

ISMB 2023



25-30 June 2023

BOOK OF ABSTRACTS

30th
International Symposium on
Molecular Beams

Rethymno, Crete, Greece

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(M. Devienne, *Peymenade, FR*)†, (J.B. Fenn (*New Haven, US*))†, J. Reuss (*Nijmegen, NL*), G. Scoles (*Princeton-Trieste, IT*), J. P. Toennies (*Göttingen, DE*), U. Buck (*Göttingen, DE*), Y.T. Lee (*Taipei, TW*) P. Casavecchia (*Perugia, IT*)

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**HONORARY
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New Frontiers in Imaging

Eric Smoll,¹ Martin Fournier,² Chris Kliewer,¹ and David W. Chandler¹

¹Sandia National Laboratory, California, USA

²Heriot-Watt University, Edinburgh, Scotland

Email: chand@sandia.gov

Over the years the imaging of charged particles has been successfully applied to many areas of research. The most popular have been unimolecular photochemistry, bimolecular collisions and reaction I crossed molecular beams and high-resolution electron spectroscopy of anions and neutrals ¹. In this contribution I will describe three new ways we are utilizing ion and electron imaging to learn about chemistry in more complex environments. The three environments are, laser induced plasmas, catalytic reactions on surfaces and details about surfaces by imaging secondary electrons in a secondary electron microscope. Each of these environments has their own set of experimental challenges to overcome to obtain qualitative data.

The first environment, a plasma, is a mix of cations and electrons that are stabilized as a “gas” through electrostatic forces. We use imaging to extract and image the electrons to understand the time evolving temperature and composition of plasmas induced by laser ionization. The second environment, above the surface of a catalyst, allows us to monitor the reactivity at the surface. The imaging challenge is that the plasma is large and moving in time making it difficult to get appropriate imaging at all times and positions. We study catalytic reactivity at the surface of a solid catalyst by ionizing the products of a reaction directly above the surface of the catalyst and image those ions in a manner that tells us where on the surface they were derived. We do this by first utilizing velocity map Imaging at a plane containing a pinhole where we select only the ions that are moving perpendicularly to the surface. Those pass through the pinhole and are imaged on a detector providing a spatial map of where they were formed within the laser beam focus. In this manner the ions report on where they were formed at the surface. The imaging challenge is to accurately determine where in your laser beam ions are formed a few hundred microns above a surface. The third environment is the surface of a material. Secondary electrons with energies between 0 and 50 volts come off of surfaces after electron beams on the order of 5 to 30KV impact those surfaces. These low energy electrons imaged in a manner that allows us to obtain their energy and angular distributions. The imaging is challenging as the surface represents an electrode that can easily distort the distributions.

Acknowledgments: This work was supported the Department of Energy, Office of Basic Energy Sciences.

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Molecular Beam Scattering from Flat Liquid Jets

Daniel Neumark

University of California, Berkeley & Lawrence Berkeley National Laboratory

Email: dneumark@berkeley.edu

Molecular beam scattering is one of the most powerful experimental techniques in all of chemical physics. It has been used to great effect to investigate gas phase chemistry under single collision conditions and the dynamics of gas interactions with solid surfaces. In the pioneering work of Nathanson and Minton, molecular beam collisions with liquid surfaces were studied for the first time, primarily using non-volatile liquids. We have recently adapted a crossed molecular beams instrument to the study of gas-liquid interactions in which the liquid is introduced to vacuum via a flat jet, enabling evaporation and scattering experiments with more volatile liquids. Results will be presented for Ne, CD₄, and D₂O interacting with liquid dodecane. Ongoing efforts to carry out experiments on cold, salty water will also be described.

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Crossed beam experiments on reactions between atomic oxygen or atomic nitrogen with small aromatic compounds

Nadia Balucani

DCBB – Università degli Studi di Perugia, Perugia, Italy

Email: nadia.balucani@unipg.it

In our laboratory we have pursued a systematic investigation of bimolecular reactions involving atomic species and hydrocarbons by means of the crossed molecular beam method with mass spectrometric detection (see, for instance, Ref. 1) for many years. Advantage has been taken of an efficient, versatile radio frequency discharge beam source for the production of atomic (C, N, O, S, Cl) and diatomic (CN, OH, C₂) radicals.²

In this contribution, I will present recent results obtained in our laboratory on the reactions involving either atomic oxygen in its ground electronic state, O(³P), or atomic nitrogen in its first electronically excited state, N(²D), with small aromatic compounds (benzene, toluene, pyridine). The investigated systems are of relevance in combustion chemistry, in the chemistry of the interstellar medium and in the chemistry of the upper atmosphere of Titan, the giant moon of Saturn with potential implications in prebiotic chemistry.

In all cases, the interpretation of the experimental results has been assisted by dedicated *ab initio* calculations of the underlying potential energy surface and statistical estimates of the product branching fractions.³⁻⁶

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Conical Intersections in Photoinduced Molecular Dynamics

Luis Bañares^{1,2,3}

¹*Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain*

²*Center for Ultrafast Lasers (CLUR), Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain*

³*Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA Nanoscience), C/ Faraday 9, 28049 Madrid, Spain*

Email: lbanares@ucm.es

The most general case of photoinduced chemical reactions occurs through non-adiabatic molecular dynamics. The complex panorama of potential energy surfaces describing the excited states of polyatomic molecules is characterized quite often by non-adiabatic crossings and the presence of multiple conical intersections. A conical intersection (CI) is a 3N-8 dimension hypersurface of intersection between two electronic states. The two remaining internal coordinates, *i.e.*, \mathbf{g} as the difference gradient vector, and \mathbf{h} as the non-adiabatic coupling vector, define the branching plane. Conical intersections can be considered as the transition states of electronic excited states and therefore the coupling between the different degrees of freedom, valence electrons and vibrations, and the timescales of these motions, are of paramount interest to understand photodynamics. The aim is to find an equivalent of “Polanyi rules” for excited state molecular dynamics, in such a way that specific vibrational dynamics at conical intersections would be as important to dynamics as are the topographical features of the conical intersections themselves.

In the present case, we highlight several cases of non-adiabatic reaction dynamics in which CIs play a determining role. We will focus on case examples including the identification of an elusive CI in the dissociative ionization of methyl iodide [1,2], the photodissociation dynamics of internally excited ethyl radicals from high Rydberg states [3], the light-induced CI in methyl iodide photodissociation under strong laser fields,[4] and the non-adiabatic dynamics in vinyl iodide [5].

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Xanthone excited-state dynamics measured with time-resolved photoionization spectroscopy

Lou Barreau¹, Léo Cantarell¹, Darius Lebeau¹ and Lionel Poisson¹

¹Institut des Sciences Moléculaires d'Orsay (ISMO) UMR 8214, Université Paris-Saclay, CNRS, Rue André Rivière, Bâtiment 520, F-91405 Orsay Cedex, France

Email: lou.barreau@universite-paris-saclay.fr

Xanthone is a prototypical molecule for photochemistry in the triplet state due to its triplet yield close to unity [1] and its fast (ps) intersystem crossing in solution [2]. However, the mechanisms at play in the isolated molecule after photoexcitation to the second singlet excited state S_2 are still under debate. Here, we investigate the femtosecond time-resolved dynamics in gas-phase Xanthone after excitation at various wavelengths within the S_2 band (310–330 nm). Photoelectron spectroscopy in a Velocity Map Imaging Spectrometer and Time-of-Flight Mass Spectrometry are performed after multiphoton ionization at 800 nm, 400 nm, or single-photon ionization at 266 nm. The experimental results are compared to recent wavepacket dynamics simulations [3].

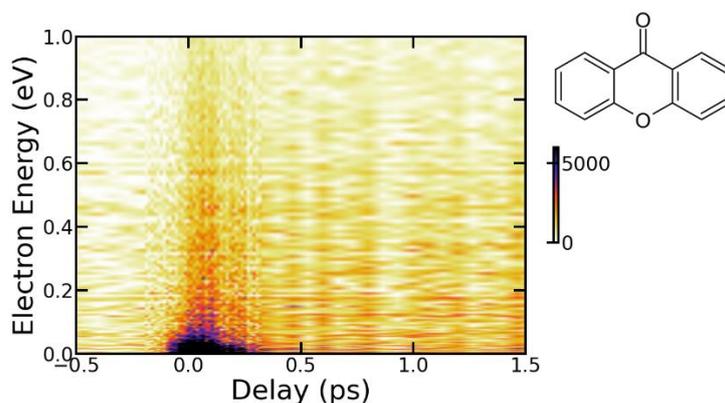


Figure: Time-resolved photoelectron spectrum of Xanthone after excitation at 322 nm and single-photon ionization at 266 nm.

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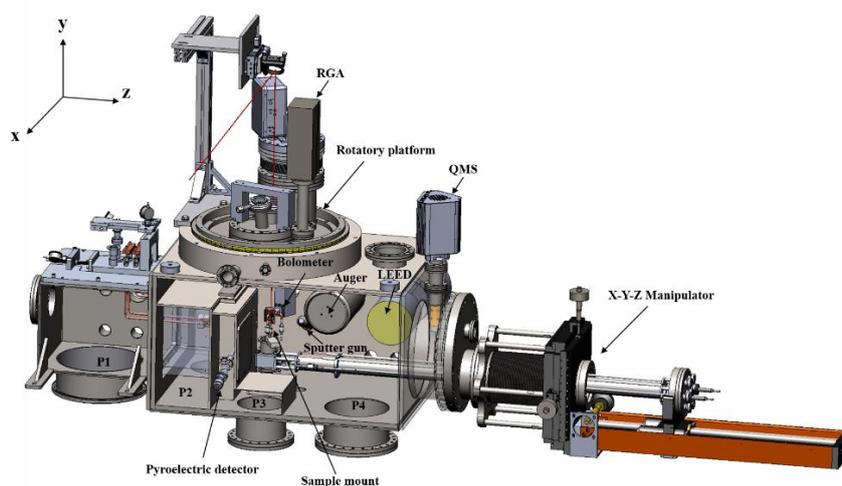
Probing surface dynamics and catalytical activity by state-to-state molecule/surface scattering

Christopher S. Reilly, Patrick Floss, Bo-jung Chen, Daniel J. Auerbach, and Rainer D. Beck

Institute of Chemical Sciences and Engineering (ISIC), École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

Email: rainer.beck@epfl.ch

We present first results for state-to-state methane scattering experiments from four different solid surfaces obtained in a new, dedicated UHV state-to-state molecule/surface scattering apparatus that combines the preparation of a surface incident molecular beam in a specific initial rovibrationally excited state with angle- and quantum-state-resolved detection of the scattered species. Our detection technique uses a cryogenic bolometer in combination with infrared laser tagging and is applicable to any molecule with an infrared active vibrational mode and a rotationally resolved infrared spectra. Comparing the extend of vibrationally inelastic scattering $\text{CH}_4(n_3 \rightarrow n_1)$ (where n_3 and n_1 are the antisymmetric and symmetric C-H stretch normal modes) from Ni(111), NiO/Ni(111), Au(111), and graphene/Ni(111), reveals a propensity for vibrational relaxation that scales with catalytic activity of the target surface as characterized by the barrier height for the methane dissociation. The experimental observations can be rationalized by quantum mechanical inelastic scattering calculations by the Jackson group¹.



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DOI:[10.1103/PhysRevResearch.2.043251](https://doi.org/10.1103/PhysRevResearch.2.043251)

Making Kinetics at Surfaces a More Exact Science

Dmitriy Borodin*, Florian Nitz, Michael Schwarzer, Daniel J. Auerbach, Theofanis N. Kitsopoulos, Alec M. Wodtke

*: Center for Quantum Nanoscience, 52 Ewhayeodae-gil, Daehyeon-dong, Seodaemun-gu
03760 Seoul, South Korea

*: Borodin.dmitriy@qns.science

Quantitative understanding of reactions at surfaces is essential for rational design of catalytic materials for large-scale chemical transformations. The quality of a catalyst is typically evaluated by the degree it enhances the product formation rate, its selectivity for the particular product and its resistance against processes leading to its deactivation. All these properties can be fully characterized when elementary rate constants of all underlying processes, like adsorption, diffusion, reaction and desorption are determined from experiment or theory. Today catalyst discovery is transitioning more and more into full *in silico* modelling. Unfortunately, many methods employed in this context remain without validation from precise experiments. Given the fact that these untested methods are likely to influence our choice of the catalytic material for a given purpose, this situation remains highly unsatisfying.

During the last few years we established the Velocity Resolved Kinetics (VRK) technique[1], which opened up the possibility to study transient surface reaction rates with extraordinary precision. We focused on characterization of elementary rate constants for desorption, site-to-site hopping and active-site specific reactions on atomically stepped and flat single crystal surfaces[2-9]. So far, a key requirement for VRK was a model catalyst which recovers within the pump-probe cycle of the experiment, preventing us to study non-stationary catalytic phenomena in detail. In my talk, I will present a new experimental scheme for VRK allowing the study of surface reaction kinetics while the catalyst is dynamically changing during the experimental investigation[10]. This technique has the potential to bridge the gap between laboratory surface kinetics experiments and real-world heterogeneous catalysis.

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Ultrafast Imaging of Molecular Dynamics with Electron Diffraction

Martin Centurion¹

¹*University of Nebraska, Lincoln, Nebraska, United States*

Email: martin.centurion@unl.edu

The conversion of light into chemical energy, at the level of single molecules, drives many biological and chemical processes such as vision and photosynthesis, and has applications in solar energy conversion and storage. In order to understand and control these reactions, it is essential to observe them as they happen on the femtosecond scale and in real space on the atomic scale. While most time-resolved studies of molecular reactions have relied on spectroscopic measurements, recent advances have allowed for the emergence of Ultrafast Electron Diffraction (UED) with femtosecond resolution, which provides previously inaccessible information. UED is directly sensitive to changes in the molecular structure, thus it provides information complementary to spectroscopic observables.

Recent advances have enabled ultrafast electron diffraction (UED) to successfully capture coherent nuclear motions on the relevant time scales [1], to spatially resolve a wave-packet traversing a conical intersection [2] and to capture ring opening and dissociation reactions [3,4]. Here, we will describe the method of UED and present a recent application to study an intramolecular proton-transfer reaction. Proton transfer reactions are widely common in nature and have many technological applications, but so far have not been studied with atomic spatial resolution to directly observe the nuclear motions. We use UED to capture the main structural changes leading to and following the proton transfer in photoexcited o-nitrophenol. We map the main structural motions and follow the wavepacket from the excited state back to the ground state through a conical intersection.

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Magnetic manipulation of rotational orientation projection states in ground state molecules

Helen Chadwick,¹ Yosef Alkoby,¹ and Gil Alexandrowicz¹

¹*Department of Chemistry, Faculty of Science and Engineering, Swansea University, Singleton Park, Swansea, SA2 8PP, Wales*

Email: h.j.chadwick@swansea.ac.uk

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. Here I will explain a unique magnetic manipulation technique¹ which has made it possible to coherently control the m_J (and nuclear spin projection, m_I) states of small ground state 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. To date, this technique has been used to obtain a scattering matrix for H_2 scattering from a LiF surface², and study the rotationally inelastic diffraction of D_2 from Cu(111)³, but also opens the possibility of exploring the role of nuclear spin and rotational orientation projection states in gas-phase scattering. The methodology is potentially applicable to a range of small ground state molecules, which will provide extremely stringent benchmarks which can be used to develop accurate theoretical models.

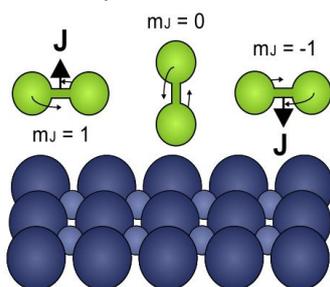


Figure: Rotational orientation projection states describe (classically) whether the molecule is rotating like a helicopter or a cartwheel.

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Hypervelocity Ice Grain Impact Mass Spectrometry

Sally E. Burke, Zachary Auvil, Karl Hanold and Robert E. Continetti

Department of Chemistry and Biochemistry, University of California San Diego,

9500 Gilman Drive, La Jolla, CA 92093-0340, USA

Email: rcontinetti@ucsd.edu

One proposed spaceflight instrument for the detection of biosignatures in small icy particles – like those ejected from Saturn’s moon Enceladus – is an impact ionization mass spectrometer. Laboratory validation of proposed flyby sampling missions is needed to show that biosignature molecules can survive an impact at hypervelocity speeds. We have constructed an Aerosol Impact Spectrometer that allows studies of the impact dynamics for single mass- and charge-selected submicron particles,¹ providing an ideal tool for validating the approach of sampling the Enceladus ice grain plume in a flyby mission for the detection of specific biosignatures. Previously, we have applied this approach to study the impact dynamics of ice grains from 40 m/s to 2.4 km/sec, examining the coefficient of restitution and post-impact behavior including rebound, adhesion and fragmentation.^{2,3} Now, using a 41-element linear accelerator (615 keV/q), this technique has been extended to allow particle velocities up to 4.2 km/sec, well above the ~2 km/sec threshold for impact ionization. Time-of-flight mass spectra obtained from the impact of ~0.8 micron diameter single charged ice grains using the Hypervelocity Ice Grain Impact Mass Spectrometer following impact have now been obtained. This technique replicates the hypervelocity impact of organic-laden submicron ice grains for in-situ mass spectrometric characterization. It is found that amino acids entrained in ice grains can be detected intact after impact at speeds up to 4.2 km/s and that the presence of salt reduces their detectability, providing an important benchmark for future missions to Enceladus.

