Björn Bastian, Tim Michaelsen, Malcolm Simpson, Alec Wodtke,
Roland Wester (Eds.)

international Conference on Molecular Energy Transfer in Complex Systems 2017 (iCOMET 2017)

January 15 – 20, 2017

Innsbruck, Austria

Book of Abstracts

Preface

The international Conference on Molecular Energy Transfer in Complex Systems iCOMET brings together researchers that study energy transfer in dynamical processes in order to obtain an atomic-scale understanding of dynamical events controlling complex physico-chemical phenomena. The field of molecular energy transfer has grown out of the study of simple systems, especially of small molecules in the gas-phase.

Today, this field is striving towards a fundamental understanding of more complex problems such as molecular interactions at surfaces, in the condensed phase, biological molecules and in technology applications. It is characterized by advanced experimental tools and a highly sophisticated level of theoretical analysis. By comparing experiment and theory at the most fundamental level, this research field seeks an atomic-level understanding of complex phenomena that is as informative and detailed as has been achieved for gas-phase binary collisions.

We would like to welcome you to Innsbruck to share your expertise in the field of iCOMET and to foster discussions and new collaborations to advance towards the grand challenge of a full dynamical understanding of complex molecular phenomena.

Alec Wodtke and Roland Wester

Previous COMET and iCOMET Conferences

Year	Location	Organizer
1971	Cambridge, United Kingdom	Anthony Callear
1975	Loccum, Germany	Peter Toennies
1979	Rodez, France	Magdeleine Huetz-Aubert
1983	Cirencester, United Kingdom	Anthony McCaffery
1987	Emmetten, Switzerland	Martin Quack
1991	Nijmegen, Netherlands	Jörg Reuss
1995	Kloster Banz, Germany	Hans-Joachim Werner and Peter Andresen
1999	Assisi, Italy	Antonio Laganà and Piergiorgio Casavecchia
2003	San Lorenzo de El Escorial, Spain	Javier Aoiz, Luis Bañares and Miguel González
2007	Arcachon, France	Michel Costes and Jean-Claude Rayez
2011	Oxford, United Kingdom	Mark Brouard
2015	Chengdu, China	Aart Kleyn and Xueming Yang

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Program

Sunday

16:00 Registration

19:00 *Dinner*

20:15 Welcome address

20:30 **Scott Kable**, University of New South Wales, Sydney, Australia

H_2 production from photolysis of aldehydes in the atmosphere

21:10 **Sang Kyu Kim**, KAIST, Daejeon, Republic of Korea

Spectroscopic characterization of the conical intersection in the photodissociation dynamics of heteroaromatic compounds

Monday

08:00 *Breakfast*

09:00 **Musa Ahmed**, Lawrence Berkeley National Laboratory, USA

Probing chemical transformations in clusters and nanoparticles with mass spectrometry and X-ray based spectroscopy

09:40 **Andrew J. Orr-Ewing**, University of Bristol, United Kingdom

State-resolved photodissociation dynamics in perfluorocarbon and chlorinated solvents

10:20 *Coffee*

10:40 **Jörg Behler**, Ruhr-Universität Bochum, Germany

Molecular dynamics simulations of solid-liquid interfaces employing high-dimensional neural network potentials

11:20 **Sebastian Trippel**, University of Hamburg, Germany

Photophysics of controlled gas-phase molecules and clusters

11:40 **Eduardo Carrascosa**, The University of Melbourne, Australia

Photoisomerization action spectroscopy of molecular switches

Break

16:00 *Coffee & Snacks*

16:30 **Joachim Paier**, Humboldt-Universität zu Berlin, Germany

Electron transfer in gold atoms on reduced ceria surfaces: Lessons learned from static density functional theory

17:10 **Sergey Levchenko**, Fritz-Haber-Institut, Berlin, Germany

Ab initio modelling of charge transfer to defects and molecules at surfaces of semiconductors at realistic temperature, pressure, and doping conditions

17:50 **G. Barratt Park**, Georg-August University, Germany

Scattering formaldehyde from the Au(111) surface

18:10 **Kai Kang**, China Academy of Engineering Physics, China

Quasiclassical study of Eley-Rideal reactions of N atoms with O/N adsorbed on a Ru(0001) surface

19:00 *Dinner*

20:30 Poster session

Tuesday

08:00 *Breakfast*

09:00 **Ludo Juurlink**, Leiden Institute of Chemistry, Leiden, the Netherlands

How does molecular hydrogen dissociate on Pt?

09:40 **Oliver Bünermann**, Georg-August University Göttingen, Germany

H atom scattering from surfaces

10:20 *Coffee*

10:40 **Yvonne Dorenkamp**, Georg-August University, Germany

Inelasticity in hydrogen atom scattering from surfaces: A probe for energy conversion

11:00 **Alexander Kaiser**, Universität Innsbruck, Austria

H_2 physisorption on $C_{60}Cs$

11:20 **Weiwei Zhou**, University of Oxford, United Kingdom

Electron impact total and partial ionization cross sections and kinetic energy releases for hydrocarbon species relevant to fusion edge plasmas

Break

16:00 *Coffee & Snacks*

16:30 **Theo Kitsopoulos**, Georg-August University, Göttingen, Germany

CO oxidation on Pt(111): Deciphering the second mechanism using slice imaging

17:10 **Martin Beyer**, Universität Innsbruck, Austria

Ion-molecule reactions with ionic water clusters

17:50 **Sven Köhler**, University of Manchester, United Kingdom

Photodesorption of NO from Au(100) using
3D surface-velocity map imaging

18:10 **Qiang Huang**, China Academy of Engineering Physics, China

Carbon dioxide dissociation in non-thermal microwave and radiofrequency plasma

19:00 *Dinner*

20:30 Tour of the city

Wednesday

08:00 *Breakfast*

09:00 **Toshinori Suzuki**, Kyoto University, Japan

Time and angle-resolved photoemission spectroscopy of electronic dynamics in aqueous solutions

09:40 **Jochen Mikosch**, Max-Born-Institute, Berlin, Germany

Molecular dynamics studied with attosecond XUV pulses

10:20 *Coffee*

10:40 **Yann Mairesse**, Université de Bordeaux, France

Probing ultrafast dynamics of chiral molecules with photoelectron and photoexcitation circular dichroism

11:20 **Neil Cole-Filipiak**, University of Warwick, United Kingdom

Ultrafast dissociation of substituted pyrroles

11:40 **Francesco Gianturco**, Universität Innsbruck, Austria

CH^+ : A building block for C-bearing molecules in the ISM: Computing its chemical rates to model its evolution under different interstellar environments

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16:00 *Coffee & Snacks*

16:30 **Julia Weinstein**, University of Sheffield, United Kingdom

Towards directing ultrafast charge transfer with IR excitation

17:10 **Chia-Chen Wang**, National Sun Yat-sen University, Kaohsiung, Taiwan

Probing valence electronic structures and interfacial solvation properties of biological and organic aqueous nanoaerosols via aerosol VUV photoelectron spectroscopy

17:50 **Thomas Penfold**, Newcastle University, United Kingdom

The importance of nonadiabatic coupling and host tuning for efficient reverse intersystem crossing in TADF molecules

18:10 **Jennifer Meyer**, Universität Innsbruck, Austria

Imaging the complex influence of the leaving group on nucleophilic substitution reactions

19:00 *Dinner*

20:30 Poster session

Thursday

08:00 *Breakfast*

09:00 **Kopin Liu**, Academia Sinica, Taipei, Taiwan

Aligning a spherical top molecule and the stereodynamics in Cl + $CH_4(v_3=1)$ reaction

09:40 **Xingan Wang**, University of Science and Technology, Hefei, China

High-resolution experimental studies of elementary chemical reactions using the ion imaging technique

10:20 *Coffee*

10:40 **Upakarasamy Lourderaj**, National Institute of Science Education and Research, Odisha, India

Computational studies of the dynamics of chemical reactions

11:20 **Jun Li**, Chongqing University, China

Full dimensional accurate potential energy surfaces and dynamical studies for the OH/Cl + CH_4 reactions

11:40 **Astrid Bergeat**, Université de Bordeaux, France

Low energy scattering in crossed molecular beams

Break

16:00 *Coffee & Snacks*

16:30 **Arthur Suits**, University of Missouri, Columbia, USA

Chirped-pulse microwave spectroscopy in uniform supersonic flows: Applications in kinetics and dynamics

17:10 **Andreas Osterwalder**, Ecole Polytechnique Fédérale de Lausanne, Switzerland

Merging and splitting beams of neutral molecules

17:50 **Stephen Hogan**, University College London, United Kingdom

Controlling resonant energy transfer in collisions between NH_3 and He Rydberg atoms using electric fields

19:00 *Conference Dinner*

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09:00	Departure

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Vibrational energy transfer at surfaces studied by TR-SFG

P-02 **Nina K. Bersenkowitsch**, Universität Innsbruck, Austria

Photodissociation cross section of sodium chloride clusters doped with nitrate

P-03 **Neil C. Cole-Filipiak**, University of Warwick, United Kingdom

Ultrafast dissociation of substituted pyrroles

P-04 **Philip M. Coulter**, University of Bristol, United Kingdom

Unraveling energy relaxation mechanisms in simple solvents

P-05 **Andreas Herburger**, Universität Innsbruck, Austria

IR spectroscopy of hydrated $CO_2^{\bullet -}$ and its reaction products

P-06 **Mario H. Vera**, Universität Innsbruck, Austria

Rotational relaxation of molecular cations in buffer gas: computing rates and decay times for $pH2^+$, $oD2^+$ and HD^+

P-07 **Hiroshi Kohguchi**, Hiroshima University, Japan

Detection of the excited state NH_2 ($\tilde{A}\ ^2A_1$) in the ultraviolet photodissociation of methylamine

P-08 **Tim Michaelsen, Björn Bastian**, Universität Innsbruck, Austria

Charge transfer reactions with Ar^+ and various neutrals

P-09 **Milan Ončák**, Universität Innsbruck, Austria

Photochemistry of $Mg^+(H_2O)_n$ clusters

P-10 **G. Barratt Park**, Georg-August University, Göttingen Germany

Scattering formaldehyde from the Au(111) surface

P-11 **Nishant Sharma**, NISER, Odisha, India

Dissociation of formaldehyde on single layer graphene

P-12 **Malcolm J. Simpson**, Universität Innsbruck, Austria

Towards evidence for the role of permanent dipoles in the formation of molecular anions in the interstellar medium

P-13 **Christian van der Linde**, Universität Innsbruck, Austria

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Invited Talks

H_2 production from photolysis of aldehydes in the atmosphere

Aaron Harrison,[1] Alireza Kharazmi,[1] Miranda Shaw,[2] Meredith Jordan[2] and
Scott Kable[1*]

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Molecular hydrogen is regarded as a potential replacement for hydrocarbons as a clean and renewable energy source providing motivation for efficient, large-scale production and storage of H_2. This will certainly lead to H_2 leakage into the atmosphere where it is an indirect greenhouse gas and has an impact on tropospheric concentration of OH and O_3. [1] This makes a full accounting of the atmospheric H_2 budget of fundamental interest in monitoring the H_2 economy in the future. Dihydrogen is found in the atmosphere at around 500 ppm, about 2.5 times the pre-industrial levels, which makes it one of the more abundant trace gases with a large anthropogenic fraction. [1] The major known sources of H_2 in the atmosphere are H_2CO photodissociation, fossil fuel and biomass combustion, and biogenic emission, while the major sink is biological uptake. [2] Models of H_2 in the atmosphere underestimate the mixing ratio by a factor of ~2. [1] While this might be an error in the biology (source or sink), it is reasoned that a missing photolytic source is to blame.

We have discovered recently, in experiments in which ethanal and propanal are photolysed in a molecular beam, that H_2 is a primary photolytic product of both aldehydes. Measurements of the quantum yield, photolysing CH_3CHO in a bulb with 1 atm N_2 buffer gas, provide a value of $\Phi \sim 1\%$. While this might not seem very high, the atmospheric half-life of CH_3CHO is measured in hours, while H_2 is 2 years, which results in a significant H_2 loading into the atmosphere. Additionally, the production of H_2 from carbonyls is likely to be ubiquitous. We estimate that photolysis of carbonyls, producing H_2, might account for about half of the missing photolytic source.

