactions by thermal desorption rates

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Prevalently reactions at catalytic surfaces proceed through the so called Langmuir-Hinshelwood mechanism. Here the molecules adsorb at the surface where they thermalize. Subsequently they diffuse on the catalyst to find an active site at which they may react. Reaction products leave the surface trough desorption. Each of the described processes can be rate determining in the overall product formation rate and thus the thermal rate constant are needed to quantitatively describe the efficiency and selectivity of a catalyst.

In this work we show that accurate measurements and analysis of thermal desorption rates from surfaces can provide more information than just molecules binding energies to the surface. On the example of NO and NH_3 desorption from Pt and Pd surfaces we show that conclusions about the mechanism and barrier for diffusion can be made. The measurement of thermal desorption rates is accomplished with the Velocity-Resolved Kinetics method[1] that combines molecular-beam surface scattering with Ion Imaging based measurement of desorption flux. Molecules are adsorbed to the surface from a short molecular beam pulse and the thermal desorption rate is followed in a pump-probe experiment where the detection laser is scanned with respect to the molecular beam pulse. In the same experiment we obtain the desorption dynamics of the molecules from which we are able to extract their sticking probabilities to the surface.

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Coherent multidimensional spectroscopy of cluster beams

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Coherent multidimensional spectroscopy (CMDS) is an extension of femtosecond pump probe spectroscopy which unifies spectroscopic information otherwise only accessible in disjunct experiments [1]. However, applying CMDS in the gas phase, in particular to dilute molecular and cluster beams, is experimentally very challenging [2]. Recently, we have overcome these challenges and have performed the first CMDS studies of doped cluster beams [2,3]. In my talk I will present our recent results about ultrafast molecular dynamics induced by a superfluid cluster environment, our high-resolution study of phthalocyanine molecules, the combination of CMDS with photoelectron spectroscopy and our recent progress in extending the method towards extreme ultraviolet (XUV) wavelengths [4,5].

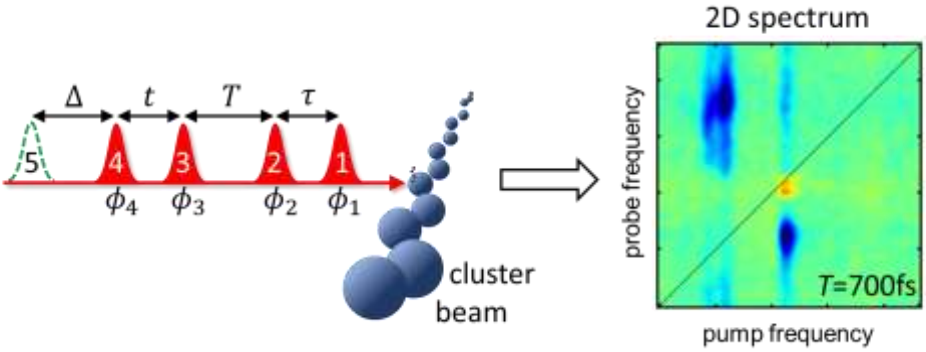

Figure: Experimental scheme. A sequence of femtosecond laser pulses excites and ionizes molecules isolated on rare gas clusters prepared in a molecular beam apparatus. Two-dimensional spectra are retrieved offering high spectro-temporal resolution and directly disclose inter-/intra-particle couplings.

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Pure-state preparation and readout of increasingly large molecules

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The use of gas phase molecules in pure quantum states for computation, measurement, and sensing relies on the ability to determine the quantum state of the molecules. This applies not only to state detection, but also state preparation (and cooling), where initialization of the molecules into pure quantum states is far more challenging for molecules than atoms due to their high density of internal states. A major advance in this regard was the identification of laser-addressable molecular species with atom-like emission properties, first demonstrated with diatomic molecules[1], and this approach has been steadily pushing to larger species[2], including the recent laser cooling of $CaOCH_3$[3]. We will discuss some approaches for extending the reach of these laser cooled atom techniques to species with carbon rings[4,5] and into the regime where the rotational structure is unresolved by the laser.

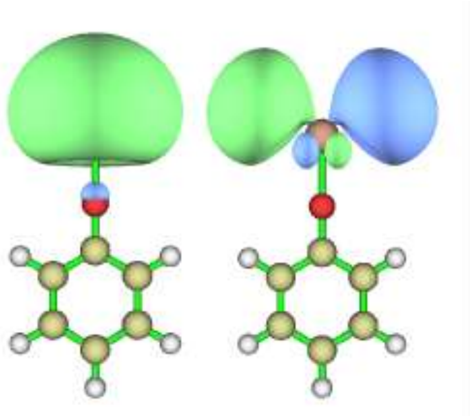

Figure: Molecular orbital isosurfaces for the ~X and $\tilde{A}$ states of $SrOC_6H_5$ show atomlike character and a lack of electron density near the bonds, in accordance with its extremely weak coupling to molecular vibration.

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Au_{10}^+: a Broadband Infrared Chromophore

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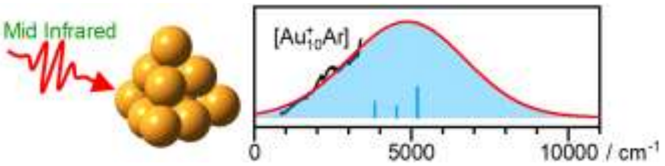
Au_{10}^+ presents a remarkable broadband mid-infrared absorption in a region in which only molecular vibrations would normally be expected.[1] In the free-electron laser infrared multiple photon dissociation (IRMPD) spectra of $Au_{10}Ar^+$, $Au_{10}(N_2O)^+$ and $Au_{10}(OCS)^+$, the smooth feature is observed between 700–3400 cm^{-1} (λ=14–2.9 µm). In contrast, electronic transitions are typically in the ultraviolet or visible region. However, calculations confirm unusually low energy allowed electronic excitations consistent with the recorded spectra. Like with many gold clusters the electronic structure of Au_{10}^+ can be qualitatively described by jellium (or uniform electron gas) models, in which electrons occupy well-defined shells, much like in isolated atoms. For all other cluster sizes studied (Au_3^+-Au_{12}^+), only absorption due to vibrational transitions of the adsorbed OCS or N_2O molecules is seen in this range, as these low energy electronic transitions are unique to Au_{10}^+.[2,3]

Here, IRMPD harnessed the sensitivity of mass spectrometry for the purpose of gas-phase molecular absorption spectroscopy but was also able to inform upon IR-induced reactivity *via* fragment enhancements (e.g., $Au_{10}(OCS)^+ + h\nu \rightarrow Au_{10}O^+ + CO$). On the surface of Au_{10}^+ IR absorption throughout the electronic band drives OCS decomposition, raising the prospect of using the unique optical properties of Au_{10}^+ for catalysis, i.e., by providing an attractive alternative method of bond activation/breaking at a wide range of photon energies.



Acknowledgments: This work was supported by EPSRC, DFG and Magdalen College, Oxford.

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Photodissociation of CF_3CHO from the decomposition of hydrofluoroolefins provides a new source of CHF_3 (HFC-23) in the atmosphere

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Hydrofluoroolefins (HFOs) are an important class of replacement compounds for older refrigerant gases banned by the Montreal Protocol. HFOs decompose readily in the atmosphere, forming smaller fluorinated compounds, including CF_3CHO. In this work, we use velocity-mapped ion imaging with some conventional and some novel molecular beam techniques to demonstrate unambiguously that CHF_3 (HFC-23, fluoroform) is a primary product of CF_3CHO decomposition and reveal it to represent the atmospheric fate of a significant fraction of emitted HFO molecules. These results may lead to reevaluation and reclassification of important HFO compounds and account for some of the recent increase in measured CHF_3 emissions for which no source is yet identified.

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Ultrafast XUV-induced Dynamics in Gas-phase Complex Molecules

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The development of modern ultrashort X-ray/XUV pulses has brought new perspectives in the real time observation of high-energy electron and nuclear dynamics in gas-phase atomic and molecular species. While great efforts have been devoted to the XUV-induced dynamics in small atomic or molecular systems, experiments on polyatomic molecules remain scarce because of the complex understanding of the associated dynamics.[1]

In this talk, I will present works investigating the ultrafast dynamics induced by XUV inner-valence photoionization in different series of complex molecules. Experiments on neutral, size-scalable polycyclic aromatic hydrocarbons (PAHs) reveal a general behavior in the femtosecond relaxation of any neutral molecule, due to the ubiquitous role of electron correlation and non-adiabatic effects (Figure 1).[2] Additionally, we recently combined ultrashort XUV sources with electrospray (ESI) technology to explore post-ionization dynamics in large alkaloid ions, where the natural charge strongly drives the dynamics.[3] These results offer new opportunities to study charged, biorelevant molecules beyond proof-of-principle systems.

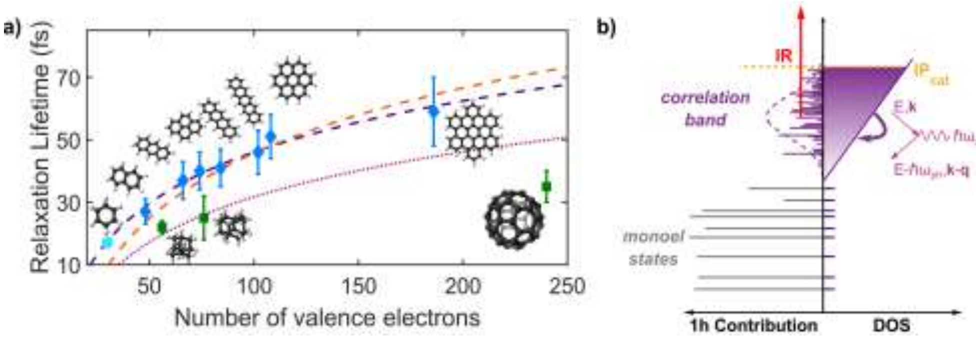

Figure: a) XUV-induced relaxation lifetime in several neutral molecules, from benzene (C_6H_6) to hexabenzocoronene ($C_{42}H_{18}$); b) the lifetime evolution with size is due to the role of correlation bands in any complex molecule, that is created by electron correlation and relaxes via electron-phonon scattering events.

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Machine learning assisted energy transfer dynamics simulations at gas-surface interface

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Chemical reactions of gas-solid interface are always accompanied by energy conversion between different degrees of freedom. Therefore, it is very important to understand the energy exchange between the molecule and surface upon gas-surface encounters. However, in comparison to gas-phase systems, the degrees of freedom of gas-surface systems are significantly increased, and the theoretical description has been facing great challenges. Our research group focus mainly on the neural network high-dimensional representations for potential energy surface (PES) and electron friction tensor (EFT) to simulate the state-to-state energy transfer dynamics during molecule-surface scattering. In this report, I will mainly present our recent progress in machine learning methods for PES and EFT. These advances allow us to discover a new mechanism of the mechanical molecule-to-surface vibrational energy transfer of NO scattering from Au(111), in a classical system showing predominant characteristics of electron-mediated energy transfer. The non-adiabatic energy transfer is also partially accounted for in our molecular dynamics simulations with electron friction on the basis of machine learned EFT surfaces, quantifying the general applicability of the electron friction model in gas-surface systems.

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Matter-Wave Diffraction from a Periodic Array of Half Planes and its

application to He_2 and He_3

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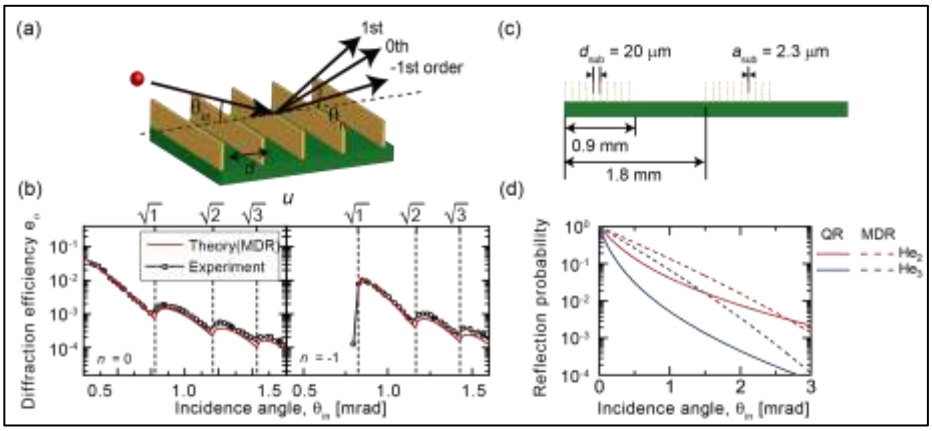
We report on reflection and diffraction of beams of He and D_2 from square-wave gratings of 400-µm period and strip widths ranging from 10 to 200 µm at grazing-incidence conditions. In each case we observe fully resolved matter-wave diffraction patterns including the specular reflection and diffracted 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 to the regime of edge diffraction from an array of half-planes. The latter is described by a single-parameter model 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. Furthermore, we applied the diffractive reflection mechanism to the diffraction of fragile He_2 and He_3 to increase their diffraction efficiencies.



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Ultrasensitive high precision microwave spectroscopy in a buffer gas cell

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Pulsed supersonic jets have been the leading method to produce cold molecules for spectroscopic experiments. Pulsed jets have certain limitations in achieving high sensitivity per unit time due to low overall duty cycles and other factors. An alternate method to produce cold molecules, that has emerged in the last decade, is cryogenic buffer gas cooling, where molecules sprayed into a buffer gas cell held cryogenically at 6 K are cooled via collisions with a Helium buffer gas. I will describe our instrument[1], that couples Chirped Pulse-Fourier Transform (CP-FT) microwave spectroscopy with cryogenic buffer gas cooling to produce ultrasensitive rotational spectra with applications in chirality detection. I will discuss future directions where buffer gas cooling may be advantageous for high precision measurements.

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Following the energy transfer between hydrogen atoms and surfaces using scattering experiments

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Hydrogen atom scattering from various surfaces under ultra-high vacuum conditions is used to investigate the process of energy transfer during the interaction of impinging atoms with a surface sample, thereby providing information about surface dynamics and important steps in surface reactions, e.g. chemical binding and adsorption. The simplicity of the system makes it particularly interesting for a detailed comparison between high-level experiments and first principle theories.

Photolysis of hydrogen halide molecules with ultraviolet or vacuum-ultraviolet photons generates nearly monoenergetic atomic hydrogen beams with translational energies in the range of 0.4 to 7 eV. These hydrogen atoms are scattered from the surface sample, and their translational energy after the collision is probed by the Rydberg-atom time-of-flight method to obtain scattering-angle resolved translational energy loss spectra.

For an insulating surface, it was shown that the collisions are nearly elastic, whereas hydrogen atoms colliding with a metal surface possess a large translational energy loss that can be explained by energy transfer to electron-hole pair excitation.[1] In contrast, for hydrogen atoms colliding with epitaxial graphene grown on a platinum (111) substrate, the formation of a transient chemical bond could be observed. Here, the scattering distributions exhibit a bimodal behaviour with a strongly inelastic and a nearly-elastic scattering channel, depending on whether the barrier to chemical bond formation is overcome or not, respectively.[2]

In a current project we investigate hydrogen atom scattering from a semiconducting, reconstructed germanium (111) surface. Again, two different scattering channels are observed. To elucidate the experimental findings, comparison with theoretical models will be required. Because of the surface reconstruction, this system represents a particularly challenging, yet very interesting task for theoretical simulations.

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Controlled Laval Expansion Facilitates Understanding Nucleation on the Molecular Level

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Abstract. Gas phase nucleation is a ubiquitous phenomenon whose progress critically depends on the properties of the initially formed nucleating clusters. A complete understanding of nucleation thus requires understanding its mechanism on the molecular level. However, this poses an experimental challenge as experiments need be conducted at precisely controlled conditions with successful concentration quantification of the delicate nucleating clusters. To meet this challenge, we combine the uniform postnozzle flow of pulsed Laval expansions, soft single-photon ionization and time-of-flight mass spectrometry [1] to directly measure the chemical composition and the concentration of the nucleating clusters in various unary [2-5] and binary [6] nucleation systems at <100 K. We present water nucleation as a representative example for unary nucleation and demonstrate the extraction of monomer-cluster association rates from the evolving mass spectra of nucleating clusters[3]. For binary nucleation systems, we focus on binary CO_2-containing vapors. Our analysis reveals that CO_2 essentially catalyzes nucleation through a Chaperone-like mechanism, i.e. CO_2 enhances the nucleation of the low vapor pressure component through the formation of transient, heteromolecular clusters. Our work opens up new avenues for the quantitative assessment of nucleation kinetics to decipher nucleation mechanisms across different temperature regimes.

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Probing and controlling reactions at sub-microkelvin temperatures

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Advances in atomic, molecular, and optical (AMO) techniques allowed the cooling of simple molecules down to the ultracold regime (< 1 mK) and opened the opportunities to study chemical reactions with unprecedented levels of control. While many prior studies investigated how long-range forces influence ultracold reactions, we extend the exploration into the short-range where the actual chemistry takes place. To this end, we developed an experimental apparatus that combines production of state-controlled ultracold molecules with highly efficient and universal ion-based detection [1]. Using such an apparatus, we probed the exchange reaction between ultracold potassium-rubidium (KRb) molecules in its entirety, detecting both the reaction intermediates and the products [2]. Such direct signals allowed us to further investigate the dynamics of this reaction, and eventually gain control over its various aspects. In this talk, I will describe the observation of an unusually long-lived reaction intermediate [3], the demonstration of product rotational state control via conserved nuclear spins [4], and a test of the celebrated statistical theory [5] using the complete pair-correlated quantum state distribution of the products [6].

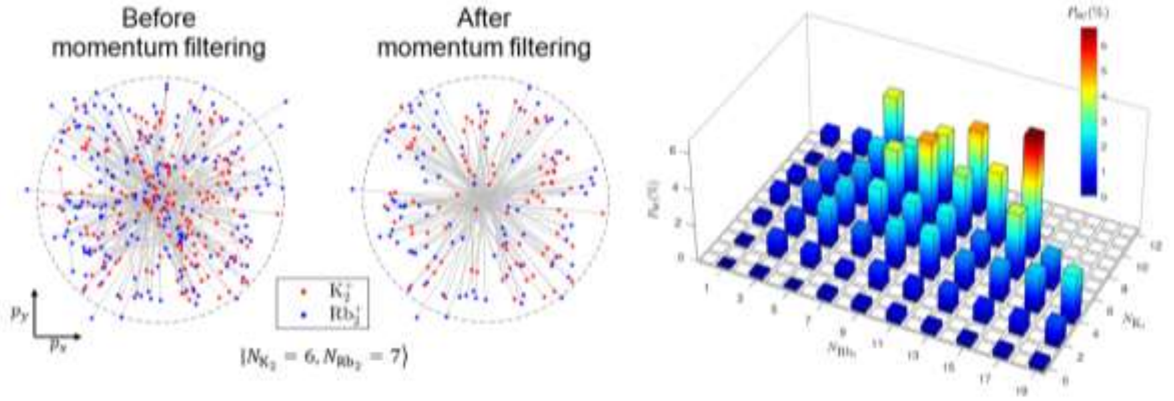

Figure: mapping the pair-correlated product state distribution for the ultracold reaction KRb + KRb → K_2 + Rb_2 using state-selective coincidence imaging (adapted from Ref [6] with permission)

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Revealing the chemistry of polycyclic aromatic hydrocarbons by plasma sources

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Polycyclic aromatic hydrocarbons (PAHs) are considered to dominate the unidentified infrared bands (UIRs) - infrared emissions, which are characteristic of the vibrational modes of aromatic species and which have been detected in many circumstellar and interstellar objects. PAHs are thought to incorporate a large fraction of the galactic carbon budget (10 to 25%) and play an extensive and ubiquitous role in interstellar chemistry. Despite their importance, the formation and destruction of PAHs, as well as their reactivity with other interstellar molecules under the harsh conditions of the ISM remain relatively unexplored.

To look at these processes in the laboratory, we have coupled an electrical discharge nozzle with chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in the 2-12 GHz frequency range. Under plasma conditions, PAHs are expected to undergo fragmentation processes and/or a recombination chemistry. The formed species are then unambiguously identified via their unique microwave signatures.

Using this technique, we investigate PAHs of different size, shape, and degree of aromaticity to understand how these different properties can influence the plasma chemistry.
Herein, we present our results obtained from electrical discharge experiments on the PAHs naphthalene ($C_{10}H_8$) and phenanthrene ($C_{14}H_{10}$), both pure and in mixture with acetonitrile (CH_3CN), a simple nitrogen-containing interstellar molecule. Among the species formed, we have observed the two isomers of cyano-naphthalene[1] and allenyl acetylene,[2] all molecules recently detected in the TMC-1. This suggests that the species generated in our experiments could be used as a basis for chemical investigation in TMC-1 and other cold clouds.

Acknowledgments: This work was supported by the ERC Starting Grant “ASTROROT” and the Alexander von Humboldt Foundation.

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Velocity map imaging and photoelectron spectroscopy as a means for determining photodissociation pathways of molecules.

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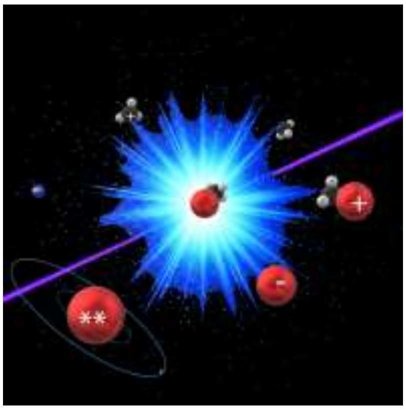

Velocity map imaging is a technique that can determine the kinetic energy of molecular fragments formed via photodissociation. By mapping the arrival positions of molecular fragments on a microchannel plate following a multi-photon ionization the total kinetic energy of each fragment can be determined. In a similar way, photoelectron spectroscopy can determine the kinetic energy of electrons following ionization of molecules or molecular fragments. Combined, these techniques form a powerful tool to analyze and determine photofragmentation pathways of molecules.