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Time-Resolved PhotoElectron Circular Dichroism: a comparative study in Camphor and Fenchone

Valérie Blanchet, Dominique Descamps, Stéphane Petit, Yann Mairesse, Bernard Pons and Baptiste Fabre

Université de Bordeaux – CNRS – CEA, CELIA, UMR5107, F33405 Talence, France

Email: baptiste.fabre@u-bordeaux.fr

PhotoElectron Circular Dichroism (PECD) [1, 2] is a well-established technique allowing to probe the chirality of complex systems in gas phase whatever the ionization regime [3]. Experimentally, it consists in characterizing the asymmetry, with respect to the direction of light propagation, of the photoelectron momentum distribution resulting from the ionization of a set of randomly oriented molecules by a circularly polarized pulse. The PECD is particularly sensitive to the molecular structure [4] and vibrational excitation [5, 6], which makes it an adequate observable for the study of dynamics initiated in chiral systems. Here we present the time-resolved PECD investigation of relaxation dynamics in 1R,4R-(+)-camphor [7] and 1R,4S-(-)-fenchone [8] molecules, which highlights the sensitivity of the PECD not only to the relaxation dynamics but also to isomerism.

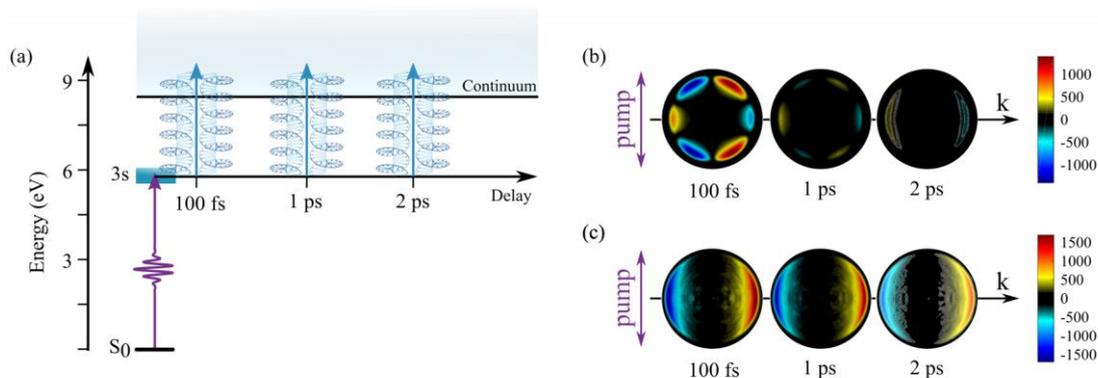


Figure: (a) Scheme of the pump-probe experiment. (b) Asymmetric 2D distribution for camphor excited with a linearly polarized photon ($S_3 = 0$) as a function of the delay. (c) Same for fenchone.

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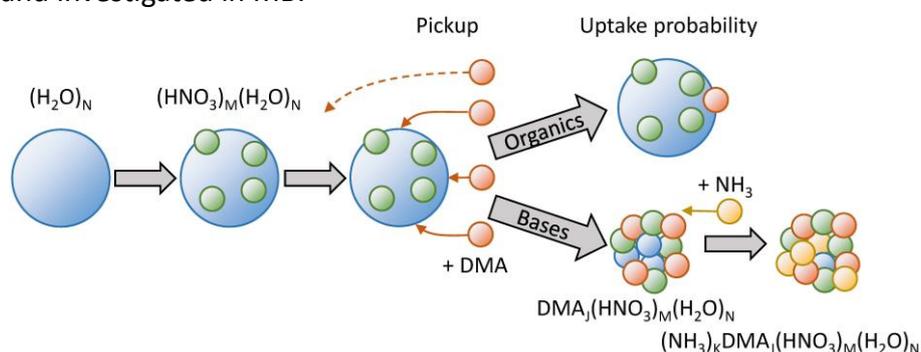
Can Clusters in Molecular Beam-Experiments Mimic Atmospheric Aerosols?

Michal Fárník¹

¹J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague 8, Czech Republic

Email: michal.farnik@jh-inst.cas.cz

The relevance of clusters for atmospheric chemistry was emphasized since the early studies of clusters in molecular beams (MB). In particular, the clusters can serve as laboratory analogues to the atmospheric aerosol particles. Recently, the clusters in MB have approached the atmospheric aerosols in terms of their size and chemical complexity.¹ At the same time, the investigation of the clusters in MB can continuously cover the size region between the isolated gas-phase molecules and nanometer sized aerosol particles (*atmospheric nanoclusters*) that are difficult to measure directly in the atmosphere. We will describe the journey from the investigations of pure large water clusters $(\text{H}_2\text{O})_N$ (ice nanoparticles), over hydrated nitric and sulfuric acids, to multicomponent acid/base/organics/water clusters generated and investigated in MB.



The experiments were performed on a versatile cluster beam apparatus CLUB in Prague, which implements several techniques:^{2,3} the clusters can be doped by different molecules in a pickup process, interactions with photons and/or electrons of different energies trigger various processes such as UV-photodissociation, IR and UV excitation, ionization, electron attachment and ion-molecule reactions, which are probed by velocity map imaging (VMI) and/or mass spectrometry. Most recent examples of these experiments will be discussed.

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Self-organization in the avalanche, quench and dissipation of a molecular ultracold plasma

Amin Allahverdian,¹ Ruoxi Wang,² Kevin Marroquín,¹ Nathan Durand-Brousseau,^{1,2} Smilla Colombini,¹ Abhinav Prem,³ John Sous,⁴ and Edward Grant^{1,2}

¹Department of Chemistry, and ²Department of Physics & Astronomy, University of British Columbia, Vancouver, BC V6T 1Z1, ³Department of Physics, Princeton University, Princeton, NJ 08540,

⁴Department of Physics, Stanford University, Stanford, CA 94305

Email: edgrant@chem.ubc.ca

In dissipative many-body Rydberg gases, long-range correlations can give rise to transient states with emergent dynamics that oppose the equipartition of energy. Small driving forces produce local fluctuations that trigger avalanche-like energy dissipation events. Driven dissipation can lead to avalanche distributions described by power laws signifying self-organization to a scale-invariant critical state. Recent experiments in Strasbourg and Durham have found such signs of self-organized criticality in the off-resonant excitation of a Rydberg gas in the anti-blockade regime, where interaction-induced line shifts and broadening cause transition avalanches reflecting a physics of self-organization. A similar mosaic of local kinetic processes and long-range interactions drives the relaxation of a molecular Rydberg gas of nitric oxide to form an ultracold plasma. Here, we find a scale-invariant, power-law avalanche-size distribution: $P(N) = N^{\alpha}$ with $\alpha = -1.37$.

An evident balance in the optimum initial density, ρ_0 , for a chosen initial principal quantum number, n_0 , reflects a sensitivity to the Rydberg orbital radius compared with the average distance between nearest neighbors. Non-linearity enters in the variation of dipole-dipole coupling and unimolecular dissociation with the evolving electron binding energy. Owing to these factors, n_0 and ρ_0 constitute important control parameters to consider in models that seek to explain the apparent self-organized criticality of this system in terms of the dynamics of microscopic interactions.

The nitric oxide ultracold plasma populates an ensemble of disordered dipoles largely confined to an energy interval within a few hundred GHz of the ionization threshold. Reading the nature of Rydberg-Rydberg coupling in the linewidths and depths of mm-wave depletion resonances, we see direct evidence that a trace residual population of $n_{0l}(2)$ states, driven to predissociation via resonance with $(n_0 \pm 1)d(2)$ states bridges the closed plasma ensemble to a continuum of free N(⁴S) + O(³P) atoms, in effect creating an open quantum system in which Griffiths-like regions couple the plasma to a thermal reservoir. Motivated by these results, we have constructed a minimal model of disordered one-dimensional spins evolving under a Lindblad master equation with local dissipation that qualitatively reproduces the experimental observations.

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Quantum Chemistry for Quantum Logic

Eric R. Hudson^{1,2,3}

¹Department of Physics and Astronomy, UCLA, Los Angeles, CA USA

²Center for Quantum Science and Engineering, UCLA, Los Angeles, CA USA

³Challenge Institute for Quantum, UCLA, Los Angeles, CA USA

Email: eric.hudson@ucla.edu

Chemists are largely absent from the world-wide effort to realize *useful* quantum technology, relegating chemistry to merely an afterthought when qubits and their associated quantum machinery are built. This talk will be a call-to-arms for the chemical community. I will argue that elevating chemical considerations in the design process would lead to improved performance for current quantum processors [1,2] and wholly new routes to quantum technology [3].

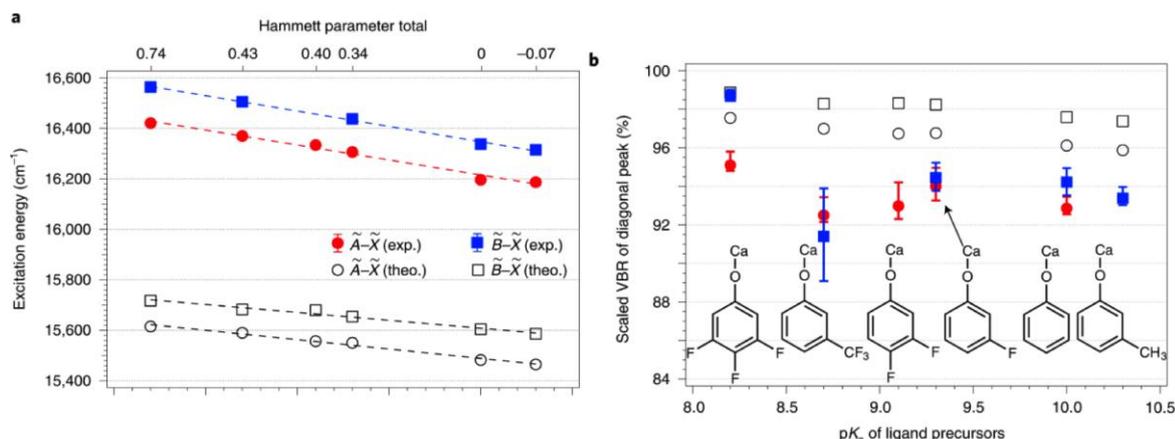


Figure: Transition energies versus $\text{p}K_a$ for all calcium phenoxide and derivatives. **b**, Scaled VBR for diagonal decay as a function of $\text{p}K_a$.

Acknowledgments: US ARO, US AFOSR, and US NSF.

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Fluoroform (CHF_3) production from CF_3CHO photolysis and implications for the decomposition of hydrofluoroolefins in the atmosphere

Joshua D. Thomson,¹ Jyoti S. Campbell,¹ Ethan B. Edwards,¹ Christopher Medcraft,¹ Klaas Nauta,¹ Maria Paula Pérez Peña,¹ Jenny A. Fisher,² David L. Osborn,³ Scott H. Kable¹ and Christopher S. Hansen¹

¹*School of Chemistry, University of New South Wales, Australia*

²*University of Wollongong, Australia*

³*Combustion Research Facility, Sandia National Labs, USA*

Email: s.kable@unsw.edu.au

Hydrofluoroolefins (HFOs) are the leading synthetic replacements for compounds successively banned by the Montreal Protocol and amendments. HFOs readily decompose in the atmosphere to form fluorinated carbonyls, including CF_3CHO in yields up to 100%, which is then photolyzed. A longstanding issue, critical for the transition to safe industrial gases, is whether atmospheric decomposition of CF_3CHO yields any quantity of CHF_3 (HFC-23), which is one of the most environmentally hazardous greenhouse gases.

In this talk, I will discuss three experimental techniques, all involving molecular beams. One technique provides true zero-pressure quantum yields in a molecular beam. The second provides low pressure, 300 K quantum yields, while the third provides quantum and molar yields up to 1 bar pressure using a combined FTIR – chirped pulse FT microwave technique. These experiments confirm this reaction occurs under at all pressures from true zero pressure to 1 bar, atmospheric conditions. We provide pressure-dependent quantum and molar yields. We have also conducted atmospheric modelling using the Master Chemical Mechanism, implemented via the AtChem box model. We estimate a maximum 100-year global warming potential, $\text{GWP}_{100} \sim 10$, demonstrating that HFOs are unlikely to contribute to the greenhouse effect significantly more than “natural refrigerants”.

Acknowledgments: This work was supported by the Australian Research Council (DP220100891, DE200100549, DP190102013), the Australian National Computational Infrastructure (NCI) and the Department of Energy (USA) as well as our institutions.

Structures of nanoclusters formed in superfluid helium droplets: crystalline or amorphous?

Marisol Trejo, Andrew Clifford, Jie Zhang, and Wei Kong

Dept. of Chem., Oregon State University, Corvallis, Oregon 97331, USA

Email: Wei.Kong@Oregonstate.edu

Superfluid helium droplets are known scavengers collecting dopants along their traveling path. The structures of the thus formed dopant clusters are of interest not just for scientific curiosity, but also for potential applications in synthesis of catalysts.¹ Using electron diffraction, we have determined that dimers and trimers are typically formed with gas phase structures,² different from any cuts from the crystalline structures. Given the fast rate of cooling of superfluid helium droplets, it is also reasonable to suspect that large nanoclusters formed in droplets are amorphous. On the other hand, evidence of crystalline structures of rare gas clusters has been reported.³ We compare structures of large benzene clusters and large argon clusters formed in superfluid helium droplets, and discuss the conditions for forming crystalline nanoclusters inside helium droplets.

Acknowledgments: This work was supported by the National Institutes of Health.

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The Competition Between Hydrogen Bonding and π -Stacking Explored with Supersonic Jets and Broadband Chirped-Pulse Microwave Spectroscopy

Wenqin Li,¹ Rizalina T. Saragi,^{1,2} Marcos Juanes,^{1,2} Camilla Calabrese,¹ Cristóbal Pérez,¹
Alberto Lesarri¹

¹*Departamento de Química Física y Química Inorgánica, Facultad de Ciencias – I.U. CINQUIMA, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid (Spain)*

²*Institut für Ionenphysik and Angewandte Chemie, Universität Innsbruck, Technikerstr. 25/4.OG, 6020 Innsbruck (Austria)*

Email: alberto.lesarri@uva.es

The combination of supersonic jets and broadband (chirped-pulse) microwave spectroscopy has greatly expanded the studies on non-covalent interactions in the gas-phase.¹ Neutral clusters up to ca. 600 Da are now rotationally accessible, offering insight into their structural and electronic properties. We will offer examples on dimerization and trimerization of model systems, in particular alcohols and thiols. The investigation of cyclic and aromatic molecules permits discerning the balance of inter and intramolecular forces, the influence of transient chirality and the emergence of isomer multiplicity, as in the six isomers of (cyclohexanol)₂ or the three isomers of (2-phenylethanol)₂. For the thiol dimers these studies are effective to discern the properties of weaker non-covalent interactions involving sulfur, specifically the O-H...S, S-H...S or S-H... π hydrogen bonds, as in (thiophenol)₂ or (benzyl mercaptan)₂.² Moreover, the extension to thiol or alcohol substituted naphthalenes has exposed the competition between hydrogen bonding and π -stacking forces. We will present the differences between the homodimers of 1- and 2-naphthalenethiol, all dominated by π -stacking forces.³

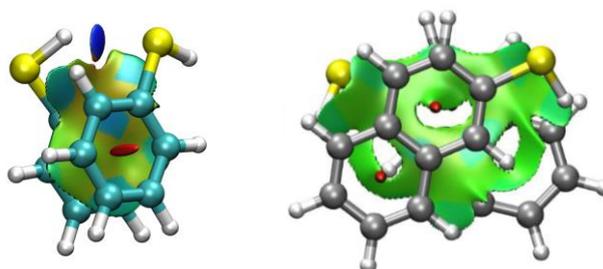


Figure: The thiophenol dimer (left) and the C_2 -symmetric 2-naphthalene dimer (only one isomer shown).