From a reaction dynamics viewpoint, the H_2-producing photolysis reaction is interesting. The mechanism of H_2 production from CH_3CHO and

CH_3CH_2CHO is completely different. H_2 is formed from acetaldehyde in a conventional 4-centre elimination with a ketene co-fragment. However, in the case of propanal, the co-fragments are CO and C_2H_4, in a, likely concerted, three-body process. The chemistry of butanal is completely different again! These observations are leading us to a set of structure-activity relationships to determine which aldehydes should produce H_2 and what the mechanism might be for these aldehydes.

Acknowledgements: This work is supported by the Australian Research Council (grant DP16 0101792)**.**

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Spectroscopic characterization of the conical intersection in the photodissociation dynamics of heteroaromatic compounds

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Nonadiabatic processes are ubiquitous in nature. Those are actually even essential in many important processes such as light-harvesting, vision, or genetic protection from irradiative damages. Despite a number of experimental and theoretical studies on such reactions for decades, chemists are still keenly interested in the detailed mechanism of nonadiabatic transitions at the molecular level. For polyatomic molecules, conical intersection where two different adiabatic surfaces touch has been widely accepted as the dynamic funnel for efficient nonadiabatic transitions. And yet, direct experimental probing of the conical intersection in terms of its topology and energetics has been quite rare. Here, we have investigated photodissociation dynamics of thioanisole, thiophenol, and their several chemical derivatives using the velocity-map ion imaging and femtosecond pump-probe methods. We have observed strong variation of the nonadiabatic transition probability depending on the nuclear configurations accessed by various initial vibronic transitions. This in turn provides the spectroscopic characterization of the conical intersection as the nonadiabatic transition probability increases when the reactive flux (or wavepacket) passes the phase space in the proximity of the conical intersection. As the excited-state structures are often hard to understand, slow-electron velocity imaging (SEVI) is employed to unravel the nature of the vibrational mode relevant to the efficient curve-crossing. Femtosecond time-resolved photo-ion and/or photoelectron spectroscopic study of the same system provides the comprehensive information regarding the temporal evolution of the wavepacket moving around the conical intersection. The study on deuterated thioanisoles gives much richer ideas about the multi-dimensional conical intersection seam indeed. Wavepacket propagation simulation has been carried out using the ab initio calculated two-dimensional potential energy surfaces for the S-H bond dissociation of thiophenol. The S-H bond elongation and CCSH dihedral angle are two degrees of freedom in the constructed analytic potential energy function.

Relaxed scan of the adiabatic potential surface for the excited state reveals the minimum energy pathway for the wavepacket prepared on the edge of the conical intersection along the reaction pathway.

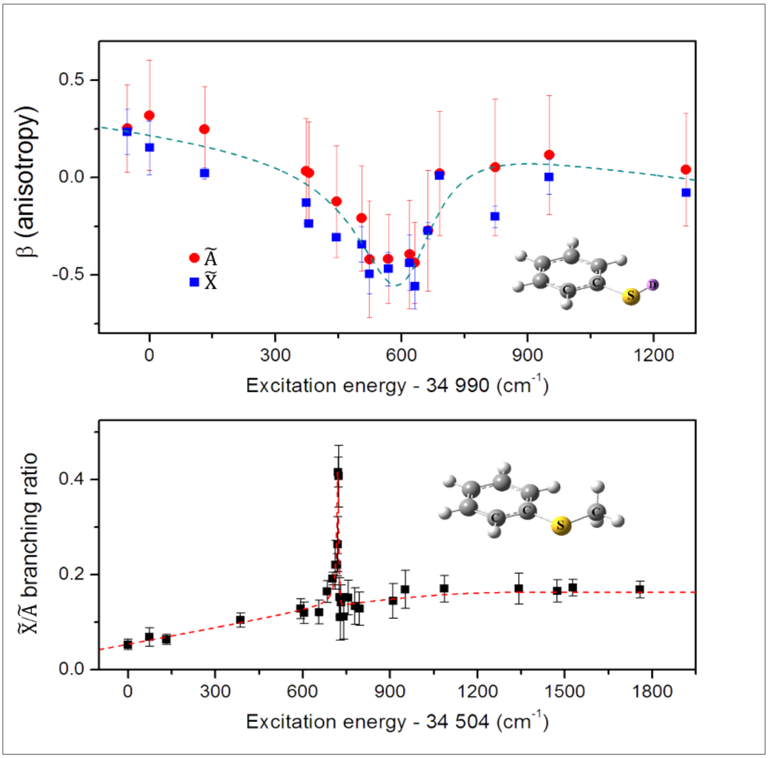

Figure 1: Conical Intersections revealed as “resonances” in photodissociation dynamics of thiophenol (top) and thioansisole (bottom).

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Probing chemical transformations in clusters and nanoparticles with mass spectrometry and X-ray based spectroscopy

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Tunable synchrotron radiation (VUV and X-rays) provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry and photoelectron spectroscopy. This provides profound insight into molecular growth mechanisms, solvation and electronic structure in clusters, complexes and nanoparticles. Efficient intra-molecular ionization-induced proton transfer for a system with no hydrogen bonds, the 1,3 dimethyuracil dimer, have been demonstrated,[1] and upon microhydration,[2] this transfer is blocked and a new pathway mediated via water occurs. I will describe recent results on the association and dissociation pathways in acetylene clusters where bonding can change from van der Waals to covalent upon ionization leading to the formation of benzene.

X-ray photoelectron spectroscopy provides a local probe of a sample's electronic structure with elemental and site-specificity. Velocity Map Imaging X-Ray Photoelectron Spectroscopy (VMI-XPS) coupled to nanoparticle beams[3] allows for the visualization of proton transfer in solvation processes. I will describe its' implementation on aqueous arginine aerosols, where by varying the pH of the constituent solution, evidence is provided that the guanidinium groups are protonated even in a very basic solution (pH 13). A molecular level picture of how charge and proton transport in aqueous solutions of arginine occur emerges by analyzing the energy shifts on the C and N X-ray photoelectron spectra.

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State-resolved photodissociation dynamics in perfluorocarbon and chlorinated solvents

M. P. Grubb[1,2], P. M. Coulter[1], H. J. B. Marroux[1], B. Hornung[1], M. N. R. Ashfold[1] and A. J. Orr-Ewing[1*]

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Weakly interacting solvents such as perfluorocarbons provide an environment in which to study the effects of a liquid medium on ultrafast photochemical processes with quantum-state resolution. We have examined the photochemical production of molecules and radicals with high levels of internal (electronic, vibrational or rotational) excitation and the subsequent relaxation dynamics through interaction with the surrounding perfluorocarbon solvent. The dynamics are compared with those observed in more conventional organic solvents such as chloroform and carbon tetrachloride. The quantum-state resolved cooling towards equilibrium in the liquid perfluorocarbons provides unique insights into the transfer of energy between solute and solvent molecules. Examples will be drawn from our recent studies of UV photolysis of BrCN [1], N_2O_4 [2], and methyl nitrite [3] in solution.

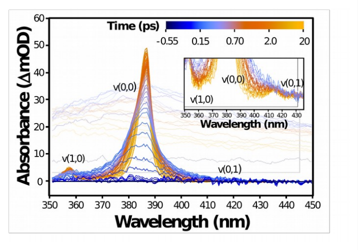

Figure 1: Transient absorption spectra of the $B^2\Sigma^+$ - $X^2\Sigma^+$ transition of CN radicals from BrCN photolysis in perfluorohexane. The faded background shows corresponding measurements in acetonitrile.

Acknowledgements: This work was funded by ERC Advanced Grant 290966 CAPRI. and Marie-Curie International Incoming Fellowship PIIF-GA-2012-326988 (for MPG).

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[3] P.M. Coulter, M.P. Grubb and A.J. Orr-Ewing, submitted (2016).

Molecular dynamics simulations of solid-liquid interfaces employing high-dimensional neural network potentials

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Understanding the structural and dynamical properties of water at solid-liquid interfaces is essential for unraveling the atomistic details of key steps in electrochemistry, heterogeneous catalysis and corrosion. In recent years, in particular ab initio molecular dynamics simulations (MD) based on density-functional theory (DFT) have contributed significantly to the understanding of these processes. Still, due to their high computational costs, ab initio MD simulations of water interacting with solid surfaces are restricted to small systems and short simulation times. This limitation can be overcome by employing high-dimensional neural network potentials (NNPs), which are constructed from a set of electronic structure data and enable carrying out large-scale simulations with close to first-principles accuracy for a variety of systems [1,2].

Here, we present NNPs for liquid water interacting with metal and oxide surfaces using copper and zinc oxide as benchmark systems. First, the convergence of various properties as a function of the supercell size and the thickness of the water layer in typical slab approaches will be investigated allowing to assess the reliability of conventional ab initio MD simulations. Then, the influence of copper and zinc oxide surfaces on the properties of water will be discussed addressing in particular the local water structure, its density profile, changes in the mobility and hydrogen bond lifetimes as well as possible dissociation processes resulting in chemical modifications of the surfaces. Finally, some perspectives for the extension to general electrolyte solutions will be given.

Acknowledgements: Financial support by the DFG (Heisenberg fellowship Be3264/6-1) and the cluster of excellence RESOLV (EXC 1069) of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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Electron transfer in gold atoms on reduced ceria surfaces: Lessons learned from static density functional theory

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Oxygen point defects in reducible oxide surfaces like ceria play a crucial role, when it comes to oxidation catalysis [1]. The activity of these surfaces may be drastically enhanced upon deposition of noble metals like gold [2]. The theoretical description of these complex systems involving electron transfer in the redox chemistry, however, represents a formidable task [3].

We present a detailed analysis of results obtained using density functional theory within the so-called DFT+*U* approach and hybrid functionals. The energy position of donor (i.e. Ce^{3+} $4f^1$) and acceptor (i.e. Au^0 $6s^1$) levels matters and steers the stability of Au atoms adsorbed on a reduced $CeO_2(111)$ surface. Benchmark *GW* calculations corroborate results obtained with hybrids.

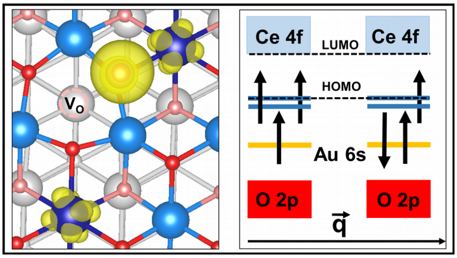

Figure 1: Top view on a reduced $CeO_2(111)$ surface showing spin-densities of two Ce^{3+} ions and Au^0 in yellow (l.h.s.). Schematic energy diagram illustrating Au diffusion from atop O^{2-} to atop a Ce^{3+} ion (r.h.s.).

Acknowledgements: COST action CM1104, “Stiftung Industrieforschung der Humboldt-Universität zu Berlin”, and the “Fonds der Chemischen Industrie” (FCI). Grants for computing time at the the high-performance computer centers HLRN (North-German Supercomputing Alliance in Berlin and Hannover) and JUROPA (Forschungszentrum Jülich) are

gratefully acknowledged.

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Ab initio modelling of charge transfer to defects and molecules at surfaces of semiconductors at realistic temperature, pressure, and doping conditions

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An important parameter influencing defect formation and molecular adsorption at semiconductor surfaces is doping. It is useful to distinguish local and global effects of doping Ref. 1. The local effects occur due to a direct chemical-bonding interaction and lattice relaxation around the dopant or adsorbed molecule. The global effect is controlled by the presence of charge-carriers (electron chemical potential) and charge separation on meso- to macroscopic length scales.