As a case example, the determination of photofragmentation pathways for CH_3I in the excitation region of 55 700 to 70 000 cm^{-1} is presented.

Acknowledgments: The case example was supported by the University Research Fund, University of Iceland, the Icelandic Research Fund (Grant No. 184693-051), the European Union's Horizon 2020 research and innovation programme LASERLAB-EUROPE (Grant Agreement No. 654148) and by HELLAS-CH (MIS 5002735) implemented under “Action for Strengthening Research and Innovation Infrastructures,” funded by the Operational Programme “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

Gas-Phase Characterization of Hypervalent Carbon Compounds: Penta- versus Tetra-Coordinated Isomers

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A hypervalent carbon compound having a penta-coordinated carbon atom is typically seen as a transition state of S_N2 reactions (Figure 1a), and thus experimental studies of its structure have been receiving great attention. Yamamoto and coworkers have succeeded in chemical synthesis of "stable" penta-coordinated carbon compounds[1] (e.g. compound **1** in Figure 1b), although the structural characterization just relied on X-ray diffraction analyses of a single crystal. It is highly desired (1) to examine intrinsic structure of the compounds by isolation in the gas phase and (2) to spectroscopically characterize the hypervalent nature.

To these ends, I herein investigated electronic and geometrical structures of **1** and **2**, with different ligands, by means of photodissociation spectroscopy (PDS)[2] with the aid of ion mobility mass spectrometry (IMMS).[3] Penta-coordinated (hypervalent) structure of **1** was dominantly identified by both of PDS and IMMS. On the other hand, coexistence of penta- and tetra-coordinated (non-hypervalent) isomers was revealed for compound **2** in the gas phase; it is in sharp contrast to its exclusive tetra-coordinated structure in a crystal (Figure 1c). The cause of such difference will be discussed on the basis of the relative stabilities, to shed new light on the origin of the hypervalent structure.

1; penta-coordinated **2**; tetra-coordinated

(In single crystal)

Figure 1: (a) Transition state of S_N2 reaction. (b, c) Schematic structures of target compounds in a single crystal. Ligands are indicated in red. *p*-Tol indicates a *para*-tolyl ($–C_6H_4–CH_3$) group.

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Molecular collisions: from molecular billiards to chemical reactions

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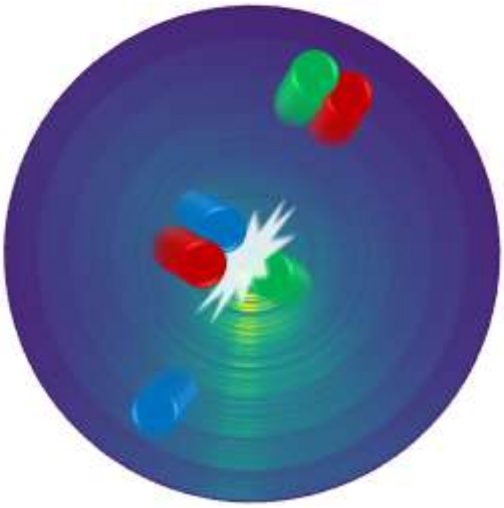
One of the important goals in physical chemistry is to get a complete understanding of fundamental molecular processes that underlie chemistry. Our aim is to investigate and control molecular scattering processes in extremely high detail and in unexplored energy regimes.

The combination of a Stark or Zeeman decelerator and Velocity Map Imaging is a powerful tool to study molecular collisions. The decelerator gives experimentalists precise control over an atomic or molecular beam, while Velocity Map Imaging in combination with near-threshold ionization allows for an accurate probing of the velocity vectors of scattered molecules. This combination of techniques therefore enables scattering experiments with extraordinary resolution, revealing intimate details of molecular collisions that are washed out otherwise.

Up to now, we used this experimental approach to investigate *inelastic* molecular collisions. We have been able to observe diffraction oscillations, scattering resonances and other quantum phenomena in various systems. In the near future, we will for the first time use our powerful combination of techniques to study *reactive* scattering processes. This will allow us to investigate fundamental chemical reactions on the molecular level in great detail.



Acknowledgments: This work receives funding from NWO, from the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Programme (Grant Agreement No. 817947 FICOMOL), and from the European Union’s Horizon 2020 Research and Innovation Programme under the Marie Skłodowska-Curie Grant Agreement No. 886046 and 889328.

Probing molecular dynamics using ultrafast XUV transient spectroscopy

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Attosecond probing of core-to-valence electronic transitions is a powerful tool for real-time observation of chemical dynamics.[1] Here, ultrafast extreme ultraviolet (XUV) transient absorption spectroscopy is employed to investigate the electronic and nuclear dynamics on small polyatomic iodinated molecules. The dynamics induced by one- or two-photon absorption using either few-femtosecond visible pulses, ranging between 500 nm and 900 nm, or 20-fs UV pulses around 260-280 nm is probed by XUV attosecond isolated pulses through iodine-4*d* core-to-valence transitions. The motion of the wavepacket on the excited states is directly mapped, allowing us to visualize the time-resolved photodynamics.[2] The results presented will include mapping coherent nuclear motion in I_2 and dissociation dynamics through a conical intersection in alkyl iodides.

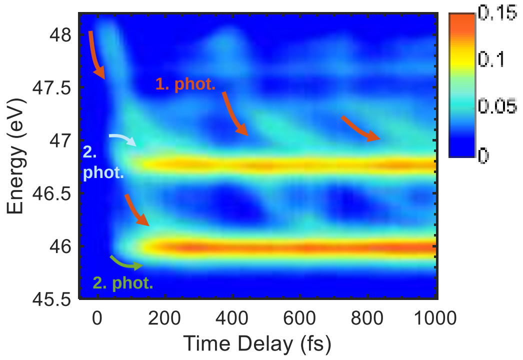

Figure: Transient absorption map measured for I_2 excitation by the visible pump pulse, as a function of the time delay and the XUV photon energy.

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Crossed-beams and theoretical studies of the O(^{3}P,^{1}D) + benzene reaction dynamics: primary products, branching fractions, and role of intersystem crossing

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Recently, we have shown that the Crossed Molecular Beams (CMB) technique with *soft* electron ionization mass-spectrometric detection and time-of-flight analysis, synergistically empowered with theoretical calculations of potential energy surfaces (PESs) and statistical computations of product branching fractions (BFs), with intersystem crossing (ISC) taken into account, permits to characterize all primary products and BFs of multichannel reactions of O(^{3}P) with unsaturated hydrocarbons[1], which are of great relevance in combustion. In this talk, we will focus on the extension of the combined CMB/theoretical approach to the investigation of the O(^{3}P,^{1}D) reactions with the prototypical aromatic hydrocarbon, benzene.[2] Despite extensive kinetic[3], dynamical[4,5], and theoretical[3,6] studies, the detailed dynamics (primary products and BFs) of the O(^{3}P)+benzene reaction are still not well understood, and this has hampered the development of reliable combustion models. CMB studies coupled to synergistic theoretical calculations of coupled triplet/singlet PESs and statistical (RRKM/Master Equation) computations of product BFs with inclusion of ISC, have permitted to achieve a detailed characterization of the O(^{3}P) (and also O(^{1}D)) + benzene reaction dynamics and ultimately predict channel-specific rate constants as a function of temperature, which are expected to be useful for improved combustion models.

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Energy Partitioning and Spin-orbit Effects in the Photodissociation of Higher Chloroalkanes as Isolated Molecules and Clusters

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We apply velocity map imaging (VMI) technique [1,2] and molecule dynamics (MD) simulations based on novel molecule dynamics continuous-wave sampling method[3] in our current research of the photolysis of four selected isolated alkyl chlorides (C_xH_YCl), i.e., methyl-, n-propyl-, i-propyl-, n-pentyl-chloride. The halogenated hydrocarbons are benchmark systems for studying intersurface dynamics of polyatomic molecules and the excess energy partitioning into internal modes of molecules and clusters within the fast ~fs photodissociation. In our experiment, the alkyl chlorides are dissociated by optically active repulsive excited singlet $^1Q_1$ and triplet $^3Q_0$ states, which are coupled by significant spin-orbital interaction and diabatically correlated with the Cl-fragment in ground and spin-orbit excited state, respectively. The molecule fragmentation is triggered by 193 nm excitation followed by resonantly enhanced ionization probe pulse to detect the ground or spin-orbit excited Cl-fragments. The energy-resolved distributions show that Cl-fragment kinetic energy is almost independent on the paternal molecule and that around 50% of the available energy after photodissociation is stored in inner modes of hydrocarbon fragment compared to only 10% in the case of CH_3Cl. This agrees well with both MD simulations and classical spectator model, which assumes low rigidity of investigated molecules. The angle-resolved distributions of Cl fragments combined with quantum yield ratio of Cl*/Cl fragments indicate according to model described in [2] enhanced spin-orbital coupling in A-band region correlated with hydrocarbon group prolongation. This leads to strong absorption to $^3Q_0$ state (15%) and over 60% probability of intersystem crossing between $^1Q_1$ and $^3Q_0$ states in both directions. These outcomes have impact on our future experiments with alkyl chlorides incorporated in water cluster environment mimicking the atmospheric aerosols.

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Oxidation reaction dynamics of aluminum atoms at low and hyperthermal collisional energy

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Using the time-sliced ion velocity imaging and crossed molecular beam apparatus, where the metal atomic beam can be generated with or without using buffer carrier gas, we studied the reaction dynamics of $Al(^2P)+O_2(X^3\Sigma^+)\rightarrow AlO(X^2\Sigma^+)+O(^3P_J)$ in the collision energy range of around 1.5 -20 kcal/mol. At a low collision energy of 1.45 kcal/mol, the Al atomic beam is generated by 532 nm laser ablation of the Al metal rod, carried out by Ar carrier gas to form a supersonic metal atomic beam, and then collides with O_2 molecular beam. The $AlO(X^2\Sigma^+)$ products can be rovibrational-state-selectively ionized via the (1+1) resonance enhanced multiphoton ionization through the intermediate state $D^2\Sigma^+$. The energetically allowed maximum rotational state N=53 of $AlO(X^2\Sigma^+, v=0)$ was detected along with the center of mass velocity almost zero from the $Al(^2P_{1/2})$ reactant. The high energy resolution at the low collisional energy in our setup allows us to distinguish the AlO products at high rotational level from the aluminum spin-orbit coupling states, i.e., $Al(^2P_{1/2})$ or $Al(^2P_{3/2})$ with an energy difference of 112 cm^{-1}. The product angular distributions characterized by the forward-backward peaks and the preference in the forward direction indicate the existence of AlO_2 complex with the lifetime comparable to its rotational period.

When no carrier gas is used and the laser ablation metal beam is directly sprayed into the reaction chamber, the ultra-fast aluminum atoms at 3000 m/s can be obtained. Under this condition, the oxidation reaction of aluminum atoms at the high collisional energy of 20.0 kcal/mol was studied. The observation with the strong backward-scattering angular distribution of AlO products indicates that the direct oxidation reaction occurs at low impact parameters.

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State-resolved spectroscopy and dynamics of large buffer-gas cooled molecules

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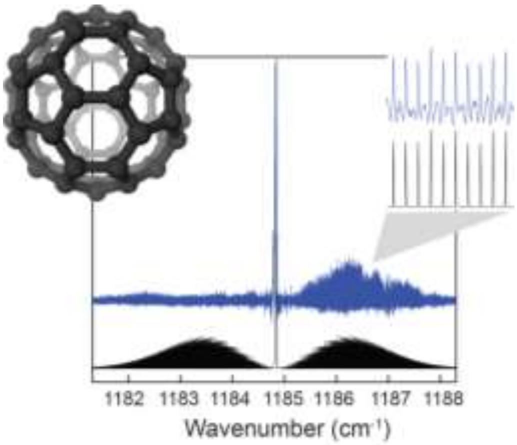
I will discuss my postdoctoral work in the Ye group at JILA/CU Boulder, harnessing mid-infrared frequency comb spectroscopy for precise interrogation of unprecedentedly large molecular species. Frequency combs are light sources consisting of thousands of evenly spaced, sharp frequency “teeth.” Cavity-enhanced frequency comb spectroscopy (CE-FCS) matches a comb’s evenly spaced spectral structure to the resonant modes of an optical cavity. This method allows for simultaneous detection of absorption signal across the comb spectrum, extremely high frequency resolution, and high sensitivity as the cavity enhances the interaction length between light and sample.[1] We combined buffer gas cooling of large molecules with CE-FCS in order to measure the rovibrational structure of buckminsterfullerene (C_{60}), a molecule of great fundamental and astrochemical interest and a longstanding spectroscopic challenge.

Our frequency comb measurements represent the first direct probe of the quantum state-resolved structure of C_{60} and establish it as by far the largest molecule for which a state-resolved spectrum has been reported.[2] We report characteristic nuclear spin statistical intensity patterns of C_{60}, as well as complex splittings of some rovibrational transitions caused by high-order centrifugal distortion. A detailed understanding of this fine structure demands a more sensitive spectroscopic measurement. We subsequently implemented a mid-IR quantum cascade laser spectrometer locked to a high-finesse cavity using optical feedback stabilization.



I will conclude by outlining the future research plans of the Weichman Lab, which launched this year in the Department of Chemistry at Princeton University. We will continue to push the boundaries of molecular spectroscopy using novel optical and cold molecule technologies for state-resolved characterization of systems of transitional size, on the brink of treatment with standard molecular tools. We are also very interested in the chemistry of polaritons, hybrid quantum states arising through strong light-matter interactions engineered inside optical cavities, which have great prospects for controlled reaction dynamics and photochemistry.

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Crossed-beam experiment of F+H_2 at collision energies down to 0.5 meV

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The reaction of F+H_2 is one of the most important reactions in the field of molecular reaction dynamics.[1] In the past decades, it has been serving as the benchmark reaction for dynamical resonances and Born-Oppenheimer (BO) approximation. Most of these experiments were carried out at collision energies above 5 meV, while some theoretical predictions have been made at lower collision energies.[2,3] To investigate the F+H_2 reaction at lower collision energies, we have developed two new techniques for the crossed-beam experiment. One is a new crossed beam machine with a small crossing angle and a multi-channel Rydberg tagging detection scheme.[4] The other is a slow and clean F atom beam source based on ultraviolet photolysis.[5] As a result, we are able to carry out crossed-beam experiments of the F+H_2 reaction at collision energies as low as 0.5 meV. In the preliminary study, significant signals were observed from the BO forbidden reaction of the spin-orbit excited F*($^2P_{1/2}$) atom with H_2, and notably, the contribution of the BO forbidden reaction to the overall reactivity in the backward scattering direction increases as the collision energy decreases. We believe the breakdown of BO approximation is due to the resonant-enhanced tunnelling of the BO forbidden reaction at low energies.[3]

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Part 2

Hot Topic Talks

(in alphabetical order, by speaker)

Hot Topic Talks List	
1	Amanda Alencar (*Universidade Federal do Rio de Janeiro, Brazil*) **Quantum State Preparation of H Atoms by Hyperfine Quenching**
2	Geetika Bhardwaj (*Tata Institute of Fundamental Research, India*) **Imaging atomically-thin thin films using neutral atom microscopy**
3	Bo-Jung Chen (*École Polytechnique Fédérale de Lausanne, Switzerland*) **State-to-state methane-surface scattering with bolometer infrared laser tagging (BILT) detection**
4	Baruch Margulis (*Weizmann Institute of Science, Israel*) **Direct Observation of a Feshbach-resonance by Coincidence-detection of Ions and Electrons in Penning Ionization Collisions**
5	Andriana Tsikritea (*University of Oxford & University of Liverpool, UK*) **Charge transfer reactions between polar molecules and rare gas ions**
6	Krystal Vo & Si Young Lee (*University of California, Santa Barbara, USA*) **UV Photodynamics of Thymine-Thymine Stacked Nucleobases in Peptide Nucleic Acids**
7	Xu-Dong Wang (*Radboud University, Netherlands*) **Cold and controlled inelastic and reactive collisions between C and O_2**

Quantum State Preparation of H Atoms by Hyperfine Quenching

Amanda Alencar,[1] Italo Prazeres,[1] Carlos R. de Carvalho,[1] François Impens,[1] Aline Medina,[1]
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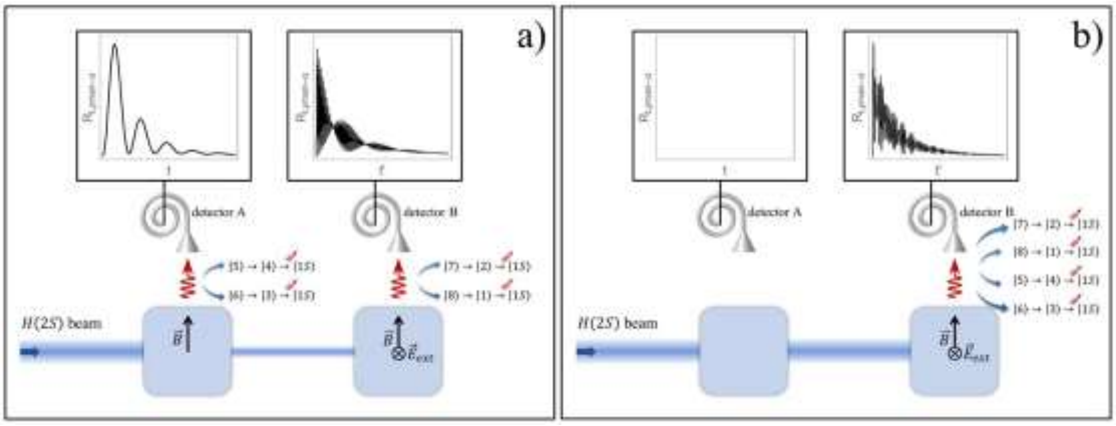
In the present work we discuss how a tuning of the metastable hydrogen energy levels by a uniform and constant magnetic field can enable the realization of a two-state polarizer for an H(2S) beam. [1] We have observed that a device with such field configuration can achieve an efficient polarization for a wide range of magnetic field intensities and atomic velocities. The role of the polarizer's magnetic field is twofold: it is used to tune the energy levels, as mentioned, and also to generate the commoving electric field responsible for shortening the lifetime of the metastable states, as shown in the references[2,3]. In addition, we establish a criterion that must be met to confirm a successful polarization. That is possible due to a specific beating pattern for the Lyman-α radiation expected for the outgoing two-state atomic beam.



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Imaging atomically-thin thin films using neutral atom microscopy

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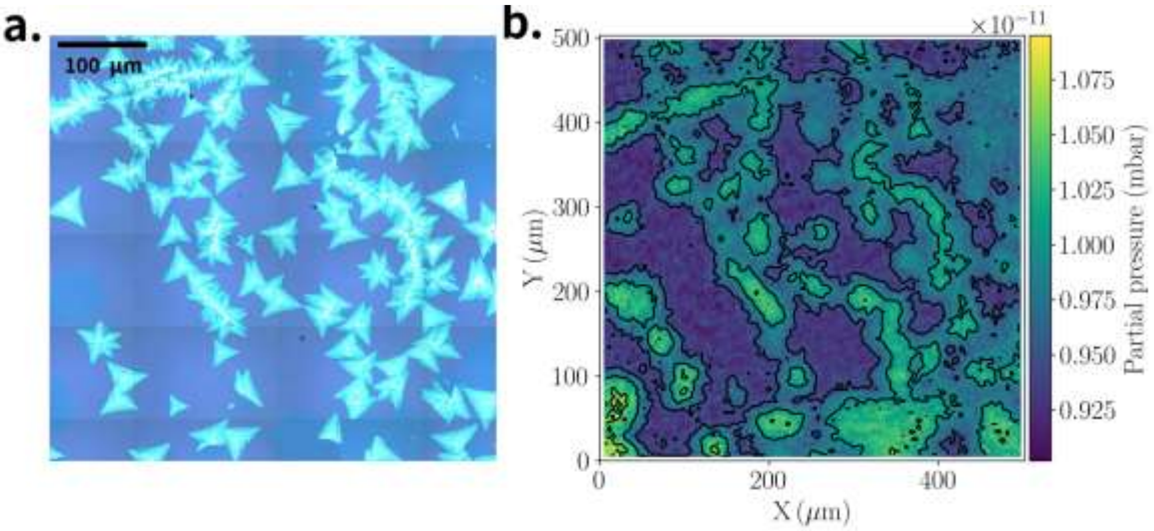
A relatively recent addition to the gamut of available microscopy techniques is based on scattering of low energy neutral atoms from surfaces and is referred to as 'Neutral Atom Microscopy' (NAM). Two key features of this microscopy are worth highlighting: Firstly, low kinetic energy (10 to 200 meV) of the incident neutral atoms used as probe makes it a soft and non-destructive probe for delicate surface structures. Secondly, owing to the neutral nature of incident atoms, conducting, insulating, magnetic, optically transparent, to name a few, can be probed directly without any elaborate sample preparation.

An interesting area that is largely unexplored is the applicability of NAM methods for imaging thin films, especially those made up of two dimensional materials. In this talk, I'll dig into the capability of this technique for imaging of thin MoS_2 films grown on SiO_2/Si substrate using our recently developed pin hole collimation based NAM apparatus. Presentation will include a detailed comparison of the NAM images[1] obtained using He atoms, optical microscopy in conjunction with Raman spectroscopy for sample characterization, to show that thin films of MoS_2, up to a single monolayer can be successfully imaged using NAM.