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Fission of Oblate Gold Superatom in $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ via Collision-Induced Core Deformation

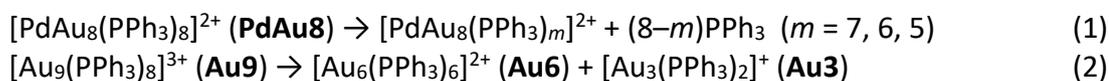
Satoru Muramatsu

Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima-shi, Hiroshima, Japan

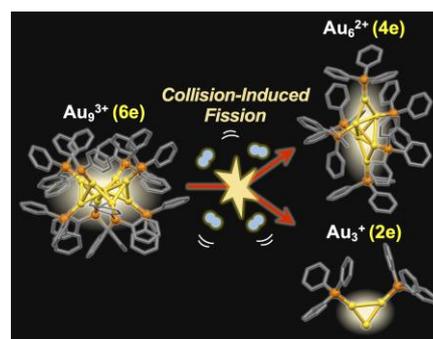
Email: smuramatsu@hiroshima-u.ac.jp

Structural fluxionality¹ is one of distinct features of ligand-protected metal clusters. A prototypical example can be found in a title cluster $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ (**Au9**), whose crown-shaped Au_9 core can easily be isomerized into butterfly-shape by controlling counter-anion packing.² Notably, this isomerization is suppressed in $[\text{PdAu}_8(\text{PPh}_3)_8]^{2+}$ (**PdAu8**), owing to its stiffer intracluster bonds.² In this talk, we present our recent unprecedented finding that the above-described difference is further reflected on collision-induced dissociation (CID) patterns.³

CID mass spectrometry of **PdAu8** identified ordinary sequential PPh_3 losses as shown in Reaction (1). In contrast, **Au9** underwent cluster-core fission (Reaction (2)), associated with splitting the number of valence electrons in the superatomic orbitals from 6e (**Au9**) into 4e (**Au6**) and 2e (**Au3**).



Density functional theory calculations revealed significantly different core shapes of **Au9** and **Au6**: oblate and prolate cores with semi-closed superatomic electron configurations of $(1\text{S})^2(1\text{P}_x)^2(1\text{P}_y)^2$ and $(1\text{S})^2(1\text{P}_z)^2$, respectively. The absence of this route in **PdAu8** is probably attributed to its stiffer intracluster bonds. From these results, we propose that the collision-induced structural deformation (oblate \rightarrow prolate) plays a critical role in the cluster-core fission.



Acknowledgments: I am grateful to following members for their collaborations in this project: Dr. Tsubasa Omoda, Dr. Shinjiro Takano, and Prof. Tatsuya Tsukuda (The Univ. of Tokyo); Mr. Yuki Nakahigashi and Prof. Yoshiya Inokuchi (Hiroshima Univ.).

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Coulomb explosion imaging to watch dynamics in molecules and molecular dimers

Rebeca de Nalda¹, María Eugenia Corrales², Jesús González Vázquez² and Luis Bañares³

¹Instituto de Química Física Blas Cabrera, CSIC, C/ Serrano 119, 28006 Madrid, Spain

²Dpto. de Química, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

³Dpto. de Química Física (Unidad Asociada I+D+i del CSIC), Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

Email: r.nalda@csic.es

Coulomb explosion occurs when more than one electron is ejected from the system, and its charged components undergo explosion due to the electrostatic repulsion. The complete measurement of the final velocity vectors of the fragments¹ can provide information on the geometry of molecules or clusters² or the alignment or orientation of a molecular ensemble in the laboratory frame³. Coulomb explosion can also be used as a probe of transient molecular structure in studies of time-dependent molecular dynamics initiated by a short pump laser pulse. In this presentation we will show how Coulomb explosion imaging can map nonadiabatic molecular dynamics in CH₃I A-band dissociation⁴ and, beyond the single molecule case, we will describe how Coulomb explosion readily happens in CH₃I dimers with laser pulses of low intensity. We will discuss the mechanisms that make this anomalous Coulomb explosion process possible and evaluate the dynamical insights that can be obtained from its observation.

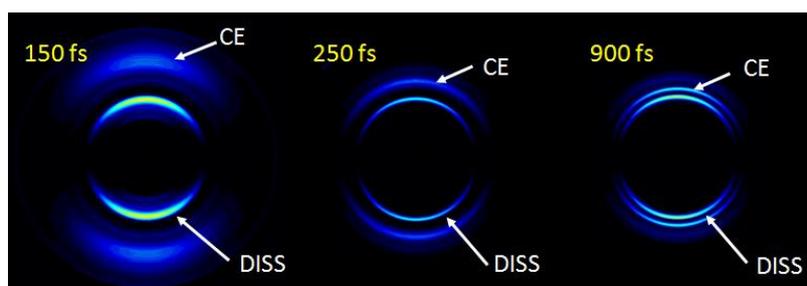


Figure. Abel-inverted CH₃⁺ images obtained after A-band dissociation of CH₃I followed by probing with an intense NIR field at selected delays. DISS: single ionization processes; CE: Coulomb explosion channels.

Acknowledgments: This work was supported by projects PID2021-122839NB-I00 and PID2019-106125GB-I00 from the MCIN/AEI/10.13039/501100011033/FEDER.

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Quantum state resolved dynamics at the gas-liquid interface: Rotating wheels, self-assembled monolayers, and liquid microjets

David J. Nesbitt

*JILA, National Institute of Standards and Technology, and University of Colorado, Boulder,
Department of Chemistry and Biochemistry, Department of Physics, University of Colorado, Boulder,
CO 80309, USA*

Email: David.Nesbitt@colorado.edu

Studies of quantum state resolved collisions in the gas phase and at the gas-solid interface have long been highlighted in ISMB meetings and have served as mature testbeds for development and testing of first-principle theories for energy transfer. By comparison, equivalent efforts for quantum state resolved collision dynamics at the *gas-liquid* interface have been more elusive. This talk will report on results in three challenging directions for the field, each based on a rovibronically quantum state-resolved perspective: i) rovibrationally inelastic scattering of OCS molecules with wetted wheel gas-liquid interfaces and high resolution quantum cascade IR laser direct absorption, ii) inelastic scattering of HCl from self-assembled monolayers (SAMs) via resonance-enhanced photoionization (REMPI)/velocity map imaging (VMI), and iii) quantum state resolved evaporation dynamics of NO at the gas-water and gas-hydrocarbon alcohol interface with laser induced fluorescence (LIF) methods. As a recurring theme, we find that molecular projectiles reactively, inelastically, or evaporatively scatter from the gas-liquid interface into internal quantum state distributions *out of equilibrium* with respect to the bulk liquid temperature (T_S). Such non-equilibrium behavior may make dynamics at gas-liquid interfaces more complicated but also even more interesting targets for further experimental/theoretical exploration.

Towards cold and controlled reactive collisions

Jolijn Onvlee¹

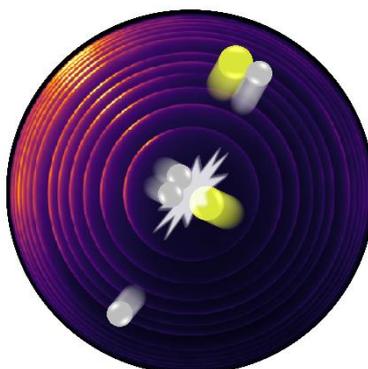
¹*Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands*

Email: J.Onvlee@science.ru.nl

One of the main aims in physical chemistry is to completely understand chemical reactions and the underlying dynamics on a molecular level. To achieve this, we investigate collisions and reactions between individual molecules and atoms in the gas-phase using the well-known crossed molecular beam technique. By utilizing a Zeeman decelerator in combination with a Velocity Map Imaging (VMI) detector in our crossed-beam setup, we can examine these molecular encounters with exceptional precision [1,2].

The decelerator produces beams of paramagnetic species with a well-defined and tunable velocity, narrow velocity spreads, and a high quantum-state purity, while VMI combined with resonance-enhanced multiphoton ionization enables us to accurately probe the velocity vectors of the scattered products. This powerful combination of techniques allows for scattering experiments with extraordinary resolution, unveiling intricate features of molecular collisions, such as scattering resonances and diffraction oscillations.

Here, I will show how we use our approach to investigate reactive collisions between excited sulfur atoms and hydrogen molecules, i.e., $S(^1D) + H_2 \rightarrow SH + H$. By investigating the collision-energy dependence of state-to-state differential cross sections, especially at low collision energies, we aim to provide an extremely sensitive test for potential energy surfaces and scattering calculations used to describe the molecular reaction dynamics in this system.



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Chemistry in merged molecular beams and in merged microjets

Andreas Osterwalder

Institute for Chemistry and Chemical Engineering (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Email: andreas.osterwalder@epfl.ch

I will be giving a status report on our experiments on stereodynamics in merged molecular beams where two reactant beams are superposed using curved electric and magnetic guides. We have studied sub-Kelvin stereodynamics in prototypical energy transfer reactions, namely between metastable $\text{Ne}(^3\text{P}_2)$ and rare gas atoms or diatomic molecules.

Such reactions can lead to Penning ionization (producing X^+) or associative ionization (producing NeX^+), respectively, and the branching ratio is highly dependent on the reactant orientation and the collision energy.

In the second part of the presentation I will review our work in liquid microjets where we have recently demonstrated a new approach to measure chemical kinetics at liquid-liquid interfaces.

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Probing molecular photodynamics using ultrafast XUV transient absorption spectroscopy

Sonia Marggi Poullain¹

¹*Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain.*

Email: smarggi@ucm.es

Ultrashort laser pulses currently available characterized by femtosecond to attosecond temporal duration has enabled the development of different sensitive tools for real-time observation of photo-induced chemical reactions. Here, ultrafast extreme ultraviolet (XUV) transient absorption spectroscopy is employed to unravel the dynamics in small polyatomic iodinated molecules. The dynamics is 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, and is then 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, due to the strong shift of the XUV core-to-valence transitions with internuclear separation and the high sensitivity of the wave packet to the electronic configuration. The results presented will include first coherent nuclear motion in the B excited state of molecular iodine (I₂) visualized with great detail [1] including the wave packet spreading and later recompression, at the outer turning point and inner turning point, respectively. Second, structural effects on the photodissociation dynamics of alkyl iodides will be presented [2, 3]. The dynamics governed by coupled electronic and nuclear dynamics at conical intersections is experimentally revealed.

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Microscopic pathways to energy dissipation and adsorption in molecule-metal surface encounter

I. Rahinov, Raanana/IL, D. Borodin, Goettingen/DE, P.R. Shirhatti, Hyderabad/IN A.

Kandratsenka, Goettingen/DE, T. Kitsopolous/DE, D. J. Auerbach, Goettingen/DE, H. Guo,

Albuquerque/US/NM and A. M. Wodtke, Goettingen/DE

Prof. Igor Rahinov, The Open University of Israel, 1 University Rd., 43553701 Raanana, Israel

Email: igorra@openu.ac.il

The most common mechanism of catalytic surface chemistry is that of Langmuir and Hinshelwood (LH). In the LH mechanism, reactants adsorb, thermalize with the surface and subsequently react. At the same time, molecular vibration is known to enhance the rates of gas-phase chemical reactions as the motion associated with bond stretching facilitates the reactant molecule approach to the transition state. However, for reactions occurring on via LH mechanism on metal surfaces, relevant for heterogeneous catalysis reactions, the ability of vibrational excitation to promote reactivity is hampered by rapid dissipation of the vibrational energy of the reactant into electronic excitation of the metal within several picoseconds. Our recent findings challenge this paradigm: we have demonstrated by quantum-state-resolved scattering of CO($v=2,1$) from Au (111), studied in temporally and spatially resolved fashion, that excited vibrational states can survive longer than expected [1] (~ 100 ps) – suggesting vibrational excitation might promote or modify heterogeneously catalyzed LH-chemistry on metals. Furthermore, we show that the vibrational relaxation time can serve as an internal clock to follow the microscopic pathways of adsorption and equilibration on the surface [2]. On the basis of molecular beam experiments and theoretical modeling we reveal the intricate interplay between physisorption and chemisorption states [2] for the prototypical CO/Au(111) system, relevant to many other heterogeneous systems.

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The “Vector-Model” Wavefunction: spatial description and wavepacket formation of quantum-mechanical angular momenta

T. Peter Rakitzis^{*1,2}, Michail E. Koutrakis^{1,2}, and George E. Katsoprinakis^{1,2}

¹ Department of Physics, University of Crete, 70013 Heraklion-Crete, Greece

² IESL-FORTH, N. Plastira 100, Heraklion-Crete 71110, Greece

*Email: ptr@iesl.forth.gr

In quantum mechanics, spatial wavefunctions describe distributions of a particle’s position or momentum, but not of angular momentum \mathbf{j} . In contrast, here we demonstrate the existence of a spatial angular-momentum wavefunction, $\mathbf{j}_m(\varphi, \theta, \chi) = e^{im\varphi} \delta(\theta - \theta_m) e^{i(j+\frac{1}{2})\chi}$, which treats \mathbf{j} in the $|\mathbf{j}m\rangle$ state as a three-dimensional entity, and is an asymptotic eigenfunction of angular-momentum operators; φ, θ, χ are the Euler angles, and θ_m is the Vector-Model polar angle, given by $\cos \theta_m = m/|\mathbf{j}|$. The $\mathbf{j}_m(\varphi, \theta, \chi)$ wavefunctions give a computationally simple description of particle and orbital-angular-momentum wavepackets (constructed from Gaussian distributions in \mathbf{j} and \mathbf{m}) which predict the effective wavepacket angular uncertainty relations for $\Delta m \Delta \varphi$, $\Delta j \Delta \chi$, and $\Delta \varphi \Delta \theta$, and the position of the particle-wavepacket angular motion in the orbital plane. The particle-wavepacket rotation can be experimentally probed through continuous and non-destructive \mathbf{j} -rotation measurements. We also use the $\mathbf{j}_m(\varphi, \theta, \chi)$ to determine geometrically well-known asymptotic expressions for Clebsch-Gordan coefficients [1], Wigner d -functions [2], the gyromagnetic ratio of elementary particles, $g = 2$ [3,4], and the \mathbf{m} -state-correlation matrix elements. Interestingly, for low \mathbf{j} , even down to $\mathbf{j} = 1/2$, these expressions are either exact (the last two) or excellent approximations (the first two), showing that the $\mathbf{j}_m(\varphi, \theta, \chi)$ give a useful spatial description of quantum-mechanical angular momentum, and provides a smooth connection with classical angular momentum.

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Molecular Beam Surface Scattering of Polyatomic Molecules

Tim Schäfer^{1,2}, Rasika E. A. Dissanayake,^{1,2} Alec M. Wodtke^{1,2}, Daniel Schaueremann,^{1,2} Arved C. Dorst,^{1,2}

¹University of Göttingen, Institute of Physical Chemistry, Tammannstraße 6, DE-37077 Göttingen

²Max-Planck Institute for Multidisciplinary Sciences, Am Faßberg 11, DE-37077 Göttingen

Email: tschaef4@gwdg.de

We combine velocity map imaging (VMI) with molecular beam surface scattering to investigate the interaction of polyatomic molecules with catalytic surfaces. VMI provides the angular-resolved velocity distributions of desorbing reaction products, so that detailed information about surface reaction dynamics are obtained.[1] Additionally, the VMI detector allows to record the photoelectron circular dichroism (PECD), enabling chirality sensitive detection of surface reaction products.

We use this technique for studies on heterogeneously catalyzed chiral surface reactions like the partial oxidation of olefins to epoxides on metal surfaces. For this, we combine PECD measurements with velocity resolved kinetics experiments, providing enantiosensitive information about reaction mechanisms at surfaces. [2]

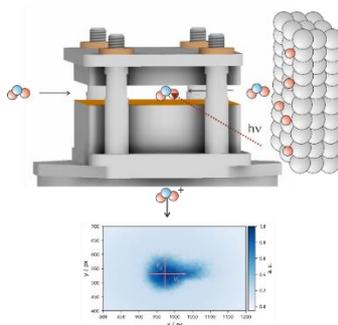


Figure: Experimental setup for molecular beam surface experiments in combination with velocity map imaging. Scattered molecules are ionized between a repeller and a grounded grid. Molecules are accelerated towards microchannel plates (MCPs) and a phosphor screen. Velocity map imaging is achieved when biasing an ion lens. The inset shows a typical raw image consisting of two parts: the symmetric signal around zero velocity is caused by background gas and is subtracted during data analysis. Desorbing molecules appear as a non-symmetric signal with velocity components parallel to the surface normal.

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Elementary Steps in Hydrogenation of α,β -unsaturated Aldehydes on Functionalized Surfaces

Swetlana Schauer mann

Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Max-Eyth-Str. 2, 24118 Kiel, Germany

[*schauer mann@pctc.uni-kiel.de](mailto:schauer mann@pctc.uni-kiel.de)

Selectivity of multi-pathway surface reactions depends on subtle differences in the activation barriers of competing reactive processes, which is difficult to control. One of the most promising strategies to overcome this problem is to introduce a specific selective interaction between the reactant and the catalytically active site, directing the chemical transformations towards the desired route. This interaction can be imposed via functionalization of a solid catalyst with ligands, promoting the desired pathway via steric constrain and/or electronic effects.¹ The microscopic-level understanding of the underlying surface processes is an important prerequisite for rational design of a new class of ligand-functionalized catalytic materials.

In this contribution, we present a mechanistic study on formation and dynamic changes of a functionalized heterogeneous Pd(111) catalyst for chemoselective hydrogenation of α,β -unsaturated aldehyde acrolein.² Deposition of allyl cyanide as a precursor of a ligand layer renders Pd highly active and nearly 100 % selective toward propenol formation by promoting acrolein adsorption in a desired configuration via the C=O end. Employing a combination of (multiple) molecular beams, real space microscopic (STM) and *in operando* spectroscopic (IRAS) surface sensitive techniques, we show that an ordered active ligand layer is formed under operational conditions, consisting of stable N-butylimin species. In a competing process, unstable amine species evolve on the surface, which desorb in the course of the reaction. The geometric and electronic effects imposed by a variety of other investigated ligands will be also discussed in the talk. Obtained atomistic-level insights into the formation and dynamic evolution of the active ligand layer under operational conditions provide important input required for controlling chemoselectivity by purposeful surface functionalization.