Using *ab initio* atomistic thermodynamics, we show Ref. 2,3 that (and how) the global effect of doping influences the transition levels and formation energies of defects, as well as adsorption energies of molecules at interface significantly. In our approach, the energy density of the electric field is considered as part of the free energy of the system. Charge-carrier doping is modelled using a variant of virtual crystal approximation Ref. 4. Two main contributions to the defect formation energy are identified: (i) the interaction of a charged defect with the compensating charge and (ii) the shift in the Fermi level due to the space-charge formation. Both contributions are present in periodic model calculations, but must be corrected for realistic defect concentrations. Similar considerations are applicable to molecular adsorption. We also discuss the interplay between defect site coordination and charge-carrier trapping at oxide surfaces, and the prospects and pitfalls of tuning the fraction of the exact exchange in hybrid functionals to improve the description of charge transfer at surfaces.

Our results for doped MgO clearly show that the global effect of doping on interface chemical properties can be significant, so that charge-carrier doping (intentional or not) must be considered as a thermodynamic variable along with temperature and pressure.

Acknowledgements: This work has the support of DFG through CoE UniCat

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How does molecular hydrogen dissociate on Pt?

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In this contribution, we address a simple but currently unresolved issue at the heart of gas-surface reaction dynamics. For the explanation of dissociative events resulting from H_2 impinging onto Pt, two models exist. The first model relies on resonant scattering into a weakly bound molecular state and frictionless diffusion to monoatomic steps where the molecule dissociates or scatters[1]. The second model assumes that the molecule dissociates or scatters upon impact without significant diffusion[2].

We probe D_2 dissociation using a curved Pt single crystal. The 30° curvature with [111] centered at the apex is shown to result from monoatomic A and B type steps, which are spatially separated by the apex. The step density ranges over 3 order of magnitude from the center of the crystal to either edge. We quantify the absolute dissociation probability with high spatial resolution using supersonic molecular beam techniques and probe how it depends on incident kinetic energy and surface temperature. HD production from a beam consisting of H_2 and D_2 tracks the initial sticking probability, indicating that the reaction mechanism for H-D exchange is rate limited by the dissociation event. We discuss the implications with respect to the two models to dissociation of hydrogen.

Acknowledgements: This work has the support of the Netherlands Organization for Scientific Research (NWO) "CO_2 neutral fuels" program.

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H atom scattering from surfaces

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Obtaining an atomic-level understanding of the dynamics of energy conversion at surfaces remains a complex and challenging area of modern research in physical chemistry. A general strategy to this field follows the lessons of gas-phase bimolecular chemical dynamics, where simple model systems are studied experimentally with great care while theoretical simulations are developed. One of the simplest systems to think of is Hydrogen atom scattering from a single crystalline surface. We study this model system experimentally with extraordinary resolution. The experiments give detailed insights about the energy exchange between atom and surface and provide a valuable benchmark for high level theoretical models describing the interaction between atoms or molecules and surfaces.

Recently, we could show that in case of H atom scattering from Au(111) a large amount of the translational energy can be transferred to electronic excitation of the metal, Ref. 1. We expanded our studies to a large parameter space, including incidence H-atom beam, surface and scattering conditions. Furthermore, the isotope effect and a wide set of metals (Cu, Ag, Au, Ni, Pd, Pt) were investigated. The experimentally observed dependencies are presented and their implication for the underlying non-adiabatic process are discussed.

In addition, another example of a very efficient energy transfer between H-atoms and a surface is presented. H-atoms were scattered from a monolayer of graphene deposited on a Pt(111) surface. H atoms can form a covalent bound with Graphene and the adsorption process exhibits a barrier. For normal incidence energies below the adsorption barrier nearly elastic and specular scattering is observed. However, for normal energies larger than the adsorption barrier a large amount of translational energy of the H-atom is transferred to Graphene. Ab intio molecular dynamics (AIMD) simulations qualitatively reproduce the experiment and suggest an adiabatic energy loss mechanism.

Acknowledgements: This work has the support of the SFB1073 under project A04, the Deutsche Forschungsgemeinschaft (DFG), the Agence Nationale de la Recherché (ANR), the Ministerium für Wissenschaft und Kultur (MWK) Niedersachsen, the Volkswagenstiftung, and the Humboldt Foundation.

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CO oxidation on Pt(111): Deciphering the second mechanism using slice imaging

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We report the results of a combined kinetics and dynamics study to elucidate the underlying mechanisms in the catalytic oxidation of CO on Pt(111). We show that there are two concurrent, competing pathways at all oxygen coverages, the classical Langmuir-Hinshelwood (LH) pathway, and a second reaction pathway that involves the reaction of a weakly bound, roaming precursor CO molecules (CO_p) with adsorbed oxygen atoms. This latter reaction pathway is significant and dominates the oxidation process at high oxygen coverage and, consequently, under industrially relevant conditions. The implementation of slice imaging detection allowed the measurement of velocity selected kinetics and determination of the rate constants for the different channels. The two reaction pathways have distinct CO_2 product velocity distributions which are identified for the first time by our velocity selected kinetics measurements, which also allow branching ratios to be extracted. The directly measured branching ratios are in excellent agreement with the ratios of rate constants reported above further supporting our proposed reaction model for the underlying kinetics.

Our observations provide experimental evidence for a precursor mechanism for surface catalyzed exothermic reactions that is intermediate between the two generally limiting mechanisms, i.e., those of Langmuir-Hinshelwood and Eley-Rideal (ER).

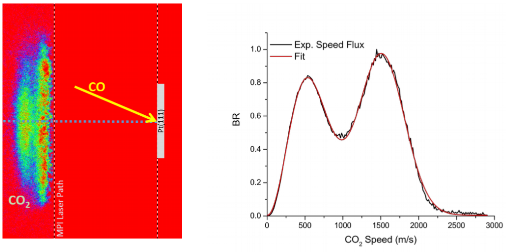

Figure 1: Typical Slice Image of the CO_2 reaction product and the corresponding speed Distribution.

Acknowledgements: This work has the support of teh Alexander-von-Humboldt-Stiftung, the Deutsche Forschungsgemeinschaft (DFG) and the Niedersächsisches Ministerium für Wissenschaft und Kultur (NMWK).

Ion-molecule reactions with ionic water clusters

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The influence of hydration on chemical reactions has many facets, involving changes in thermochemistry, kinetics and reaction dynamics. Ionic water clusters in the gas phase are ideal model systems to study and disentangle these effects. Some examples will be presented that highlight specific aspects of water cluster reactivity.

Already one water molecule changes the reaction product and enhances the rate by almost two orders of magnitude for the reaction of $CO_3^{\bullet-}$ with HCl. In the lower troposphere, where $CO_3^{\bullet-}(H_2O)$ dominates, $Cl^-(HCO_3^{\bullet})$ is efficiently formed. At higher altitudes, where $CO_3^{\bullet-}$ prevails, the product is $Cl^-(OH^{\bullet})$. An intriguing aspect is the low rate of the unhydrated species, which can only be explained with arguments from reaction dynamics.

In larger water clusters containing up to 130 water molecules, electron attachment to and electron transfer between CO_2 and O_2 has been studied at different temperatures. These studies reveal clearly that the charge transfer from $CO_2^{\bullet-}$ to O_2 in the cluster involves a $CO_4^{\bullet-}$ intermediate, which is confirmed by ab initio molecular dynamics simulations.[1]

Another puzzling ion embedded in water clusters is $O^{\bullet-}$, which may be converted to OH^- and $OH^{\bullet}$. We prepared a mixture of $O^{\bullet-}(H_2O)_n$ and $OH^-(H_2O)_n$ by reacting $(H_2O)_n^-$ with N_2O. Infrared spectroscopy in the O-H stretch region reveals no difference between the two species, but both exhibit the signature of the mobile proton, a weak, broad absorption below 3000 cm^{-1}. Here dynamics simulations are employed to interpret the spectra and to understand the structure of the $O^{\bullet-}$ core ion.

Acknowledgements: This work has the support of Austrian Science Fund (FWF) via Lise Meitner Grants M 1983 and M 2001, as well as Single Project P 28896, of the DFG via Project BE2505/4-3, and City University of Hong Kong, Project No. 7004401.

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Time and angle-resolved photoemission spectroscopy of electronic dynamics in aqueous solutions

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Chemical reactions are strongly affected by solvents, particularly polar solvents. To explore static and dynamic influences of polar solvents on electronic dynamics, we are investigating non-adiabatic dynamics of an excess electron in polar solvents using time-resolved photoemission spectroscopy (TRPES).

Atomic iodine anion has no stable excited state in the gas phase, while metastable excited states are created by solvation. These metastable states are short-lived, and they undergo rapid charge-transfer-to-solvent (CTTS) reactions to produce a solvated neutral atom and a solvated electron in sub-picoseconds. Since the polarization field of solvents are essential for the CTTS states, their electronic relaxation processes are strongly coupled with solvation dynamics. Absence of rovibrational degrees of freedom makes I^- to be an ideal solute to illuminate strongly-coupled electron-solvation dynamics.

The CTTS reaction creates a solvated electron, which is also an intriguing target of research in relation to radiation chemistry and biology. We studied ultrafast internal conversion of a hydrated electron from the *p* to *s* state using time and angle-resolved photoemission spectroscopy. The angle-resolved measurement disentangled the overlapping signals from the *p* and *s* states and also revealed ultrafast depolarization of the *p* orbital of a hydrated electron in solution.

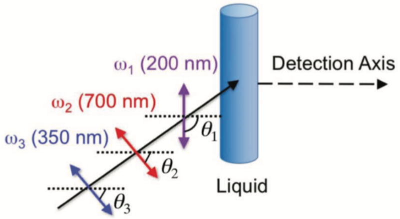

Figure 1: Geometry of three pulse photoemission experiment, in which ω1 is the generation pulse of a hydrated electron in the s state, ω_2 is the pump pulse, and ω_3 is the probe pulse.

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Molecular dynamics studied with attosecond XUV pulses

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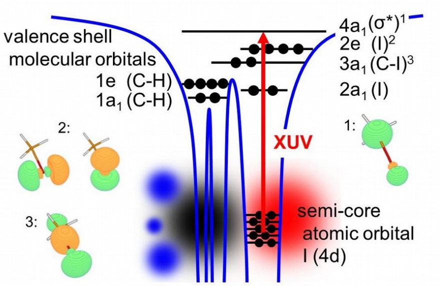
There are exciting ways in which studies of chemical dynamics can hugely benefit from the technological developments pushed forward in the vibrant field of Attosecond Science. We present two experiments involving different schemes of utilizing ultrashort XUV pulses derived from High Harmonic Generation.



Core-to-valence transitions are element-specific probes of the intramolecular local chemical environment. An electron from a highly localized and energetically distinct core orbital is lifted to a hole in the valence shell, affected by chemical bonding. We present time-resolved XUV transient absorption spectroscopy of iodomethane and iodobenzene photodissociation at the iodine pre-$N_{4,5}$ edge [1]. For both molecules the molecular core-to-valence absorption lines fade immediately, within the pump-probe time-resolution. Absorption lines converging to the atomic iodine product emerge promptly in CH_3I but are time-delayed in C_6H_5I. We attribute this delay to the initial $\pi \rightarrow \sigma^*$ excitation in iodobenzene, which is distant from the iodine reporter atom. We measure a continuous shift in energy of the emerging atomic absorption lines in CH_3I, attributed to relaxation of the excited valence shell.

Detailed understanding of dynamics beyond the adiabatic Born-Oppenheimer approximation remains one of the most formidable challenges in physical chemistry. Particular relevance as a model system has the benzene cation, for which Köppel and coworkers have theoretically investigated the multimode and multistate vibronic coupling around the lowest lying conical intersections in an extended series of work. In contrast, time-resolved experiments were not within reach until recently. We present a time-resolved study of internal conversion in the benzene cation following XUV preparation of the lowest electronic states [2]. Signature fragments single out the population transfer from the E to D state on a time scale of 11fs, and from the D to the B state on the time scale of 115fs. Detailed comparison of experiment and theory is drawn within a collaboration with the groups of Horst Köppel and Alexander Kuleff.