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State-to-state methane-surface scattering with bolometer infrared laser tagging (BILT) detection

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We introduce a novel, widely applicable, quantum-state-resolved detection technique for surface scattered molecules which combines state specific infrared laser tagging with highly sensitive detection by a cryogenic bolometer. We applied our BILT detection method to study methane scattering both from a catalytically active nickel surface and a nickel surface passivated by a single layer of graphene. We find that the vibrational state distribution of the scattered methane differs dramatically for the two surfaces[1]. Quantum mechanical inelastic scattering calculations show that these differences are related to the catalytic activity of the surface impact site. Our results demonstrate how inelastic scattering can be used to probe the reactive potential energy surfaces of molecule/metal systems important to heterogeneous catalysis.

To exploit the full potential of the BILT technique, we recently constructed a dedicated surface scattering machine optimized for BILT detection and equipped with a rotatable bolometer detector which allows for independent variation of the incident and the scattering angle. We used our new machine to record angular distributions of scattered CH_4 from a Ni(111) surface as function of incident energy and surface temperature and compare it to other scattered species such as Ne and CO_2. I will present first results obtained with our new BILT scattering machine.

Acknowledgments: This work was supported by the Swiss National Science Foundation.

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Direct Observation of a Feshbach-resonance by Coincidence-detection of Ions and Electrons in Penning Ionization Collisions

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Observation of molecular dynamics with quantum state resolution is one of the major challenges in molecular physics. Complete characterization of collision dynamics leads to the microscopic understanding and unraveling of different quantum phenomena such as scattering resonances. We present a new experimental approach for observing molecular dynamics involving neutral particles and ions. Our approach utilizes Penning ionization (PI) reaction as a preparation step of the ionic system with the energy of ejected electron serving as an indicator of the formed quantum state. The coincidence detection of momenta of PI products serves as a state-to-state detection of the post-ionization ion-neutral dynamics. For $He^*(^3S,^1S)+Ar$ PI reaction, we observe a Feshbach resonance arising from the coupling between an electronically excited bound $HeAr^+$ A_2 state to the scattering electronically ground $He + Ar(^3P_{1/2})$ state.

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Charge transfer reactions between polar molecules and rare gas ions

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Charge transfer reactions between NH_3 or ND_3 and ground-state Xe^+, Kr^+ and Ar^+ ions are studied within the cold and controlled environment of Ca^+ Coulomb crystals. Rate coefficients are experimentally calculated and are compared with capture theory models. The models' predictions overestimate the rate coefficients of all six reaction systems studied. Additionally, an inverse kinetic isotope effect (KIE) is observed; ND_3 reacts faster than NH_3. The magnitude of the KIE shows a dependence on the mass of the rare gas ion. Capture theories cannot account for the presence of the observed KIEs. Detailed *ab initio* calculations show no energetically-accessible crossing between the reactant and product potential energy curves; the mechanism responsible for electron transfer is not straightforward. We speculate that the properties of the reaction complex, such as its density of vibrational states and lifetime, play a role in the probability of product formation.[1,2]

Conversely, charge transfer reactions between water isotopologues (H_2O or D_2O) and ground-state Kr^+ ions, studied under similar conditions, do appear to be well-described by capture theory. Furthermore, no significant KIE is observed.

Astrochemical models often adopt capture theories to predict low-temperature reaction rate coefficients of experimentally unmeasured reactions. As such, accurately accounting for the reactivity of species such as small rare gas ions and polar molecules (the charge transfer reactant species are known to be present in the interstellar medium) is important. Our work suggests that capture theories do not consistently describe the reactivity of ion-molecule systems. Further work is needed to establish when capture theories can be confidently utilised.

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UV Photodynamics of Thymine-Thymine Stacked Nucleobases in Peptide Nucleic Acids

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Biological nucleobases exhibit sub picosecond excited state lifetimes, preventing potential damage from UV radiation and suggesting photochemical selection of the building blocks of life on a prebiotic earth. This intrinsic property shifts when as nucleobases are complexed with a sugar moiety or paired with another base, as changes to their electronic energies provide alternative decay pathways. For example, stacked bases are known in solution to exhibit an ultrafast exciplex formation channel, which safely decays to the ground state via charge recombination in the order of 100 picoseconds. We explore stacking effects in the gas phase by probing the excited state dynamics of two stacked homodimers: guanine-guanine (G-G) and thymine-thymine (T-T) bound to peptide nucleic acid (PNA), an analog of the negatively charged backbone of DNA. Laser desorption jet cooling coupled with resonance enhanced multiphoton ionization (REMPI) allows us to survey detailed stacking interactions in the gas phase in conjunction with theoretical calculations. We measured excited state lifetimes from picosecond pump-probe measurements, finding a lifetime in the order of 100 nanoseconds for T-T PNA. IR-UV double resonance spectroscopy revealed the diketo tautomeric form of T-T PNA. . We conclude that in the absence of solvent an excimer decay channel is unavailable in isolated T-T PNA suggesting that solvation may be necessary for stabilization of base stacking.

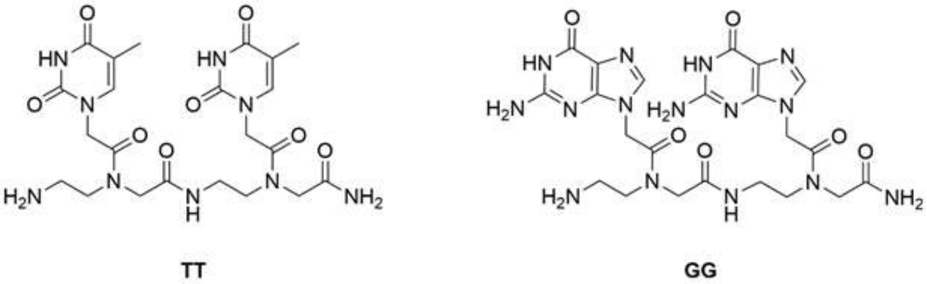

Figure: Structure of thymine-thymine (TT) and guanine-guanine (GG) peptide nucleic acid homodimers.

Acknowledgments: This work was supported by the National Science Foundation

Cold and controlled inelastic and reactive collisions between C and O_2

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Studies of cold inelastic and reactive collisions open many new possibilities to study the most fundamental aspects of molecular interactions and bring the goal of manipulating chemical reactions within reach. For the $C(^3P) + O_2$ system there has, on the one hand, been considerable interest in the nonadiabatic dynamics of collision-induced fine-structure (de-) excitation. On the other hand, reactions involving this system have attracted special interest because of their importance in interstellar chemistry.

We use a multistage Zeeman decelerator to prepare beams of chemically relevant species with a magnetic dipole moment (such as carbon and oxygen atoms) with small spatial and angular spreads and almost perfect quantum state purity.[1,2] These controlled beams in combination with a small beam intersection angle offer us an opportunity to investigate scattering processes in high detail and in unexplored energy regimes. Detecting the collision products with velocity map imaging and 1+1' (VUV + UV) near-threshold resonance-enhanced multiphoton ionization allows high-resolution measurements of differential cross sections. Here, we will present the dynamics of state-to-state inelastic collisions between carbon atoms and oxygen molecules at low temperatures. In the future, we will use our powerful combination of experimental technologies to investigate reactive collisions of C and O_2, forming CO and O.

Acknowledgments: This work has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Program (grant agreement No. 817947 FICOMOL), and from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 886046 and 889328.

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Part 3

Posters

(in alphabetical order, by presenter)

	Posters List
1	**Single color isomer-resolved spectroscopy** Presenter: Grite L. Abma (*Radboud University, Netherlands*) Poster type: PDF
2	**Solvation dynamics of the excited DABCO molecule deposited on an argon cluster** Presenter: Slim Awali (Université Paris-Saclay, France) Poster type: VIDEO
3	**Size- and Time-Resolved Electron Solvation Following Below Band Gap Photoexcitation of Neutral Water Clusters** Presenter: Loren Ban (*ETH Zürich, Switzerland*) Poster type: Not presented
4	**Sticking probability of ammonia on tungsten and 316L stainless steel** Presenter: Regis Bisson (*Aix-Marseille Université, France*) Poster type: PDF
5	**Hybrid electrostatic ion beam trap (HEIBT): Towards merged beam experiments** Presenter: Alon Bogot (*The Hebrew University of Jerusalem, Israel*) Poster type: PDF
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7	**Magnetic Manipulation of Rotational Orientation Projection States in Ground State Molecules** Presenter: Helen Chadwick (*Swansea University, UK*) Poster type: PDF
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12	**Coulomb Explosion Imaging of Methyl Iodide** Presenter: Lingfeng Ge (*University of Bristol, UK*) Poster type: PDF
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15	**Reflectron Time-of-Flight Mass Spectrometer with Improved Convergence of an Ion Beam** Presenter: Takefumi Handa (*Kyushu University, Japan*) Poster type: PDF
16	**Potential energy surfaces of LiH_2^+ for singlet and triplet states and quasiclassical trajectory study of LiH^+ + H and LiH + H^+** Presenter: Javier Hernández (*Univ. Autónoma de Madrid, Spain*) Poster type: PDF
17	**Buffer gas cooling, optical cycling and radiative deflection of AlF molecules** Presenter: Simon Hofsäss (*Fritz Haber Institute of the Max Planck Society, Germany*) Poster type: PDF
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23	**Time-resolved photoelectron imaging using hollow-core photonic crystal fibers and capillaries** Presenter: Nikoleta Kotsina (*Heriot-Watt University, UK*) Poster type: PDF
24	**Scattering resonances in cold ND_3-H_2 and ND_3-HD collisions: towards external field control** Presenter: Stach Kuijpers (*Radboud University, Netherlands*) Poster type: PDF
25	**High-resolution UV spectroscopy of 1-indanol** Presenter: JuHyeon Lee (*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*) Poster type: VIDEO
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27	**Revealing the complex network of PAH formation pathways** Presenter: Alexander K. Lemmens (*University of Amsterdam & Radboud University, Netherlands*) Poster type: VIDEO & PDF

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30	**Elucidating elementary steps of CO_2 hydrogenation over copper clusters with IR spectroscopy** Presenter: Olga V. Lushchikova (*Radboud University, Netherlands*) Poster type: PDF
31	**Crossed beams and theoretical study on two reactions relevant to Titan's atmosphere: $N(^2D)$ + propyne and $N(^2D)$ + allene** Presenter: Demian Marchione (*Università degli Studi di Perugia, Italy*) Poster type: PDF
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33	**Cryogenic ion trap to study cold and controlled ion-radical reactions** Presenter: Chloé Miossec (*University of Oxford & University of Liverpool, UK*) Poster type: PDF
34	**Femtosecond XUV-IR induced photodynamics in the methyl iodide cation** Presenter: Marta L. Murillo-Sánchez (*Universidad Complutense de Madrid, Spain*) Poster type: PDF
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36	**Total Integral Cross Sections and Potential Energy Surfaces from Molecular Beam Scattering Experiments on Propylene Oxide – He and Propylene Oxide – Ne** Presenter: Federico Palazzetti (Università degli Studi di Perugia, *Italy*) Poster type: VIDEO
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39	**Unraveling the Mechanism of the Electronic Quenching of NO ($A^2\Sigma^+$) with CO** Presenter: Andrew S. Petit (*California State University, Fullerton, USA*) Poster type: VIDEO
40	**High-resolution imaging of C-He and C-H_2 collisions using a Zeeman decelerator** Presenter: Vikram Plomp (*Radboud University, Netherlands*) Poster type: PDF

41	**Investigating the origin of coincident fragments from the H_2 molecule** Presenter: Italo Prazeres (*Universidade Federal do Rio de Janeiro, Brazil*) Poster type: VIDEO
42	**Predissociation dynamics of the $A^2\Sigma^+$ state of SH radical** Presenter: Yuan Qin (*University of California, Riverside, USA*) Poster type: PDF
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44	**Theoretical Study - Long Range on LiH_2** Presenter: Carolina Rio (*Universidade do Algarve, Portugal*) Poster type: PDF
45	**Stepwise Microhydration of Isoxazole: Infrared Spectroscopy of Isoxazole-$(Water)_{n\leq 2}$ Clusters in Helium Nanodroplets** Presenter: Tarun Kumar Roy (Ruhr-Universität Bochum, Germany) Poster type: PDF
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47	**Looking at the Bigger Picture: Photoproducts of Pyruvic Acid** Presenter: Bibek R. Samanta (University of Southern California, *USA*) Poster type: VIDEO
48	**VMI Photoelectron Spectroscopy Probing the Rotational Cooling Dynamics of Hot Trapped OH^- Ions** Presenter: Abhishek Shahi (*Weizmann Institute of Science, Israel*) Poster type: PDF
49	**Flash pyrolysis of 1,1,2,2-tetramethyldisilane: the role of tetramethyldisilene in the decomposition mechanism** Presenter: Kuanliang Shao (*University of California, Riverside, USA*) Poster type: PDF
50	**Imaging photodesorption from low temperature O_2 ice** Presenter: Zhongfa Sun (*Radboud University, Netherlands & Anhui Normal University, China*) Poster type: PDF
51	**Coriolis Coupled Dynamics of the $H(^2S) + CH+(X^1\Sigma^+)$ Reaction: A Full-Dimensional Quantum Wavepacket Study** Presenter: P. Sundaram (*Pondicherry University, India*) Poster type: PDF
52	**Methods for Accelerating the Prediction of Anharmonic Spectra of Cold Molecules and Clusters** Presenter: Daniel P. Tabor (*Texas A&M University, USA*) Poster type: Not Presented
53	**Fully quantum state resolved dipolar molecular collisions** Presenter: Guoqiang Tang (*Radboud University, Netherlands*) Poster type: PDF
54	**Towards the coherent control of Penning collisions between metastable helium atoms** Presenter: Alexandra Tsoukala (*University of Freiburg, Germany*) Poster type: Not Presented

55	**Coherent two-dimensional photoelectron spectroscopy** Presenter: Daniel Uhl (*University of Freiburg, Germany*) Poster type: PDF
56	**Probing for mode specificity in the chemisorption of CO_2 on H-Cu(111)** Presenter: Harmina Vejayan (*École Polytechnique Fédérale de Lausanne, Switzerland*) Poster type: PDF
57	**Conformationally selected polar Diels-Alder reactions in the gas phase** Presenter: Jia Wang (*Deutsches Elektronen-Synchrotron, Germany*) Poster type: VIDEO
58	**Kinetic and dynamic studies of the $O(^1D) + H_2O(X^1A_1)$ reaction** Presenter: Wenli Wang (*Universidade do Algarve, Portugal*) Poster type: PDF
59	**The Enolic Form of Curcumin Studied in Gas Phase** Presenter: Ann Williams (*University of California, Santa Barbara*) Poster type: Not presented
60	**Producing a Cold, Controlled Source of Radicals** Presenter: Lok Yiu Wu (*University of Oxford & University of Liverpool, UK*) Poster type: PDF
61	**Photoionization and photodissociation of furan by mass spectrometry and photoelectron imaging** Presenter: Yihui Yan (*Nanjing University of Information Science & Technology, China & Technical University of Munich, Germany*) Poster type: PDF
62	**Low-pressure yields of stabilized Criegee intermediates produced from ozonolysis of a series of alkenes** Presenter: Lei Yang (*University of California, Riverside*) Poster type: PDF
63	**Observation of a π-Type Dipole-Bound State in Molecular Anions** Presenter: Dao-Fu Yuan (*Brown University, USA*) Poster type: PDF
64	**High-dimensional quantum dynamics in OH(A)+H2 and H+CD4** Presenter: Bin Zhao (*University Bielefeld, Germany*) Poster type: VIDEO

Single color isomer-resolved spectroscopy

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Structural isomers, such as conformers or tautomers, are of significant importance across chemistry and biology, as they can have different functionalities. In gas-phase experiments using molecular beams, formation of many isomers cannot be prevented and their presence significantly complicates assignment of spectral lines. Current isomer-resolved spectroscopy techniques heavily rely on theoretical calculations or make use of elaborate double-resonance schemes. We show here that isomer-resolved spectroscopy can also be performed using a single laser wavelength. In particular, we demonstrate single-color isomer-resolved spectroscopy by utilizing electrostatic deflection to spatially separate the isomers. We show that for 3-aminophenol we can spatially separate the *cis* and *trans* conformers and use these pure samples to perform high-resolution REMPI spectroscopy, making the assignment of all transitions to an isomer trivial, without any additional *a priori* information. We further demonstrate that we can gain isomer-resolved spectroscopic insight about the corresponding cation through photoelectron imaging by detecting the photoelectrons from the REMPI process. The combination of these approaches enables isomer-resolved ultrafast electronic relaxation measurements through isomer- and time-resolved photoelectron imaging.

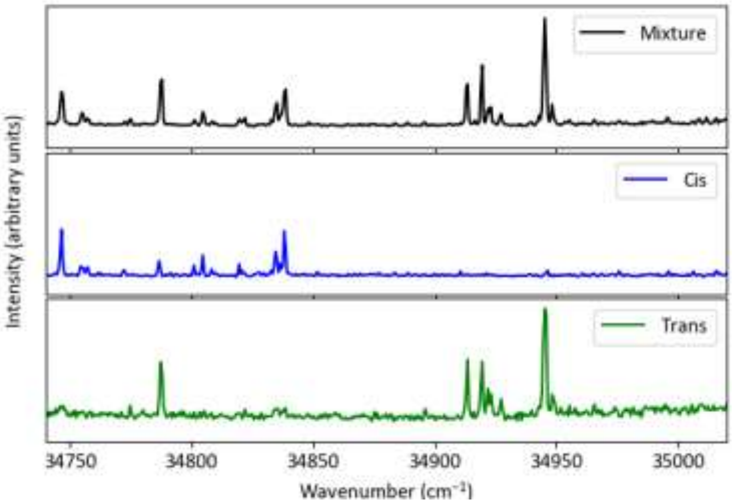

Figure1: REMPI spectroscopy of 3-aminophenol performed in a conventional molecular beam (top), and for pure cis (middle) and pure trans (bottom) samples obtained by electrostatic deflection.

Acknowledgments: This work was supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO), as well as the Spectroscopy of Cold Molecules Department and the Institute for Molecules and Materials at Radboud University Nijmegen.

Solvation dynamics of the excited DABCO molecule deposited on an argon cluster

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Observing the spectroscopy and the dynamics of a species in interaction with a cluster is a method of choice to study energy relaxation in guest-host systems following guest excitation. Of particular interest is the situation where a small guest exchanges electronic, kinetic and vibrational energy with a host having many degrees of freedom (the cluster). We investigate here the photo-induced dynamics of the DABCO molecule bound to an argon cluster. The DABCO molecule was chosen because it has a very long excited lifetime when isolated.

This allowed us studying a multiscale dynamics ranging from a rapid solvation dynamics (**4 ps** time scale) **[1]** to a thermalization dynamics occurring in a much longer time **[2].**

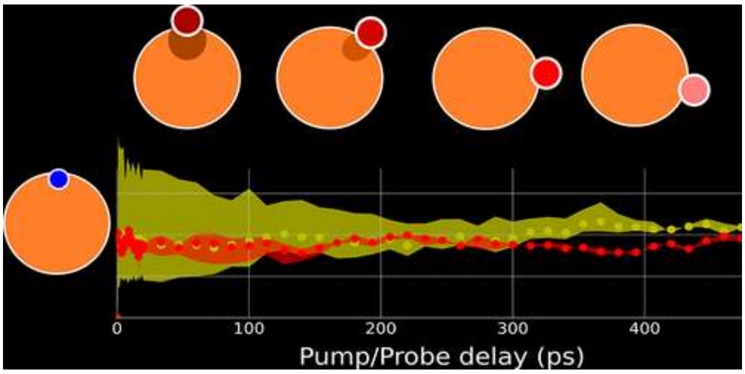

Figure 1: scheme of the DABCO relaxation dynamics deposited on argon cluster.

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Size- and Time-Resolved Electron Solvation Following Below Band Gap Photoexcitation of Neutral Water Clusters

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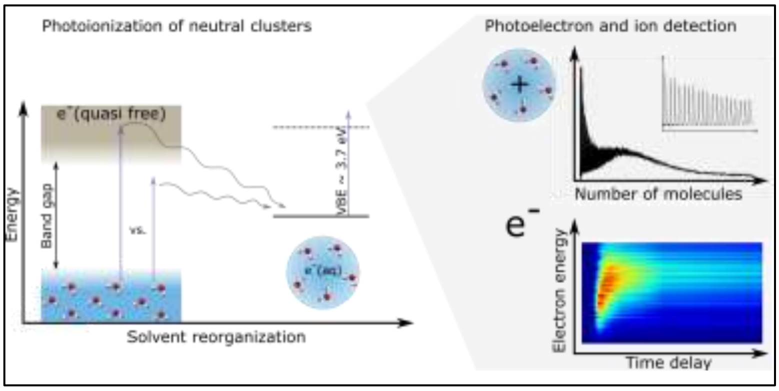
Recent time-resolved photoelectron studies on electron solvation upon direct photoexcitation of water allowed for a direct comparison between neutral water clusters[1,2,3] and water liquid jet[4]. Observed relaxation timescales are essentially independent of the aqueous environment (clusters vs. bulk) and the excitation energy[1]. However, some questions regarding the formation mechanism and dynamics remain open.

In this contribution, we build upon the abovementioned studies and present an experiment to further investigate electron solvation following below band gap excitation. The hydrated electron is formed by photoexcitation of neutral water clusters ($(H_2O)_n$ with $n < 200$ molecules) with femtosecond laser pulses of 7.8 eV photon energy from high-harmonic generation. The subsequent relaxation dynamics are probed with laser pulses of 4.7 eV by means of pump-probe mass spectrometry. In this way, we obtain time-dependent yields of ions which originate from photoionization of the hydrated electron. From this we infer size-resolved information on hydrated electron formation and relaxation dynamics. Combining these results with the time-dependent photoelectron study[1], we will discuss the current understanding of electron solvation following below band gap excitation of water.