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Chaperon complexes and dielectrons in supersonic expansions

Ruth Signorell¹

¹*Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 2, CH-8093 Zurich, Switzerland*

Email: rsignorell@ethz.ch

Transient species play a crucial role in reaction dynamics. With the help of supersonic expansions, such species can be isolated and their role in the dynamics be studied. Here, we report on chaperon complexes and their role in gas phase nucleation [1], and on dielectrons as a source of low-energy electrons for reduction reactions [2].

New particle formation through vapor condensation is an important source of atmospheric aerosols. However, the question how the volatility of different vapor components affects the nucleation kinetics has hardly received any attention yet - mainly due to the lack of suitable experiments to answer this question. To solve this problem, we have developed a special nucleation instrument that combines a Laval expansion with soft mass spectrometric cluster detection. The setup allows us to probe transient heteromolecular clusters (chaperon complexes) directly during the very first step of vapor nucleation. We find that higher volatility vapor components catalyze the nucleation of lower volatility vapor components, thus providing an alternative, previously unknown route for more efficient nucleation [1].

Electrons solvated in liquid ammonia or water are powerful reducing agents. Here we report a new way to generate low-energy electrons in situ that might even enhance such reduction reactions [2]. Using double-imaging photoelectron-photoion coincidence spectroscopy, we demonstrate for sodium-doped ammonia cluster how ultraviolet photoexcitation generates spin-paired solvated dielectrons, which subsequently relax through electron-transfer-mediated decay. When the dielectrons decay, an electron is formed that recombines with the solvent molecules together with a second low-energy electron that is ejected. The latter is available for reduction reactions.

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CRESU inside an extended nozzle: Detection by rotational spectroscopy and characterization by REMPI

Shameemah Thawoos,¹ Nicolas Suas-David,² Ranil Gurusinghe,³ Matthew Edlin¹, and Arthur G. Suits^{1,*}

¹Department of Chemistry, University of Missouri, Columbia MO 65211 USA

²Univ Rennes, CNRS, Institut de Physique de Rennes - UMR 6251, F-35000 Rennes, France

³Department of Chemistry, Tennessee Technical University, Cookeville, TN 38505 USA

Email: suitsa@missouri.edu

Chirped-Pulse Fourier-Transform Microwave (CP-FTMW) spectroscopy is a groundbreaking, near-universal detection method which enables rapid “fingerprint” detection of quantum state specific reactants and products within mixtures. We have successfully coupled this method with a pulsed CRESU system (CRESU is a French acronym for reaction kinetics in uniform supersonic flow) to study reaction kinetics at very low temperature, which we refer to as CPUF (“Chirped-Pulse/Uniform flow”). The uniform supersonic flow is generated by expanding a gas from stagnation to a low-pressure region through a Laval nozzle. The traditional method of detection coupled with CRESU is laser induced fluorescence (LIF). One of the major drawbacks of LIF is the limited number of species that can be probed, and this range can be greatly expanded with the CPUF method. Detection by CPUF requires monitoring the free induction decay of the species. However, the high collision frequency in high-density uniform supersonic flows can interfere with the free induction decay and attenuate the signal. One way to overcome this is to use sampling methods, such as airfoil or skimmer sampling. However, this requires complicated experimental designs with differential pumping systems and can have interference from shocks in the sampling region and thus may not be ideal for studying reaction kinetics. This has led us to develop an extended Laval nozzle which creates a uniform flow within the nozzle itself, after which the gas undergoes a *shock-free secondary expansion* to a cold, low pressure condition ideal for CP-FTMW detection. However, impact pressure measurements, commonly used to characterize Laval flows, cannot be used to monitor the flow within the nozzle. Hence, we have implemented a REMPI (resonance-enhanced multiphoton ionization) detection scheme which allows interrogation of the conditions of the flow directly inside the extended nozzle, confirming fluid dynamics simulations of the flow environment. We have built an extended nozzle designed for a 20 K He flow and characterized the flow within the nozzle using (1+1) REMPI of a very dilute sample of NO. We will describe the development of the new extended flow along with its characterization using REMPI and application to studies of the low temperature reaction kinetics of HCO with NO and O₂ as co-reactants.



Imaging metal-atom collision dynamics with laser ablation plasma-crossed molecular beam

Fangfang li, Yujie Ma, Dong Yan, Ang Xu, Jiaying Liu, Fengyan Wang*

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM), Fudan University, Shanghai 200438, China

*Email: fengyanwang@fudan.edu.cn

Exploring two-state or multi-state mechanism is important for how to understand and improve the activation efficiency of many reaction systems. The study of the reaction dynamics of electronically excited states or spin-orbit splitting states associated with the nonadiabatic transitions has long been a challenge both experimentally and theoretically.

In recent years, we have carried out crossed-beam reaction dynamics studies of electronic ground and excited state of metal atoms using laser ablated metal atom beam and time-sliced ion velocity imaging experimental setup. Laser ablation of metal targets generates plasma containing metal atoms in electronic ground and excited states, from which we can study the reaction dynamics of atoms and molecules with different spin states, as well as different spin-orbit splitting states. Currently, we have studied the collision dynamics of Al(²P) and Al(⁴P) through reactive collision scattering and nonreactive collision scattering methods, and revealed different pathways.

The collision dynamics of metal atoms with different collision partners, including O₂, CO₂, CH₄, etc. were also studied experimentally. Two different electron transfer mechanism are suggested. one is that the electrons of metal atoms can be transferred back, such as Al + O₂, in which system collisions form anion/cation pairs, and then induce the reaction to occur, and meanwhile the transferred electrons can return to metal cations, forming metal atoms that can have different spin-orbit splitting states. The other electron transfer mechanism is that the electrons from metal atoms cannot return after transferring to the oxidant, as in the case of CO₂, once the electrons are gained from the metal atom, a conformational change occurs, which then leads to subsequent chemical reactions.

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Real-time tracking of electron-driven dynamics in chiral molecules

Vincent Wanie

Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg, 22607,
Germany

Email: vincent.wanie@desy.de

Exploiting the ultrafast electronic motion triggered by molecular photoexcitation is a promising avenue to manipulate the outcome of photophysical and photochemical processes. I will showcase a combined experimental and theoretical work that reveals electron currents in chiral molecules and their impact on the molecular properties.

Photoionization of randomly oriented chiral molecules by circularly polarized radiation leads to an asymmetric photoelectron angular distribution with respect to the light propagation axis. This forward/backward asymmetry is known as PhotoElectron Circular Dichroism (PECD). In the time domain, PECD has recently provided insights on ultrafast molecular dynamics of gas-phase chiral molecules, such as internal conversion [1], photoemission delays [2] and photodissociation [3]. Here, I will present an investigation of *coherent electron dynamics in neutral chiral molecules* via time-resolved (TR)-PECD [4].

We used ultrabroadband UV pulses [5] in order to photoexcite below the ionization threshold and trigger the electron dynamics in the Rydberg states of chiral methyl-lactate molecules. These are probed via photoionization by a delayed circularly polarized near-infrared probe pulse. TR-PECD with an exceptional time resolution of ~ 3 fs reveals electronic coherences and disclose their impact on the molecular chiral response. We observe that the amplitude and direction of the PECD can reverse on a sub-10 fs timescale. I will also discuss important perspectives that our results provide towards applying the concept of charge-directed reactivity to enantio-sensitive processes such as molecular orientation.

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Ion-molecule reactive scattering: from classical to quantum dynamics

Roland Wester

*Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck
Technikerstraße 25, 6020 Innsbruck, Austria*

Email: roland.wester@uibk.ac.at

Crossed-beam scattering experiments are a unique approach to study reaction dynamics. In this talk I will present reactive scattering results for several ion-molecule reactions that we have recently studied using our velocity map imaging spectrometer [1]. Nucleophilic substitution reactions have been studied in the gas phase for more than 50 years [2] and quasiclassical trajectory calculations have shown excellent agreement with experimental data [3,4]. Nevertheless, an unexpected dynamical isotope effect has been observed in the reaction of fluorine anions with methyl iodide, $F^- + CH_3I$ [5]. The differential scattering data are compared with quasiclassical and quantum scattering calculations and the evidence for quantum dynamics in this reaction will be discussed. At present we are setting up a new crossed-beam velocity map imaging spectrometer with higher energy and angular resolution to better resolve product internal quantum states, e.g. in the reaction $H_2^+ + H_2$ [6]. Finally, results will be presented on the quantum dynamics in the proton transfer reaction $D^- + H_2$, which was studied in a cryogenic radiofrequency ion trap. At low temperature, this reaction proceeds via tunneling with an extremely small rate coefficient of only $5.2 \times 10^{-20} \text{cm}^3/\text{s}$ [7].

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VUV photoionization spectroscopy of nitrile-substituted PAHs

Madhusree Roy Chowdhury¹, Gustavo A. Garcia¹, Helgi Hrodmarsson², Jean-Christophe Loison³ and Laurent Nahon¹

¹Synchrotron SOLEIL, L'Orme des Merisiers, Départementale 128, 91190 Saint Aubin, France

²LISA Laboratory, Universités Paris Est-Paris Diderot-Paris 7, UMR CNRS 7583, Créteil, France

³Université Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, Talence F-33400, France

Email: madhusree.roy-chowdhury@synchrotron-soleil.fr

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the interstellar medium (ISM), acting as reservoirs of carbon and accounting for about a quarter of the total carbon mass of the ISM. The aromatic infrared emission bands (AIBs) in the 3-20 μm range are the signatures of the existence of PAHs in the interstellar and circumstellar medium which are exposed to ultraviolet radiation. Although their presence is well acknowledged, the individual detection of PAHs by rotational spectroscopy is notoriously difficult owing to their highly symmetric structures. In this context, substituted PAHs being less symmetric are promising candidates, leading to the detection of the two isomers of cyanonaphthalenes¹ (naphthalene with the $\text{-C}\equiv\text{N}$ unit attached at the 1st and 2nd C atom) in the dark, cold TMC-1. Upon absorbing the VUV radiation emitted by the hot stars, the PAHs relax via photoionization and photodissociation processes in competition with radiative cooling. The electrons emitted during ionization leads to the gas heating of the ISM by dissipating their kinetic energy to the surrounding gas molecules by collision mechanism². On the other hand, photodissociation accounts for the chemical evolution of the PAHs giving rise to smaller molecules and radicals.

In the present work, we study the VUV photoionization and fragmentation of 1- and 2-cyanonaphthalenes using a double imaging photoelectron photoion coincidence spectrometer (*i*²PEPICO)³, DELICIOUS 3 connected to the permanent molecular beam endstation at one of the branches of the DESIRS undulator based VUV beamline. The high resolution threshold photoelectron spectra obtained experimentally and compared with *ab initio* calculations show an overall good agreement between the predicted and observed bands yielding precise ionization energies. The state-selected fragmentation of the cation over an extended photon energy sheds light on the photostability of the cyanonaphthalenes in comparison to the unsubstituted PAHs. The kinetic energy distribution of the photoelectrons obtained as a function of photon energy is useful to model the photoelectric heating for any incoming photon flux distribution, while the thermochemical values obtained here—adiabatic ionization energies and OK appearance energies—will be useful to model their VUV photochemistry.

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Measuring the photodetachment cross-section of a dipole-bound state using microhydrated nucleobase anions

Connor J. Clarke and Jan R. R. Verlet

Durham University, Department of Chemistry, Durham, DH1 3LE, United Kingdom

Email: connor.clarke@durham.ac.uk

Isolated nucleobases have been previously observed to form dipole-bound state (DBS) anions.¹ These are enabled by the strong permanent dipole moment of the neutral core, which allow an extra electron to reside in a diffuse non-valence molecular orbital, located on the positive end of the dipole. Although the extra electron is weakly bound (<100 meV), the DBS is the ground-state of the uracil and thymine nucleobase anions. This is no longer the case upon solvation, as a valence resonance state of each anion (π_1^*) becomes stabilised.² Even a single water molecule sufficiently stabilises the π_1^* state to be the ground state in $U^-(H_2O)$ and $T^-(H_2O)$ anion clusters. Our experiment simultaneously generates these monohydrated nucleobase anions in their π_1^* and (excited) DBS forms. Using photoelectron spectroscopy, we unravel their different electronic properties, and notably, compare their relative photodetachment cross-sections.

The photodetachment cross-section of a DBS is expected to peak when the de Broglie wavelength of the outgoing photoelectron approximately matches the spatial width of the diffuse DBS orbital. At higher photoelectron energies, one earlier study reported the cross-section to depend on photon energy as $\sigma_{rel} \sim (h\nu)^{-2}$, although the range of reported data was limited.³ We measure the relative photodetachment cross-section by comparing the amount of photoelectron signal generated from the DBS to that from the π_1^* state, using different wavelengths. With the aid of electronic structure calculations, we find the photon energy dependence to be closer to $\sigma_{rel} \sim (h\nu)^{-3}$. Additionally, we find the DBS binding energy to be surprisingly high for both nucleobase anions (≈ 250 meV).

Acknowledgments: This work was supported by the EPSRC.

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High-resolution scattering imaging of charge transfer processes between spin-orbit selected $\text{Ar}^+(\text{}^2\text{P}_{3/2, 1/2})$ ion and neutrals N_2 and H_2

Hong Gao

Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Email: honggao2017@iccas.ac.cn

Ion-molecule reactions play vital roles in determining the physicochemical properties of interstellar medium, planetary atmospheres, and plasma. To study quantum state-to-state ion-molecule scattering dynamics, we have recently built a crossed ion-molecule scattering setup, where the ions can be prepared in selective electronic, vibrational, and rotational states by laser photoionization, and the product velocity is measured by the three-dimensional velocity-mapped ion imaging method^{1, 2}. In this study, we prepared spin-orbit selected $\text{Ar}^+(\text{}^2\text{P}_{3/2, 1/2})$ ion by using resonance enhanced multiphoton ionization (REMPI) method, and the high-resolution scattering images for the prototype charge transfer reactions $\text{Ar}^+(\text{}^2\text{P}_{3/2, 1/2})+\text{N}_2\rightarrow\text{Ar}+\text{N}_2^+(\nu)$ and $\text{Ar}^+(\text{}^2\text{P}_{3/2, 1/2})+\text{H}_2\rightarrow\text{Ar}+\text{H}_2^+(\nu)$ are obtained, as shown in Figure 1. The features of scattering images show substantial dependence on the specific spin-orbit state of the Ar^+ ion, which indicates that the charge transfer processes are strongly affected by the spin-orbit state of the Ar^+ ion.

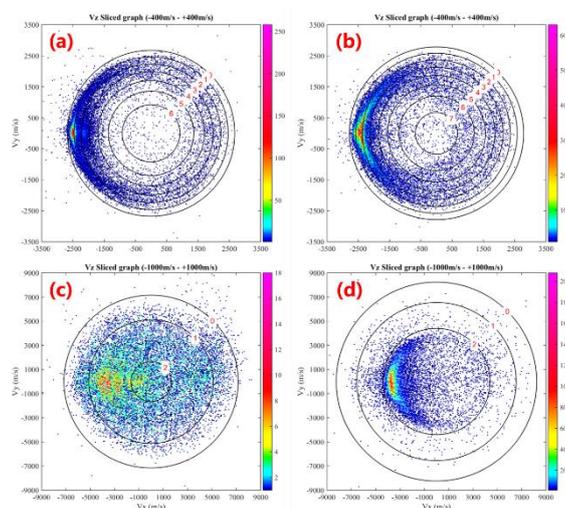


Figure: Scattering images for the charge transfer reactions (a) $\text{Ar}^+(\text{}^2\text{P}_{3/2})+\text{N}_2\rightarrow\text{Ar}+\text{N}_2^+(\nu)$, (b) $\text{Ar}^+(\text{}^2\text{P}_{1/2})+\text{N}_2\rightarrow\text{Ar}+\text{N}_2^+(\nu)$ at the collision energy of 1.588 eV; (c) $\text{Ar}^+(\text{}^2\text{P}_{3/2})+\text{H}_2\rightarrow\text{Ar}+\text{H}_2^+(\nu)$ and (d) $\text{Ar}^+(\text{}^2\text{P}_{1/2})+\text{H}_2\rightarrow\text{Ar}+\text{H}_2^+(\nu)$ at the collision energy of 0.224 eV. The rings represent the vibrational levels of the product ions N_2^+ and H_2^+ .