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Probing ultrafast dynamics of chiral molecules with photoelectron and photoexcitation circular dichroism

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Chiral molecules exist as two forms (enantiomers) which are mirror images of each other but are non superimposable. Understanding the fundamental processes at play in chiral reactivity requires measuring the dynamics of chiral molecules on their natural timescales - femtoseconds to attoseconds. The vast majority of chiroptical processes are forbidden within the electric dipole approximation and are thus extremely weak, incompatible with ultrafast measurements in the gas phase. Photoelectron Circular Dichroism (PECD) is the exception to this rule: it is a pure electric dipole effect, consisting of a strong (up to 30%) forward/backward asymmetry in the angular distribution of electrons ionized from *randomly aligned* chiral molecules by circularly polarized light [1-5].

We used time-resolved PECD to track the ultrafast relaxation of Rydberg wavepackets in chiral molecules. We demonstrate that PECD reveals dynamics invisible in the angle-integrated photoelectron spectra, with high sensitivity to rotations, vibrational and electronic relaxation.

In a second experiment, we demonstrate a new type of chiroptical signal: PhotoeXcitation Circular Dichroism (PXCD). Using a circularly polarized pump pulse, we create a bound electron wavepacket with a forward/backward asymmetry, which is probed by ionizing with a linearly polarized probe pulse. This phenomenon offers new opportunities to track bound wavepacket and coherences in chiral molecules.

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Towards directing ultrafast charge transfer with IR excitation

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Ultrafast electron transfer (ET) in condensed-phase molecular systems is often strongly coupled to intramolecular vibrations that can promote, suppress and direct electronic processes. Recent experiments exploring this phenomenon proved that light-induced electron transfer *in solution* can be strongly modulated by vibrational excitation[1,2], with up to 100% effect [1]. However, predictive and directive control over ET in condensed phase has not yet been achieved. Yet theory predicts that it should be possible to direct electron transfer along one of the preselected pathways.[3]

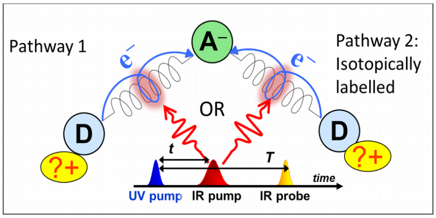

Figure 1: Modulation of electron transfer between D and A by transient IR excitation. The two electronically identical pathways are made structurally distinct by ^{13}C-isotopic labelling of one of the bridges, enabling independent vibrational perturbation of either.

The realization of such vibrational control will be presented, on an example of a Pt(II)-acetylide charge-transfer Donor-Bridge-Acceptor-Bridge-Donor “fork” system (Fig. 1). The frequency-domain Transient 2-Dimensional IR (T-2DIR) pulse sequence, UV$_{pump}$- IR$_{pump}$-IR$_{probe}$, is applied to exploit the interplay between vibrational and electronic processes and to direct ET along one of the pathways. It was observed that the pathway that is vibrationally perturbed in the course of ET is drastically slowed down compared to its unperturbed counterpart. The results will be discussed in the context of the previous reports on IR-modulation of ET in linear D-Bridge-A systems.[1] The findings deliver a new opportunity for perturbative control of electronic energy propagation in molecular devices.

Acknowledgements: This work has the support of the EPSRC, STFC, and the University of Sheffield, UK.

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Probing valence electronic structures and interfacial solvation properties of biological and organic aqueous nanoaerosols via aerosol VUV photoelectron spectroscopy

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Aqueous aerosols are complex systems that exist ubiquitously in nature. The crucial roles of aqueous aerosols have been recognized in a variety of important fields, encompassing the aerosol science, atmospheric chemistry, marine chemistry and environmental science. To better understand the physicochemical activities of these complex systems, it is particularly important to assess their valence electronic properties under either physiologically or atmospherically relevant aqueous environments. Recently, we applied the recently built aerosol VUV photoelectron spectroscopy to investigate the valence electronic structures and interfacial solvation characteristics of several complex systems that are of particular biological or environmental significance, including cysteine (Cys), a highly bioactive amino acid [1], glutathione (GSH), a thiol-containing tripeptide [2] and some small amphiphilic organic species such as phenol and duhydroxybenzenes in the form of aqueous nanoaerosols, using the undulator-based VUV radiation as the ionization source (U9, BL21B2, NSRRC, Hsinchu, Taiwan). The pH-dependent valence electronic properties of chosen aqueous nanoaerosols have been interrogated, revealing their electronic evolution and interfacial solvation behaviors. The newly developed aerosol VUV photoelectron spectroscopy apparatus sheds new light for one to assess the valence electronic structures of nanoscaled aerosols, complex molecular assemblies and other novel nanomaterials in a size-selective and composition-controlled way. With this new aerosol technique, it is promising to address numerous fundamental but critical issues regarding aerosols in various related fields, including the environmental science, the atmospheric chemistry and the biomedical science.

Acknowledgements: This work is supported by the Ministry of Science and Technology of Taiwan, R.O.C. under the project numbers of NSC 102-2113-M-110-005-MY2, MOST 104-2113-M-110-011 and MOST 105-2119-M-110-002.

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Aligning a spherical top molecule and the stereodynamics in Cl + $CH_4(v_3=1)$ reaction

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Two complementary experimental approaches to understand the steric effects in the title reaction were adopted in a crossed-beam, product-imaging apparatus. First, the initial rotational-mode specificity was examined in reaction with *un*polarized-$CH_4(v_3=1, |JNl\rangle)$ over the collisional energy (E_c) range of 1 − 6 kcal mol^{-1} [1]. We found that the initial rotational $|JNl\rangle$-state selection of the vibrationally excited reactants exerts significant effects on the reaction rate. More detailed product state and angular distributions are, however, nearly invariant to the selected $|JNl\rangle$-states − a surprising result that defies conventional wisdom. We term this phenomenon a "loss of memory" effect, as the product distributions appear to be independent of the reactant rotational excitation.

An alternative, yet more revealing approach is to actively pre-align the reactant $CH_4(v_3=1)$ in space. By exploiting the linear polarization of the IR excitation laser, we investigated (1) how a spherical top molecule as CH_4 is optically aligned by an infrared laser [2], and (2) once aligned, what consequences will be in terms of stereo-requirement in reaction with a Cl atom [3-5]. A huge steric effect was found, and the observed polarization-dependent differential cross sections depend sensitively on the initially aligned $|JNl\rangle$-states of $CH_4(v_3=1)$ reactant, in sharp contrast to the above experiment with *un*polarized reactants.

In this talk, I will discuss both results with polarized and *un*polarized reactants, and try to delineate a coherent picture about the stereo-specificity of the reaction of Cl + $CH_4(v_3 = 1)$.

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High-resolution experimental studies of elementary chemical reactions using the ion imaging technique

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The crossed molecular beam technique plays a very important role in the development of chemical reaction dynamics and molecular physics. In combination with the velocity mapping ion imaging technique, researchers have successfully studied the molecular scattering dynamics of reactive collisions [1-3]; In particular, very high resolution has been achieved in elastic scattering experiments with a Stark decelerated molecular beam [4].

We report in this talk the experimental studies of reactive collisions using a new crossed molecular beam apparatus [5] in University of Science and Technology of China. We employed the time-sliced ion imaging technique and the state selected ionization detection to study the elementary reactions between the Hydrogen atom and small molecules (such as CD_4 and D_2). Ion images with high resolution were acquired. These results are of great importance for researchers to understand quantum effects in reactive scattering experiments.

Acknowledgements: This work was supported by the National Natural Science Foundation of China, Strategic Priority Research Program of the Chinese Academy of Sciences, and the Ministry of Science and Technology of China.

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Computational studies of the dynamics of chemical reactions

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Computational studies on the mechanism and dynamics of chemical reactions are of fundamental importance since they help us understand how and why chemical reactions happen. If quantum mechanical effects are not important, the dynamics of a reaction can be described classically. To this end, ab initio chemical dynamics simulations have been used to follow the dynamics and mechanisms of chemical reactions. Here, dynamical studies on two reactions: (i) Protonation and lithiation of ferrocene and (ii) Denitrogenation of pyrazoline will be discussed.

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Low energy scattering in crossed molecular beams

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This presentation aims at giving a flavour of what happens when molecular collisions (reactive or inelastic) occur at low energy / temperature, in the *near cold* regime (1-50 K). In this domain, resonances are predicted by theory for many systems.

I shall report on experimental studies of such systems, using a crossed molecular beam apparatus with variable crossing angle to determine the integral cross sections (ICSs) [1] as a function of the collisional energy down to a few wavenumbers. Reactants and products are probed using REMPI time-of-flight spectrometry.

The $S(^1D) + D_2(j=0)$ reaction which is barrierless and exoergic, is a prototypical insertion atom + diatom reaction. The experimental results will be compared with the theoretical ones obtained with different methods and with data for its isotopic variants [2]. The ICSs for spin orbit excitation of $C(^3P_0) + He \rightarrow C(^3P_1 \text{ or } ^3P_2) + He$, observed experimentally for the first time, will also be presented with an assignment of the resonances.

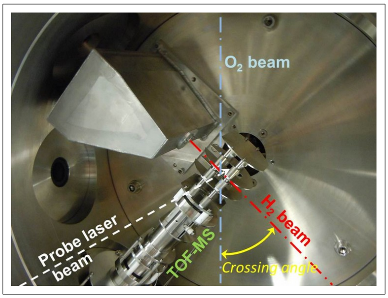

Figure: Open view of the scattering chamber of our crossed molecular beam apparatus.

Acknowledgements: This work has the support of the "Agence Nationale de la Recherche" (ANR-HYDRIDES, contract ANR-12-BS05-0011-01) and by the CNRS national program "Physico-Chimie du Milieu Interstellaire".

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Chirped-pulse microwave spectroscopy in uniform supersonic flows: Applications in kinetics and dynamics

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We describe development and application of a new instrument combining two powerful techniques: chirped-pulse Fourier-transform microwave spectroscopy and pulsed uniform supersonic flows. The objective is to join the virtues of microwave spectroscopy: quantitative, near universal detection affording structural information, with Laval flows offering thermalized conditions at low temperature and high density, to study reaction dynamics of polyatomic molecules with unprecedented detail in product characterization. This combination, which we term "CPUF" (chirped-pulse/uniform flow), delivers broad-band rotational spectra with MHz resolution and allows monitoring, on the μs timescale, of the appearance of transient reaction products with quantitative determination of product branching, yielding isomer and in some cases vibrational level specificity. We have applied this technique to study multichannel product branching in the reaction of CN radicals with unsaturated hydrocarbons at low temperature as well as a number of photochemical systems. The approach will be described and recent examples of the capabilities of the technique will be presented.

Acknowledgements: This work has the support of the NSF under award number CHE-1634760.

Merging and splitting beams of neutral molecules

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Merged neutral beams have enabled the investigation of sub-Kelvin chemical reactions in molecular beams. In the past years we have conducted several Penning ionization studies of polyatomic molecules, targeting characteristics arising from the presence of multiple rotational degrees of freedom and from the anisotropic shape of such systems are accessible. Here I will give an overview of our recent experiments on stereo dynamical aspects where we orient, e.g., the angular momentum of a metastable rare gas atom prior to reaction. Strong orientation-dependent changes in the branching ratio between different reaction channels permit the determination of state-specific reaction cross sections for levels that differ only by their magnetic quantum number.

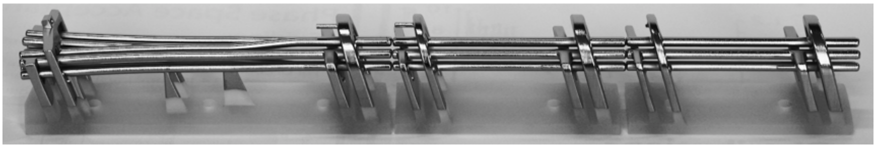

Figure 1: 3D printed, electroplated beam splitter for polar neutral molecules.

I will also present a beam splitter for neutral polar molecules which we have recently developed [1]. With this device a single supersonic expansion is split, using electrostatic guides, into two nearly identical components. This permits, for example, differential measurements with correlated probe and reference beams. Here, only the former is made to interact with a laser or a second molecular beam, while the latter is left unchanged. I will present our device, shown in figure 1, which we have produced by a novel production method: the 3D printing of a plastic structure using stereo lithography, followed by electroplating to obtain conductive surfaces. This new manufacturing approach opens many possibilities for the generation of scientific apparatus, and it will greatly simplify and accelerate the design, production, testing, and exchange of experimental components.