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Sticking probability of ammonia on tungsten and 316L stainless steel

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Ammonia production has been observed in fusion reactors when nitrogen is injected at the edge plasma to maintain power fluxes to plasma facing components within tolerable limits. The international experimental reactor ITER, under construction in France, will use a deuterium-tritium mix to obtain an energy gain from the fusion plasma. Tritium is radioactive and nuclear safety regulation imposes a stringent control of tritiated species within the reactor. It is thus necessary to understand where tritiated ammonia will stick on the reactor vessel, which is made of tungsten and stainless steel.

In this contribution, we exposed tungsten and 316L stainless steel samples to a supersonic molecular beam of ammonia. Using the King & Wells method, we measured the evolution of the sticking probability with the ammonia surface coverage, the samples temperature and the ammonia kinetic energy. We observe similar sticking features on both surfaces, consistent with a non-dissociative adsorption mediated by two precursors.

First, the initial sticking probability decreases with increase in the surface temperature. Second, the sticking probability increases with the surface coverage up to near-saturation coverage, where it declines. Both features cannot be described together with the Kisliuk model (intrinsic + extrinsic precursors with identical trapping probabilities) or the modified Kisliuk model (direct adsorption + extrinsic precursor). Thus, we derive a generalized and separable Kisliuk (GSK) model that is able to reproduce quantitatively these two experimental observations thanks to intrinsic and extrinsic precursors having different trapping probabilities. Finally, we measure that the sticking probability does not decline to zero, i.e., steady-state sticking is observed that is consistent with NH_3 multilayer adsorption and can be reproduced with a zeroth-order desorption from the edge of NH_3 islands in the multilayer regime. These experimental results and their fitting with the GSK and the multilayer models offer the starting point to a predictive determination of the fusion fuel inventory related to ammonia sticking on the metallic vessel of the international experimental reactor ITER.

Acknowledgments: The views and opinions expressed herein do not necessarily reflect those of the ITER Organization. ITER is the Nuclear Facility INB no. 174. This paper applies new physics analysis related to tritiated ammonia formation, which is not yet incorporated into the ITER technical baseline. The nuclear operator is not constrained by the results presented here.

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Hybrid electrostatic ion beam trap (HEIBT): Towards merged beam experiments.

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Trapping of fast ion beams between two electrostatic mirrors offers many experimental advantages for the study of atomic, molecular and cluster ions.[1,2] The Hybrid Electrostatic Ion Beam Trap (HEIBT) expands the field of ion trapping by introducing a "dichroic" electrostatic mirror, which can reflect a fast ion beam while transmitting a counterion beam through the mirror.[3] We present the HEIBT design that implements such dichroic mirrors for simultaneous trapping of velocity matched, merged cation and anion beams. The planned mutual neutralization studies in low energy collisions, SIMION simulations and experimental trapping tests "through the counter-ion electrostatic mirror" will be reported.

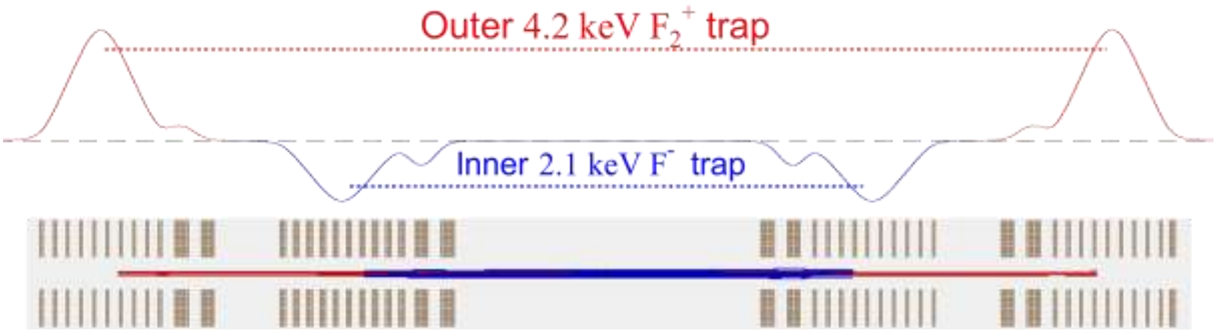

Figure: Potential energy landscape along the HEIBT optical axis, optimized for trapping velocity matched F2+ cations and F- anions.

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Towards cold ammonia collisions

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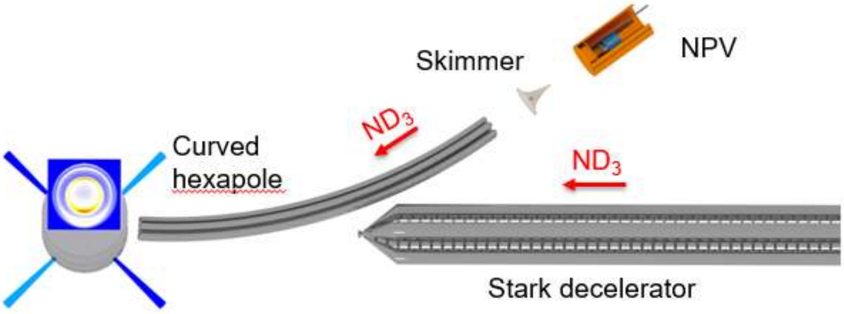
In the last decade, big steps have been made towards probing and understanding atom-molecule and molecule-molecule collisions with the highest possible resolution[1]. The collisions of our interest are between two dipoles, because the anisotropic and long-range nature of dipole-dipole interaction allows for interesting collision phenomena. These phenomena are most pronounced for (ultra)cold collisions, where the interaction energy and collision energy become similar in magnitude. Dipolar systems are thought to be relevant for quantum information processing applications, such as in an optical dipole lattice[2].

In our lab in Nijmegen, we run a merged-beam collision machine. One of the two molecular beams, created by home-made NPV's[3], passes a Stark decelerator and merges with the other beam bending through a curved hexapole. This experimental set-up allows us to reach collision energies down to 10mK. Preliminary measurements of ND_3-ND_3 collisions at various collision energies have shown that the signal is highly forward scattered. Due to a reprojection of the M-states of the low-field-seeking |JK> = |11> level of ND_3 in zero field conditions in combination with hexapole deflection, we currently see both M-levels at different spots on our VMI detector, hindering us to conduct collision experiments in the cleanest fashion.



Acknowledgments: This work is part of the research program of the Netherlands Organization for Scientific Research (NWO), and supported by the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Program (Grant Agreement No. 817947 FICOMOL).

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Magnetic Manipulation of Rotational Orientation Projection States in Ground State Molecules

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The most detailed insights into collisions at a molecular level are provided by quantum state resolved experiments, as they remove the averaging over the many degrees of freedom that can influence the outcome of the collision. One quantum state that was particularly difficult to control for ground state molecules is the rotational orientation projection (m_J) state. This limitation has recently been overcome, with the development of a magnetic manipulation technique[1] which has made it possible to coherently control the m_J (and nuclear spin projection, m_I) states of small ground state molecules. The unique methodology will be presented, and results shown for the control of the projection states for both ground state H_2 and D_2 molecules. Simulations of the experiments will also be described, and shown to reproduce the measured signals, demonstrating that the coherent evolution of the projection states can be modelled accurately. This technique opens the possibility of exploring the role of nuclear spin and rotational orientation projection states in both gas-phase and gas-surface[2] scattering, potentially for a range of small ground state molecules, which will provide extremely stringent benchmarks which can be used to develop accurate theoretical models.

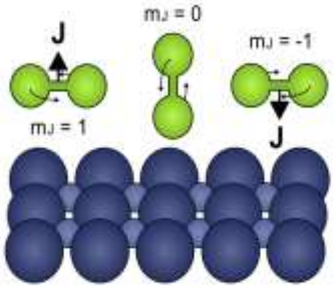

Figure: Rotational orientation projection states describe (classically) whether the molecule is rotating like a helicopter or a cartwheel.

Acknowledgments: This work was supported by the Horizon 2020 Research and Innovation Programme Grant Number 772228.

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The design and construction of a near-ambient pressure velocity-mapping imaging apparatus

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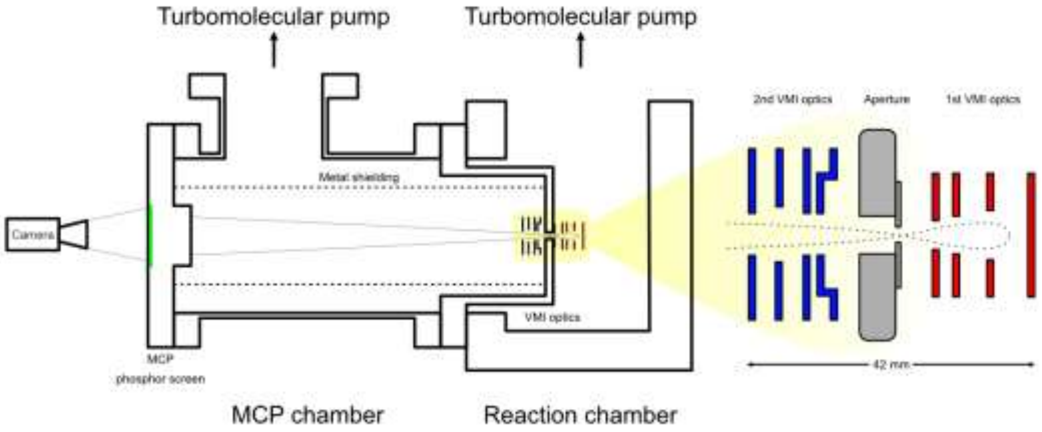
We present a new velocity-map imaging[1] system that can be used to study processes occurring at near-ambient pressure. The required differential pumping between ionization and detector regions is achieved by the addition of a small aperture. Ions are guided to a hard focus at the aperture by the extraction optics before being velocity mapped by a second set of electrodes. VMI and DC slicing[2,3] at pressures up to 8×10^{-4} mbar are demonstrated for photodissociation of N_2O.[4] The use of a smaller aperture and/or additional differential pumping will allow even higher pressures. This system is being developed as part of a molecular beam surface scattering instrument, but the technique may be applied in a range of other areas where higher pressures are either interesting or unavoidable, e.g. with liquid jets and surfaces.



Schematic of near-ambient pressure velocity-mapping imaging apparatus.

Acknowledgments: This work is supported by the Swedish Foundation for Strategic Research (ITM17-0236)

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Design of de Laval nozzles for gas-phase molecular studies at very low temperature in uniform supersonic flow

Olivier Durif

We present a program to design a Laval nozzle to generate uniform supersonic flows for gas-phase molecular studies at very low temperature. It is based on a code written in the 80's at the former aerodynamic laboratory of Meudon, France. Its implements the calculation of an isentropic kernel following the method of supersonic nozzle design for rarefied gas flows developed by Owen and correcting the turbulent boundary layer following the Michel integral method. This approach has already largely shown its potency and has been widely used for 30 years in the field of experimental molecular physics or laboratory astrophysics (sometimes known under the french acronym CRESU for *Cinetique de Réaction en Écoulement Supersonique Uniforme)*. Until now, such a program to design de Laval nozzle has never been published.

Proton in a double-well potential: acetylacetone derivatives by microwave and core level spectroscopy

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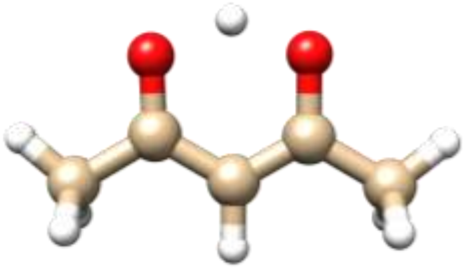
The extended nature of the proton wave function, the shape of the ground and final state potentials in which the proton is located has been investigated in gaseous acetylacetone and three of its derivatives, benzoylacetone, dibenzoylmethane [1] and 3,5-heptanedione by quantum chemical calculations, microwave spectroscopy and core level photoemission study. These molecules show intramolecular hydrogen bonds, in which a proton is located in a double well potential, whose barrier height is different for the four compounds, allowing us to examine the effect of the shape of double well on photoemission and rotational spectra. For all of them, two distinct O 1s core hole peaks are observed, previously assigned to two chemical states of oxygen in the ground state. We provide an alternative assignment by taking full account of the finite temperature of the samples based on quantum chemical calculations and symmetry consideration.



Acknowledgments: This work was supported by University of Bologna.

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Quasiclassical trajectory study of the dynamics of the $O + D_2^+ \longrightarrow OD^+ + D$ gas phase reaction

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The ground potential energy surface ($1^2A''$ PES) of the selected system correlates with H_2O^+(X^2B_1) and the first excited one ($1^2A'$ PES) correlates with H_2O^+(1^2P_u), and both PESs become degenerate in $D_{\infty h}$ symmetry.[1] Besides, the $O(^3P) + H_2^+$ reaction is related with other interesting ionic systems as, e.g., the $X + H_2^+$ (see, e.g., He, Ne, Ar + H_2^+)[2] and $O^+(^4S) + H_2$ [3] reactions. The $O + H_2^+$ system can lead adiabatically to proton transfer ($OH^+ + H$) on the ground PES and to hydrogen atom transfer ($OH + H^+$) on the first excited PES, with both PESs being barrierless [$O(^3P) + H_2 \longrightarrow OH^+ + H$, ΔD_o=-2.44 eV (1); $O(^3P) + H_2 \longrightarrow OH + H$, ΔD_o=-1.741 eV (2)]. The analytical PESs, dynamics and kinetics of this system have been investigated quite recently for the first time, using the multireference configuration interaction (MRCI) *ab initio* method[1] and the quasiclassical trajectory (QCT)[1,4] and the quantum coupled-channel time dependent real wave packet (RWP-CC)[5] methods. Moreover, the influence of the nonadiabatic Renner-Teller effect, which couples the $1^2A''$ and $1^2A'$ PESs for geometries not far from collinearity, has also been analyzed.[5] Here, we have compared the theoretical QCT results with crossed molecular beams measurements on $O + D_2^+ \longrightarrow OD^+ + D$,[6] where D_2^+ was produced following a Franck-Condon vibrational states distribution and the collision energy range (E_{col}) between 0.002 and 10.1 eV was explored. The QCT integral cross sections (ICSs) agree well with the experimental data in a wide E_{col} interval (0.4-5.0 eV) if relative units are used. The QCT products relative translational energy distributions ($P(E_T')$) are rather similar to the experimental ones until around 0.96 eV; and the QCT differential cross sections (DCSs) show a similar shape as the experimental DCSs but the last ones are clearly more forward.

Acknowledgments: This work was supported by the Spanish Ministry of Science, Innovation and Universities (MDM-2017-0767). Some support was provided by the Autonomous Government of Catalonia (2017SGR 348).

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Coulomb Explosion Imaging of Methyl Iodide

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Coulomb explosion experiments have been performed using ultrashort (40 fs) 805 nm strong laser fields on a jet-cooled CH_3I molecular beam. Mass spectra were recorded with TOF mass spectrometry, and ion images were recorded with velocity map imaging. When the peak intensity of the laser field reached 1300 TW cm^{-2}, a range of I^{q+} ions, with q up to 6, were observed. Simulations of Coulomb explosion dynamics of CH_3I^{Z+} were also performed, with $Z = 2 – 14$. Trajectories of ion fragments were simulated step by step, each step (0.1 fs) involving an ab initio calculation of the electronic structure followed by a classical propagation. The simulated recoil velocities of I^{q+} ions ($q = 1 – 6$) have been compared with the observed ones, and some interesting mismatches between them were found. This poster will show you these mismatches and the nonadiabatic model that could potentially explain the mismatches.

Influence of the nanodroplet size, interaction potential and vibrational energy gap on the vibrational relaxation of diatomic molecules in superfluid helium nanodroplets

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The vibrational energy relaxation (VER) of a homonuclear diatomic molecule in a ^{4}He superfluid nanodroplet (HeND; T=0.37 K) was studied using a hybrid quantum approach proposed by us.[1,2,3,4] This work extends a previous contribution of our own on the VER of I_2(X) in HeNDs,[3] and corresponds to the second theoretical investigation reported so far on this interesting problem. The VER from $\nu = 1$ to $\nu = 0$ of I_2(X) embedded in a 100 ^{4}He atoms nanodroplet is taken as reference system[3] and a number of hypothetical situations has been simulated, where variations in the number of HeND atoms (from 50 to 200 He atoms), He-I_2 interaction potential (from 0.5 to 1.5 times the real He-I_2 interaction potential energy) and energy gap between the I_2 vibrational levels (from 0.75 to 1.5 times the real I_2 energy gap) have been considered, in order to determine the influence of these three properties on VER. The size of the nanodroplet has none or little effect, as the first solvation shell, which plays a dominant role, is completely defined for all the HeND sizes examined. Moreover, vibrational relaxation becomes faster when the strength of the I_2-HeND interaction increases and this also happens when the $\nu = 1$-$\nu = 0$ energy gap decreases. The dependence of the relaxation time with the energy gap is linear, differing from what happens for the dependence with respect to the interaction potential, and both factors show a strong influence on VER. In spite of the simpler dependence observed in the former case its results are more difficult to rationalice than in the second case, where an almost linear dependence is obtained between the transition frequency (1/transition time) and the coupling term between the two vibrational levels ($<V_{01}^2>$). We hope that these results will encourage other researchers to study this interesting relaxation process about which we still know very little.

Acknowledgments: This work was supported by the Spanish Ministry of Science, Innovation and Universities (MDM-2017-0767). Some support was provided by the Autonomous Government of Catalonia (2017SGR 348).

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Nitric Oxide Scattering off Graphene using Surface-Velocity Map Imaging

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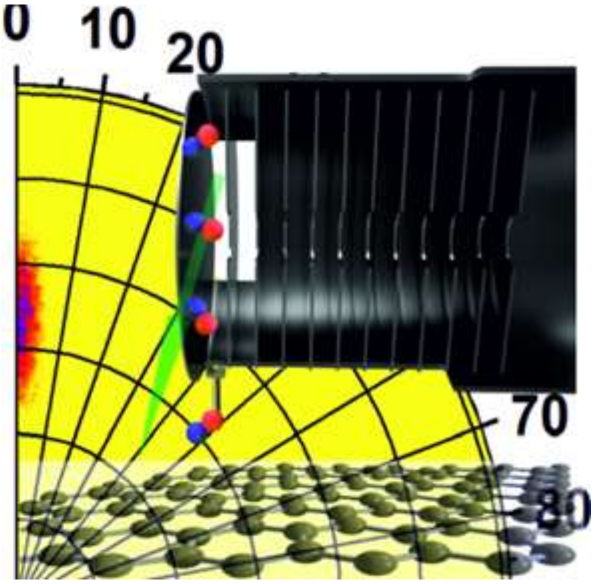
We investigated the scattering of nitric oxide, NO, off graphene supported on gold. We directed a molecular beam of NO in helium at 0° incidence angle onto graphene and detected the scattered molecules using surface-velocity map imaging. In contrast to previous scattering studies off graphite which detected only a modest reduction of the translational energy of the NO, we observe a loss of ~80% of the molecules' kinetic energy. Our accompanying classical molecular dynamics simulations do not agree quantitatively, but still predict a loss of ~60% of the translational energy in the scattering process. This energy appears to partly go into the NO rotations, but mostly into collective motion of the carbon atoms in the graphene sheet. We also observe a very narrow angular scattering distribution. Both findings may be unique to pristine graphene on gold as 1) the 2D honeycomb structure is perfectly flat, and 2) the graphene is only loosely held to the gold at a distance of 3.4 Å, thus it can absorb much of the projectiles' kinetic energy, much like a 'worn-out trampoline'. If time allows, results of on-going measurements of the internal energy distributions as a function of the translational energy of the scattered NO molecules will be presented.



Acknowledgments: We thank the Royal Society for funding (IEC\R2\181028).

Reflectron Time-of-Flight Mass Spectrometer with Improved Convergence of an Ion Beam

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A reflectron time-of-flight mass spectrometer (RTOF-MS)[1] is widely employed for mass analysis of various ions. As it is often supposed that analyte ions are generated in a small volume in the ion-extraction region, its performance is not optimized for ions spread over a large volume. Such a situation causes not only a degraded mass resolution but also significant divergence of an ion beam after it is reflected from an ion reflector. In our trajectory simulation by SIMION, a conventional gridless ion reflector[2] has the diverging nature, where ions with dispersed kinetic energies travel along different trajectories and are subject to a diverging lens effect upon leaving the reflector (Fig. 1). Therefore, ions that extremely spread over a large volume in the ion-extraction region could reach even out of the detector.

In the present study, we developed a novel ion reflector to overcome this problem.[3] The key finding in our simulation is that an ion beam converges by the electric field gradient at reflector's aperture if it passes through the center of the aperture. Our new ion reflector has two apertures for incoming and outgoing beams separately (Fig. 2). An eyeglasses-frame electrode was installed additionally at the very front of the ion reflector to further enhance the converging effect. The performance was examined both by ion trajectory simulations (Fig. 3) and by experiment. The experiment was performed on Ag_3^+ ions extracted from a volume of 6.3 cm^3, i.e., a cylinder with 20-mm length and 20-mm diameter. A two-dimensional image on an ion detector clearly displayed a converged ion beam with 9 mm in diameter. Mass resolution was evaluated as well, showing that isotopologues of Ag_3^+ are well resolved.

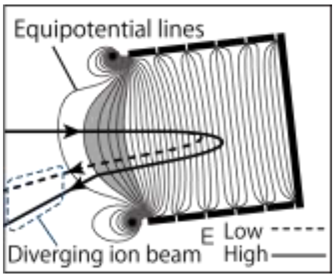

Fig.1: A cross-sectional view of a conventional ion reflector with calculated equipotential surfaces.