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Unravelling the photo-detachment and dissociation dynamics of a dianion

Jemma A. Gibbard¹

¹*Department of Chemistry, Durham University, Durham, UK*

Email: jemma.gibbard@durham.ac.uk

Gas-phase dianions present a playground for rich excited state dynamics, with most excited states being electronic resonances behind repulsive Coulomb barriers, and many being unstable with respect to dissociation. Here, recent unexpected results are presented following photo-excitation of the fluorescein dianion (Fl^{2-}).^{1,2} Electron loss is observed via resonant tunnelling through two distinct repulsive Coulomb barriers (RCB_1 and RCB_2), which link different excited dianion (S_1 and S_2) and anions states (D_0 and D_1).¹ This is the first experimental observation of resonant tunnelling mediated via a highly excited electronic state ($\geq S_2$) and, provides clear evidence for an analogue of Kasha's rule controlling electron emission in polyanions. Furthermore, the resonant electron tunnelling pathways of a dianion are shown to adhere to Koopman's correlations for the first time. Following photodetachment, decarboxylation of Fl^{2-} can occur, with competition seen between the formation of stable Fl^- and decarboxylated Fl-CO_2^- , suggesting that $\text{Fl}^-[\text{D}_1]$ is dissociative in character, whereas $\text{Fl}^-[\text{D}_0]$ is stable. Rapid, slow, and multiple photon CO_2 loss channels are identified, which follow electron loss via specific resonant tunnelling pathways. For example, the dominant CO_2 loss pathway is attributed to the rapid decarboxylation of $\text{Fl}^-[\text{D}_1]$, formed exclusively via resonant tunnelling through RCB_2 .

Acknowledgments: This work was supported by a Ramsay Memorial Fellowship.

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Unravelling the fragmentation dynamics of molecular polycations

Joseph W. McManus,^{1*} Tiffany Walmsley,¹ Michael Burt,¹ Mark Brouard,¹ Ruaridh Forbes,² and Felix Allum²

¹Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford, UK

²Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, California, USA

*Email: joseph.mcmanus@chem.ox.ac.uk

Molecular polycations play an important role in chemistry of planetary ionospheres,¹ where they are formed through interaction with high-energy photons. They are generally metastable and decay quickly via an assortment of processes. Fragmentation occurs through sequential and concerted mechanisms,² and yields an array of combinations of charged and neutral products. In recent years, the fragmentation behaviour of polycations has attracted further interest due to the development of time-resolved Coulomb explosion imaging (CEI) as a method to probe ultrafast photochemistry.³ In such experiments, the target is rapidly multiply-ionised and the resulting fragment velocities measured in correlation to infer the nuclear structure immediately prior to breakup. A detailed understanding of many-body fragmentation dynamics of polycations is therefore essential to fully exploit CEI as a structural probe.

In this work we discuss the complex nature of many-body fragmentation dynamics following multiple-ionisation, using the isomers of iodopropane (IP) as an exemplary system. Target species were studied in an ion imaging experiment following irradiation with intense femtosecond extreme-ultraviolet laser pulses. Using covariance analysis, a range of fragmentation pathways of the resulting polycations can be isolated and interrogated in detail. This includes three-body breakups of dications (example in Fig. 1) and trications, as well as contributions from highly charged polycations which split completely into atomic

fragments. Combining the results of experiment with simple simulations provides detailed physical insights into the fragmentation dynamics, such as how the initial dissociation step in a sequential mechanism influences the nuclear dynamics in the intermediate during its lifetime.

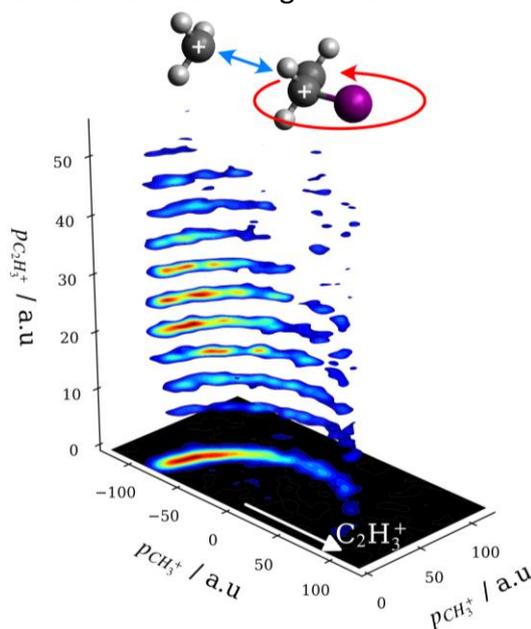


Figure 1. Momentum distribution of CH_3^+ covariant with C_2H_3^+ , produced by sequential breakup of 1-IP^{2+} involving primary loss of CH_3^+ and secondary loss of neutral I. The momentum of C_2H_3^+ defines the +x direction. Vertical slices correspond to the different absolute momenta of C_2H_3^+ . xy-projection is the sum of these vertical slices.

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Dynamics of the oxygen atom transfer reaction between carbon dioxide and the Ta⁺ cation

Marcel Meta,¹ Maximilian E. Huber¹, Atilay Ayasli¹, Tim Michaelsen²,
Milan Ončák², Roland Wester² and Jennifer Meyer¹

¹*Fachbereich Chemie und Forschungszentrum OPTIMAS, RPTU Kaiserslautern-Landau, Erwin-Schrödinger Straße 52, 67663 Kaiserslautern, Germany*

²*Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria*

Email: jmeyer@chemie.uni-kl.de

We present first results from our new crossed beam imaging experiment dedicated to the dynamics of transition metal ion molecule reactions. We record energy and angle differential cross sections to trace the atomic level rearrangement during a reaction¹. We chose to study the model reaction of oxygen atom transfer (OAT) reaction between a transition metal cation and carbon dioxide $M^+ + CO_2 \rightarrow MO^+ + CO$ with tantalum and transition metal ion. This four-atom reactions present model systems for multi-state reactivity often found in transition metal ion chemistry. The reaction is endothermic and associated with a high barrier on the quintet ground state surface of Ta⁺ but exothermic with only a submerged barrier for the first electronically excited state of Ta⁺. The reaction is highly efficient at room temperature which can only be explained by multi-state reactivity²⁻⁴.

We recorded energy dependent velocity map images of for the Ta⁺ + CO₂ → TaO⁺ + CO reaction at relative collision energies of up to 2eV. The product ion velocity distributions show indirect dynamics to be dominant even at high collision energy. But we found unexpected direct rebound to contribute at the highest collision energy. Besides a fraction of internal excitation, additional collision energy is preferentially partitioned into internal excitation. This leads to a near constant kinetic energy release which is associated with a bottleneck along the reaction coordinate.

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Planar laser-induced fluorescence (pLIF) imaging to determine the dynamics of inelastic hydroxyl radical collisions with organic liquid surfaces

Daniel R. Moon¹, Maks J. Roman², Adam G. Knight¹, Paul D. Lane¹, Matthew L. Costen¹, and Kenneth G. McKendrick¹

¹ *Institute of Chemical Sciences, Heriot-Watt University Edinburgh EH14 4AS, United Kingdom*

² *Department of Physics, University of Liverpool L69 3BX, United Kingdom*

Email: d.moon@hw.ac.uk

We present a recently developed novel spectroscopic method to image the scattering of a molecular beam of hydroxyl radicals (OH) from liquid surfaces, which is providing insight into the dynamics of crucial oxidation reactions that occur on atmospheric organic aerosol surfaces. The method employs the pulsed, planar laser-induced fluorescence (pLIF) technique.¹ The probe laser beam is shaped into a sheet and directed into an ultra-high vacuum chamber parallel to the surface of an enclosed rotating wheel submerged in a bath of the liquid of interest. A rotationally and vibrationally cold pulsed molecular beam of OH is fired at the rotating wheel, with the ingoing beam and scattered OH transecting the probe region. The resulting LIF emission is projected onto an image intensifier to obtain real-space images of the scattered OH number density. The delay between firing the molecular beam and the probe sheet is varied, producing a sequence of images before and after the scattering event. The notable advantages over more established techniques² are that it is state-specific and scattered molecules at a broad range of angles can be detected simultaneously, including those that are backscattered towards the molecular-beam source. Novel image analysis methodologies have been developed to obtain OH angular scattering distributions, correlated with speed and rotational quantum state. Integrated number densities also provide the survival probability, referenced to an inert liquid (PFPE).

Extensive Monte Carlo (MC) simulations of the experiment were conducted that validated the image-analysis methodology, helped to interpret results, and tested the sensitivity of the observed image to various experimental parameters. By far the most important parameter is the ratio of the incident molecular-beam diameter to the distance from the surface at which the scattered molecules are probed. The lessons learnt from the proof-of-concept apparatus and MC simulations have fed into the design and build of a new upgraded purpose-built apparatus that offers significant improvements to experiments that can be conducted.

Results obtained so far with this methodology include the scattering of a beam of OH with a kinetic energy of around 30 kJ mol⁻¹ from squalane, squalene and PFPE liquid surfaces. A representative example for PFPE is shown in Figure 1. The results overall show that most of the inelastic scattering from all three liquids must be impulsive, based on the asymmetry in the angular distributions for non-normal incidence and super-thermal speeds. The surfaces also do not appear molecularly flat, leading to relatively broad and sub-specular scattering angular distributions. There are subtle differences between the angular distributions for different rotational levels. Systematic differences in the angular distributions for squalene relative to squalane can be interpreted as enhanced reactive loss of partially accommodated OH due to addition reactions at double-bond sites on squalene.

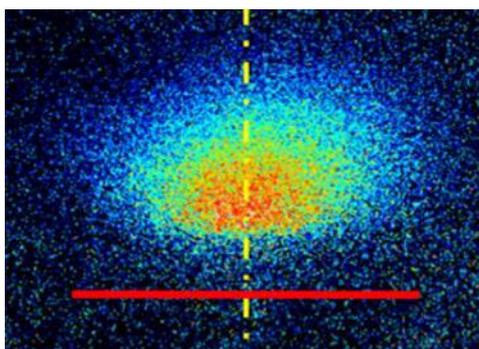


Figure 1: Image at the peak of the scattered wave of OH ($N'=3$) from PFPE for an incidence angle of 45° .

Acknowledgments: This work was supported by the EPSRC Programme Grant EP/T021675/1 'New Directions in Molecular Scattering: Multiple Pathways and Products'

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Excited state Ion-pair formation dynamics in bromobutane and formic acid clusters

Scott G. Sayres¹

¹Arizona State University, Tempe AZ, 85282, United States

Email: ssayres@asu.edu

The ion-pair formation mechanisms in small organic molecules and clusters through UV light absorption have attracted substantial attention due to their prominent role in acid-base chemistry, atmospheric ozone depletion, and acid rain. I will present new results on the photodynamics of ion-pair formation that operate within bromobutane¹ and formic acid clusters,^{2,3} as revealed through femtosecond time-resolved mass spectrometry and density functional theory calculations. Femtosecond UV excitation accesses the Rydberg manifold within the Franck-Condon region. The subsequent excited state relaxation and coupling to the valence/ion-pair state is monitored through the transient growth of the cation component on the ultrafast timescale. Predissociation from the 5p-Rydberg state of bromobutane leads to the ion-pair $[C_4H_9^+ - Br^-]$ state within 10.8 ± 0.5 ps. A similar mechanism occurs on the sub-picosecond timescale within formic acid clusters, $(FA)_n$, where $n < 10$. Comparison of the rate constants and cross-sections of $[(FA)_nH^+ - COOH^-]$ demonstrates that the potential energy surfaces attributed to the ion pair shift to longer bond distances and become more deeply bound with increased clusters size. Thus, the solvent rearrangement time increases by ~ 72 fs per additional formic acid molecule, ranging from 213 ± 51 fs for FA_3 to 667 ± 116 fs for FA_9 .

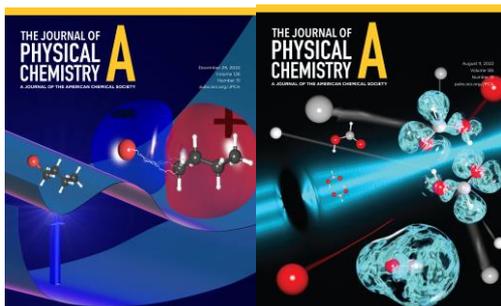


Figure: Recent cover art from our group that highlights the excited state dynamics and ion pair formation mechanisms in bromobutane and in formic acid clusters.

Acknowledgments: This work was supported by W.M. Keck Foundation, Lightworks, and ASU startup funds

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The impact of replacing CC by BN on the excited state dynamics of BN-9,10-naphthalene

Floriane Sturm,¹ Michael Bühler¹, Christoph Stapper¹, Johannes Schneider², Holger Helten², Merle Röhr¹ and Ingo Fischer¹

¹*Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, 97074 Würzburg, Germany*

²*Institute of Inorganic Chemistry, University of Würzburg, Am Hubland, 97074 Würzburg, Germany*

Email: floriane.sturm@uni-wuerzburg.de

Substituting CC by the isoelectronic BN units is an excellent means to modify the optoelectronic properties of polycyclic aromatic hydrocarbons.¹⁻³ While computational studies have already addressed the impact of isosterism, accurate experimental data are still scarce. In our research, the excited state spectroscopy and dynamics of BN-9,10-naphthalene were studied by picosecond time-resolved photoionization in a supersonic jet together with an implemented velocity map imaging set-up. A resonance-enhanced multiphoton ionization spectrum (REMPI) reveals the S_1 origin at $\tilde{\nu} = 33841 \text{ cm}^{-1}$, which is in very good agreement with theory. Several vibrational bands were resolved and assigned by comparison with computations. A [1+1] photoelectron spectrum via the S_1 origin yielded an adiabatic ionization energy of 8.27 eV. Selected vibrational bands were subsequently investigated by pump-probe photoionization. While the origin as well as several low-lying vibronic states exhibit lifetimes in the ns-range, a monoexponential decay is observed at higher excitation energies, ranging from 409 ps, at $+1708 \text{ cm}^{-1}$ to 13 ps at $+3361 \text{ cm}^{-1}$. Based on quantum chemical calculations, the deactivation is attributed to an internal conversion between the optically excited S_1 and the S_2 state.

Acknowledgments: This work was supported by the Deutsche Forschungsgemeinschaft, DFG contract FI 575/16-1. F.S. thanks the Rosa-Luxemburg-Foundation for a PhD fellowship.

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Investigating solvent effects in the electronic and ionization dynamics of pyrrole and pyrrole-water clusters

Sebastian Trippel^{1,2}, Melby Johny¹, Constant Schouder⁴, Ahmed Al-Refaie¹, Ivo S. Vinklárek¹, Wuwei Jin¹, Henrik Stapelfeldt⁴, and Jochen Küpper^{1,2,3}

¹ Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

² Center for Ultrafast Imaging, Universität Hamburg, Germany

³ Department of Physics, Universität Hamburg, Germany

⁴ Department of Chemistry, Aarhus University, Denmark

Email: sebastian.tripple@cfel.de

Molecular and chemical properties, including molecular dynamics, strongly depend on the environment. For instance, for a protein in an aqueous solution, the hydrogen bonds between the protein and surrounding water molecules strongly affect its folding and thereby also its function.

We investigated pyrrole, relevant for the photophysics of tryptophan, and its binary pyrrole-water complex, which serve as model systems for studying the photophysics of the interaction between proteins and water. We produced pure samples of pyrrole and the pyrrole-water complex in the gas phase using the combination of a cold molecular beam and the electrostatic deflector. The pure samples were locally photoionized at the pyrrole moiety with 50 fs laser pulses with a central wavelength of 800 nm and a peak intensity on the order of 10^{14} W/cm². The photofragments were recorded with a velocity-map-imaging spectrometer in combination with a time- and position-sensitive Timepix3 camera [1].

For single ionization, a strong suppression of the pyrrole fragmentation was observed for the hydrogen-bonded cluster, showing the efficient protective nature of the solvation environment [2]. Furthermore, for the pyrrole-water cluster highly-charged carbon ions were detected [3]. Such systems could serve as new sources of highly-charged ions for various applications, e.g., tumor therapy.

In addition, recent results obtained on the ultrafast UV-induced dynamics of pyrrole-water, probed by x-ray ionization at the European XFEL, will be presented.

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Cold supersonic beam spectra for hot exoplanet atmospheres

Ondrej Votava¹, Jozef Rakovský¹, and Vít Svoboda^{1,2}

¹ *J. Heyrovský institute of physical Chemistry ASCR, Dolejškova 2155/3, Prague 8, 182-23, Czech Republic*

² *JILA, University of Colorado, Boulder and the National Institute of Standards and Technology, 440 UCB, Boulder, CO 80309, United States*

Email: votava@jh-inst.cas.cz

Several thousand exoplanets have been discovered in past 25 years and with improved instrumentation we start to probe the composition and properties of their atmospheres. Substantial numbers of exoplanet fall into “hot-Jupiter” and “hot-super-Earths” class. Their atmospheres are expected to contain large number of molecular species exhibiting rich and complex spectral features. Detailed knowledge of the expected spectra under the local conditions is a prerequisite for their astronomical detection. With improving level of theory¹ there is increasing need for reliable experimental data for validation the theoretical approaches, particularly for the highly vibrationally excited molecules, observed via overtone and combination bands. Unfortunately the spectra measured by traditional techniques at room temperature are usually too dense and irregular to be successfully assigned, which makes them virtually useless for rigorous comparison with the theory.