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Hot Topic Talks

Photophysics of controlled gas-phase molecules and clusters

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The properties of atoms and molecules are strongly dependent on their environment. So-called hydrogen bonds are one of these interactions, which are of universal importance in chemistry and biochemistry. Thus, it is of great interest to study their microscopic details in order to bridge the gap between single, isolated molecules and solvated molecules.

Here, we present results on the photofragmentation of indole, the chromophore of the amino acid tryptophan, and indole-water, i.e., indole 'solvated' by a single water molecule, upon x-ray ionization. These solvated-indole molecules were spatially separated from monomeric indole using the electric deflector [1,2]. The photofragmentation was induced by side specific 1*s* core hole ionization of indole's nitrogen atom, leading to a relaxation of the highly excited molecules and clusters via an emission of electrons and/or photons and subsequent Coulomb explosion. Photoelectrons and ionic fragments were recorded in coincidence with a double-sided velocity map imaging (VMI) spectrometer. The photofragmentation of indole and indole-water was analyzed by means of (photoelectron-)photoion-photoion coincidence (PIPICO) maps. Charge/electron, proton, and hydrogen-atom transfer, as well as different Coulomb explosion channels were observed. These results will be discussed based on the fragmentation channels of the different species, photoelectron and ion VMI images for different ionic fragments, and the 3D reconstruction of the molecule's orientation. The prospects of pump-probe experiments for unraveling the intermolecular solvation interactions is discussed.

Acknowledgements: This work was carried out in a collaboration with DESY and Kansas State University. The experiment was conducted at the Variable Polarization XUV Beamline P04 of PETRA III at DESY.

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Photoisomerization action spectroscopy of molecular switches

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Organic molecules such as diazobenzenes, spiropyrans, and styryl dyes are light-absorbing units that constitute the basis of modern molecular photoswitches and devices for data storage [1]. Most molecular switches undergo reversible structural changes in response to visible and ultraviolet light or heat. Recently, a combination of ion mobility-mass spectrometry with laser or collision induced excitation has opened new opportunities for the investigation of fundamental isomerization and dissociation dynamics of mobility selected conformers [2,3].

Here we present first results on the isomerization behaviour of a series of charged azobenzene switches (Figure 1). Efficient *trans* to *cis* isomerization following absorption of a photon in the visible range is demonstrated for all molecules. In some cases, a photodissociation channel with multiphoton character is observed. Overall, the absorption profiles of the protonated cations appear red-shifted compared with those for neutral azobenzenes in the gas phase or solution. The experimental data are supported by electronic structure calculations. These studies represent the first gas phase photoisomerization action spectra of this family of molecular switches.

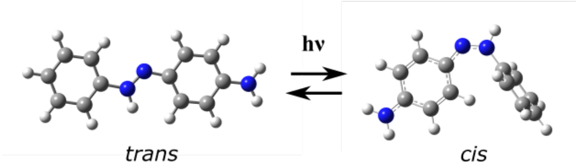

Figure 1: Geometric isomers of 4-aminoazobenzene.

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Scattering formaldehyde from the Au(111) surface

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A number of recent studies have demonstrated the importance of orientation and mode-specific vibrational excitation on reactions of polyatomic molecules at surfaces [1]. The conversion of translational to rotational motion often plays a major role in the trapping of small molecules at surfaces, a crucial first step for a wide variety chemical processes that occur at gas-surface interfaces. However, to date most quantum-state resolved surface scattering experiments have been performed on diatomic molecules, and very little detailed information is available about how the structure of non-linear polyatomic molecules influences the mechanisms for energy exchange with surfaces. In the current work, we employ a new rotationally-resolved 1+1′ resonance-enhanced multiphoton ionization (REMPI) scheme to measure rotational distribution in formaldehyde molecules directly scattered from the Au(111) surface at incident kinetic energies in the range 0.3−1.2 eV. The results indicate a pronounced propensity to excite *a*-axis rotation (twirling) rather than *b*- or *c*-axis rotation (tumbling or cartwheeling), and are consistent with a rotational rainbow scattering model. Classical trajectory calculations suggest that the effect arises—to zeroth order—from the three-dimensional shape of the molecule (steric effects). Figure 1 shows the distribution of *a*-axis rotational energy obtained from fitting the observed spectra to a rainbow model.

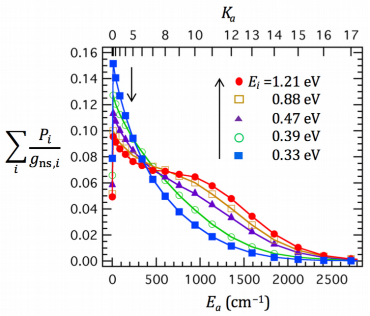

Figure 1: The summed population (divided by the nuclear spin degeneracy, gns), obtained from our fit model, is shown as a function of *a*-axis rotational energy (E_a) and incident kinetic energy (E_i).

Acknowledgements: This work has the support of the Alexander von Humboldt Foundation**.**

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Quasiclassical study of Eley-Rideal reactions of N atoms with O/N adsorbed on a Ru(0001) surface

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Eley-Rideal (ER) reactions between neutral atoms heavier than hydrogen and adsorbed atoms of similar mass were first observed in recent molecular beam experiments.[1] Through analysis of two types of measurements different estimations for the N-O ER reaction cross section were obtained. The unexpectedly high value of N-O ER reaction cross section (34 $Å^2$) was qualitatively accounted for by invoking a secondary effect whereby the presence of N adatoms on the surface acted to "shield" O adatoms from prompt recombinative desorption.

In the kinetic analysis[2] with a rate equation model including two ER processes involving different adsorbed species ($N\text{-}O_{ad}$ and $N\text{-}N_{ad}$) and an N adsorption process to the full-beam exposure subset of the experimental data, the measured N_2 response can be well described, but it is insufficient to completely describe the NO response. And it shows that the "shielding effect" may be not large enough to explain the unexpectedly high value of N-O ER reaction cross section. To understand these reactions rigorous theoretical study is needed.

Here we employ a first-principles divide and conquer approach based on a six-dimensional potential energy surface within the frozen surface approximation. Neural networks are used to interpolate the grid data from density-functional theory to a continuous representation. Dynamical properties are obtained by the quasi-classical trajectory method. The analysis of our computational results gives detailed mechanistic information of the processes. In addition, the reverse dissociative adsorptions of NO and N_2 are studied.

Acknowledgements: This work has the support of the European Research Council through an ERC-2013 advanced grant (Nr. 338580) and a VIDI grant of the Netherlands Organisation for Scientific Research (Nr. 723.014.009).

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Inelasticity in Hydrogen atom scattering from surfaces: A probe for energy conversion

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Developing an understanding of energy conversion at surfaces is of great fundamental and practical interest and the subject of extensive investigation over many years. Measuring the change in momentum and quantum state in collisions of atoms and molecules with surfaces are fundamental tools to evolve an understanding of how atomic and molecular degrees of freedom couple to those of a surface.

Recently, we have developed an apparatus to measure energy conversion in H-atom surface collisions: A mono energetic H-atom beam is pointed towards a surface at defined incidence angles. Employing Rydberg Atom Tagging the final scattering angular and kinetic energy distributions are measured. A first experiment showed that drastic differences are observed when Hydrogen atoms are scattered from a metal versus an insulator surface. Comparison of the experimental results to resent theoretical work indicate that electron-hole-pair excitation plays an important role in scattering processes with metals.[1,2]

We studied in detail which factors affect the dissipation of translational energy to the surface. The influence of various experimental parameters was investigated: Kinetic energy, incidence angles, isotope of the incident beam, surface temperature and structure of the surface. Furthermore, a variety of different metals were studied. The obtained experimental data were put into context with theoretical concepts.

Acknowledgements: We acknowledge support from the Humboldt Foundation, the SFB1073 under project A04, the Deutsche Forschungsgemeinschaft (DFG), the Agence Nationale de la Recherché (ANR), the Ministerium für Wissenschaft und Kultur (MWK) Niedersachsen, and the Volkswagenstiftung.

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H_2 physisorption on $C_{60}Cs$

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Low physisorption energies render H_2 storage on pure carbon based materials impracticable. Doping of carbon materials with alkali, earth alkali or other metal atoms has been proposed as a means to enhance adsorption energies, and some experiments have shown promising results [1-3]. In the present work the upper bounds of hydrogen storage capacities are investigated for $C_{60}Cs$ clusters grown in ultracold helium nanodroplets. On bare C_{60}^+, a commensurate phase with 32 H_2 molecules was identified in previous experiments. Doping C_{60} with a single cesium atom leads to an increase in relative ion abundance for the first 10 H_2 molecules, and the closure of the commensurate phase is shifted from 32 to 42 H_2 molecules. DFT calculations indicate that thirteen energetically enhanced adsorption sites exist. The quantum nature of the hydrogen molecule can significantly decrease the adsorption energies. Harmonic zero-point corrections, which represent an upper bound to corrections for dissociation energies (D_e to D_0) amount to around 50% for $(H_2)C_{60}Cs$ and up to 80% for $(H_2)C_{60}$. Five normal modes of libration and vibration of H_2 physisorbed on the substrate contribute primarily to the large ZPE correction. A similar effect has been calculated for H_2 physisorbed on benzene [4] and is expected to be found for any other weakly H_2-binding substrate.

Acknowledgements: This work has the support of the Austrian Science Fund (FWF Projects I978, P23657, P26635, P28979). The computational results have been achieved using the HPC infrastructure LEO of the University of Innsbruck. A.K. acknowledges support by the Tirolean Science Fund (TWF grant). R.P. thanks the Austrian Agency for International Cooperation in Education and Research ORGANISATION (OeAD-GmbH), Centre for International Cooperation & Mobility (ICM) for Ernst Mach-Nachbetreuungsstipendium (EZA).

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Electron impact total and partial ionization cross sections and kinetic energy releases for hydrocarbon species relevant to fusion edge plasmas

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The electron ionization cross section (EICS) quantifies the probability that an atom or molecule will be ionized in a collision with an electron. Accurate absolute electron ionization cross sections are needed for modelling a range of plasma processes, including fusion and industrial plasmas, as well as naturally occurring plasmas such as those found in the upper atmosphere and interstellar space [1]. We have recently upgraded an existing instrument (Figure 1 left) for measuring electron total ionization cross sections [2], and will report recent progress on these measurements, such as experimental total ionization cross section (TICS) data for an important interstellar molecule, Carbon dioxide (Figure 1 right).

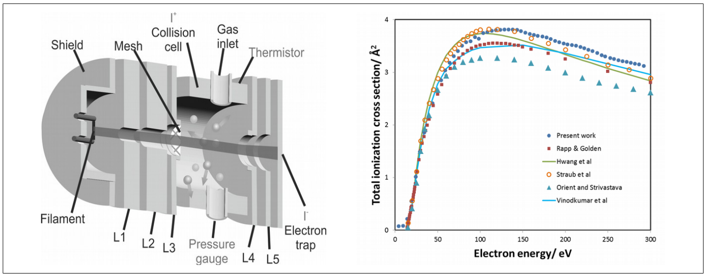

Figure 1 Left: Schematic representation of ionization cell. Right: Present TICS data for CO_2, together with literature experimental data (dots) and theoretical data (line).

Acknowledgements: This work is supported by EPSRC Programme Grant EP/L005913/1.

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Photodesorption of NO from Au(100) using 3D surface-velocity map imaging

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We measured the fully-resolved 3-dimensional velocity distributions of nitric oxide photodesorbed from a gold single crystal. These experiments combine time-of-flight measurements and the velocity map imaging technique to yield fully resolved velocity distributions *in three dimensions* for a prototypical surface-adsorbate system. The detection of fragments within a relatively large volume requires soft extraction conditions to ensure that all ionised fragments adhere to VMI conditions (Ref. 1).