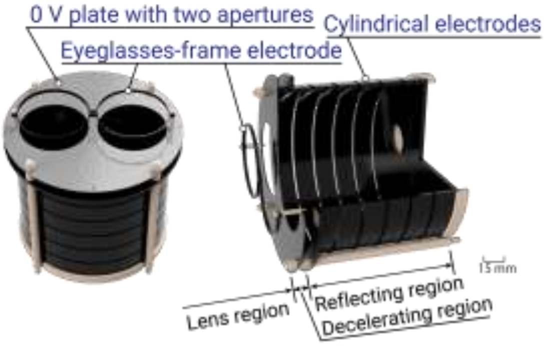

Fig.2: A rendered view of the newly designed ion reflector.

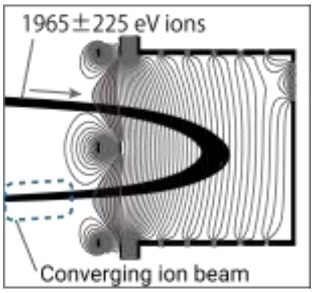

Fig.3: A cross-sectional view of our new ion reflector with calculated ion trajectories.

Acknowledgments: This work was supported by JSPS KAKENHI Grant Numbers JP18H03901 and JP21J21716.

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Potential energy surfaces of LiH_2^+ for singlet and triplet states and quasiclassical trajectory study of LiH^+ + H and LiH + H^+

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The lithium chemistry has been the subject of much attention, due to its relevance in the early universe, and, in particular, the LiH_2^+ system has been rather studied in the context of chemical reaction dynamics and kinetics; considering so far only the ground potential energy surface ($1^1A'$ PES) and the first excited singlet one ($2\ ^1A'$).[1-5]

Here, a new set of six accurate ab initio PESs is presented for the first three singlet and triplet states of LiH_2^+ ($1,2\ ^1A'$, $1\ ^1A''$, $1,2\ ^3A'$, $1\ ^3A''$). These states are relevant for the study of the reactions $Li^+ + H_2$, $Li + H_2^+$, $LiH^+ + H$ and $LiH + H^+$. More than 40,000 energy points have been calculated using the multi-reference configuration interaction (MRCI) level of theory using explicitly correlated methods, which provide a dramatic improvement of the basis set convergence. These points have been fitted to suitable analytical expressions.

Quasiclassical trajectory (QCT) calculations have been carried out on the PESs of the reactions $LiH^+(v=0,j=0) + H \longrightarrow Li^+ + H_2$ and $LiH(v=0,j=0) + H^+ \longrightarrow Li + H_2^+$ (where different electronic states are involved), in a rather wide collision energy interval (E_{col} up to 1.0 eV); and paying also attention to the other possible reaction channels (exchange and collision induced dissociation). The contribution of each channel to the reactivity depends on the PES and collision energy considered. These PESs will be useful for further QCT and quantum dynamics studies on the selected reactions and their reverse ones, which are in progress.

Acknowledgments: This work was supported by the Spanish Ministry of Science, Innovation and Universities under the grants: MDM-2017-0767 and FIS2017-83473-C2. Some support was provided by the Autonomous Government of Catalonia (2017SGR 348).

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Buffer gas cooling, optical cycling and radiative deflection of AlF molecules

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Aluminium monofluoride (AlF) is a promising candidate for a high-density magneto-optical trap (MOT) of molecules.[1,2,3] Here, we show that AlF can be produced efficiently in a bright, pulsed cryogenic buffer gas beam, and demonstrate rapid optical cycling on the Q rotational lines of the $A^1\Pi \leftrightarrow X^1\Sigma^+$ transition at 228nm.[1] We measure the brightness of the molecular beam to be $>10^{12}$ molecules per steradian per pulse in a single rotational state and present a new method to determine its velocity distribution accurately in a single molecular pulse. The photon scattering rate is measured using three different methods and compared to theoretical predictions of the optical Bloch equations and a rate equation model. An exceptionally high scattering rate of up to $42(7) \times 10^6$ s^{-1} can be sustained despite the large number of Zeeman sublevels (up to 216 for the Q(4) transition) involved in the optical cycle. We demonstrate that losses from the optical cycle due to vibrational branching to $X^1\Sigma^+$, v=1 can be addressed efficiently with a repump laser, allowing us to scatter about 10^4 photons using two lasers. Further, we investigate two other loss channels, photo-ionisation and parity mixing by stray electric fields. The upper bounds for these effects are sufficiently low to allow loading the molecules into a MOT.

Acknowledgments: This work was supported by ERC grant no. 949119.

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Imaging the vibrational predissociation of Ar-tagged protonated water clusters

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Infrared photodissociation of molecular clusters has been widely studied to investigate intra- and intermolecular vibrational relaxation processes. Here we report imaging experiments for vibrational predissociation of Ar-tagged protonated water monomer (H_3O^+-Ar) and dimer ($H^+(H_2O)_2$-Ar). The experiments are based on our own imaging apparatus designed for photodissociation of mass-selected ionic species.[1] In this study, H_3O^+-Ar and $H^+(H_2O)_2$-Ar were irradiated with a mid-infrared laser to excite one of the OH-stretching modes.[2] After Ar predissociation, resultant photofragment ions were observed as images to determine translational energy (E_t) distributions.

The E_t distributions are plotted against E_t fractions of total available energies (E_{avl}) as shown in Fig. 1. In H_3O^+-Ar, the E_t distribution for the *bound*-OH excitation was a broader one toward large E_t/E_{avl} as compared to that for the *free*-OH excitation. On the other hand, different features were found in $H^+(H_2O)_2$-Ar. First, the *bound*-OH excitation exhibited a smaller E_t fraction than that for H_3O^+-Ar, indicating a propensity for internal excitation in the photofragment $H^+(H_2O)_2$. Second, the E_t distribution for *bound*-OH excitation was almost identical to that for the *free*-OH excitation of the other H_2O molecule. Thus, mode dependence disappeared in the E_t distributions for $H^+(H_2O)_2$-Ar. These observed features are discussed in terms of energetics of vibrational modes of the photofragment ions.

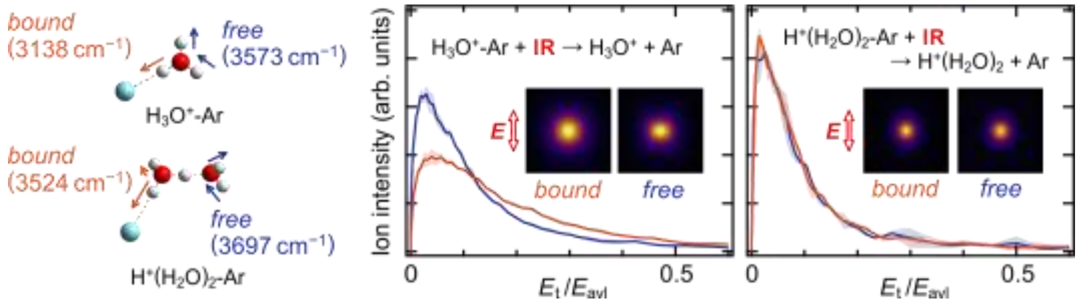

Figure 1: OH-stretching modes of H_3O^+-Ar and $H^+(H_2O)_2$-Ar (left), the corresponding ion images and the E_t distributions plotted against E_t/E_{avl} (right). ***E*** is a polarization direction of the dissociation laser.

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Vibrational Spectroscopy of Benzonitrile – (Water)$_{1-2}$ Clusters in Helium Droplets

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Author Contribution :[‖] Tarun Kumar Roy, and Kuntal Chatterjee contributed equally.

Polycyclic aromatic hydrocarbons (PAH) are considered as primary carriers of the unidentified interstellar bands (UIRs). Despite its ubiquity, any specific PAH molecule has not been observed in the interstellar medium (ISM). Recently, the Benzonitrile molecule is observed in the interstellar medium[1]. Therefore, the Benzonitrile molecule can act as a precursor for these PAH molecules. Herein, we report the microhydration of Benzonitrile using mass-selective infrared spectroscopy inside the helium nanodroplets. By comparison of the experimental spectra with the ab-initio calculation at MP2/6-311++G(d,p) level of theory reveals the formation of a local minimum structure, where the solvent water forms a nearly linear hydrogen bond (H-bond) with the nitrile nitrogen of Benzonitrile. The predicted most stable cyclic H-bonded isomer is not observed. This can be rationalized by the unique cluster growth condition that exists in helium droplets. Further, the addition of a second water molecule results in the formation of two different isomers. In one of the observed isomers, a H-bonded water chain linearly binds to the nitrile nitrogen similar to the monohydrated Benzonitrile-water complex. In the other observed isomer, the water dimer forms a ring-type structure, where a H-bonded water dimer simultaneously interacts with the nitrile nitrogen and the adjacent *ortho* CH group. Finally, we compare the water-binding motif in the neutral Benzonitrile-water complex with the corresponding positively and negatively charged Benzonitrile-water monohydrates to characterize the charge-induced alteration of the solvent binding motif.

Acknowledgments: This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy-EXC 2033-390677874-RESOLV.

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Detection of astrochemically relevant reaction products in skimmer sampled uniform supersonic flows using chirped-pulse Fourier transform mm-wave spectroscopy

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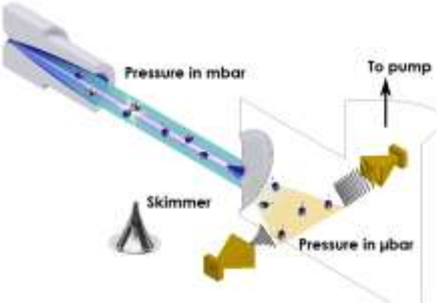
Numerous chemical processes take place in the interstellar medium, where temperatures go below 10 K. We are combining the CRESU (Reaction Kinetics in Uniform Supersonic Flow) technique[1] to provide a very low temperature flows with the chirped pulse Fourier transform mm-wave/microwave (CPFTMW) spectroscopic technique to study gas-phase collisional processes under the interstellar conditions. The objective is to determine the branching ratios of astrochemically relevant bimolecular reactions. Two CPFTMW spectrometers have been built in the Ka band (26.5-40 GHz)[2] and the E-band (60-90 GHz)[3]. While reaction products have been successfully detected at temperatures down to 10 K in continuous CRESU flows, the sensitivity of the CPFTMW technique is reduced by collisional broadening. Reducing the collisional frequency rate is critical, to achieve this aim, the high pressure CRESU flow is sampled via a skimmer to create an expansion into a much higher vacuum environment where both the temperature and pressure of the gas are lowered. This creates a nearly collision-free environment with favourable conditions for the detection of the molecular signal.



Chirped pulse in skimmer chamber

Acknowledgments: This work is supported by the European research council, the European Regional Development Fund, the Region of Brittany and Rennes Metropole.

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Dynamical Probes of NO ($A^2\Sigma^+$) Electronic Quenching with O_2 ($X^3\Sigma_g^-$)

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Nitric oxide (NO) radicals are prevalent in combustion and in the atmosphere, playing key roles in important chemical reaction pathways. Determination of fluorescence quantum yields using laser-induced fluorescence has been extensively used to quantify NO concentrations to monitor its sources and sinks. However, nonradiative electronic quenching of NO ($A^2\Sigma^+$) to NO ($X^2\Pi$) from atomic and molecular collision partners affects quantum yield measurements. While studies have primarily focused on atomic collisions, electronic quenching studies of NO ($A^2\Sigma^+$) with molecular partners are more rare. Results will be presented on the electronic quenching dynamics of NO ($A^2\Sigma^+$) with O_2 ($X^3\Sigma_g^-$) under single collisions using velocity map imaging.[1] The dynamical signatures imprinted on the product internal energies and relative recoil velocity arise from the NO-O_2 collision pair funneling through a conical intersection towards products. The formation of a collision complex and the non-statistical rovibronic levels populated report on the mechanism following electronic quenching.

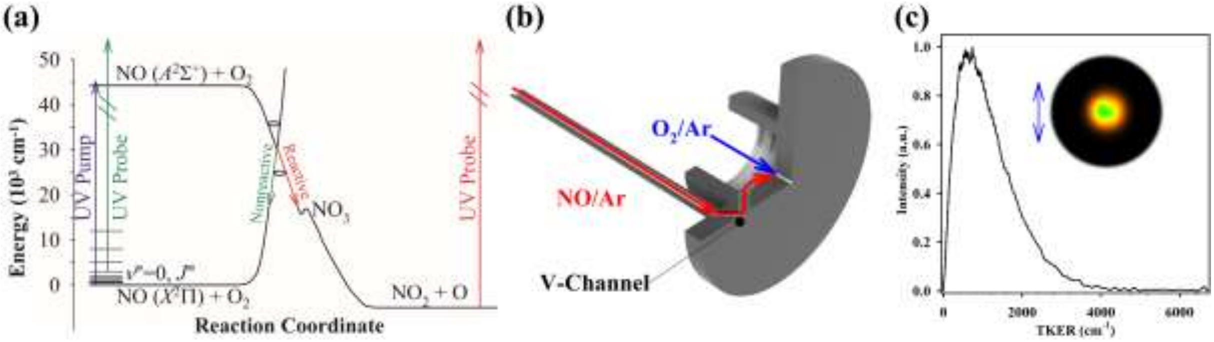

Figure 1: (a) Reaction coordinate for the electronic quenching of NO ($A^2\Sigma^+$) with O_2. (b) Dual-flow nozzle used to study the quenching dynamics, in which NO flows through a ‘v-channel’ and encounters O_2 at the valve exit. (c) NO ($X^2\Pi$) product ion imaging results from quenching.

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Formation of Metal Cluster Ion Beams Investigated by Mass Spectrometry and Optical Emission Spectroscopy

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Metal clusters, consisting of several to several hundreds of metal atoms, exhibit physical and chemical properties highly dependent on their size (the number of constituent atoms). A magnetron-sputtering cluster-ion source is one of the powerful tools to produce an intense metal-cluster ion beam.[1] It generates a large amount of metal atoms by sputtering a metal plate with an argon gas efficiently ionized by electrons confined in a magnetic field. The atoms and atomic ions are allowed to aggregate and grow into clusters by collision with a cold helium gas. The cluster ions thus generated are not monodispersed; various sizes coexist in a cluster-ion beam. The size distribution is dependent on parameters of the cluster source such as its discharge power, the gas flow rates, etc. Here we study the cluster-growth condition as well as the resulting size distribution by optical emission spectroscopy and mass spectrometry.[2]

An ion beam of silver clusters, Ag_n^+, was generated by magnetron sputtering. The emission spectrum of sputtered atoms, which are excited in the magnetron plasma, was recorded to monitor an amount of atoms in the cluster source. The beam was admitted into a quadrupole mass analyzer to measure a cluster-size distribution. These measurements were performed as a function of DC discharge power of the magnetron up to 12 W, while argon and helium gas flow rates were kept constant.

The size distribution, as measured by mass spectrometry, shifted toward larger clusters as the discharge power was raised, i.e., the maximum size was $n \sim 40$ at 6 W, while sizes over $n = 100$ were enhanced at 12 W. A statistical model explains the size shift to be a result of an increased atomic density of silver in the cluster source. On the other hand, the emission spectra give us an insight into the amount of silver atoms. Combining the information from mass and emission spectra, we were able to estimate the effective volume of the cluster-growth region, which was found to be enlarged as the discharge power was increased. This result suggests that one should keep the cluster-growth volume small even at high power for generating a large metal-cluster beams.

Acknowledgments: This work was supported by JSPS KAKENHI Grant Numbers JP18H03901 and JP21J12060.

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Time-resolved photoelectron imaging using hollow-core photonic crystal fibers and capillaries

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Time-resolved photoelectron imaging (TRPEI) is a highly differential technique for the detailed study of non-adiabatic energy redistribution dynamics operating in the electronically excited states of molecules following the absorption of ultraviolet light (UV) [1]. To utilise the technique to its full extent, minimizing the temporal duration of pump/probe pulses and the choice of probe wavelength is crucial. Ultrashort pulses ensure improved time-resolution and shorter wavelength probes offer extended views along the reaction coordinate, and thus both are highly desirable for TRPEI studies [2]. Rare-gas filled hollow-core photonic crystal fiber (HCPCF) and hollow capillary fiber (HCF) sources have been demonstrated to generate ultrashort (<10 fs), tunable (from visible to vacuum UV) light pulses with high efficiency in a compact bench-top configuration [3]. We will show the first demonstration of HC-PCF in TRPEI experiments on the molecule styrene [4], and present potential upgrades and improvements that may be achieved through the incorporation of HCF sources.

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Scattering resonances in cold ND_3-H_2 and ND_3-HD collisions: towards external field control

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Recently it has become possible to image differential cross sections of collisions between NO and He, state-to-state selectively and at energies *below* 1 K.[1] In this cold regime, the wavelike quantum nature of matter starts to dominate the collision process, leading to rich resonance behaviour that is directly observable as sharp increases in the cross section.

As a next step, we plan to add a level of control to these low-energy collisions by tuning scattering resonances using external electric fields. To this end, collisions involving ammonia are of great interest, as its large dipole moment makes it susceptible to electric fields.

However, two main hurdles remain. First, until now the limiting factor in performing low-energy collision experiments with ammonia has been its laser detection. Experimental images become blurred by the conventional 2+1 REMPI scheme at 317 nm as excess energy from the ionising photon transfers to the molecule as a randomly oriented recoil.[2] At small collision energies, this recoil largely exceeds the size of the image itself, hindering the observation of any structure. Second, to achieve a significant field interaction, the corresponding Stark shift should be comparable to the collision energy itself, on the order of 1 K. This calls for a newly designed velocity map imaging detector that is able to apply fields above 40 kV/cm, while maintaining good imaging resolution.

During this poster presentation, we will present our current results on scattering resonances in the zero-field integral cross section of ND_3-H_2 and ND_3-HD collisions. Furthermore, we will discuss our progress towards imaging differential cross sections for ammonia at high resolution and enabling external field control.

Acknowledgments: This work was supported by ERC and NWO

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High-resolution UV spectroscopy of 1-indanol

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Chiral alcohols are commonly used in the preparation of hormones, flavors, and fragrances. Moreover, they are important intermediates in the synthesis of many chiral medicines. During this talk I will focus on 1-indanol. This chiral alcohol is a relatively simple and rigid molecule composed of a phenyl ring fused with a 5-membered aliphatic ring. Recently, we have built an experimental apparatus that can perform both vibrationally resolved resonance-enhanced multiphoton ionization (REMPI) spectroscopy and high-resolution laser induced fluorescence (LIF) measurements under identical conditions, in a jet-cooled pulsed molecular beam. We recorded and understood the rotationally resolved LIF spectra of the $S_1 \leftarrow S_0$ origin band of the two most stable conformers as well as a transition to a vibrationally excited level in the S_1 state of the lowest energy conformer.[1] From the obtained molecular parameters, it was clear that upon excitation both conformers expand slightly along all three axes due the expansion of the aromatic ring. In addition, the high-resolution spectrum of Ne-eq1 complex was measured and the geometric structures in the S_0 and S_1 states will be discussed. Furthermore, the lifetimes of the S_1 state have been measured through two-color REMPI delay scan. To confirm the Lorentzian lifetime-contribution to the observed lineshapes, Lamb-dips were measured on selected rotationally resolved electronic transitions. I will discuss recent experimental results as well as details of our new experimental setup.

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Excited State Intramolecular Proton Transfer and Hydrogen Transfer in Indigo Dye

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Indigo is the dye that makes jeans blue. It was already used in several ancient cultures, and some of their artifacts retain their distinct blue color to this day. indigo thanks this tremendous photostability to ultrafast return to the ground state from the excited state. The photophysics of indigo can be very sensitive to its environment, and to understand the fundamental properties of the chromophore, we studied the intrinsic photodynamics of isolated indigo in the gas phase. Indigo was laser-desorbed, jet cooled. and studied with resonance enhanced multiphoton ionization (REMPI) spectroscopy. We performed IR double resonant spectroscopy to distinguish between tautomers and observed the di-keto tautomer in the molecular beam. We performed pump-probe measurements in the range from 60 ps to 24 ns to study deactivation processes in the excited state. We observed a barrier to relaxation of about 700 cm^{-1} , beyond which decay was dominated by fast excited state dynamics. Below this barrier we observed slow decay and, computation at the ADC(2)/MP2/cc-pVDZ level predicts two processes that compete with decay from the S_1 state. Both processes lead to tautomerization from the di-keto to the keto-enol form intramolecular proton transfer, occurring in the order of 1 nanosecond and intramolecular hydrogen transfer, occurring in the order of 10 nanosecond. Both cases undergo drastic charge distribution changes upon de-excitation. To further disentangle these pathways, we are now studying the effects of selective deuteration. This study may help in understanding the photostability of indigo dye and the remarkable long preservation of its rich blue color.

Acknowledgments: This work was supported by the National Science Foundation

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Revealing the complex network of PAH formation pathways

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Infrared signatures of polycyclic aromatic hydrocarbons (PAHs) are detected towards all phases of star and planet formation in the interstellar medium (ISM). As a result of their stability, they are expected to be a major player in the carbon chemistry of the ISM, thereby forming the connection between small hydrocarbons and large fullerenes.[1] However, there are still significant gaps in our knowledge regarding the formation and dissociation of PAHs in relevant environments.[2]

In our experiments, we incite gas-phase chemical reactions of PAHs with an electrical discharge in a molecular beam environment. The resulting complex mixture, consisting of newly formed molecules and fragments from the parent molecule, is then cooled down in a supersonic expansion. Subsequently, the product species composition and structures are elucidated with mass selective IR laser spectroscopy. The rapid cooling process and on-line probing enables us to identify not only PAH growth, but also shows the presence of radicals and intermediates.

Using either naphthalene[3] or benzene as a precursor, we reveal multiple reactions leading to PAH growth to occur collectively. The structural assignments, supported with quantum chemical calculations, allow for disentangling the complex and interconnected network of PAH formation pathways. The results of this study serve as a key ingredient for constructing reliable models that describe the carbon chemistry in our universe.