In this contribution I will present an approach taken in our laboratory where high resolution overtone spectra are measured at low temperatures (~20K) in the supersonic molecular beams.²⁻⁴ On the examples of several typical molecules of increasing complexity (NH₃, CH₃Cl, HCOOH) I will demonstrate the clear advantage provided by measurements in cold molecular beams - in addition to the well known simplification of the spectra I will discuss spectral analysis approaches applicable specifically to such measurements, in particular the two-temperature analysis for experimental determination of lower state rotational energies and ground state combination difference pattern recognition approach we developed. In essence, instead of obtaining a large number of nonassignable spectral transitions we deliver a sub-set of transitions with reliably determined and cross-checked quantum assignments for rigorous bench-marking of the theory used for hot spectra predictions.

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Creating state- and velocity-selected molecular beams of pure radicals

Lok Yiu Wu,^{1,2} Maksymilian J. Roman¹ and Brianna R. Heazlewood¹

¹*Department of Physics, University of Liverpool, Oxford Street, Liverpool, L69 7ZE, UK*

²*Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK*

Email: L.Wu23@liverpool.ac.uk

Beams of slow hydrogen radicals with very narrow speed distributions have been produced by the application of external magnetic fields using a “magnetic guide”. This magnetic guide is made up of a series of magnets (in Halbach arrays) and skimming blades.^{1,2} The technique relies on an optimised vertical displacement of the arrays and blades from the longitudinal beam axis to form a “velocity filter”, allowing only the radicals travelling at a selected target speed to pass through the guide without being obstructed. Moreover, the guide also acts as a state selector, as only target radical species in low-field seeking states can successfully pass through the guide. This results in a beam with no radicals in high field seeking states, seed gas, or any by-products of radical formation. This combination of capabilities makes the magnetic guide a very enticing option for studies of radical reactions, such as those present in the atmosphere or the interstellar medium. We present here the successful development of a new “second-generation” magnetic guide, designed to manipulate beams of larger (and not only atomic) species. We will present the first results from this new apparatus, with the guiding of O₂ molecules, and discuss our goal to apply the method to other molecular radicals in the near future.

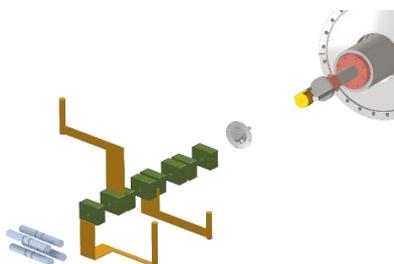


Figure: A schematic of the second-generation magnetic guide interfaced with a linear Paul trap (not to scale).

Acknowledgments: This work was supported by the European Research Council, the Royal Society, the Engineering and Physical Sciences Research Council, and the Community for Analytical Measurement Science.

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Development of a Narrow-Pulsed Molecular Beam System for the Study of Cold Ion-Molecule Reactions

Yurun Xie, Yue Xiao, Heyang Liu, Jie Han, Yongxu Peng, Liping Wen, Zhichao Li, Xueming Yang, Tiangang Yang*

Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong 518055, P. R. China.

*Email: yangtg@sustech.edu.cn

The study of low-temperature reactions is essential for understanding fundamental chemistry and the interstellar medium, where quantum effects are more prominent and significantly impact the chemistry, challenging existing models[1, 2]. To investigate these reactions, experimental tools are necessary to lower reaction temperature and control the translational and internal energies of reactants. In this context, our recent progress in cold ion-molecule chemistry has involved the development of a Narrow-Pulsed and velocity-adjustable Molecular Beam System, laser-cooled ion sympathetic cooling, and a Time-of-Flight (TOF) mass spectrometer in an RF Paul trap. In this presentation, our latest advancements in this project will be reported.

Acknowledgments: This work was supported by National Natural Science Foundation of China (Grant No. 22103023, and 22173040).

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25-30 June 2023

POSTERS

30th
International Symposium on
Molecular Beams

Rethymno, Crete, Greece

ISMB2023 Poster List

Posters with odd numbers (P1, P3, P5, ... P21) will be presented on Monday, June 26th (Poster Session I).

Posters with even numbers (P2, P4, P6, ... P22) will be presented on Tuesday, June 27th (Poster Session II).

P1	Understanding intersystem crossing through the S⁺+H₂ reaction dynamics Presenter: Alexandre Zanchet (<i>CSIC, Spain</i>)
P2	Laser-Induced Desorption for Velocity-Resolved Surface Kinetics Presenter: Jessalyn DeVine (<i>University of Göttingen & Max Planck Institute for Multidisciplinary Sciences, Germany</i>)
P3	Formation of multiply charged atomic ions from nanoclusters in moderately intense nanosecond laser fields: an extraordinary observation Presenter: Wei Kong (<i>Oregon State University, United States</i>)
P4	Photodissociation dynamics and alignment of CH₂BrI in the third absorption band at 193 nm Presenter: Pedro Recio (<i>University Complutense of Madrid, Spain</i>)
P5	Dynamics of the photodissociation of methylamine: H and CH₃ displacement channels Presenter: Pedro Recio (<i>University Complutense of Madrid, Spain</i>)
P6	Comparison of the photodissociation dynamics of alkyl nitrites in the A and B absorption bands Presenter: Pedro Recio (<i>University Complutense of Madrid, Spain</i>)
P7	Ion molecule reaction dynamics of the radical anion O⁻ with CH₃I Presenter: Atilay Ayasli (<i>Universität Innsbruck, Austria</i>)
P8	A detailed experimental view into the strong-field induced fragmentation of water dimer Presenter: Ivo S. Vinklárek (<i>Deutsches Elektronen-Synchrotron DESY, Germany</i>)
P9	Probing the valence electronic properties, interfacial solvation structures and oxidation products using aerosol VUV photoelectron spectroscopy Presenter: Chia Wang (<i>National Sun Yat-sen University, Taiwan</i>)
P10	Reaction dynamics of state- and speed-selected radicals with trapped ions Presenter: Maksymilian Roman (<i>University of Liverpool, United Kingdom</i>)
P11	Characterizing the multi-dimensional reaction dynamics of CH₂I₂ using XUV-induced electron transfer and covariance analysis Presenter: Tiffany Walmsley (<i>University of Oxford, United Kingdom</i>)
P12	Molecular-ion tagging spectroscopy with helium droplet beams Presenter: Fabio Zappa (<i>Universität Innsbruck, Austria</i>)

P13	Scattering Nitric Oxide off Graphene using Surface-Velocity Map Imaging Presenter: Sven Koehler (<i>Hannover University of Applied Sciences, Germany</i>)
P14	The influence of fluorination on the reaction dynamics and branching ratios of F⁺ + CH₃CH₂I Presenter: Tim Michaelsen (<i>Universität Innsbruck, Austria</i>)
P15	New Setup for High-Resolution Ion-Molecule Crossed Beam Imaging Presenter: Dasarath Swaraj (<i>Universität Innsbruck, Austria</i>)
P16	Experimentally motivated molecular dynamics comparative study of C₆₀ impact interactions with low mass targets Presenter: Bernstein Victor (<i>Technion, Israel</i>)
P17	Gas-phase investigation of conformational and rotational-state effects in chemical reactions under single collision conditions Presenter: Chao He (<i>University of Basel, Switzerland</i>)
P18	Conformationally selected ions for reactions with conformationally selected molecules Presenter: Lei Xu (<i>University of Basel, Switzerland</i>)
P19	Photodissociation of CH₂Br₂ and CHBr₃ at 242nm Presenter: Nektarios Findrilis (<i>University of Crete & IESL-FORTH, Greece</i>)
P20	Detecting chirality in mixtures using ns-PECD Presenters: Ioannis Giannakidis & Nikolaos Fragkoulis (<i>University of Crete & IESL-FORTH, Greece</i>)
P21	Photodissociation of CH₂Br₂ & CHBr₃ at 193 nm Presenter: Apostolos Banoutsos (<i>University of Crete & IESL-FORTH, Greece</i>)
P22	The impact of replacing CC by BN on the excited state dynamics of BN-9,10-naphthalene Presenter: Floriane Sturm (<i>University of Würzburg, Germany</i>)

Understanding intersystem crossing through the $S^+ + H_2$ reaction dynamics

Alexandre Zanchet¹

¹*Instituto de Física Fundamental, CSIC, Serrano 123, Madrid, Spain*

Email: alexandre.zanchet@csic.es

SH^+ is a widespread molecular ion in diffuse interstellar clouds, and has also been detected in emission toward the Orion Bar photodissociation region (PDR). In warm and dense PDRs, SH^+ is thought to form by exothermic reactions of S^+ with vibrationally excited H_2 ($v>1$). The viability of this hypothesis have been confirmed by theoretical simulations reaction which demonstrate that for vibrational level $v=2$ or higher of H_2 , the reaction exhibit high rate constants[1].

From an experimental point of view, scarce data are available[2]. As the reaction of the ground state ion is endothermic by almost 1 eV, the SH^+ product is observed only at high collision energies where translational energy brings the needed energy to reach products, as predicted by the theoretical simulations. Interestingly, it appears from this experimental study that spin-orbit couplings may play a significant role on the reaction, motivating a new theoretical study of the reaction, now including the spin-orbit interactions.

Exact quantum dynamics calculations show that spin-orbit interaction does indeed play an important role in this reaction, and that for energies below the threshold of formation of SH^+ , long lived H_2S^+ complex may form, opening the possibility of a radiative association. To check this hypothesis, and check the accuracy of the calculations, a new series of experiments were performed using the CERISE setup at synchrotron SOLEIL.

Acknowledgments: This work was supported by the Grants No. PID2019-107115GB- C21 and PID2021-122549NB-C21 from MICINN (Spain)

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Laser-Induced Desorption for Velocity-Resolved Surface Kinetics

Jessalyn A. DeVine,^{1,2} Jan Fingerhut,² Fotios Anastasiadis,² Michael Schwarzer,² Kai Golibrzuch,^{1,2} Theofanis N. Kitsopoulos,^{1,2} Daniel J. Auerbach,¹ Alec M. Wodtke^{1,2}

¹*Dynamics at Surfaces, Max Planck Institute for Multidisciplinary Sciences, Göttingen, Germany*

²*Institute for Physical Chemistry, University of Göttingen, Göttingen, Germany*

Email: Jessalyn.devine@mpinat.mpg.de

Velocity-resolved kinetics (VRK) is an experimental method used for measuring the kinetics of surface reactions by monitoring the flux of desorbing product molecules after reaction is initiated by an incident pulsed molecular beam.¹ This information-rich technique has great potential to provide key information, such as the rate constants of elementary reaction steps; however, its dependence on thermal desorption means that it can be difficult to interpret traditional VRK data for systems involving more complex reaction mechanisms, such as oxidation of H₂ or NH₃ at metal surfaces. In such systems, it is common for the desorption kinetics themselves to dominate the observed data, thus obscuring the true kinetics of surface processes. Laser-induced desorption (LID), where an ultrafast laser pulse rapidly heats a surface to several thousand Kelvin, has been shown previously to be a useful approach to observation of surface adsorbates.² We describe recent efforts to use this LID-VRK technique (Figure 1) to tackle true chemical transformations, where the goal is to observe surface-bound intermediates in catalytically important reactions, which are invisible to the traditional VRK approach.

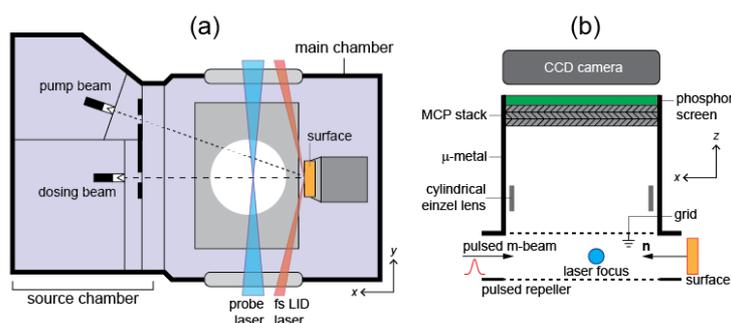


Figure 1: Experimental setup of the LID-VRK apparatus. (a) The dosing beam is run asynchronously to set up steady-state concentrations of one reactant. Reaction is initiated with the pump beam. A femtosecond laser (<300μJ/pulse) focused at the surface desorbs molecules; these, along with thermally-desorbed molecules, are then ionized with multi-photon ionization. (b) Ions generated in the laser focus are extracted into an orthogonal ion-imaging apparatus. Gated MCPs allow for mass selection. Ultimately this provides the velocity distributions of molecules desorbed from the surface.

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Formation of multiply charged atomic ions from nanoclusters in moderately intense nanosecond laser fields: an extraordinary observation

Steven Tran, Kim Cuong Tran, and Wei Kong

Dept. of Chem., Oregon State University, Corvallis, Oregon 97331, USA

Email: Wei.Kong@Oregonstate.edu

Formation of multiply charged atomic ions (MCAI) from nanoclusters is considered a signature of Coulomb explosion in intense fields, typically on the order of or above 10^{15} W/cm². However, several research groups have reported observations of MCAI in moderately intense visible nanosecond laser fields from molecular clusters, rare gas clusters, and rare gas clusters mixed with a variety of molecular species.¹⁻³ In a nanosecond laser field at 532 nm (photon energy = 2.3 eV) with intensities as low as 10^9 W/cm², Arⁿ⁺ ($1 < n \leq 16$) and Cⁿ⁺ ($1 < n \leq 4$) have been identified from argon and mixed argon-organic clusters, while the ionization of Ar¹⁶⁺ requires thousands of photons.⁴ We stumbled into this extraordinary phenomenon and embarked on this journey of discovery, from initial characterizations of the ionization state to measurements of kinetic energy distributions of the atomic products, to the effect of the organic compounds embedded in the atomic clusters.⁵⁻⁷ We compare the physical and chemical conditions of this process with those of intense fields, and discuss the potential pitfalls of existing theories in explanations of the observed phenomenon.

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

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Photodissociation dynamics and alignment of CH₂BrI in the third absorption band at 193 nm

Pedro Recio,¹ Javier Cachon,¹ Luis Rubio-Lago,¹ David V. Chicharro,¹ Sonia Marggi Poullain,¹ Alexandre Zanchet,² Peter C. Samartzis,³ and Luis Bañares¹

¹ Chemical Physics Department, University Complutense of Madrid, Spain

² Fundamental Physics Institute, Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain

³ Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology-Hellas (FORTH), Voutes, Heraklion, Greece

Email: pedrecio@ucm.es

The photodissociation of dihalomethanes have received significant attention due to its role in producing pollutant species and ozone depletion.¹ Moreover, CH₂BrI presents an intricate structure of excited electronic states and a high bond selectivity. For instance, the A absorption band was attributed to C-I dissociation, while the A' band corresponds to C-Br bond fission.² However, the third band (B band) has not been investigated deeply.³

The detection of atomic iodine I(²P_{3/2,1/2) and bromine Br(²P_{3/2,1/2), using a combination of laser pump-and-probe and slicing imaging techniques coupled to (2+1) REMPI, show the presence of two main contributions. Combining the experimental results with high *ab initio* calculations, we assigned the faster contribution to a predissociation through the 9A' state. Meanwhile, the slower contribution was attributed to a secondary dissociation after absorbing a second 193 nm photon. Due to geometrical restrictions, this process was favored through the C-Br dissociation rather than the C-I bond cleavage. The calculated anisotropy parameter supports the proposed mechanism.}}

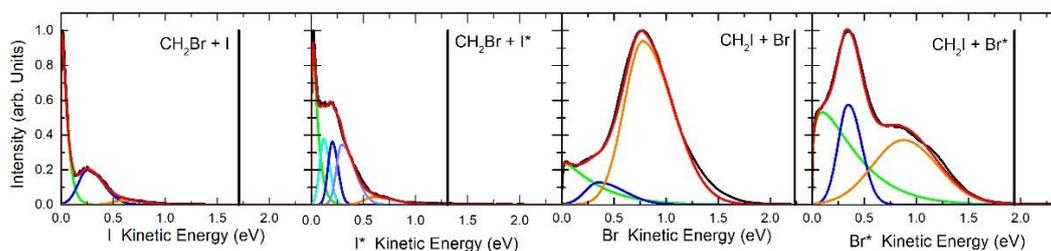


Figure: Kinetic energy distribution of the four detected fragments, I(²P_{3/2}), I*(²P_{1/2}), Br(²P_{3/2}), and Br*(²P_{1/2}), from left to right, after excitation at 193 nm.

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Dynamics of the photodissociation of methylamine: H and CH₃ displacement channels

Pedro Recio,¹ Javier Cachon,¹ Luis Rubio-Lago,¹ Sonia Marggi Poullain,¹ Alexandre Zanchet,² and Luis Bañares¹

¹ Chemical Physics Department, University Complutense of Madrid, Spain

² Fundamental Physics Institute, Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain

Email: pedrecio@ucm.es

Due to its similarity with ammonia (NH₃) and because it has been observed in the interstellar medium,¹ methylamine (CH₃NH₂) has received considerable attention in the last decades. The molecular photodissociation of methylamine was studied using the pump-probe method with nanosecond laser pulses. The molecule was excited in the 198 - 203 nm range, and the generated photofragments were detected with the velocity map imaging (VMI) technique, studying the H-atom elimination and the N-C bond fission channels separately, combining experiment and theory.