Nitric oxide adsorbed on Au(100) was photodesorbed using a 355 nm laser beam. The desorbed NO molecules were ionised in the gas-phase by resonance-enhanced multi-photon ionisation within a set of velocity map imaging optics. The NO molecules preferentially leave the surface along the surface normal with a very narrow angular distribution, indicating a non-thermal desorption process.

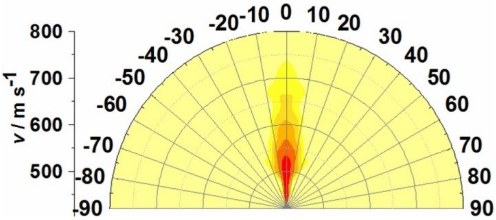

Figure 1: Plot of the NO flux as a function of overall speed and angle after 355 nm photodesorption from a Au(100) single crystal. Color scheme from red (most intense) to faint yellow (zero intensity). Note that the geometry of our 3D surface VMI setup allows NO molecules desorbing from the surface at angles of up to 53° to be detected.

Acknowledgements: We thank the Dalton Cumbrian Facility program in part funded by the Nuclear Decommissioning Authority for funding; HAS and SA thank the Saudi and Libyan government, respectively, for funding.

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Carbon dioxide dissociation in non-thermal microwave and radiofrequency plasma

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Non-thermal plasma, which contains chemically active species such as high energy electrons, ions, and excited gas molecules, is expected to achieve chemical activation at low gas temperature and has wide applications in both industry and scientific research. We have designed and installed a versatile experimental system to study the energy transfer process and induced chemistry activated by non-thermal plasma. The system comprises microwave (MW) and radiofrequency (RF) plasma sources connected to a vacuum system, in-situ Fourier Transform infrared spectroscopy (FTIR), emission spectrometry, Langmuir probe and differentially pumped quadrupole mass spectrometer (QMS).

Electron collisions in the plasma can excite vibrational modes in the molecule. Taking CO_2 dissociation reaction as an example, the major portion of the discharge energy could be transferred from plasma electrons to molecule vibrations at electron temperature typical for non-thermal discharges ($T_e \approx 1eV$). Other degrees of freedom rotation and translation are heated less. Meanwhile, the vibrational energy loss through relaxation is relatively slow. The vibrationally excited molecules will further interact with each other or collide with other plasma electrons, leading to a successive "vibrational pumping" up along the energy scale to reach the dissociation limit, which explains the high energy efficiency of the CO_2 dissociation, while keeping the other degrees of freedom cooler.

Recently, we have carried out the CO_2 dissociation experiments in RF and MW non-thermal plasma discharges at low gas pressure. The highest energy efficiency up to now is about 60%, which exceeds the maximum value of about 45%, in case of thermodynamic equilibrium. This proves that electron induced vibrational excitation plays an important role in the CO_2 dissociation process. Addition of a noble gas, such as Ar, was found to improve the energy transfer from the plasma to the molecular vibrational modes via tuning the electron energy distribution. Results obtained using various diagnostic methods will be shown, and we will demonstrate that plasma is an efficient and practical tool to drive chemical reactions in an energy efficient way.

Acknowledgements: This work has the support of the National Natural Science Foundation of China (51561135013, 21603202)

Ultrafast dissociation of substituted pyrroles

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The lowest lying electronic excited singlet state present in the aromatic heterocycles of many biologically relevant systems [1] has attracted significant attention as photoexcitation to these states results in prompt H-atom loss. As the prototypical chromophore in biomolecules such as tryptophan or heme, the photodissociation of pyrrole (c-C_4H_5N) from the S_1 state has been extensively studied in the gas phase (see, for example, Ref. 2), where H-atom appearance lifetimes range from 130 to 40 fs as the photon wavelength is decreased [3]. While the effects of ring substitution on the H-atom photo-fragment translational energies have been investigated [4], the ultrafast photodissociation has remained largely unexplored. Recently, our group invest-igated the photodissociation of 2,4-dimethyl pyrrole [5], finding significant changes in the N–H photochemistry due to methylation. Here, we report on our current work to continue exploring the structure-property relationship of the ultrafast photochemistry of pyrrole derivatives.

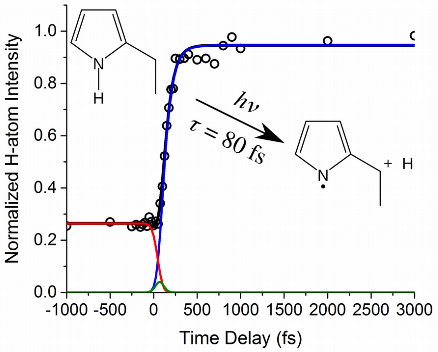

Figure 1: H-atom appearance measurement from the photodissociation of 2-ethyl pyrrole.

Acknowledgements: This work has the support of the Leverhulme Trust, the EPSRC, the Royal Society, the Ecole Normale Supérieure (ENS) de Cachan and the French state, and the University of Warwick.

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CH^+ : A building block for C-bearing molecules in the ISM: Computing its chemical rates to model its evolution under different interstellar environments

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The formation of large C-bearing molecules in the Interstellar Space and in protostar regions is usually linked to a complex network of reactions that involve initially C^+, CH^+, $C2^+$ and other small polyatomic species which effectively come into the building of the larger PAHs components (e.g. see[1]).

A detailed analysis of a crucial ionic reaction which is considered to play a significant role in the carbon chemistry of the interstellar medium (ISM) is carried out by employing a recently discussed reactive potential energy surface [2,3] and by computing ab initio reactive cross sections with a quantum method [5,6], thus obtaining the corresponding CH^+ destruction rates over a range of temperatures that shows good overall agreement with existing experiments [7].

The differences found between all existing calculations and the very low-T experiments are discussed and explored via a simple numerical model that links these cross section reductions to collinear approaches where non-adiabatic crossing is expected to dominate [4]. The new rates are further linked to a complex chemical network that models the evolution of the CH^+ abundance in photodissociation region (PDR) and molecular cloud (MC) environments of the ISM. The abundances of CH^+ are obtained and analysed by numerical solutions of a large set of coupled, first-order kinetics equations which employs our new chemical package developed in our group, K-ROME [7]. The analysis that we carry out reveals that the important thermal region for CH^+ destruction is that above 100 K, hence showing that, at least for this reaction, the differences with the existing low-T laboratory experiments are of essentially no importance within the astrochemical environments where this molecule has been observed. A detailed analysis of the chemical network involving CH^+ also shows that a slight decrease in the initial oxygen abundance leads to higher CH^+

abundances since the main chemical carbon ion destruction channel is reduced in efficiency. This finding provides an alternative chemical route for the reason why general astrochemical models fail when matching the observed CH^+ abundances with the outcomes of calculations.

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The importance of nonadiabatic coupling and host tuning for efficient reverse intersystem crossing in TADF molecules

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The communication between low lying singlet and triplet excited states is of great importance in the field of organic electronics and plays a fundamental role in determining key molecular and material properties such as the lifetime and mobility of charge separated states. Herein we present a quantum dynamics study on the reserve intersystem crossing (rISC) mechanism, which plays a central part in the thermally activated delay fluorescence (TADF) mechanism, Figure 1b, of 3rd generation OLEDs [1].

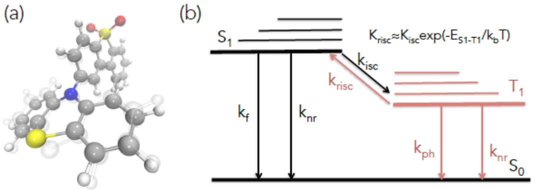

Figure 1 (a) Ground state of PTZ-DBTO2. The transparent overlaid structure is the optimised geometry in the S_1 state. (b) A simplified energy diagram representing a general schematic of the up-conversion of triplet states to a higher energy singlet state.

We show that the rISC mechanism for a high performing complex (Figure 1a) depends upon non Born-Oppenheimer effects. Indeed, they can increase it by over 4 orders of magnitude! Crucially this insight, which explains recent experimental observations, shows the dynamical mechanism of rISC. It also demonstrates the importance of not just tuning the ΔE_{S1-T1} gap but playing close attention to the gaps between multiple excited states. We extend these simulations to show how changing the local environment within an OLED device, 'host tuning' can dramatically improve its performance.

Acknowledgements: TJP acknowledges the EPSRC, Project EP/N028511/1 for funding.

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Imaging the complex influence of the leaving group on nucleophilic substitution reactions

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Predicting the outcome of a reactive encounter is of fundamental importance for processes in synthetic chemistry, catalysis or astrochemistry. Our group has investigated the dynamics of several gas phase bimolecular substitution S_N2 reactions of the type $X^- + CH_3Y$ where X (nucleophile) and Y (leaving group) are halide atoms and has identified a number of distinct dynamical features [1] additional to the backside attack.

Here, we report on the influence of the leaving group on the dynamics of S_N2 reactions [2]. Our experimental approach combines crossed beam scattering with 3D velocity map imaging. This allows us to record differential scattering cross sections which contain the full three dimensional velocity information. Specifically, we have studied the reaction of F^- with CH_3Cl. We expected similar dynamics as for $F^- + CH_3I$ [3] because both systems show very similar energetics in the entrance channel. However, we found a significantly different dynamical behavior in case of chlorine as leaving group. High level chemical dynamics simulations revealed that the differences in interaction of the nucleophile F^- and the respective leaving group leads to this distinct differences in the dynamics [2].

Recently, we extended our investigations of gas phase organic reactions to the competition of based induced elimination E2 with bimolecular nucleophilic substitution S_N2 reactions. These two reaction channels are in constant competition, if the molecule contains at least two carbon atoms in its backbone. To disentangle both channels by experimental methods is challenging because the same ionic product is formed in both S_N2 and E2 reactions. We used ion imaging to identify the dynamical fingerprint of the E2. First results will be shown on the transition from S_N2 to E2 dynamics.

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Full dimensional accurate potential energy surfaces and dynamical studies for the OH/Cl + CH_4 reactions

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An important pre-requisite for studying dynamics of chemical reactions is an accurate representation of the Born-Oppenheimer potential energy surfaces (PESs). Our recent work combining the two approaches led to the so-called permutation invariant polynomials-neural network (PIP-NN) method [1-3], which has been demonstrated to be both accurate and efficient in representing global PESs for molecular systems of up to seven atoms with the permutation symmetry [4-8]. We here report our recent theoretical investigations on the title reactions, which have served as prototypes in understanding dynamics of bimolecular reactions in the gas phase. For the two systems, ∼135,000 / ~70,000 *ab initio* points were calculated at the explicitly correlated coupled cluster singles, doubles, and perturbative triples level with the augmented correlation corrected valence triple-zeta basis set (UCCSD(T)-F12a/AVTZ) and fit using the PIP-NN approach, with a total root-mean square error (RMSE) of only 3.9 / 6.0 meV. Dynamical, and kinetics calculations are performed on these PIP-NN PESs, and the results agree well with experiment. Mode selectivity was found and rationalized by the sudden vector projection (SVP) model [9].

Acknowledgements: This work has the support of National Natural Science Foundation of China (21573027 to JL) and US Department of Energy (DE-FG02-05ER15694 to HG).

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Controlling resonant energy transfer in collisions between NH_3 and He Rydberg atoms using electric fields

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The large electric dipole moments associated with high Rydberg states of atoms and molecules make them very well suited as model gas-phase systems with which to perform experimental studies of resonant energy transfer in inelastic scattering from ground-state polar molecules [1,2]. The sensitivity of the Rydberg states to static electric fields, and to thermal radiation can be exploited to investigate environmental contributions to the energy transfer process, while strong electric dipole interactions within the ensembles of Rydberg atoms or molecules allows opportunities for studies of collective or many-body effects [3,4].

With studies of this kind in mind, we report here the results of new experiments in which electric fields of 0 - 20 V/cm have been employed to control resonant energy transfer in collisions between NH_3 in the X $^1A_1$ ground electronic state, and Rydberg He atoms in triplet states with principal quantum numbers $n = 36 – 41$. For these values of n electric dipole allowed transitions between s- and p-states can be tuned into resonance with the inversion splitting in NH_3 using externally applied electric fields with energy transfer occurring via Förster resonance.