Pulsed discharge source with skimmer

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A Combined Crossed Molecular Beam and Theoretical Investigation of the CN ($X^2\Sigma^+$) + HCCCN and CN ($X^2\Sigma^+$) + H_2CCHCN Reactions and Astrophysical Implications

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CN is one of the most abundant and widespread radicals in the interstellar medium. The fast reactions between CN and unsaturated hydrocarbons generate various nitriles[1,2], including HC_3N and H_2CCHCN, which are alleged to be prebiotic molecules. HC_3N is ubiquitous in interstellar environments. Similarly, H_2CCHCN has also been detected in numerous objects, such as the dark cloud TMC-1, massive star-forming regions Sgr B2 and Orion KL, the circumstellar envelope of the C-rich star IRC +10216, and Titan's atmosphere. Because of the wide distribution of these species, it is interesting to explore if the reactivity of CN with HC_3N and H_2CCHCN can produce more complex nitriles. Kinetics studies confirmed that the rate constant for the CN($X^2\Sigma^+$) + HC_3N reaction increases rapidly as the temperature decreasing from 300 K to 22 K[3] while few studies have focused on the CN($X^2\Sigma^+$) + H_2CCHCN reaction. Furthermore, there are no experimental data on the reaction products and their branching ratios. Given these unsolved problems, it is essential to gain further insights into these elementary reactions, either experimentally or theoretically. In this contribution, I will illustrate the reaction mechanism of the CN($X^2\Sigma^+$) + HCCCN and CN($X^2\Sigma^+$) + H_2CCHCN reactions by combining crossed molecular beam experiments and electronic structure calculations. Rate coefficients have also been estimated at the temperatures of relevance in interstellar clouds. Our preliminary results reveal that in both cases the reactions proceed with the barrierless addition of CN to the unsaturated carbon-carbon bond leading to a bound intermediate, followed by the fission of a C-H bond to produce NCCCCN (from CN + HCCCN) or Z, E-NCCHCHCN and 1,1-dicyanoethylene (from CN + H_2CCHCN).

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Probing Molecular Growth, Interactions and Networks

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Our effort in molecular reactivity in complex systems is from two directions: molecular cluster chemistry and the growth of polycyclic aromatic hydrocarbons (PAH). The two projects are explored using synchrotron-based time-of-flight mass spectrometer, corroborated by theoretical calculation and modeling.

We have explored the behavior of gas-phase argon-acetylene clusters formed via weak van der Waals interactions and extracts their structural features to shed light on mechanisms of electronic excitation and concomitant energy transfer leading to ionization. The resemblance between the appearances of photoionization efficiency (PIE) curves of the $(C_2H_2)Ar_n$ ($n = 1 – 7$) clusters and the excitation spectra of Ar_n clusters are explained by Penning ionization. The growth of PAHs has been explored in collaboration with Ralf Kaiser (Hawaii) et al. The self-combination reaction of propargyl (C_3H_3) to benzene isomers (C_6H_6) was investigated in dilute environments. The branching ratios of C_6H_6 isomers are quantified experimentally and verified with the aid of *ab initio* calculations, fluid dynamics simulations and kinetic modeling. These results uncover valuable insights for a better understanding of the hydrocarbon chemistry of our universe.

We will continue the study of photo-induced reactivity of hydrogen-bonded clusters in the future, expecting to form different cluster and hydrogen-bonding networks. Another direction that is to study the molecular mechanisms of water evaporation within confined volumes and in mixtures.

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Elucidating elementary steps of CO_2 hydrogenation over copper clusters with IR spectroscopy

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The catalytic recycling of CO_2 to liquid fuels, such as methanol, may help to control the atmospheric CO_2 content. Methanol can be produced by the hydrogenation of CO_2. Although this reaction is thermodynamically favorable, the strong C-O and H-H bonds require the use of a catalyst to initiate the reaction. $Cu/ZnO/Al_2O_3$ catalysts have been the industrial standard, where recently nm-sized Cu particles have been identified as the active sites. A molecular-level understanding of the elementary steps of CO_2 hydrogenation is required for the rational design of an improved catalyst.

To get this knowledge, we study the interaction of CO_2 and H_2 with copper clusters as well-defined model systems with many under-coordinated adsorption sites. The structure of the formed complexes is investigated by a combination of infrared photodissociation spectroscopy and density functional theory calculations. We here present IR spectra of cationic Cu clusters reacted with H_2 and CO_2 individually, and with both together. We find evidence for H_2 dissociation, but CO_2 remains unactivated. In contrast, anionic Cu_nC^- show size-selective activation and dissociation of CO_2.

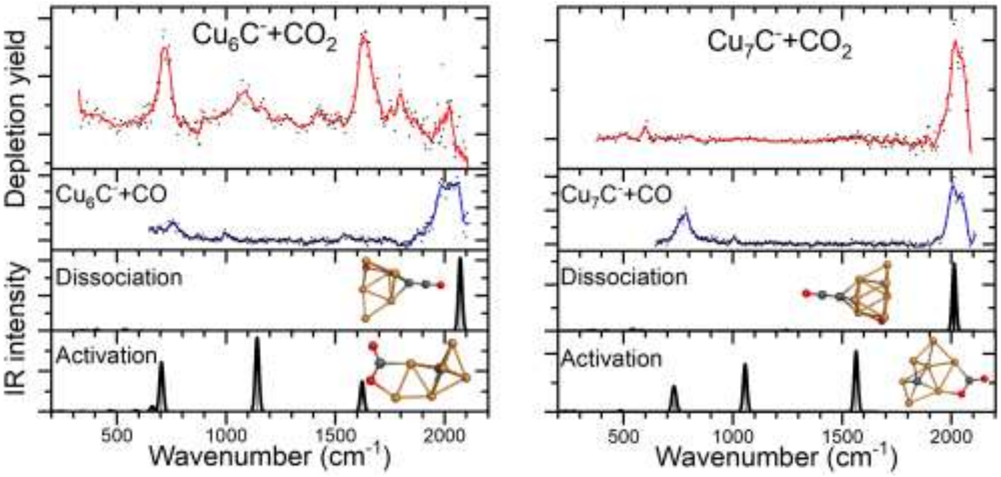

Figure: The IRMPD spectrum (red) of Cu_6C^-+ CO_2 in the left column compared to the reference IRMPD spectrum (blue) of Cu_6C^-+ CO and calculated spectra (black). The right column illustrates the same graphs for complexes with Cu_7C^-.

Crossed beams and theoretical study on two reactions relevant to Titan’s atmosphere: N(^{2}D) + propyne and N(^{2}D) + allene

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Several hydrocarbons, with formula CxHy, have been detected in the atmosphere of Titan.[1,2] These molecules are key to the abiotic nitrogen (N) fixation *via* gas-phase reactions. This rich chemistry, leading to a variety of N-containing organic species, is triggered by the dissociation of N_2 through energetic processes that seed the upper atmosphere of Saturn’s moon with a large reservoir of atomic N, both in the first excited ^{2}D and ground ^{4}S electronic states, and in its ionic form N^+.[3] Particularly, the N addition/H elimination reactive channels *via* neutral-neutral reactions lead to the formation of several isomers of the type C_3H_3N, including cyclic species as observed for similar reactions,[4] and vinyl cyanide (H_2CCHCN) which was mapped in Titan’s atmosphere and might form cell membranes/vesicle structures in Titan’s hydrocarbon-rich lakes and seas. [5,6]

The knowledge of the possible reaction products and how they form (reaction dynamics) is of utmost importance for astrochemical model as much as the values of rate constants (obtained from kinetic studies) are.

Within this context, we have investigated the N(^{2}D) + CH_3CCH (propyne) reaction and the N(^{2}D) + H_2CCCH_2 (allene) reaction by the crossed molecular beams (CMB) technique with mass spectrometric detection and time-of-flight analysis in combination with electronic structure calculations of stationary points and product energetics to elucidate the nature of the primary products and the micromechanism at play from the analysis of our data. Furthermore, RRKM statistical calculations were performed to derive the product branching ratios under the conditions of the present experiments and of the atmosphere of Titan. Astrophysical implications will be discussed.

Acknowledgments: This work was supported by the Italian Space Agency (DC-VUM-2017-034, Grant n° 2019-3 U.O Life in Space) and the Marie Sklodowska-Curie project ``Astro-Chemical Origins” (ACO), grant agreement No 811312.

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Resolving the F_2 Bond Energy Discrepancy Using Coincidence Ion Pair Production (Cipp) Spectroscopy

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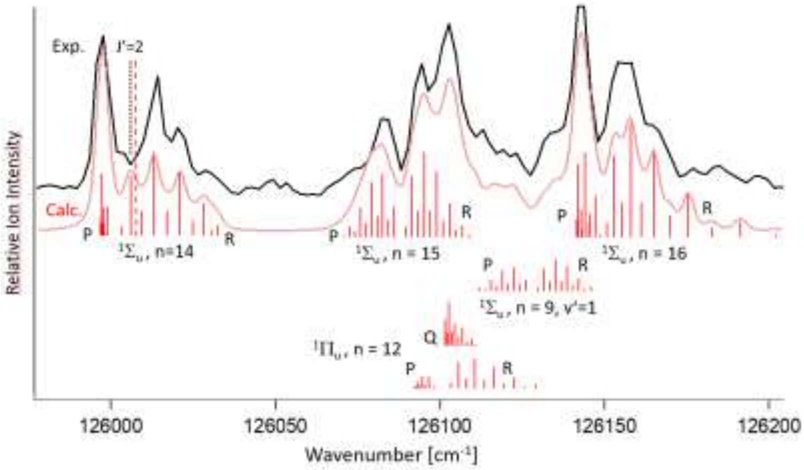
Cipp spectra of F_2 were recorded on the DELICIOUS III coincidence spectrometer[1] in the one-photon excitation region of 125 975–126 210 cm^{-1}. The $F^+ + F^-$ signal in this frequency range shows rotational band head structure, corresponding to F_2 Rydberg states crossing over to the ion pair production surface. Through a simulation of the spectra and quantum defect analysis, five Rydberg states spectra were characterized and assigned, four $^1\Sigma_u$ states and one $^1\Pi_u$ state. One of the key features of the simulation was the lack of the $J' = 2$ rotational peak in the first sigma state of the experimental spectrum (at around 126 000 cm^{-1}). This finding allowed us to estimate, with high certainty, the $F_2 \longrightarrow F^+ + F^-$ dissociation threshold, which could then be used to determine the F–F bond dissociation energy.



Acknowledgments: This work was funded by the National Science Foundation (grant no. CHE-1665464). Experiments were performed at the DESIRS VUV beamline of the Soleil Synchrotron under proposal numbers 20180455 and 20190866 and we thank the beamline staff for their support, in particular Dr. Laurent Nahon for helpful discussions in the design and preparation of the experiment. The financial support of the University Research Fund, University of Iceland and the Icelandic Research Fund (Grant No. 184693-051) is gratefully acknowledged. We are grateful to Dr. Krisztián Torma for his help with the cipp and PEPICO experiments and to Dr. Branko Ruscic for fruitful conversations and running our data on top of the latest development version of the Active Thermochemical Tables

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Cryogenic ion trap to study cold and controlled ion-radical reactions

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Ion-radical reactions are an important part of the gas phase chemistry that takes place in extreme environments such as the interstellar medium or outer regions of our atmosphere. However, their complexity and high reactivity makes them difficult to study in isolation.
We have built an ion trap which, combined with a Zeeman decelerator [1], will give us enough control to study ion-radical reactions under cold, controlled conditions. To achieve such control, the ion trap is cryogenically cooled to less than 10 K, and features an anti-vibration system and a new optical system designed for the imaging of Coulomb crystals. The optical system has previously been tested ex-vacuo at room temperature [2]. We now characterize it in vacuo, under both room temperature and at low temperature conditions.
Analysis of our experimental characterisation studies confirms that the ion trap reaches the low temperatures expected (≈ 10 K). It also shows that the resolution of the images recorded with the new optical system is not impacted by the cryogenic temperatures of the ion trap.
Final characterisation work is still underway, but the first results regarding the new optical system are promising for the study of ion-radical reactions using Coulomb crystals.

Acknowledgments: This work was supported by the EPSRC (Engineering and Physical Sciences Research Council of the UK) and the ERC (European Research Council).

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Femtosecond XUV-IR induced photodynamics in the methyl iodide cation

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Ultrashort extreme ultraviolet pulses obtained from high harmonic generation (HHG) allow for studies of molecular cations dynamics, nevertheless using the full bandwidth of HHG sources leads to a manifold of signals from different states which are mixed and so difficult to interpret. Here, we employ a time-delay-compensating XUV monochromator,[1] which defines the photon energy preserving the temporal resolution, to investigate the time-resolved dissociation of the methyl iodide cation (CH_3I^+) prepared in electronically excited states, and, in particular, the role of a time-delayed moderately strong IR probe pulse on the electronic and vibrational dynamics. The ground $\widetilde{X}\,^2E_{1/2,1/2}$ and excited $\widetilde{A}\,^2A_1$ states of CH_3I^+ are populated using the 9th harmonic of 800 nm (13.95 eV), the latter leading to CH_3^+ and I^+ fragments through different dissociation pathways, which are modified by the IR probe pulses. Velocity map imaging is employed to detect selected fragment ions – in particular CH_3^+ and I^+ – as well as photoelectrons. The experimental results are complemented by high level *ab initio* calculations of the potential energy curves, in combination with full dimension on-the-fly trajectory calculations on the $\widetilde{A}\,^2A_1$ state in the absence and presence of the IR pulse. The results provide a detailed picture of the CH_3I^+ cation dissociation and the action mechanisms of the probe IR pulse.

Acknowledgments: This work received financial support from LaserLab Europe through the project MBI002239.

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Detection of Polar Structures Assembled by Long-Range Intermolecular Forces via Electrostatic Deflection of Doped Helium Nanodroplets

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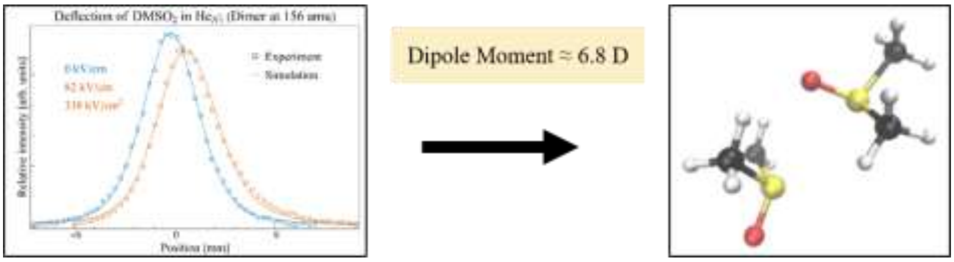
Experiments utilizing pendular state laser spectroscopy have shown that polar molecules sequentially captured in helium droplets may configure themselves into unusual polar geometries[1]. In the cold, inert helium nanodroplet environment, the “decision” to assemble into a given formation made by the trapped polar molecules is governed by their mutual long-range dipole-dipole forces. Ultimately, metastable states may form in the droplet where a complex of dopant molecules is frozen out of its ground state configuration.

In this work we examine the formed geometries of two polar molecular species: the solvent, dimethyl sulfoxide (DMSO) and the protein constituent, imidazole (IM). We probe the geometry of dimers and trimers of both DMSO and IM using our electrostatic beam deflection technique[2]. The helium droplets are multiply doped, and then a strong, inhomogeneous electric field is used to orient their constituents and deflect the droplets. The resulting beam deflection profiles for different trapped molecule combinations allow us to determine the electric dipole moment of the formed structure. Our deflection measurements clearly demonstrate that for both types of molecules the dipole moment of their configuration implies an aligned geometry[3,4]. Specifically, in the case of $(DMSO)_2$ the final state is polar in contrast with its nonpolar ground state. More recent work with alkali halide dimers suggests similar behavior. Configurations for $(DMSO)_{n=2,3}$ and $(IM)_{n=2,3}$ will be discussed and compared with theoretical simulations.



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Total Integral Cross Sections and Potential Energy Surfaces from Molecular Beam Scattering Experiments on Propylene Oxide – He and Propylene Oxide – Ne

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Interactions of propylene oxide with He and Ne have been studied in the gas phase by molecular beam techniques[1]. The total integral cross sections have been measured as a function of the selected collision velocity, under high angular and velocity resolution conditions[2]. It permits to obtain resolved quantum "glory" interference effects and provides information on the absolute scale of the long-range attraction and of the average binding energy in the range of equilibrium distances[3]. The experimental results, combined with a theoretical-phenomenological approach, have been used to derive and test the potential energy surfaces of these systems as a function of the distance and the angles that describe the mutual orientation of the interacting species[4]. These potential energy surfaces, defined in the full space of relative configurations, can be implemented in molecular dynamics simulation codes. Their formulation can be extended to more complex systems, such as heavier rare-gas atoms, diatomic molecules, and propylene oxide dimers.

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Crossed-beams and theoretical study of the reaction dynamics of O(^{3}P) with cyanoacetylene and acrylonitrile

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Some of the most dangerous air pollutants are undoubtedly the well-known nitrogen oxides NO_x. The major anthropogenic source of NO_x is the combustion of heavy fuels, like coals and coal-derived liquids: they contain a huge amount of nitrogen in pyrrolic and pyridinic structures, from which decomposition at high temperature produces many NO_x precursors.[1]

In this work we have focused on the oxidation reactions of two of these precursor molecules: O(^{3}P) + cyanoacetylene (CHCCN) and O(^{3}P) + acrylonitrile (CH_2CHCN). In fact, the pyrolysis of many heterocyclic compounds, such as pyridine[2] and pyrrole,[3] gives rise to CHCCN and CH_2CHCN: so, the study of their subsequent reactions with oxygen atoms, always present in a combustion environment, is central to unveil the NO_x evolution. We have exploited a crossed molecular beam apparatus, working under single-collision conditions, coupled to a rotating mass spectrometer to detect the primary products of the reactions, determine their branching fractions, and assess the role of intersystem crossing. In particular, there is a competition between the rupture of the carbon chain and the H-elimination pathway: we have observed the CO + HCCN and H + OCCCN channels for the O(^{3}P) + CHCCN reaction, while the oxidation of CH_2CHCN has led to CO + H_2CCNH and H + HCOCHCN. The experiments were supported by theoretical calculations of triplet and singlet potential energy surfaces to elucidate the reaction mechanisms.

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Simulation of dissociation and caging inside helium clusters

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The dissociation dynamics of molecules embedded in a condensed matter matrix is theoretically and experimentally well studied for macroscopic situations. Generally, excitation above a molecular fragmentation limit can lead to two scenarios depending on the details of the energy dissipation dynamics. The first one is fast recombination (the cage effect)[1] and the second the long time survival of separated fragments. In a cluster environment a third scenario becomes possible, namely fragments leaving the cluster with or without attached cluster particles. Helium clusters are a very cold (about 0.5 K) but still liquid and dense environment with particularly challenging properties due to the pronounced collective quantum behavior of helium leading to unusual energy dissipation dynamics. We present first results of simulations of the photo dissociation of molecular iodine, I2, at various excitation energies inside helium clusters with several thousand atoms using a technique based on quantum effective potentials[2] to account for the quantum effects. We obtain cluster size dependent threshold energies for caging, velocity distributions of photo fragments exiting from the clusters and statistics about the number of helium solvent atoms carried along by the iodine atoms similar to experimental results obtained for CH3I[3].

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Unraveling the Mechanism of the Electronic Quenching of NO ($A^2\Sigma^+$) with CO

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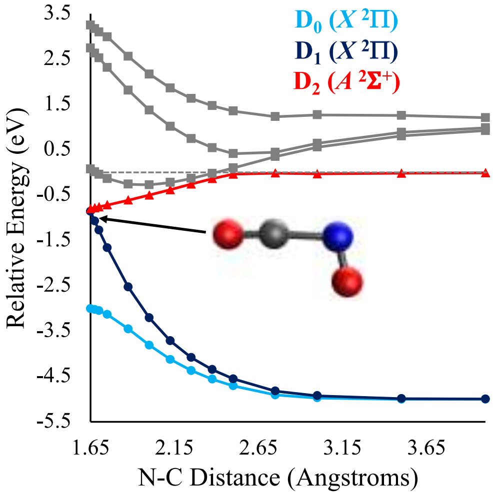
NO is an important reactive intermediate in combustion and atmospheric chemistry. The experimental detection of NO commonly utilizes laser-induced fluorescence (LIF) on the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition band. However, the electronic quenching of NO ($A^2\Sigma^+$) with other molecular species provides alternative photochemical pathways that compete with fluorescence. For example, the cross section for the nonreactive electronic quenching of NO ($A^2\Sigma^+$) with CO is 6 Å^2 at 300 K and approximately 16 Å^2 at 125 K. The underlying photochemical mechanisms responsible for this electronic quenching are not well understood.

Here, we describe the development of high-quality potential energy surfaces (PESs) that provide new physical insights into the long-range interactions and conical intersections that facilitate the nonreactive electronic quenching of NO ($A^2\Sigma^+$) with CO. The PESs are calculated at the EOM-EA-CCSD/d-aug-cc-pVTZ//EOM-EA-CCSD/aug-cc-pVDZ level of theory, an approach that ensures a balanced treatment of the valence and Rydberg electronic states as well as an accurate description of the open-shell character of NO. Our PESs show that the long-range interactions between NO ($A^2\Sigma^+$) and CO are highly anisotropic and weakly attractive. At intermediate intermolecular distances, the ON+CO PES becomes strongly attractive and funnels population to a conical intersection between NO ($A^2\Sigma^+$) + CO and NO ($X^2\Pi_{3/2}$) + CO. We demonstrate that this increase in intermolecular attractions reflects the presence of long-range electron transfer from NO ($A^2\Sigma^+$) to CO, i.e. the harpoon mechanism. Overall, our work shines new light into the impact of coupled PESs on the dynamics of open-shell systems.