On the one hand, the H-atom displacement channel presents two main dissociation pathways. One attributed to the formation of CH₃NH(\tilde{X}) via a conical intersection (CI),^{2,3} while the other to CH₃NH(\tilde{A}), observed for the first time. On the other hand, the recorded images for the NH₂ + CH₃ channel show unstructured Boltzmann-type distributions; however, the speed-dependent anisotropy parameters reveal the presence of two dissociation mechanisms. With a similar landscape of the computed potential energy curves to the N-H bond fission, prompt dissociation of the C-N bond through the CI is proposed as a minor channel. In contrast, the kinetic energy distribution reflects a major slow dissociation in the ground state, which can arise from frustrated N-H bond cleavage trajectories or vibrationally-hot ground state NH₂ fragments.

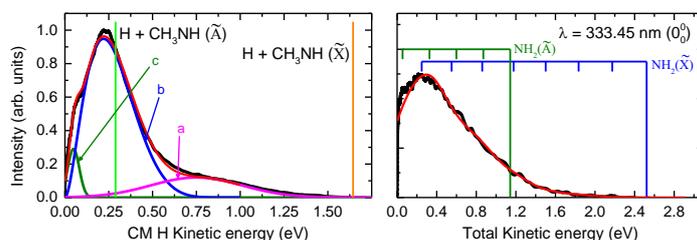


Figure: Measurements at 198 nm excitation energy for the CH₃NH + H (right) and CH₃ + NH₂ (left) channels.

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Comparison of the photodissociation dynamics of alkyl nitrites in the A and B absorption bands

Pedro Recio,¹ Javier Cachon,¹ Luis Rubio-Lago,¹ Sonia Marggi Poullain,¹ Genesis Mahecha,² Gustavo Pino,² and Luis Bañares¹

¹ Chemical Physics Department, University Complutense of Madrid, Spain

² Chemistry department, National University of Córdoba, Córdoba, Argentina

Email: pedrecio@ucm.es

Alkyl nitrites (R-ONO, R=CH₃, *n*-C₃H₇, *t*-C₄H₉) have been widely studied due to the efficient photodissociation and formation of NO fragment.^{1,2} The absorption spectra of all these molecules present two bands. A first band characterized by a clear vibronic structure, and a second more intense band which extends to the VUV energy region.^{2,3} In this work, three different alkyl nitrites were studied, CH₃ONO, *n*-C₃H₇ONO, and *t*-C₄H₉ONO, so a comparison of the hydrocarbon chain on the photodissociation dynamics could be made.⁴ The study was performed in the two absorption bands (A and B) independently. Pump-probe experiments using nanosecond laser pulses in combination with velocity map imaging detection of NO by 1+1 REMPI were carried out.

The results in the A band show a shift in the kinetic energy distributions as higher vibrational states for a fixed rotational quantum number J=19.5 of the NO fragments were detected. By comparing the three molecules, a larger shift in energy is also present, a displacement previously observed in the studies of alkyl halogen molecules.⁴ Several differences in the shape of the kinetic energy distributions, and in the angular distributions, were also detected. Meanwhile, the B band shows a parallel transition in contrast to the perpendicular transitions observed in the A band. In this case, several contributions could be observed for each of the measurements performed.

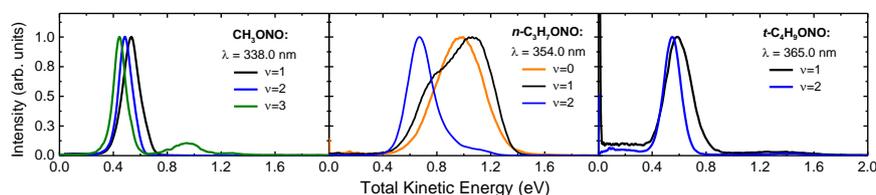


Figure: Total energy distributions of the NO(v , J =19.5) fragments for the molecules studied in this work in the first absorption band.

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Ion molecule reaction dynamics of the radical anion O^- with CH_3I

Atilay Ayasli¹, Arnab Khan², Tim Michaelson¹, Thomas Gstir¹, Milan Ončák¹, and Roland Wester¹

¹*Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, 6020 Innsbruck, Austria*

²*Department of Physics, Indian Institute of Science Education and Research, Bhopal, India*

Email: atilay.ayasli@uibk.ac.at

Our group studies ion-molecule reactions using a crossed-beam setup with kinematically complete velocity map imaging (VMI).¹ This has proven to be a powerful tool to obtain experimental insight into molecular reaction dynamics of ion-molecule reactions. Using velocity mapping in combination with crossed beams, we can obtain energy and angle dependent scattering cross sections. These can be used to look for dynamic fingerprints which help us identify different reaction mechanisms during reactive collisions.

We recently did reactive scattering studies of methyl iodide CH_3I with atomic oxygen anions O^- . Energy-dependent experiments ranging from 0.3 to 2.0 eV relative collision energy revealed a rich variety of different pathways for different angles of attack of the O^- nucleophile on methyl iodide. Attacking the backside of CH_3I on the carbon side forms iodide I^- , which can either be created through an oxygen insertion reaction or bimolecular substitution S_N2 . Additionally, an incoming O^- can attack the iodine on the frontside of CH_3I forming IO^- as a competing product.³ Furthermore, we observe proton transfer forming $CH_2I^- + OH$ and combined hydrogen/proton transfer $CHI^- + H_2O$.² The differential cross-sections show that product ions from both channels are predominantly forward scattered. Our results suggest that the combined hydrogen/proton transfer is formed over a two-step process, an incoming O^- abstracts a hydrogen forming OH^- . The transient OH^- additionally removes a proton forming H_2O .

We will discuss energy-dependent differential cross sections and branching ratios of different product pathways, accompanied by quantum chemical calculations to understand the dynamics of this rich system.

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A detailed experimental view into the strong-field induced fragmentation of water dimer

Hubertus Bromberger,¹ Ivo S. Vinklárek,¹ Nidin Vadassery,¹ Wuwei Jin,¹ Jochen Küpper,^{1,2,3,4} and Sebastian Trippel^{1,2}

¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, Hamburg, Germany

²Center for Ultrafast Imaging, Universität Hamburg, Luruper Chaussee 149, Hamburg, Germany

³Department of Physics, Universität Hamburg, Luruper Chaussee 149, Hamburg, Germany

⁴Department of Chemistry, Universität Hamburg, Martin-Luther-King-Platz 6, Hamburg, Germany

Email: ivo.vinklarek@cfel.de

Hydrogen bonding is pivotal for the vast majority of chemical reactions such as proton transfer or the topological stability of biomolecules^{1,2,3,4}. This study employed a combination of electrostatic deflection¹ to generate a pure beam of (H₂O)₂ and multi-mass imaging detection to get a thorough understanding of the hydrogen bonding's role in charge, energy, and mass transfer in an ionized water environment. The decay of the water ionized by cosmic radiation is considered essential for astrochemistry occurring on ice mantles and can act as a crucial step in chemical evolution in interstellar space medium³.

Our experimental approach enables us to directly take a full picture of the fragmentation pathways of the singly ionized (H₂O)₂⁺ dimer, and to evaluate their importance through branching ratios determination. The preliminary observation points out several new pathways, which were not included in the prior theory results². Moreover, the applied photoion-photoion coincidence analysis of the Coulomb explosion channels after double ionization to (H₂O)₂⁺² supports the previous estimation of the proton migration rate³ and provides angular and kinetic energy distributions for further investigations of the mechanism of strong field ionization in water clusters.

Acknowledgments: We acknowledge financial support by Deutsches Elektronen-Synchrotron DESY, a member of the Helmholtz Association (HGF), also for the provision of experimental facilities and for the use of the Maxwell computational resources operated at DESY.

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Probing the valence electronic properties, interfacial solvation structures and oxidation products using aerosol VUV photoelectron spectroscopy

Chia C. Wang^{1,2}

¹Department of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan, R.O.C. 80424

²Aerosol Science Research Center, National Sun Yat-sen University, Kaohsiung, Taiwan, R.O.C. 80424

Email: chiawang@mail.nsysu.edu.tw

Aerosols can be produced from a variety of sources, which exhibit distinct chemical composition, formation mechanisms, evolution kinetic and dynamic properties, and physicochemical characteristics. Once released or formed directly in the environment, aerosols can greatly influence the cloud formation microphysics, climate, environmental ecosystem, and even public health once inhaled. It is of fundamental importance to develop novel experimental tools to advance our understanding of aerosols formed via various possible sources. I will address our efforts in developing aerosol VUV photoelectron spectroscopy¹ and utilizing it to probe the valence electronic properties, interfacial solvation structures and oxidation products of aerosols of interest.² Specifically, we utilize the aerosol VUV photoelectron spectroscopy to study the valence electronic properties of limonene aerosols and SOAs derived from limonene ozonolysis, with a special focus on the effects of water in affecting the physico-chemical characteristics of Lim-SOAs. Combining with DFT theoretical calculation, we show that water actively modifies the valence electronic structures of Lim-SOAs via intervening the Criegee intermediate chemistry by acting both as a catalyst and a reactant. The atmospheric implication is discussed.

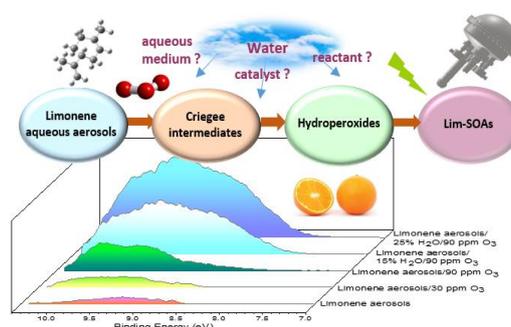


Figure: VUV photoelectron spectroscopy of limonene-derived secondary organic aerosols reveals multifunctional roles of water.

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Reaction dynamics of state- and speed-selected radicals with trapped ions

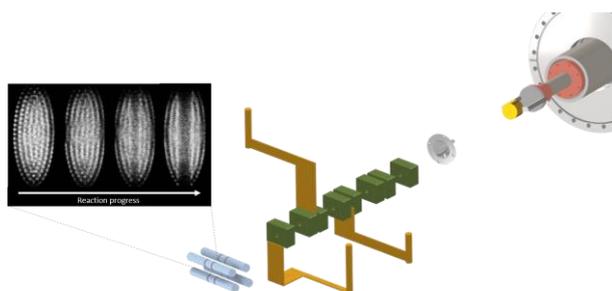
Maksymilian J. Roman,¹ Lok Yiu Wu,^{1,2} Vincent Richardson,¹ Jake Diprose,¹ and Brianna R. Heazlewood¹

¹Department of Physics, University of Liverpool, Oxford Street, Liverpool, L69 7ZE, United Kingdom

²Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom

Email: m.j.roman@liverpool.ac.uk

Establishing control over the external and internal energies of collision partners has always been at the forefront of invention in reaction dynamics experiments. This poster presents an overview of a novel method for controlling a radical molecular beam, allowing us to study the dynamics of ion-radical reactions. The radical beam is created *in situ* using an Even-Lavie valve coupled with a discharge device. A newly designed “magnetic guide” [1,2] permits only radicals in specific internal states and with selected speeds to pass into a linear Paul trap, where reactant ions are sympathetically cooled by Doppler-cooled Ca⁺ ions (within a so-called “Coulomb crystal”). A camera allows for non-destructive tracking of the reaction by imaging the change in spatial distribution of the fluorescing Ca⁺ ions as they are displaced by reaction products. Additionally, the trapped species can be ejected at a selected reaction time for time-of-flight mass spectrometry measurements. Radical reaction dynamics studies traditionally suffer from issues caused by impure radical samples and lack of tuneable properties, but the unique combination of features offered by this experimental technique overcomes these restrictions. Moreover, the tuneable radical beam can be used in a variety of other applications, such as crossed molecular beams or gas-liquid scattering experiments.



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Characterizing the multi-dimensional reaction dynamics of CH₂I₂ using XUV-induced electron transfer and covariance analysis

T. Walmsley,¹ J. Unwin,¹ F. Allum,¹ S. Bari,² R. Boll,³ K. Borne,⁴ M. Brouard,¹ P. Bucksbaum,⁵ N. Ekanayake,² B. Erk,² R. Forbes,⁵ A. J. Howard,⁵ P. Eng-Johnsson,⁶ J. W. L. Lee,² Z. Liu,¹ B. Manschwetus,² R. Mason,¹ C. Passow,² J. Peschel,⁶ D. Rivas,³ D. Rolles,⁴ A. Rörig,³ A. Rouzée,⁷ C. Vallance,¹ F. Ziaee,⁴ and M. Burt¹

¹Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, United Kingdom, ²Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany, ³European XFEL, Holzkoppel 4, 22869 Schenefeld, Germany, ⁴J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, United States of America, ⁵Stanford PULSE Institute, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, United States of America, ⁶Department of Physics, Lund University, 22100 Lund, Sweden, ⁷Max-Born-Institute, Max-Born-Straße 2A, 12489 Berlin, Germany

Email: tiffany.walmsley@chem.ox.ac.uk

Coulomb explosion imaging is a technique that utilizes the momenta of fragments produced in an electrostatic repulsion to extract molecular structural information. When coupled with pump-probe spectroscopy, it becomes a powerful tool for determining changes to molecular geometries over the course of a chemical reaction.^[1] Here, we investigate the photodissociation dynamics of CH₂I₂ at 200 nm, by site-selectively probing the iodine 4d edge using 13.1 nm pulses produced at the free electron LASER Hamburg (FLASH).

Ion momentum distributions, characteristic of electron charge transfer processes,^[2] showed that CH₂I₂ underwent concerted, three-body dissociation. These distributions were used in conjunction with time-resolved recoil frame covariance (Fig. 1) between all pairs of highly charged I^{q+} states (q=2-5) to distinguish structural and dynamic information describing the reaction mechanism, such as the iodine-iodine separation velocity, I-C-I recoil angle, and CH₂ momenta. Our results demonstrate the sensitivity of electron charge transfer processes arising from inner-shell ionization to multi-dimensional reaction dynamics and their potential ability to map multiple degrees of freedom during the structural evolution of an initially neutral molecule when coupled with particle correlation techniques and time-resolved photoelectron spectroscopy.

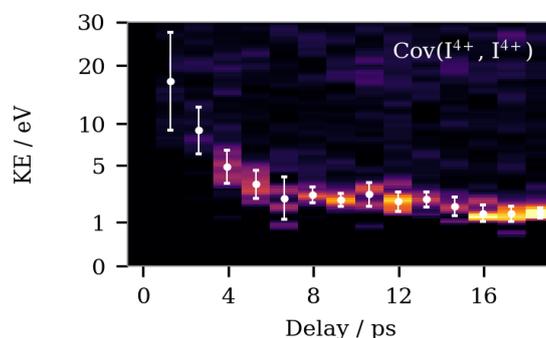


Fig. 1: Time dependent kinetic energy distribution of I⁴⁺ ions produced in a Coulomb explosion with a second I⁴⁺ ion, following dissociation at 200 nm, obtained through time dependent recoil frame covariance.

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Molecular-ion tagging spectroscopy with helium droplet beams

Fabio Zappa, Stefan Bergmeister, Lisa Ganner, Johannes Locher, Elisabeth Gruber, and Paul Scheier

Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25, A-6020, Innsbruck, Austria.

Email: fabio.zappa@uibk.ac.at

Spectroscopy of isolated ionic species presents a series of difficulties when compared to neutral substances. Ways to circumvent these difficulties include embedding the ions in solid matrices or, for instance, cooling them in cryogenic ion traps.¹ In the latter case, a distinct advantage is the possibility of attaching a weakly bound species to the ion, i.e. helium atoms, and detecting the photon absorption via depletion of the complex in the mass spectrometer signal.

In recent years, our group has developed two new methods to produce abundant beams of helium-tagged ionic species, both positive and negative, via fragmentation of multiply charged, doped helium droplets, instead of using ion traps.^{2,3} The relatively short transit time and high helium coverage of the ions allow for the detection of extremely weakly bound or transient species. Therefore, combining these newly developed methods with spectroscopy techniques is of great interest.

In the present work, we will briefly overview a new experiment in our group designed to perform spectroscopy of helium-tagged, mass-selected, ionic molecular species.⁴ The performance of the instrument will be illustrated by a few examples, namely argon clusters and C₆₀, and the results are compared with the literature.

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Scattering Nitric Oxide off Graphene using Surface-Velocity Map Imaging

Thomas Greenwood,¹ Isabella Murcia,² Samuel Franco² and Sven Koehler²

¹Manchester Metropolitan University, Chester Street, M13 9PM, United Kingdom

²Hannover University of Applied Sciences, Ricklinger Stadtweg 120, 30459 Hannover, Germany

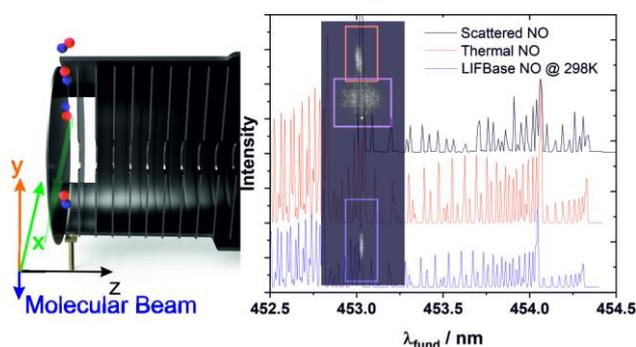
Email: sven.koehler@hs-hannover.de

We investigated the scattering of nitric oxide, NO, off graphene supported on gold. This is of fundamental importance to chemistry as collisions are the necessary first step to chemical reactions on graphene, and nitric oxide molecules are inherently radicals, with the potential to bond to graphene.