The experiments were performed in pulsed supersonic beams of metastable He, excited by two-colour two-photon laser photoexcitation to the selected Rydberg states. After excitation the Rydberg atoms crossed an effusive beam of NH_3, interacting for times from 5 to 10 μs. Resonant transfer of population between each pair of *n*s and *n*p Rydberg states for each value of *n* was identified by state-selective electric field ionization of the atoms, and exhibits a significant dependence on the strength of the applied electric field. The observations are in good agreement with a simple dipole-dipole coupling model describing the interactions between the atoms and molecules.

Acknowledgements: This work is supported by the Engineering and Physical Sciences Research Council under Grant No. EP/L019620/1, and the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 683341).

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Poster Contributions

P-01

Vibrational energy transfer at surfaces studied by TR-SFG

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Vibrational sum-frequency generation (SFG) employing femtosecond infrared (IR) laser pulses is used to study the energy transfer through three self-assembled monolayers grown on gold by probing the terminal CH_3 stretch vibration. The length of the alkyl chain was varied (C3, C6, and C18) to identify the relation between energy transfer and chain length. In this work, we used a 120 fs pulse at 800 nm to irradiate the front of the samples. The results show a decrease in the SFG signal intensity in both the symmetric and asymmetric terminal CH_3 stretches suggesting that disorder is induced, as the energy is transferred along the chain, Figure 1. Changing the chain length can tell us whether the heat is transferred along the chain ballistically or diffusively. We will also report preliminary results on time-resolved experiment on functionalised graphene to gain insight into energy transfer processes through grapheme sheets.

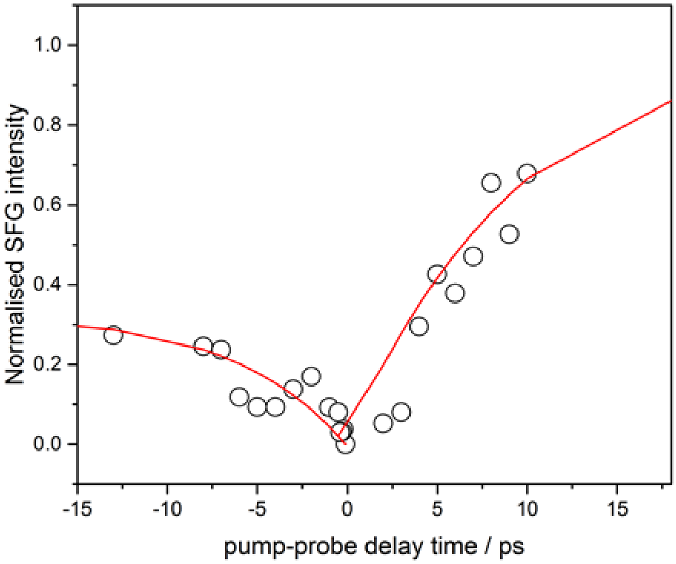

Figure 1: Total SFG integrated intensity as a function of pump-probe delay for asymmetric terminal CH_3 stretch of ODT(C18) on gold.

P-02

Photodissociation cross section of sodium chloride clusters doped with nitrate

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As sodium chloride is the main component of marine aerosols, the present study shows investigations on the photodissociation cross section of sodium chloride clusters doped with nitrate. Nitrate anions are found with high concentration in sea salt aerosols[1] and in Arctic Snowpack. The clusters are produced with electrospray ionization and are then trapped in a Fourier transform ion cyclotron resonance mass spectrometer. Photodissociation spectra are recorded by irradiating the ions with light from an optical parametric oscillator, tunable from 225-2600 nm.

The investigations revealed that the most intense fragmentation pathway at small wavelengths is where an NO_3^- in the cluster is photolyzed into NO_2 and O^-, while the negatively charged oxygen remains in the cluster (Figure 1).

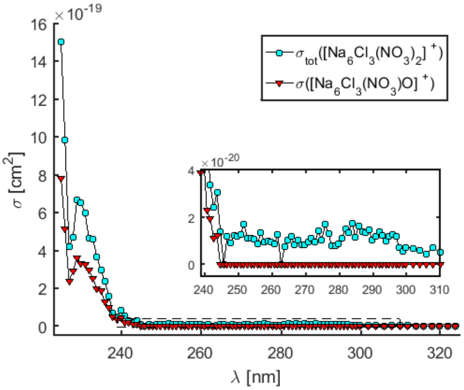

Figure 1: The Photodissociation Cross Section of $[Na_6Cl_3(NO_3)_2]^+$ and the specific contribution of the fragment $[Na_6Cl_3(NO_3)O]^+$ is shown. The subplot reveals the blueshifted absorption of nitrate[2] which is visible due to the fragment $[Na_5Cl_3(NO_3)]^+$.

Acknowledgements: This work has the support of Austrian Science Fund (FWF) within the DK-ALM: W1259-N27.

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P-03

Ultrafast dissociation of substituted pyrroles

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The lowest lying electronic excited singlet state present in the aromatic heterocycles of many biologically relevant systems [1] has attracted significant attention as photoexcitation to these states results in prompt H-atom loss. As the prototypical chromophore in biomolecules such as tryptophan or heme, the photodissociation of pyrrole (*c*-C_4H_5N) from the S_1 state has been extensively studied in the gas phase (see, for example, Ref. 2), where H-atom appearance lifetimes range from 130 to 40 fs as the photon wavelength is decreased [3]. While the effects of ring substitution on the H-atom photo-fragment translational energies have been investigated [4], the ultrafast photodissociation has remained largely unexplored. Recently, our group invest-igated the photodissociation of 2,4-dimethyl pyrrole [5], finding significant changes in the N–H photochemistry due to methylation. Here, we report on our current work to continue exploring the structure-property relationship of the ultrafast photochemistry of pyrrole derivatives.

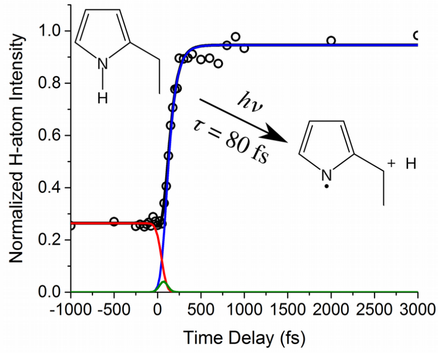

Figure 1: H-atom appearance measurement from the photodissociation of 2-ethyl pyrrole.

Acknowledgements: This work has the support of the Leverhulme Trust, the EPSRC, the Royal Society, the Ecole Normale Supérieure (ENS) de Cachan and the French state, and the University of Warwick.

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P-04

Unraveling energy relaxation mechanisms in simple solvents

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The mechanisms of energy relaxation in solution are often difficult to disentangle due to the complexity of solvent solute interactions. However, by systematic choice of solvents, common relaxation mechanisms can be uncovered for molecules with electronic or vibrational excitation. Perfluorocarbon solvents provide a simplified solvent system, where hard collisions dominate, for study of both vibrational and rotational relaxation. Such simple systems eliminate directional interactions and common vibrational relaxation processes such as Förster resonance transfer while providing information about solvation environments [1, 2]. Ultrafast transient absorption spectroscopy measurements with quantum state resolution reveal the mechanisms of energy relaxation. By comparing perfluorocarbon solvents with common organic solvents such as chloroform and carbon tetrachloride we can deduce the importance of dipolar versus collisional interactions when quenching from either high or low levels of vibrational excitation [2].

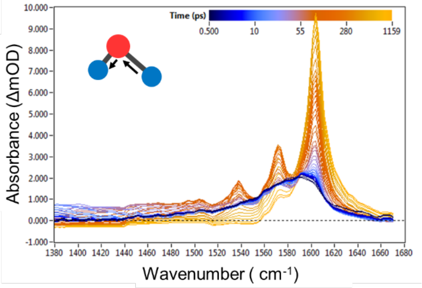

Figure 1: Transient vibrational absorption spectra of NO_2 in the anti-symmetric stretch region. The NO_2 is formed vibrationally hot through UV

photolysis of N_2O_4 in carbon tetrachloride solution and equilibrates through solute-solvent interactions.

Acknowledgements: This work has been funded by ERC grant 290966 CAPRI and Marie-Curie International Incoming Fellowship PIIF-GA-2012-326988 (for MPG).

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P-05

IR spectroscopy of hydrated $CO_2^{\bullet -}$ and its reaction products

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Gas phase studies have provided significant contributions to the understanding of activated CO_2 [1]. The metastable $CO_2^{\bullet -}$ is stabilized by a solvation shell and $CO_2^{\bullet -}(H_2O)_n$ can be studied readily by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. An EKSPLA NT 277 optical parametric oscillator system is coupled into the reaction cell, covering the 2235-4000 cm^{-1} region at 1000 Hz pulse repetition rate.

The products of the reaction between $CO_2^{\bullet -}(H_2O)_n$ and small organic molecules, as well as $CO_2^{\bullet -}(H_2O)_n$ itself (Fig. 1), are investigated via IR photodissociation spectroscopy. This provides information about the formation of covalent bonds and the structure of the reaction products. Special attention is given to the potential formation of ring structures.

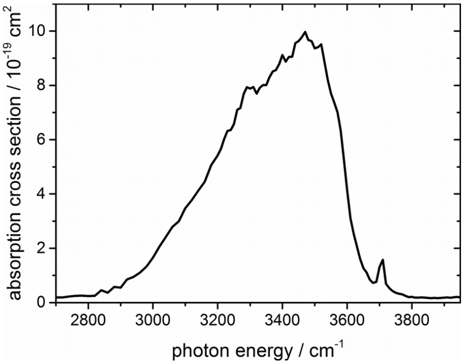

Figure 1: IR spectrum of $CO_2^{\bullet -}(H_2O)_n$, $n = 38 - 42$ at the start of irradiation, in the region 2700 – 4000 cm^{-1}. The band at ~3710 cm^{-1} corresponds to outer-shell water molecules with free OH-groups [2]. The spectrum is corrected for the contribution of black-body infrared radiative dissociation.

Acknowledgements: This work has the support of the FWF, Wien, Austria.

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P-06

Rotational relaxation of molecular cations in buffer gas: computing rates and decay times for $pH2^+$, $oD2^+$ and HD^+

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Precision vibrational spectroscopy of the molecular hydrogen ions is of significant interest for determining fundamental constants and for testing quantum electro-dynamics calculations[1] . The experiments demand a suitable preparation of these systems in specific quantum states. In the present work we discuss the dynamical processes guiding the relaxation of the internal rotational energy of three isotopes variants of a diatomic cation, the $H2^+$, in collision with He atoms in cold ion traps. The state changing cross sections and rates are computed using a 3D PES obtained from accurate ab initio calculations[2]. The decay times into their respective ground states are obtained from solving the the relevant state equation. For the homonuclear ions (p-$H2^+$, o-$D2^+$), direct laser cooling of the rotational degree of freedom is not feasible. We show that rotational cooling by cold He buffer gas is an effective approach. In the case of HD^+, we also explore the latter approach taking into account the contribution of the spontaneous downward rates among rotational levels in the ground vibrational level. A detailed comparison of the results from the tree isotopic molecules allow us to obtain a deeper insight into the relative efficiencies of the relaxation processes in cold ion traps.

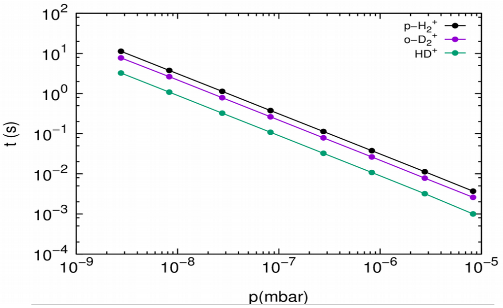

Figure 1: Cooling time as a function of helium pressure at 20K.