High-resolution imaging of C-He and C-H_2 collisions using a Zeeman decelerator

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We recently demonstrated that employing the technique of Zeeman deceleration to control collision partners in combination with velocity map imaging (VMI) to probe collision products enables controlled and high-resolution scattering studies for systems like NO-Ne and NO-O_2[1]. The level of control and the resolution in these crossed beam experiments were proven to be similar to studies in which the more established Stark decelerator was used. However, Zeeman deceleration can address a large class of chemically relevant species that exclusively have a magnetic dipole moment, and thus offers new and exciting possibilities to study collisions and reactions with an unprecedented level of precision and in unexplored energy regimes.

The carbon atom, which is amenable to Zeeman deceleration, is an abundant species of significant importance to interstellar chemistry. For example, the non-adiabatic dynamics of collision-induced fine-structure (de-)excitation in C-He collisions has already attracted considerable interest[2]. Here, we combine our Zeeman decelerator and VMI setup with a novel resonance-enhanced multiphoton near-threshold ionization scheme for carbon atoms employing VUV light. The resulting high-resolution measurements of both C-He and C-H_2 collisions reveal fine details of the state-to-state angular scattering distributions, like diffraction oscillations, and show excellent agreement with simulations based on *ab initio* calculations of the cross sections. This underlines the prospects for planned investigations of scattering resonances in low-energy C-He collisions as well as reactive collisions of C and O_2.

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Investigating the origin of coincident fragments from the H_2 molecule

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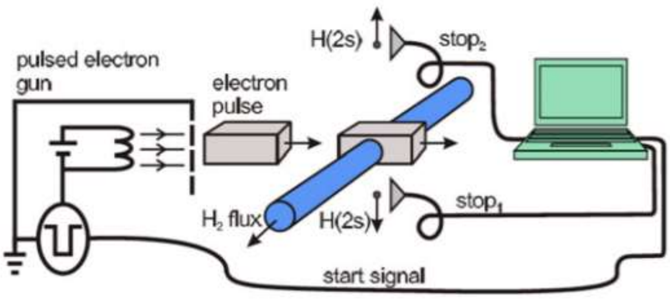
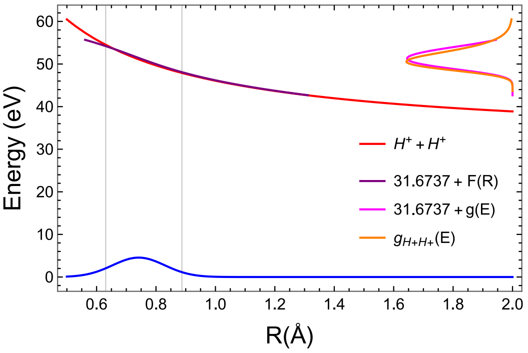
The aim of the present work is to investigate the dissociation channel of the H_2 molecule that gives origin to the peak observed in our coincidence spectra. The experiment was performed at Laboratoire Aimé Cotton in Orsay, France and is described in a previous work [1]. The target was an H_2 molecular supersonic jet crossed by pulsed electron beam. A pair of neutral and/or ionic fragments from the same H_2 molecule can be detected in coincidence after travelling free of electric fields.

Considering the dynamics of the collision and applying the inverse reflection method, where the wave function of the fundamental state of the molecule was considered, we found the potential energy curve of the excited H_2 molecule in the Franck-Condon region, except for its dissociative limit. An analysis was carried out on the experimental data for different electron energies to determine the origin of the coincident fragments; by considering the coincidence production threshold, we can say that the measured peak must come from a potential energy curve located near the double ionization energy.





Acknowledgments: This work is supported by FAPERJ, CNPq, CAPES, and CNRS.

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Predissociation dynamics of the $A^2\Sigma^+$ state of SH radical

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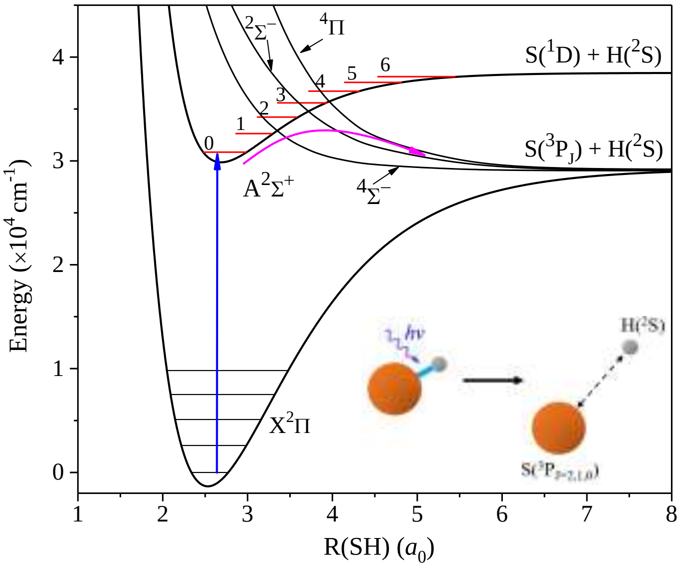
Photo-predissociation dynamics of rovibrational levels of SH ($A^2\Sigma^+$, v' = 0-6) are studied using the high-*n* Rydberg atom time-of-flight technique. Spin-orbit branching fractions and angular distributions of the $S(^3P_{J=2,1,0})$ product are measured in the product translational energy distributions. The $A^2\Sigma^+$ v' = 0 state of SH predissociates mainly through adiabatic coupling to the $^4\Sigma^-$ repulsive state. As the vibrational level v' increases, the predissociation dynamics change dramatically, and all three repulsive states ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$) are involved in the dissociation pathways. Quantum interferences among these dissociation pathways affect the fine-structure state distribution of the $S(^3P_{J=2,1,0})$ product. The experimental branching fractions of the $S(^3P_J)$ product from $A^2\Sigma^+$ (v' = 0-4) are in agreement with the close-coupling quantum scattering calculations by Alexander and co-workers, while those from $A^2\Sigma^+$ (v' = 5-6) differ significantly from the calculations. The product angular distributions reasonably agree with the prediction from the theoretical model.[1] The measured anisotropy parameters are influenced by the excited state lifetimes and depolarization.



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Modification of H_2 rotational alignment upon scattering from Si(100)

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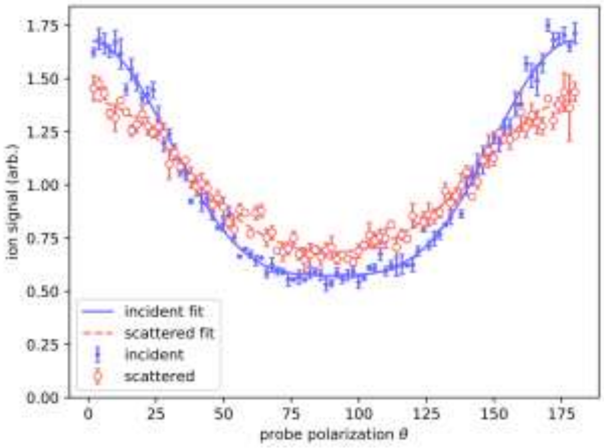
We present here our results from a state-prepared, state-resolved experiment of rotational scattering of a diatomic molecule from a solid surface. In the experiment, H_2 molecules with 80 meV kinetic energy are rotationally aligned in the j=3 rotational state via stimulated Raman pumping and then scattered from a Si(100) surface at normal incidence. The rotational alignment of the scattered molecules is determined by measuring, for both the incident and scattered molecules, the ionization yield of a probe laser, tuned to selectively ionize molecules in the j=3 rotation level, as the probe laser polarization is rotated. The measurement is performed for two initial rotational alignments: a ``helicoptering'' alignment with the bonds constrained to lie primarily parallel to the surface, and a ``cartwheeling'' alignment with the bonds lying primarily normal to the surface. For both initial alignments, the modulation of the probe ionization with laser polarization for the scattered molecules, while still pronounced, is found to be significantly weaker than the incident molecules. This indicates a definite modification but not total elimination of the initial alignment. In addition, the ionization modulation is found to be somewhat stronger for cartwheeling molecules than for the helicoptering molecules. These results provide valuable experimental input towards the goal of understanding molecular-surface interactions.



The reduction in the relative modulation of the H_2 ionization with the polarization of the ionizing laser reflects a surface-collision-induced modification of the H_2 rotational alignment.

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Theoretical Study - Long Range on LiH_2

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The lithium chemistry has received a great attention in recent years due to the importance that LiH molecules and its ionic variants can have in the primordial universe[1,2]. The reaction $LiH + H \rightarrow Li + H_2$ is considered to contribute to LiH depletion, while the hydrogen-exchange reaction $LiH + H \rightarrow LiH + H$ leads to the retention of LiH in this process.

In this work we report our recent studies on the long-range interactions between the reactants of those reactions. For the LiHH system, the main contribution for the long-range interactions is the dispersion interaction. To modeling the dispersion interaction, the parallel and perpendicular values of the polarizabilities, α, for the diatomics (H-H and Li-H) have been calculated and fitted.

The dispersion interaction coefficients C_6 have been computed as C_8 and C_{10} have been semiempirically estimated from C_6 using a universal correlation. The total dispersion interaction was obtained as a function of Cn and inter-atomic distances[3]. The dynamical correlation energy has been obtained for the interaction H-LiH and Li-HH (see figure).

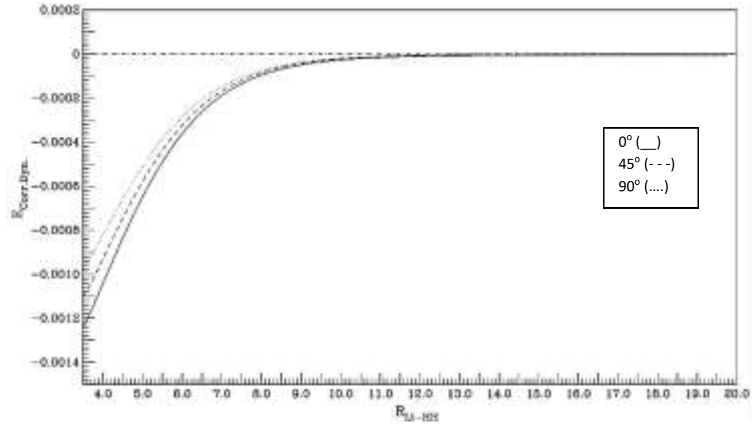

Figure: Total dynamical correlation energy for the interaction Li-HH at 0°, 45° and 90°.

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Stepwise Microhydration of Isoxazole: Infrared Spectroscopy of Isoxazole-(Water)$_{n\leq 2}$ Clusters in Helium Nanodroplets

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Hydration of heterocyclic molecules plays a crucial role in biological and chemical recognition. Here, we present an infrared (IR) spectroscopic investigation of microhydrated, heterocyclic isoxazole molecule.[1] The IR spectra of isoxazole-(water)$_{n\leq 2}$ clusters are recorded using helium nanodroplet spectroscopy and are analysed by quantum chemical calculations at the MP2/6-311++g(d,p) level. In the most abundant isoxazole-water dimer, the solvent water participates in a N⋯HO hydrogen bonding (H-bond) interaction, while in another observed structure, water simultaneously interacts with the ring nitrogen and the neighbouring CH group via N⋯HO and CH⋯O H-bonds. The addition of a further water molecule to the monohydrated cluster results in the formation of a single isomer that features a seven-membered ring, in which the water dimer simultaneously interacts with the skeletal nitrogen and the adjacent CH group through N⋯HO and CH⋯O bonds.

Acknowledgments: This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany´s Excellence Strategy–EXC 2033–390677874–RESOLV.

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Fast high-resolution method for forward and inverse Abel transforms of velocity-map images

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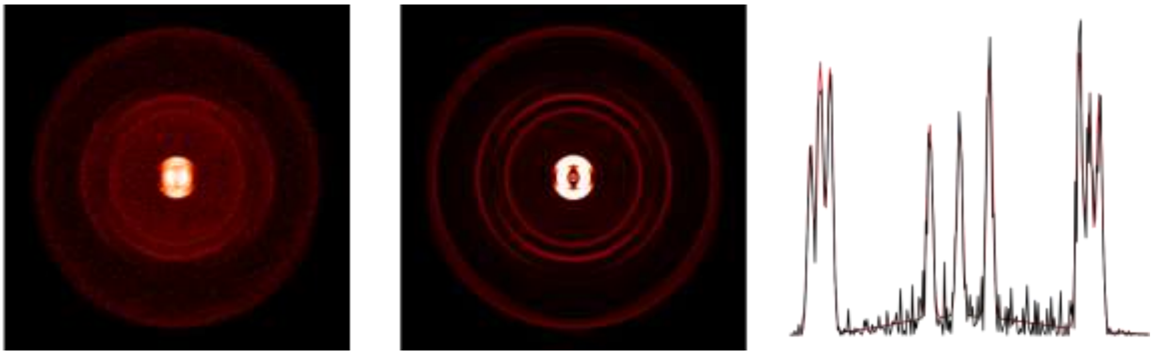
Velocity-map imaging (VMI) is a versatile experimental tool, often combined with molecular beams, but widely used in studies of surfaces and nanoparticles as well. Although a gradual shift towards its "slicing" variant or 3D detection is happening, in many cases only the 2D projection of the electron/ion cloud is recorded, thus a numerical inverse Abel transform is still required to recover the underlying 3D velocity distribution. Multiple numerical methods have been developed over the years, many of them are implemented and compared in the PyAbel software package.[1] Here I present a recent addition to PyAbel, a new “rBasex” method, based on my previous developments on maximum-likelihood analysis of VMI data,[2] but implemented in a much faster simplified variant.

The new method is similar to the popular pBasex method,[3] being designed specifically for VMI data composed of spherical harmonics. However, the use of a separable basis set with analytical projections greatly improves its performance and usability. In particular, the basis sets can be calculated on the fly (in milliseconds instead of hours), even for megapixel images with single-pixel resolution. The transform time is also on par with the fastest numerical Abel-transform methods, ∼10 ms for a megapixel image, allowing real-time processing of high-definition video. Like other “polar” methods, it produces cleaner images, without the “center-line noise” typical for general-purpose Abel-transform methods, facilitating visual inspection of the results. Several provided regularization methods can further reduce the experimental noise in the transformed images, as well as the velocity and anisotropy distributions.



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Looking at the Bigger Picture: Photoproducts of Pyruvic Acid

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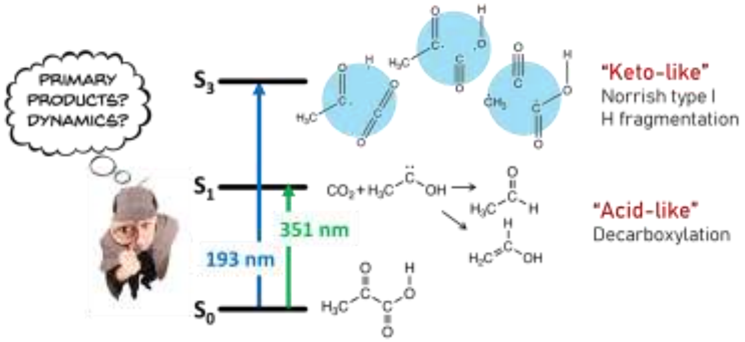
Pyruvic Acid (PA), $CH_3C(O)COOH$, a prototypical alpha-keto carboxylic acid present in the troposphere, is one of the few molecules destroyed mainly by solar radiation than by reactions with free radicals.[1] Previous research has examined only its stable products resulting from photodissociation and subsequent chemical reactions.[2] We have used the complementary methods of velocity-map imaging and multiplexed photoionization mass spectrometry to gain a broad understanding of the primary dissociation events following photoexcitation at 193 nm (S_3) and 351 nm (S_1). Using these two techniques we observe several primary products of PA photodissociation 193 nm, including CO_2, CO, H, OH, HCO, CH_2CO, CH_3CO, and CH_3. In 351 nm photodissociation, the main products are the three isomers of C_2H_4O, namely acetaldehyde, vinyl alcohol, and the proposed, but never-before observed, methylhydroxycarbene. By using energetics and multivariate analysis to constrain dissociation pathways, and the excited state framework laid out by theoretical studies,[3,4] we provide the first comprehensive description of the dissociation dynamics of PA following its excitation to the S_3 and S_1 states.



Acknowledgments: This research used resources of the Advanced Light Source, DOE Office of Science User Facility contract DE-ACO2-05CH11231. HR thanks USDOE-BES grant DE-FG02-05ER15629. Sandia National Laboratories is a multimission laboratory managed and operated for the USDOE's National Nuclear Security Administration under contract DE-NA0003525.

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VMI Photoelectron Spectroscopy Probing the Rotational Cooling Dynamics of Hot Trapped OH^- Ions

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VMI photoelectron spectroscopy inside an electrostatic ion beam trap (EIBT)[1,2] is used to probe the time dependent dynamics of rotational states relaxation of "hot" OH^- ion, produced in a cesium sputter ion source. The photodetachment of OH^- ion results in the population of two neutral states ($\Pi_{3/2}$ and $\Pi_{1/2}$)[3-5]. The corresponding VMI photoelectron images of the unresolved P-branch transitions are shown in the Figure below for different storage times in the EIBT. As the storage time increases, the peak radius of the P-transition decreases, indicating that the rotational population shift from high to low rotational levels. The calculated rotational temperature resulting from the fitted rotational line intensities ranges from 4100 to 900K during the 0.1-2.8 sec trapping time. Further, we have explored the relative population change of the individual rotational states population as a function of the storage time in order to the extract relaxation rate coefficients for a broad range of rotational states of OH^-.

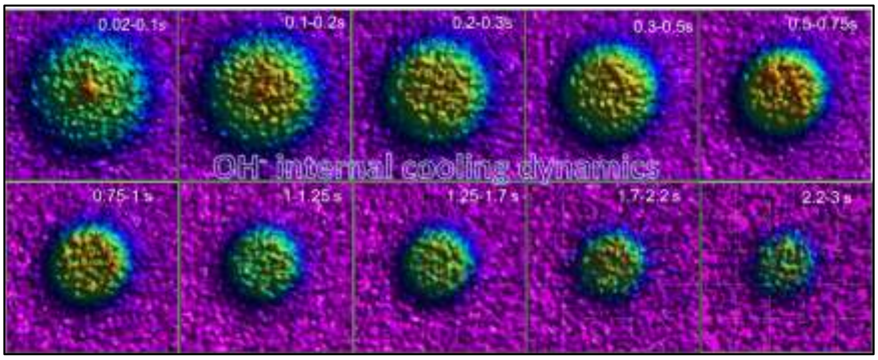

Figure: VMI spectra of OH^- probed via electron detachment by a CW laser (682 nm) as a function of time.

Acknowledgments: This work was supported by Israel Science Foundation, grant No. 1214/17.

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Flash pyrolysis of 1,1,2,2-tetramethyldisilane: the role of tetramethyldisilene in the decomposition mechanism

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Thermal decomposition of 1,1,2,2-tetramethyldisilane was performed by flash pyrolysis in a SiC microreactor in the temperature range from 295 K to 1340 K, followed by molecular beam sampling and vacuum ultraviolet photoionization mass spectrometry analysis. Density functional theory investigations on the energetics of reactants, intermediates, and products were carried out to support the experimental observations. Dimethylsilane, dimethylsilyl radical, dimethylsilylene, and tetramethyldisilene were determined as the primary reaction products in the initiation decomposition of 1,1,2,2-tetramethyldisilane. Further decomposition reactions of tetramethyldisilene allowed in situ observations of the thermal dissociation behaviors of tetramethyldisilene. The dimethylsilene (m/z = 72) and SiC_3H_4 (m/z = 68) fragments were believed to be produced by a series of isomerization reactions of tetramethyldisilene. Other products from secondary reactions of dimethylsilane and dimethylsilylene such as SiC_2H_{2-6} and $SiCH_{0-4}$ were also observed. The comprehensive pyrolysis mechanism of 1,1,2,2-tetramethyldisilane was proposed.

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Imaging photodesorption from low temperature O_2 ice

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Here we present the most recent work from our group on combining Velocity map imaging, VMI,[1-2] with laser desorption on cold molecular ice surfaces. Using a new approach – "Atomic Fragment Imaging Mass Spectrometry (AFI-MS)" that we've developed, we can now measure both the kinetic and internal energy of mass-selected species ejected by laser desorption from different ices held at low temperature. Taking O_2 ice as an example, with the advantage of the rich information available from $O(^3P)$ and $O(^1D)$ fragment images, the intermediate products and their photochemical pathways can be clearly indicated, such as the detection of the $A'^3\Delta_u$ Herzberg state of O_2 and the production of ozone.[3] Many surprising aspects of photochemistry at ice surfaces are revealed by this approach.

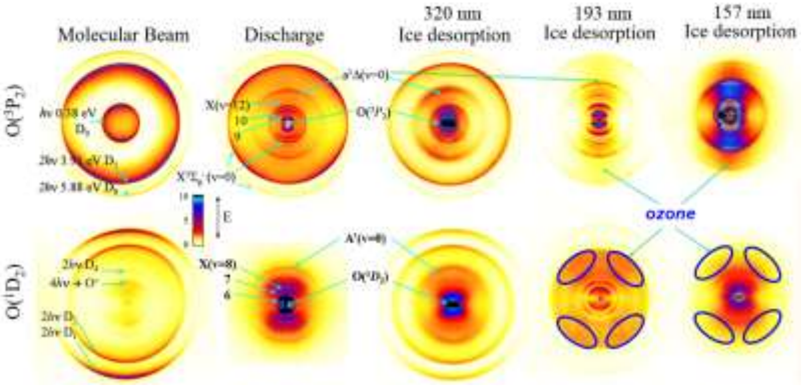

Figure: Atomic fragment images from low temperature O_2 ice with different desorption light, in comparision with velocity mapped images from O_2 molecular beam and discharged O_2 beam, revealing rich photochemistry information on ice.

Acknowledgments: This work was supported by DAN II, NWO grant number 715.013.002.