We directed a molecular beam of NO in helium onto graphene and detected the directly 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 classical molecular dynamics simulations still predict a loss of ~60% of the translational energy in the scattering process.

A much smaller trapping-desorption component is also detected, in agreement with our classical molecular dynamics simulations which also observe a small proportion of two- and multi-bounce collisions events. Surface-velocity map imaging also allows us to record velocity-dependent internal energy distributions.

Since speeds can be measured from both time-of flight distributions as well as from velocity images, we are able to extract residence times which can be as long as 100 microseconds.



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The influence of fluorination on the reaction dynamics and branching ratios of $F^- + CH_3CH_2I$

Thomas Gstir,¹ Tim Michaelsen,¹ Atilay Ayasli,¹ Dasarath Swaraj,¹ Fabio Zappa¹ and Roland Wester¹

¹Institut für Ionenphysik und Angewandte Physik Universität Innsbruck, Technikerstraße 25/3, Austria

Email: tim.michaelsen@uibk.ac.at

Investigating the competition of reaction pathways is the first step in the often-desired control of the products. Bimolecular nucleophilic substitution (S_N2) and base-induced elimination (E2) usually appear in competition and their control is a regular objective in organic synthesis. In a previous study, we disentangled the contributions in one of the simplest systems where both appear, by comparison of experimental differential cross sections to state-of-the-art quasi-classical trajectory calculations.¹ In the work presented here, we instead suppress the E2 pathway by fluorination of the β -carbon to obtain pure S_N2 reaction dynamics in a similar system.

The differential cross sections and branching ratios are obtained using a crossed-beam velocity map imaging spectrometer² for the reaction of F^- with both CH_3CH_2I and CF_3CH_2I . The trends in the branching ratios are extended down to thermal collision energies in a collaboration with the Viggiano group³. The interpretation of the results is supported by transition state energies and geometries calculated by the Czako group.⁴

We also present recent results on the reaction of $F^- + ClCH_2I$, where two S_N2 pathways leading to either I^- or Cl^- are feasible.

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New Setup for High-Resolution Ion-Molecule Crossed Beam Imaging

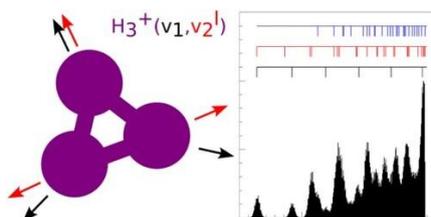
Dasarath Swaraj¹, Jerin Judy¹, Tim Michaelsen¹, Arnab Khan¹, Fabio Zappa¹, Robert Wild¹ and Roland Wester¹

¹*Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria*

Email: dasarath.swaraj@uibk.ac.at

Crossed-beam reactive scattering experiments offer a detailed understanding of the dynamics involved in elementary reactions occurring in the gas phase. By employing velocity map imaging (VMI), it is possible to acquire angle and energy differential cross-sections, as demonstrated in previous studies^{1,2}. In this study, we present a comprehensive design plan and relevant simulations for an experimental setup intended to investigate ion-molecule reactions with enhanced precision to achieve state-to-state resolution for ion-molecule reactions. Additionally, Monte Carlo simulations were conducted³ to determine the expected resolution of the product energy for the reaction: $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$.

To generate H_2^+ ions, we employ laser-induced ionization of H_2 using the 3rd or 4th harmonic of a pulsed Nd:YAG laser, ensuring that the ions primarily occupy the vibrational ground state⁴. The ion beam is then overlapped with a beam of neutral molecules, and the resulting collision products are collected and analyzed using the VMI spectrometer. Furthermore, we plan to implement coincidence detection to simultaneously observe both the ionic and neutral products subsequent to the reaction.



Acknowledgments: This work is supported by the European Research Council (ERC)

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Experimentally motivated molecular dynamics comparative study of C_{60} impact interactions with low mass targets

Victor Bernstein and Eli Kolodney

Schulich Faculty of Chemistry, Technion (IIT), Haifa 3200004, Israel

Email: chr21vb@technion.ac.il

The so-called velocity correlated cluster emission (VCCE) effect is the recently reported emission of nearly equal velocity large clusters following impact of a C_{60}^- projectile on a metallic surface at the keV kinetic energies regime^{1,2}. In contrast to cluster emission induced by the impact of a heavy monoatomic ion, for a large polyatomic projectile such as C_{60} it was found that all clusters are emitted in a velocity correlated fashion, moving with nearly the same most probable velocity. The results were supported by modelling of the initial phase of the formation of the collisionally induced thermal spike and molecular dynamics (MD) simulations of the extremely fast (deep subpicosecond) thermalization of the collisional cascade nanovolume^{2,3}. The VCCE effect was found to be most pronounced for atomically heavy targets (e.g., Au, Ag, Cu) while getting weaker for lower mass targets (e.g., Al^A). To gain a deeper microscopic insight into the underlying emission mechanism we have carried out MD simulations (employing the LAMMPS⁵ package) of the impact interaction of the C_{60} projectile with several low mass targets (*Be, C, Al, Si*), compared with that of the heavier (*Cu, Ag, Au*) targets. We have focused on the sub-ps evolution of the average kinetic energy and number density of the target atoms contained within the sub-surface impact excited zone and the sub-ps dynamics of the evolution of the impact crater at the nanoscale. We have analyzed systematic differences between the heavy and low-mass targets, as well as between the softer (*Be, Al, Si*) and harder (*C, BN*) low-mass targets. The trends observed comparing the different targets (experiment and simulation) rationalized the gradual weakening of the VCCE effect with decrease in target mass. Some preliminary results of the very low energy impact interactions of C_{60} with soft molecular solids will also be presented.

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Gas-phase investigation of conformational and rotational-state effects in chemical reactions under single collision conditions

Amit Mishra¹, Ludger Ploenes¹, Patrik Stranak¹, H. Gao, Chao He¹, Sang K. Kim², Stefan Willitsch¹

¹ Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

² Department of Chemistry, KAIST, Daejeon 34141, Republic of Korea

Email: Stefan.Willitsch@unibas.ch

The influence of molecular conformations and individual quantum states is critical to understand the mechanisms and dynamics of reactions. However, due to thermal interconversion, the isolation and control of individual states and conformers is still a challenge in the experimental investigation until now. Consequently, very few single-collision studies that characterizing the impact of conformational effects on chemical reactivity has been reported.¹ Experimental methods that are used to study conformational effects in ion-molecule reactions under single-collision conditions have been successfully developed by our group over the past years.^{2,3} Here, we furthermore built a new crossed-molecular-beam machine to extend our methodology to neutral-neutral reactions recently.⁴ This setup is equipped with an electrostatic deflector which enables the spatial separation of different conformers or individual rotational states of molecules according to their different effective dipole moments. As the pioneer application of this new method, rotational-state-dependent chemi-ionisation reactions of carbonyl sulfide (OCS) with metastable neon atoms were first studied. A remarkable state-specific effect on the product branching ratio was observed. The experimental results reveal that OCS molecules in the rotational ground state $j = 0$ are a factor of 2.5 more reactive for dissociative ionisation than Penning ionisation compared to the $j = 1$ state.⁴ Further, we chose to study the chemi-ionisation reaction of 1,2-dibromoethylene (DBE), the conformers of which can be chemically separated.⁵ And we are currently undertaking a comparative study of the photochemistry, photoionization, and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene (DBE) as a prototypical system.⁶ In brief, the aforementioned studies target to gain a comprehensive understanding of the role of individual quantum states and molecular conformations in unimolecular and bimolecular reactivities.

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Conformationally selected ions for reactions with conformationally selected molecules

Lei Xu¹, Jutta Toscano¹ and Stefan Willitsch¹

¹Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

Email: stefan.willitsch@unibas.ch

The conformation of a molecule plays an important role in the chemistry of complex molecular systems necessitating the development of experimental methods for the characterization of the chemical reactivity of individual conformers. Previously, we spatially separated the *cis* and *trans* conformers of neutral 3-aminophenol in the gas phase using an electrostatic deflector based on their different dipole moment and reacted with trapped laser-cooled calcium ions in the gas phase [1]. Under these conditions, the ions form Coulomb crystals which can be used to cool other trapped ionic species sympathetically. Building up on this methodology, ionic Diels-Alder reactions were studied between conformationally selected neutral dibromobutadiene (DBB) molecules and sympathetically cooled propene ions. These studies provided new insights into conformationally dependent reaction mechanisms of cycloaddition reactions [2].

In order to gain an even deeper understanding of conformational effects of chemical reactions, conformational control of not only the neutral, but also the ionic reactants in ion-molecule reactions would be beneficial. Towards that purpose, we report here our first results on the sympathetic cooling of conformationally selected *meta*-aminostyrene (mAS) ions. One-color (1 + 1) and two-color (1 + 1') resonance-enhanced multiphoton ionization (REMPI) spectra of mAS [3] were recorded and individual conformations of the molecule were selected spectroscopically in the intermediate electronic state. Subsequently, a specially designed (1 + 1') threshold photoionisation scheme to generate individual conformers of the mAS ion was established. We were thus able to load the *cis*- and *trans*-mAS ions into the ion trap and sympathetically cool them into a Coulomb crystal. The process was characterized by mass spectrometry and with the help of molecular dynamics simulations.

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Photodissociation of CH₂Br₂ and CHBr₃ at 242nm

Nektarios E. Findrillis,^{1,2} Ioannis C. Giannakidis,^{1,3} Apostolos N. Banoutsos,^{1,2} Meng-Xu Jiang,⁴ Ágúst Kvaran⁴ and Petros C. Samartzis¹

¹*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Vassilika Vouton, 70013 Heraklion, Greece.*

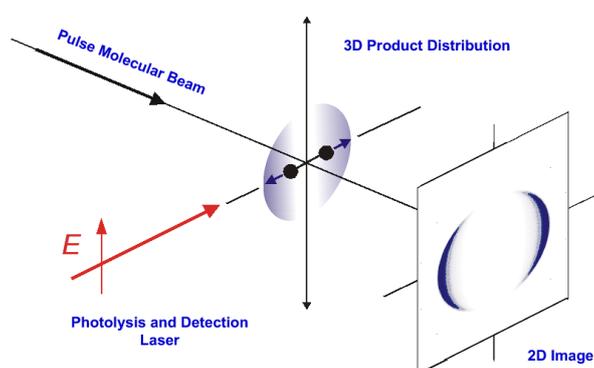
²*Department of Physics, University of Crete, 70013, Heraklion, Greece.*

³*Department of Materials Science and Technology, University of Crete, 71003, Heraklion, Greece.*

⁴*Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavík, Iceland.*

Email: nfindrillis@iesl.forth.gr

The UV photochemistry of bromine-containing molecules has been the subject of significant attention due to their contribution to stratospheric ozone depletion by bromine radicals [1]. In this study, we investigated the photodissociation dynamics of dibromomethane (CH₂Br₂) and bromoform (CHBr₃) using Velocity Map Imaging (VMI) at 242nm. By analyzing the nascent photofragments' images e.g. C⁺, Br⁺, CH₂⁺, and their kinetic energy release, as well as photoelectrons, we identified the most active photoexcitation and photodissociation pathways for each molecule.



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Detecting chirality in mixtures using ns-PECD

Ioannis C. Giannakidis^{1,2} Simon T. Ranecky,⁴ G. Barratt Park,^{5,6,7} Dirk Schwarzer,⁶ Arne Senftleben,⁴ Nikolaos Fragkoulis,^{1,3} Thomas Baumert,⁴ Tim Schäfer^{5,6} and Peter C. Samartzis¹

¹*Institute of Electronic Structure and Lasers, Foundation for Research and Technology - Hellas (FORTH), P. O. Box 1527, Heraklion 70013, Greece*

²*Department of Materials Science and Technology, University of Crete, Heraklion 71003, Greece*

³*Department of Chemistry, University of Crete, Heraklion 71003, Greece*

⁴*Universität Kassel, Heinrich-Plett-Str. 40, Kassel 34132, Germany*

⁵*Georg-August-Universität Göttingen, Tammannstr. 6, Göttingen 37077, Germany*

⁶*Max Planck Institut für Biophysikalische Chemie, Am Fassberg 11, Göttingen 37077, Germany*

⁷*Department of Chemistry and Biochemistry, Texas Tech University, Box 41061, Lubbock, TX 79409-1061, USA*

Email: giannakidis@iesl.forth.gr

Photoelectron Circular Dichroism (PECD) was predicted in 1976 by Ritchie¹ and demonstrated experimentally in the 2000s.^{2,3} It is based on the forward-backward asymmetry of photoelectrons distribution produced when chiral molecules are ionized by circularly polarized light. The main light sources used in PECD experiments are synchrotron radiation, ultrafast lasers, and, more recently, nanosecond lasers.⁴⁻⁶ We present nanosecond PECD enantio-sensitive measurements in mixtures of fenchone and camphor (structural isomers). Using pulsed molecular beams, resonance-enhanced multi-photon ionization (REMPI), and a velocity map imaging (VMI) spectrometer, enantiomeric detection was achieved in the mixtures due to the specific transition of each component.

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Photodissociation of CH₂Br₂ & CHBr₃ at 193 nm

Apostolos N. Banoutsos^{1,2}, Ioannis C. Giannakidis^{1,3}, Nektarios E. Findrillis^{1,2}, Meng-Xu Jiang,⁴
 Ágúst Kvaran⁴, Petros C. Samartzis¹

¹*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Vassilika Vouton, 70013 Heraklion, Greece.*

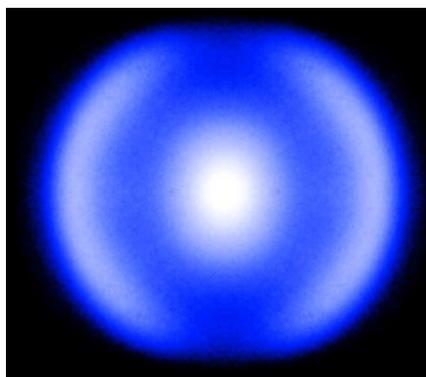
²*Department of Physics, University of Crete, 70013, Heraklion, Greece.*

³*Department of Materials Science and Technology, University of Crete, 71003, Heraklion, Greece.*

⁴*Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavík, Iceland.*

Email: abanoutsos@iesl.forth.gr

The photodissociation of halogen-containing molecules, especially those containing Cl and Br, has received the attention of scientists due to the role these species play in stratospheric ozone depletion [1]. In this study, we report results on the photodissociation dynamics of CHBr₃ and CH₂Br₂ at 193 nm using the Velocity Map Imaging technique. We recorded images of C⁺, CH⁺, CH₂⁺, Br⁺, CH₂Br⁺ and CH₂Br₂⁺ for dibromomethane and H⁺, C⁺, CH⁺, Br⁺, CBr⁺, CHBr₂⁺ and CHBr₃⁺ for bromoform. By analyzing the kinetic energy release of the photofragments, we were able to identify the most probable dissociation channels for both molecules.



C⁺ after photodissociation of CHBr₃.

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The impact of replacing CC by BN on the excited state dynamics of BN-9,10-naphthalene

Floriane Sturm,¹ Michael Bühler¹, Christoph Stapper¹, Johannes Schneider², Holger Helten², Merle Röhr¹ and Ingo Fischer¹

¹*Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, 97074 Würzburg, Germany*

²*Institute of Inorganic Chemistry, University of Würzburg, Am Hubland, 97074 Würzburg, Germany*

Email: floriane.sturm@uni-wuerzburg.de

Substituting CC by the isoelectronic BN units is an excellent means to modify the optoelectronic properties of polycyclic aromatic hydrocarbons.¹⁻³ While computational studies have already addressed the impact of isosterism, accurate experimental data are still scarce. In our research, the excited state spectroscopy and dynamics of BN-9,10-naphthalene were studied by picosecond time-resolved photoionization in a supersonic jet together with an implemented velocity map imaging set-up. A resonance-enhanced multiphoton ionization spectrum (REMPI) reveals the S_1 origin at $\tilde{\nu} = 33841 \text{ cm}^{-1}$, which is in very good agreement with theory. Several vibrational bands were resolved and assigned by comparison with computations. A [1+1] photoelectron spectrum via the S_1 origin yielded an adiabatic ionization energy of 8.27 eV. Selected vibrational bands were subsequently investigated by pump-probe photoionization. While the origin as well as several low-lying vibronic states exhibit lifetimes in the ns-range, a monoexponential decay is observed at higher excitation energies, ranging from 409 ps, at $+1708 \text{ cm}^{-1}$ to 13 ps at $+3361 \text{ cm}^{-1}$. Based on quantum chemical calculations, the deactivation is attributed to an internal conversion between the optically excited S_1 and the S_2 state.

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