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P-07

Detection of the excited state NH_2 ($\tilde{A}\ {}^2A_1$) in the ultraviolet photodissociation of methylamine

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Methylamine (CH_3NH_2) has analogous electronic structure and photochemical property with NH_3 as the simplest ammonia-derivative. The non-adiabatic dynamics around the conical intersection of NH_3 has been intensively investigated as a typical mechanistic model that controls the branching to the electronic ground and excited products: $NH_3 + h\nu \rightarrow NH_2(\tilde{X}\,{}^2B_1) + H\ /\ NH_2(\tilde{A}\,{}^2A_1) + H$. [1] Substitution of a H atom of NH_3 to a CH_3 group allows the system to have the competing product pathways: the N-H and N-C bonds fission channels. [2] These two σ-bonds are known to dissociate in the UV photoabsorption, however the details of the reaction mechanisms have not been understood. Especially, generation of the electronically excited species state is not established in both experimental and theoretical studies.

Ion-imaging and dispersed fluorescence spectroscopy are employed for the photodissociation dynamics study of methylamine in the photolysis wavelength range of 205 – 213 nm. The methyl radical product is found to populate a wide range of ro-vibrational states, among which the CH_3 fragment generated in the $v = 0$ state shows the bimodal kinetic energy distribution. The internal energy analysis of the NH_2 counter-product indicates that the lower kinetic energy component that was observed only with the $CH_3(v = 0)$ fragment energetically matches the electronically excited $\tilde{A}\,{}^2A_1$ state.

The dispersed fluorescence spectrum, whose band structure is assigned to the $\tilde{A}\,{}^2A_1 \rightarrow \tilde{X}\,{}^2B_1$ transition, provides evidence of the $CH_3(v = 0) + NH_2(\tilde{A}\,{}^2A_1)$ pathway. The branching mechanism of the product pathway is discussed in terms of nuclear dynamics in the long-range region, (Ref.3) where the conical intersection between the excited and ground state potential energy surfaces can play a significant role.

Acknowledgements: This work is supported by JSPS KAKENHI Grant No. 15KT0065 and Toray Research Fund for Science and Technology.

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P-08

Charge transfer reactions with Ar^+ and various neutrals

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The crossed-beam technique has become the method of choice for the analysis of reaction dynamics [1] as it allows to precisely assess the complete kinematics of both reactants and products. In the last decade, it could be extended from neutral partners to ion neutral reactions [2]. The combination with three-dimensional velocity map imaging has allowed us to obtain energy- and angle-differential cross sections for the $Ar^+ + N_2$ charge transfer reaction [3], opposing previous experimental results and in agreement with theoretical predictions [4]. Recently, a radio-frequency ion trap has been added to our setup that allows to achieve an improved energy resolution of the ion beam.

Here, we present the results of experiments that extend our previous work on the charge transfer reaction with Ar^+ to the neutral partners H_2, D_2, CO, NO and O_2. While state specific reaction cross sections have already been investigated for the individual spin-orbit states of Ar^+ [5, 6], our measurements reveal the specific excitation of vibrational levels of the product ions. The prediction of an energy resonance in the charge transfer reaction with H_2 but not with D_2 [5] is already supported by first results with hydrogen that show a dominant vibronic coupling between the $Ar^+(^2P_{1/2}) + H_2(\upsilon = 0)$ entrance and $Ar + H_2^+(\upsilon = 2)$ exit channel. Such a near resonance of the energy levels of initial and final states is not present in the other systems. Yet, the qualitatively different ratios between the $P_{1/2}$ and $P_{3/2}$ cross sections for N_2 (<1), CO (>1) [6] and O_2 (near 1) [7] suggest interesting differences in the dynamical features of the proposed reactions.

Acknowledgements: This work has the support of FWF and ÖAW.

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P-09

Photochemistry of $Mg^+(H_2O)_n$ clusters

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Microhydrated metal ions allow us to understand fundamental aspects of solvation under well-defined conditions and to trace evolution of various properties (dissociation energy, reactivity, IR/UV spectra…) from the gas phase to bulk. While properties of microhydrated metals in the ground state have been studied extensively for several decades, there is only limited knowledge available with respect to their photochemistry: Which reactions take place in the excited state? What is their mechanism? How does increasing hydration influence photochemical properties of metal ions?

In the present contribution, we investigate the photochemistry of $Mg^+(H_2O)_n$ clusters. We combine various methods of theoretical chemistry (single/multirefence *ab initio* calculations, absorption spectra modelling, molecular photodynamics) and mass spectrometry experiments to provide a comprehensive overview of the main photochemical features and their evolution with the increasing number of water molecules.

Already for small $Mg^+(H_2O)_n$ clusters ($n = 1$-5), complicated photoreactivity was observed.[2] Excitation into first three excited states ($3s$-$3p_{x,y,z}$) forms a bound state and our calculations predict that for a low amount of internal energy, all reactions take place in the ground electronic state, most probably after radiative transfer. For larger clusters, a solvated electron is formed, leading to hydrogen atom dissociation already in the ground electronic state for $n = 6$-14, $MgOH^+(H_2O)_{n-1}$, and forming a stable ion pair for $n \geq 15$, $Mg^{2+}(H_2O)_n^-$.[3] These changes are then reflected in the electronic spectrum and in the photochemical behavior.

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P-10

Scattering formaldehyde from the Au(111) surface

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A number of recent studies have demonstrated the importance of orientation and mode-specific vibrational excitation on reactions of polyatomic molecules at surfaces [1]. The conversion of translational to rotational motion often plays a major role in the trapping of small molecules at surfaces, a crucial first step for a wide variety chemical processes that occur at gas-surface interfaces. However, to date most quantum-state resolved surface scattering experiments have been performed on diatomic molecules, and very little detailed information is available about how the structure of non-linear polyatomic molecules influences the mechanisms for energy exchange with surfaces. In the current work, we employ a new rotationally-resolved 1+1′ resonance-enhanced multiphoton ionization (REMPI) scheme to measure rotational distribution in formaldehyde molecules directly scattered from the Au(111) surface at incident kinetic energies in the range 0.3−1.2 eV. The results indicate a pronounced propensity to excite *a*-axis rotation (twirling) rather than *b*- or *c*-axis rotation (tumbling or cartwheeling), and are consistent with a rotational rainbow scattering model. Classical trajectory calculations suggest that the effect arises—to zeroth order—from the three-dimensional shape of the molecule (steric effects).

Acknowledgements: This work has the support of the Alexander von Humboldt Foundation

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P-11

Dissociation of formaldehyde on single layer graphene

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Dissociation of H_2CO on single graphene sheet was studied using classical trajectory simulations. Effect of vibrational energy of H_2CO, orientation of H_2CO, collision energy and sheet temperature on the dynamics of H_2CO dissociation were investigated. Orientations with O atom facing the graphene sheet gave high reaction probabilities and orientation with H atom facing the graphene sheet resulted in more H + HCO products. The reaction probability was found to increase with increasing collision energy. Rotationally cold CO and vibrationally excited H_2 products were observed due to roaming atom pathway as seen in the gas phase reaction. Total reaction probabilities along with reaction probabilities for both the channels was found to increase with increase in H_2CO vibrational energy.

P-12

Towards evidence for the role of permanent dipoles in the formation of molecular anions in the interstellar medium

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The interstellar medium (ISM) is known to consist of atomic and molecular species in both neutral and ionic form [1]. However it was only in 2006 that the first molecular anion C_6H^- was discovered. Since then a further five species have been detected (C_4H^- , C_8H^- , CN^- , C_3N^- , and C_5N^-). Despite dispelling the belief that negative ions were unable to exist in space, there remain open questions regarding the mechanisms behind their formation [2].

A potential pathway for anion formation involves neutral species with a permanent dipole moment greater than the critical value of 1.625 D. These are capable of supporting two types of intermediate metastable resonances between the valence bound state and the continuum [3]. The dipole bound state (DBS) is a highly excited anionic state. The dipole scattering state (DSS) describes the neutral/electron system in the near-threshold continuum. Theoretical studies [4] of the role played by such large dipole moments in the creation of stable anionic valence bound states (VBS) through the pathway of radiative electron attachment (REA)

$$C_nN + e^- \rightarrow C_nN^- + h\nu,$$

have identified the molecule C3N, with associated dipole moment in the region 3.6 D, as being capable of hosting both metastable resonances and hinted at their involvement in the electron capture process.

Absolute photodetachment cross-sections for the species C_nH^- , n = 2, 4, 6 [5] and C_nN^- , n = 1, 3 [6] have previously been measured in our group. We propose to further this work by undertaking near- threshold photodetachment measurements of C_3N^- in order to both identify the prevalence of dipole bound states and to pursue the signature of dipole scattering states. In this way, this work aims to shed light on a potential mechanism for the formation of astrochemical anions.

Acknowledgements: This work has the support of the FWF (Austria Science Fund).

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P-13

Reactions of CO_3^- with formic acid and HCl

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The $CO_3^{\bullet-}$ radical anion is an important intermediate in tropospheric anion chemistry. However, only a small number of reactions have been reported in the literature. $CO_3^{\bullet-}$ is produced in the atmosphere from the reaction of ozonide with CO_2 via O^- transfer. Gas phase reactions of $CO_3^{\bullet-}$ with formic acid and HCl are studied via FT-ICR mass spectrometry and will be presented here.

The reaction of $CO_3^{\bullet-}$ with formic acid leads to signal loss, indicating the formation of neutral reaction products. The released electrons can efficiently be scavenged by SF_6 - or in the atmosphere be used for production of new $CO_3^{\bullet-}$, closing a catalytic cycle (Figure 1). Quantum chemical calculations of the potential energy surface of the reaction reveal that oxidation to CO_2 and water is the thermochemically favored reaction path.

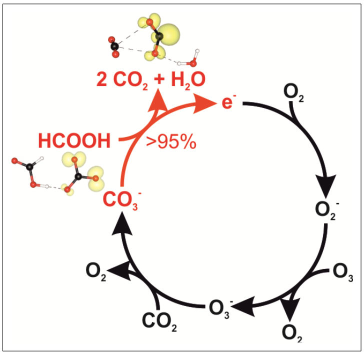

Figure 1: Cycle for $CO_3^{\bullet-}$ generation and reaction with formic acid. [1]

In contrast to formic acid, reactions with HCl show no signal loss. In a first slow reaction step $[OH,Cl]^-$ is formed that quickly reacts with another HCl molecule to form HCl_2^- or Cl_2^-. Solvation of $CO_3^{\bullet -}$ with one water molecule, the most abundant form in the lower troposphere, significantly increases the reaction rate.

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	Sunday	*Monday*	*Tuesday*	*Wednesday*	*Thursday*	*Friday*
08:00		*Breakfast*	*Breakfast*	*Breakfast*	*Breakfast*	*Breakfast*
09:00		Musa Ahmed	Ludo Juurlink	Toshinori Suzuki	Kopin Liu	Departure
09:40		Andrew Orr-Ewing	Oliver Bünermann	Jochen Mikosch	Xingan Wang	
10:20		*Coffee*	*Coffee*	*Coffee*	*Coffee*	
10:40		Jörg Behler	Yvonne Dorenkamp	Yann Mairesse	Upakarasamy Lourderaj	
11:20		Sebastian Trippel	Alexander Kaiser	Neil Cole-Filipiak	Jun Li	
11:40		Eduardo Carrascosa	Weiwei Zhou	Francesco Gianturco	Astrid Bergeat	
		Break	*Break*	*Break*	*Break*	
16:00	Registration	*Coffee & Snacks*	*Coffee & Snacks*	*Coffee & Snacks*	*Coffee & Snacks*	
16:30		Joachim Paier	Theo Kitsopoulos	Julia Weinstein	Arthur Suits	
17:10		Sergey Levchenko	Martin Beyer	Chia-Chen Wang	Andreas Osterwalder	
17:50		Barratt Park	Sven Köhler	Thomas Penfold	Stephen Hogan	
18:10		Kai Kang	Qiang Huang	Jennifer Meyer		
19:00	*Dinner*	*Dinner*	*Dinner*	*Dinner*	*Conference Dinner*	
20:30	Scott Kable	Poster session	Tour of the city	Poster session		
21:10	Sang Kyu Kim					

Invited Talks are 35min + 5min for discussion
Hot Topic Talks are 15min + 5min for discussion