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Coriolis Coupled Dynamics of the H(^{2}S) + CH$^+$(X$^1\Sigma^+$) Reaction: A Full-Dimensional Quantum Wavepacket Study

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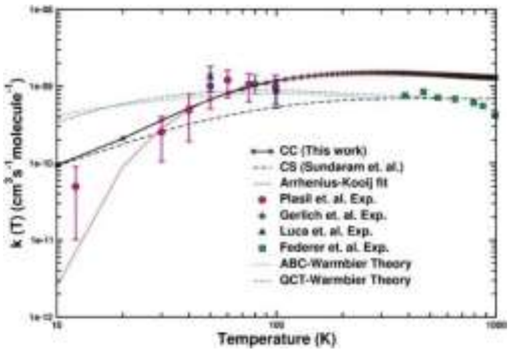
Coriolis coupling (CC) is an intramolecular process, through the molecular collision one could understand the molecular structure, energies and dynamics of the chemical system. We here report the CC effects on the initial state-selected dynamics of the H(^{2}*S*) + CH$^+$(X$^1\Sigma^+$) reaction in its electronic ground state (1 ^{2}A′)$^{(1)}$ by a time-dependent wavepacket approach. In the present study, exact quantum scattering calculations were obtained and the results were compared with our previous results, obtained by neglecting the CC terms (off-diagonal) within the centrifugal sudden (CS) approximation $^{(2)}$ [Phys. Chem. Chem. Phys. **19**, 20172 (2017)]. All partial wave contributions up to the total angular momentum $J_{max} = 60$ were considered to obtain the converged integral cross section up to a collision energy range 1.0 eV, and the projection quantum number K was varied from 0 to K_{max}. A significant contribution of coupling effects noticed in the CC reaction probabilities for different ro-vibrational levels of CH$^+$ reagent (v=0, j=3), and the CC probabilities are higher than the CS results. We predicted that the CS approximation is underestimating the results for the R1 and R2 channels compared to the exact (CC) method in the ground electronic state. At the outset, we calculated that the CC predicts theexact rate constants (at 10 - 100 K ultra-cold T), on par with the experimental results, for overallT range (10-1000 K) of astrochemical interests of the complex-forming ion-molecule type reactions $^{(3)}$.



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Methods for Accelerating the Prediction of Anharmonic Spectra of

Cold Molecules and Clusters

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We present our efforts to accelerate the prediction and simulation of infrared spectra for systems that contain high levels of resonances and other anharmonicities. These predictions are often most useful in cold molecular beam studies, for providing both firm structural assignments and for gaining insights into the fundamental chemical physics interactions that drive the structure and dynamics of system.

For our work presented here, our systems of interest are the initial clusters that form larger secondary organic aerosols, both from terpene and brown carbon sources. Their structure and growth are dictated by the interplay of hydrogen-bonding interactions of the organic molecules with water and water with itself, and thus, there are many potential conformers. We model the OH and NH stretching region of the clusters' IR spectra through a suite of approaches that have favorable computational scaling and cost compared to standard anharmonic approaches. Finally, we leverage the wealth of computational spectral data to build data-driven “inverse” spectroscopic models.

Fully quantum state resolved dipolar molecular collisions

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A detailed understanding of molecular interactions is crucial for the interpretation of microscopic dynamics. The crossed molecular beam technique proved to be a sophisticated approach to obtain detailed information of potential energy surface. Despite the success studying collisions between bimolecules[1], complete quantum-state resolved bimolecular collisions are experimentally more challenging because of the low particle density in the colliding beams.

We combined a Stark decelerator and a hexapole in a crossed molecular beam configuration to produce two molecular beams of NO radicals and ND_3 molecules with an almost perfect quantum-state purity. State-resolved inelastic collisions between NO ($X^2\Pi_{1/2}$, j=1/2, f) and ND_3 (jkp=11-) molecular beams are studied. From the measurement, we can study the interactions in NO-ND_3 collisions.

Acknowledgments: This work was supported by the European Research Council (ERC) and the Netherlands Organization for Scientific Research (NWO).

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Towards the coherent control of Penning collisions between metastable helium atoms

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The coherent control of reactive collisions, which relies on the interference between two or more reaction paths, has been long sought for.[1] We are in the process of realizing an experiment, in which we coherently control the Penning collisions between metastable helium atoms in the 2^3S_1 and 2^1S_0 states.

Our control scheme is based on the preparation of a coherent superposition of the M_J=-1 and M_J=+1 quantum states in the He (2^3S_1) via an off-resonant two-photon Rabi excitation scheme. The two states are coupled by light of counter-rotating circular polarization, which also imprints its phase onto each state. By varying the phase difference between the two circularly polarized light components, the relative phase between the involved reaction pathways follows the same trend. This control scheme will allow for a precise tuning of the overall reaction cross section. Our detection scheme is based on monitoring of ions, produced in the collision process, on a time-of-flight detector. In this contribution, I will describe our experimental apparatus and its characterization.

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Coherent two-dimensional photoelectron spectroscopy

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Coherent multidimensional spectroscopy is a powerful ultrafast spectroscopic technique which provides information otherwise only accessible in disjunct experiments[1,2,3]. Another spectroscopic tool is photoelectron spectroscopy which provides detailed information about the chemical composition and electronic states of the sample by analyzing photoelectrons released from the sample[4].

Here we present a combination of both methods in a single experiment, realized with the implementation of efficient single-counting detection and multichannel software-based lock-in amplification[5]. The approach offers high temporal, spectral and kinetic energy resolution. It enables differential CMDS experiments with unprecedented selectivity and enhances the dynamic range of CMDS by up to two orders of magnitude. The demonstrated principle opens-up a perspective for atomically-resolved CMDS experiments using X-ray photoelectron spectroscopy.

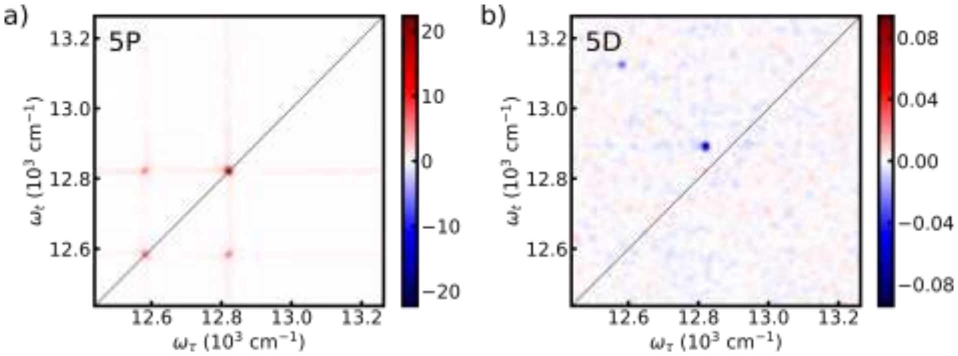

Figure: Differential 2D spectra extracted from selected regions of the photoelectron kinetic energy (atomic Rb, 5P (a) and 5D (b)).

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Probing for mode specificity in the chemisorption of CO_2 on H-Cu(111)

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The rising CO_2 concentration in the atmosphere due to man-made emissions is causing global warming and poses a major threat to the life on our planet through extreme weather and sea level rise. A potential solution to this problem is to capture CO_2 and to convert it into green fuels, thereby closing the carbon cycle. Formate ($HCOO^-$) synthesis by reacting CO_2 with hydrogen on a copper catalyst can be used as an initial step in CO_2 conversion and has therefore been studied recently by both experiment and theory [1-3]

Recently, Nakamura *et al.* reported formate synthesis via an Eley-Riedel mechanism in which 'hot' CO_2 molecules in a molecular beam react with H atoms pre-adsorbed on either Cu(111) or Cu(100) to form $HCOO^-$ adsorbates[4]. They demonstrated that this reaction is enhanced by vibrational excitation of CO_2 reactant. Nakamura and co-workers used thermal methods to excite all the vibrational modes of the incident CO_2 molecules simultaneously, according to the Boltzmann factor.

In our lab, we are able to prepare gas phase reactants such as CH_4, H_2O and CO_2 in specific vibrational quantum states using infrared laser excitation in a molecular beam incident on a catalyst surface[5]. In contrast to the thermal methods used by Nakamura and co-workers, state specific laser excitation enables the preparation of CO_2 selectively in different rovibrational eigenstates making it possible to probe for mode specificity in gas/surface reactions[5]. Information on which vibrational mode enhances formate formation most efficiently provides valuable information on the transition state structure of the chemisorption reaction. Furthermore, infrared laser pumping by polarized laser can be used to align the CO_2 molecules in the laboratory frame to study the stereodynamics of its gas/surface reactions[6]. Our aim is therefore to perform state-specific reactivity measurements with steric control for formate synthesis on a copper catalyst. Surface bound formate is detected by reflection absorption infrared spectroscopy (RAIRS). In my presentation, I will give a progress report of the state resolved study of this interesting and important reaction.

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Conformationally selected polar Diels-Alder reactions in the gas phase

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The Diels-Alder (DA) cycloaddition in which a conjugated diene reacts with a dienophile is one of the most important reactions for the synthesis of cyclic compounds in organic chemistry.[1] Over the past decades, this reaction has been extensively investigated both experimentally and computationally.[2] However, its mechanistic details are still a subject of debate.[3] Here, we present experimental results on the kinetics and mechanisms of polar DA cycloadditions studied under single-collision conditions in the gas phase. By spatially separating different conformers of the diene using inhomogeneous electric fields[4] and combining conformationally selected molecular beams with Coulomb crystals techniques,[5,6,7] we investigated conformationally specific mechanisms of ionic DA cycloadditions in the model reactions of dibromobutadiene (DBB)[8] and methyl vinyl ketone (MVK)[9] with propene ions. Pronounced conformational effects were observed in both systems which were elucidated with the help of theoretical calculations.

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Kinetic and dynamic studies of the $O(^1D) + H_2O(X^1A_1)$ reaction

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The reactivity of the oxygen atom in the first excited electronic state, $O(^1D)$, is important in various fields of chemistry, and its reaction with water plays an important role in the HO_x chemistry, which in turn participates in the stratospheric ozone depletion.[1]

Several years ago a full dimensional potential energy surface (PES) for the ground state hydrogen peroxide molecule, H_2O_2, was developed by our group.[2] Recently, this PES was improved to accurately reproduce all the reaction channels and the minimum energy pathways for the different chemical reactions involved in the $O(^1D) + H_2O(X^1A_1)$ reaction system (see Figure 1). The aim of this work is to study theoretically the gas phase reactions involved in the $O(^1D) + H_2O(X^1A_1)$ system, considering this new full dimensional ground state PES.

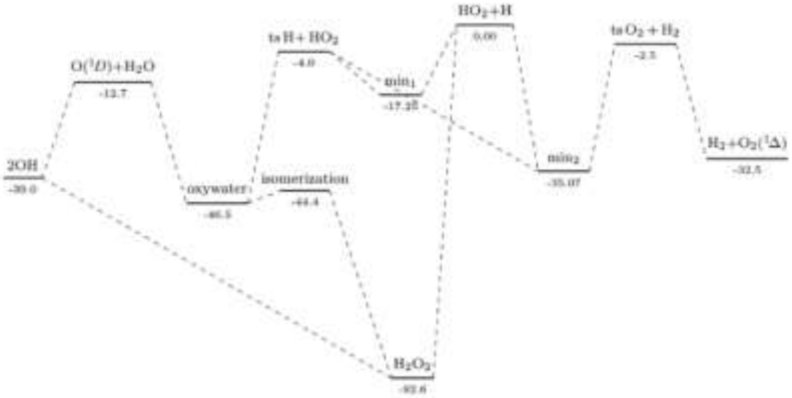

Figure 1. Energy diagram, in $kcal mol^{-1}$, connecting the stationary points and dissociation channels for the round state potential of the H_2O_2 system. The energies are given in relation to the $H + HO_2$ dissociation energy.

Acknowledgments: This work was supported by the FCT under the PTDC/QUI-QFI/31955/2017 research project.

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The Enolic Form of Curcumin Studied in Gas Phase

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Curcumin has been widely studied for its variety of possible medicinal properties. Understanding the tautomerization and spectroscopic characteristics of curcumin can help elucidate its medicinal properties. We study curcumin and several of its isotopomers in the gas phase using laser-desorption, jet-cooling, mass spectrometry coupled with resonance enhanced multi-photon ionization (REMPI). We find curcumin exists as only a single tautomer, the mono-enol, in agreement with past theoretical calculations. Broad vibronic absorption bands exist for this tautomer to both the S_1 and S_2 excited state. Pump probe spectra show a bi-exponential decay measured at the six transitions with a short decay varying from 150-600 ps and a long decay of 15,000 ps. In addition, we obtained absorption and pump probe spectra for three isotopomers of deuterated curcumin. While deuteration slightly red-shifts the absorption to the S1 and S2 excited electronic states, it has no effect on their excited state dynamics. Many studies have proposed the importance of excited state intramolecular hydrogen or proton transfer (ESIHT/PT) as a key decay mechanism of curcumin. However, ESIHT/PT would be expected to be ultrafast, so the long lifetimes of our decays as well as the lack of isotope effect rule out this process. Instead, our observed decay is likely fluorescence or an unknown nonradiative pathway that dissipates the electronic energy of curcumin.

Producing a Cold, Controlled Source of Radicals

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Producing a pure, state-selected beam of gas-phase radicals – with a tuneable velocity – in the laboratory is rife with challenges. Yet, it is one of the most important tools we need in our arsenal to precisely study ion-radical reactions that are astrochemically and atmospherically relevant. [1] Taking advantage of the paramagnetic behaviour of radicals, we can use external magnetic fields to filter out only the target species (that are travelling at a selected velocity) from a beam containing a mixture of other species. A CMA-ES evolutionary algorithm[2] has been applied to optimise the passage of a beam of H atoms, starting from a source with a mixture of species present through to the detection region, passing through a 12-stage Zeeman decelerator and a magnetic guide composed of 4 Halbach arrays and 2 skimming blades. The combined optimised switching sequence and vertical displacements of the arrays and blades from the central beam axis significantly improves on previous best[3] methods, achieving a 3.4-fold increase in particle numbers and a narrower velocity distribution of transmitted particles. Based on these findings, a second-generation magnetic guide is being designed to act as a stand-alone radical filter. The second-generation guide will feature additional Halbach arrays, to improve transverse focusing of the beam and to target O and OH radicals. This will be interfaced with a liquid surface, expanding the scope of relevant chemical reactions that can be studied with unprecedented precision.

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Photoionization and photodissociation of furan by mass spectrometry and photoelectron imaging

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Furan, a simple oxygen-containing aromatic molecule, undergoes a dissociation yielding two carbene intermediates.[1] In order to clarify the exact decomposition pathways, we performed two distinct experiments. In the first one, a single photon absorption is used to probe the photoionization efficiency (PIE) of precursor and fragment ions by mass spectrometry and synchrotron radiation. The measured ionization potential of fragment ions such as $C_4H_4O^+$ agrees with the theoretical value predicted by DFT.[2] Based on the changes in PIE curves of fragment ions, we conclude that with the increase of energy, β-carbene will dominate, and $C_3H_3^+$ becomes the main dissociation product.

The second one gives the energy scheme of furan at 400 nm femtosecond laser combined with photoelectron imaging.[3] The ground and excited electronic states of furan are analyzed after four-photon absorption process and multiple energy bands were identified. Briefly, the energy band I relates to the ionization from the S_2 state to the D_0 state, and the appearance of the energy band II can be inferred to the rapid internal conversion from the S_2 state to the S_1 state after two-photon absorption. The energy bands III and IV are classified as the energy produced by the transition of the two filling states of the D_1 state. At the same time, the energy bands V and VI are classified as the excitation energy of the two filled states, in which furan absorbs the four-photon transition to the D_0 state.

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Low-pressure yields of stabilized Criegee intermediates produced from ozonolysis of a series of alkenes

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Ozonolysis of alkenes is an important oxidation pathway of alkenes in the troposphere because it is involved in the production of organic aerosol and OH radicals. The mechanism of ozonolysis of alkenes involves the formation of a primary ozonide (POZ), which then decomposes into a carbonyl and a high-energy carbonyl oxide (Criegee intermediate). Criegee intermediates are produced with a broad internal energy distribution. High energy Criegee intermediates decompose into atmospherically important compounds (e.g. vinoxy, OH radical). Stabilized Criegee intermediates (sCIs) undergo reactions to produce secondary ozonides and organic aerosols.

Cavity ring-down spectroscopy (CRDS) was utilized in combination with chemical titration with sulfur dioxide (SO2) to quantify sCIs. The reaction is carried out under various flow and low-pressure conditions. Reference cross-sections of products and reactants are fitted with spectral features to obtain product number densities.

The yields of sCIs were measured at different low pressures and the nascent yields were determined by extrapolation to zero pressure. Endocyclic alkenes show no sCI production at the pressures studied. However, acyclic alkenes show pressure-dependent sCI yields. Formaldehyde oxide (CH_2OO) from the alkenes studied has a high nascent yield due to its relatively high energy barrier for dissociation. Cis-2-butene produces higher nascent sCI than trans-2-butene, possibly due to different syn- and anti-CI branching ratios, or different POZ conformations. There is an indication that alkenes larger than 2,3-dimethyl-2-butene would have higher nascent sCI yields. The information on low-pressure yields from the current studies can be used as a benchmark for theoretical calculations.

Observation of a π-Type Dipole-Bound State in Molecular Anions

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Polar molecules with sufficiently large dipole moments can form highly diffuse dipole-bound anions, and possess noncovalent dipole-bound states (DBSs) just below the electron detachment threshold.[1] DBSs have been proposed as the "doorway" to the formation of valence-bound anions, and exploited as a means to develop high resolution resonant photoelectron spectroscopy.[2] The π-type DBS (π-DBS) with one additional angular node in the wave function was predicted to exist as an excited electronic state in addition to the σ-type ground state.[3] However, π-type noncovalent states have never been observed in isolated molecular systems. Here we report the observation of a π-DBS in cryogenically cooled 9-anthrolate anions ($9AT^-$, $C_{14}H_9O^-$) by resonant two-photon photoelectron imaging.[4] A DBS is observed 191 cm^{-1} (0.0237 eV) below the detachment threshold, and the existence of the π-DBS is revealed by a distinct (s + d)-wave photoelectron angular distribution. The π-DBS is stabilized by the large anisotropic in-plane polarizability of 9AT. The population of the dipole-forbidden π-DBS is proposed to be via a nonadiabatic coupling with the dipole-allowed σ-type DBS mediated by molecular rotations.

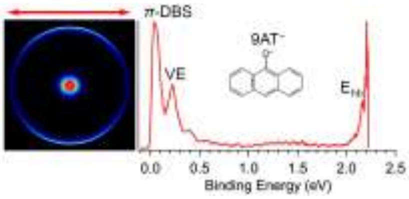

Figure: Resonant two-photon photoelectron image and spectrum of $9AT^-$

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High-dimensional quantum dynamics in OH(A)+H_2 and H+CD_4

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First-principles based study of quantum reactive scattering has achieved great success in predicting and explaining fascinating quantum effects in various tri-atomic systems. This field has now advanced to reaction systems involving more atoms, and four-atom and six-atom systems are the mostly studied polyatomic systems.[1, 2, 3]

Non-adiabatic quenching of electronically excited OH($A^2\Sigma^+$) by collisions with H_2

The study of the OH(A)+H_2 reaction has been performed with full-dimensional quantum dynamics calculations on high-quality coupled diabatic potential energy surfaces.[4] Good agreement with experiment is found for the OH($X^2\Pi$) ro-vibrational distribution. The nonadiabatic dynamics is shown to be controlled by stereodynamics, namely the orientation of the two reactants. The uncovering of a major (in)elastic channel, neglected in a previous analysis but confirmed by a recent experiment, resolves a long-standing experiment-theory disagreement concerning the branching ratio of the two electronic quenching channels.

Product state pair-correlated differential cross sections of the H+CD_4→HD+CD_3 reaction

Velocity and angle resolved state-specific differential cross section (DCS) of the H+CD_4 reaction are calculated with the time-dependent wave packet method.[5] At a collision energy of 0.72 eV, energy is largely disposed into the translational motion. The HD product has no vibrational excitation, and the CD_3 product shows multiple excitation in the umbrella bending mode. Furthermore, the correlation of the HD rotational states to the CD_3 vibrational and rotational states are analyzed in detail. Product pair correlation is only visible in the angular distribution.

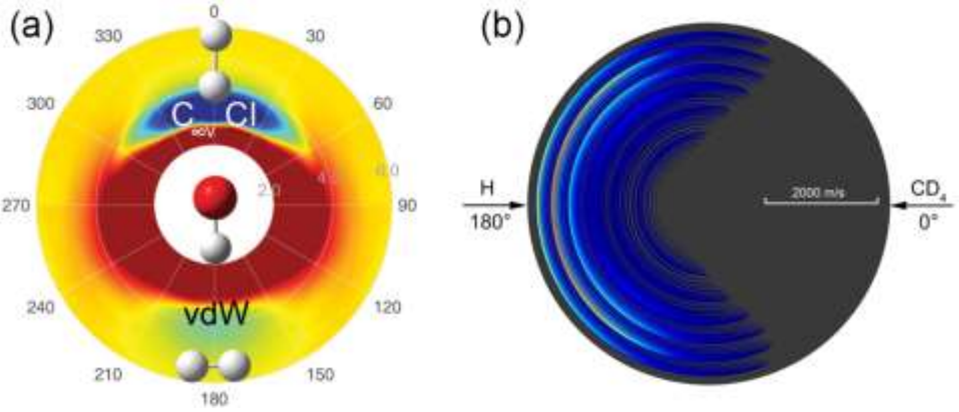

Figure: (a) Polar plot of the adiabatic 3^2A surface of tOH(A)+H2 (b)DCS of the H+CD_4 reaction.

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