Tim Michaelsen, Martin Beyer, Paul Scheier, Roland Wester (Eds.)

XXIIIrd Symposium on Atomic, Cluster and Surface Physics 2022 (SASP 2022)

February 13 – 17, 2022

Obergurgl, Austria

Contributions

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Preface

The international Symposium on Atomic, cluster and Surface Physics, SASP, is a continuing biennial series of conferences, founded in 1978 by members of the Institute of Atomphysik, now Institute of Ionphysics and Applied Physics of the University of Innsbruck, Austria. SASP symposia aim to promote the growth of scientific knowledge and effective exchange of information among scientists in the field of atomic, molecular, cluster and surface physics, stressing both fundamental concepts and applications across these areas of interdisciplinary science.

Since the beginning, the SASP format has been similar to that of a Gordon Conference, with invited lectures, hot topic oral presentations, posters and ample time for discussions. SASP 2020 was one of the last conferences that took place in presence before the corona virus pandemic hit Europe. With SASP 2022 we hope to rekindle scientific exchange in person, which many of us have dearly missed during the last two years.

SASP traditionally takes place in Austria every second time, and is held in another alpine country in between. So far, the SASP conferences took place in the following locations:

1978 Zirog, Italy
1980 Maria Alm, Austria
1982 Maria Alm, Austria
1984 Maria Alm, Austria
1986 Obertraun, Austria
1988 La Plagne, France
1990 Obertraun, Austria
1992 Pampeago, Italy
1994 Maria Alm, Austria
1996 Engelberg, Switzerland
1998 Going, Austria
2000 Folgaria, Italy
2002 Going, Austria
2004 La Thuile, Italy
2006 Obergurgl, Austria
2008 Les Diablerets, Switzerland
2010 Obergurgl, Austria
2012 Alpe d´Huez, France
2014 Obergurgl, Austria
2016 Davos, Switzerland
2018 Obergurgl, Austria
2020 St. Moritz, Switzerland

SASP Erwin Schrödinger Gold Medal 2022

The „SASP Award for Outstanding Scientific Achievements“ was initiated in 1992 by the SASP International Scientific Committee. This award is granted during the biennial SASP meeting to one or two scientists, chosen among those who have strong connections to the activities of SASP.

The recipient of the SASP Award 2022 – in the form of the „Erwin Schrödinger Gold Medal” designed by Zdenek Herman – is

Gereon Niedner-Schatteburgl from the Technical University Kaiserslautern, Germany. He has received this award in recognition of his contributions to the spectroscopy and reactivity of ionic clusters and complexes in molecular beams and cold electromagnetic traps and his long-term commitment to SASP as attendee, poster presenter and speaker.

At previous SASP meetings the Schrödinger Gold Medal was awarded to:

1992	David Smith, Birmingham, UK
1994	Zdenek Herman, Praha, Czech Republic
1996	Werner Lindinger and Tilmann Märk, Innsbruck, Austria
1998	Eldon Ferguson, Boulder, USA and Chava Lifshitz, Jerusalem, Israel
2000	Jean H. Futrell, Richland, USA
2002	Eugen Illenberger, Berlin, Germany
2004	Anna Giardini-Guidoni, Roma, Italy
2006	Davide Bassi, Trento, Italy and Martin Quack, Zürich, Switzerland
2008	Helmut Schwarz, Berlin, Germany
2010	Kurt Becker, New York, USA
2012	Dieter Gerlich, Chemnitz, Germany and John Maier, Basel, Switzerland
2014	Stephen D. Price, London, United Kingdom
2016	Roberto Marquardt, Strasbourg, France and Paul Scheier, Innsbruck, Austria
2018	Tom Rizzo, Lausanne, Switzerland
2020	Frédérik Merkt, Zürich, Switzerland

Program

	Sunday	Monday	Tuesday	Wednesday	Thursday
		Breakfast	Breakfast	Breakfast	Breakfast
08:30:00		Marquardt	Küpper	Ernst	Cederbaum
			Wild		
09:15:00		Narevicius		Koch	Ascenzi
			Coffee		
10:00:00		Coffee	Neumark	Coffee	Coffee
10:30:00		Zimmermann		Reilly	Jelinek
			Meyer		
		Lushchikova		Borodin	Hertl
11:15:00					
					Conclusion
12:00:00		Break	Break	Break	Departure
16:00:00	Arrival	Coffee	Coffee	Coffee	
16:30:00	Coffee	Ončák	Kokoouline	Schlemmer	
	Welcome		Cizek		
17:15:00	Willitsch	Worth		SASP Award: Niedner-Schatteburg	
			Martins		
18:00:00	Salzburger	Comte	Sixt		
19:00:00	Dinner	Dinner	Dinner	Conf. Dinner	
20:30:00		Posters	Posters		

Invited Papers

Hot Topic Papers

Contributed Papers

Invited Papers

State and conformationally selected reactions in the gas phase

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Recent advances in experimental methods for the manipulation, cooling and trapping of molecules and ions have opened up new avenues for studies of chemical dynamics in the gas phase [1]. Using the electrostatic deflection of molecular beams, molecules can be spatially separated based on their effective dipole moments thus enabling the isolation of individual rotational states and molecular conformations [2]. Employing this methodology, we have recently developed new experimental approaches for studies of rotational and conformational effects in both ionic and neutral chemical reactions.

First, we have combined electrostatically deflected beams with Coulomb-crystallised ions in traps for the investigation of conformationally specific reactivities [3] as well as combined rotational and hyperfine effects [4] in ion-molecule reactions. Very recently, we have applied this method to the characterisation of polar cycloadditions, i.e., ionic Diels-Alder (DA) reactions, which constitute one of the key routes for the formation of cyclic compounds in synthetic chemistry. In these reactions, a conjugated diene and an alkene, the dienophile, react to form a cyclohexene compound. The ‘canonical’ mechanism of the DA cycloaddition assumes a concerted reaction proceeding via a single transition state in which bond formation and bond breaking occur synchronously [5]. This picture often breaks down in highly asymmetric or charged systems in which the reaction becomes asynchronous to the extent that a stepwise mechanism is preferred [6]. In this context, we have established a new approach for investigating the mechanistic details of these reactions by probing the conformational specificities of the reaction in the entrance channel. The concerted mechanism imposes that the reaction proceeds exclusively from the s-*cis* (or possibly *gauche*) conformer of the diene and not from the s-*trans* conformer, while a stepwise process would also enable the s-*trans* species to participate in the formation of the cycloadduct. For the model polar cycloaddition of *gauche*/s-*trans*-2,3-dibromo-1,3-butadiene with trapped propene ions, we indeed found that both conformers are reactive [7]. This result is rationalised by a simultaneous competition of concerted and stepwise reaction pathways, revealing an interesting mechanistic borderline case.

Second, we have recently developed a new crossed-molecular-beam experiment for investigating reactions of rotational-state- and conformationally selected strong-field-seeking molecules (Fig. 1). The apparatus combines an electrostatically deflected beam which was crossed in a first series of experiments with a beam of metastable rare-gas atoms. In chemi-ionisation reactions of rotationally state selected OCS molecules with Ne (^{3}P) atoms, we found a pronounced dependence of the branching ratio of dissociative vs. Penning ionisation on the rotational state of OCS [7]. In the chemi-ionisation of conformationally selected hydroquinone, similarly marked dependencies of the product branching ratios on the specific conformation of the molecule were observed. In the presentation, we will discuss these results and outline future prospects of this experiment.

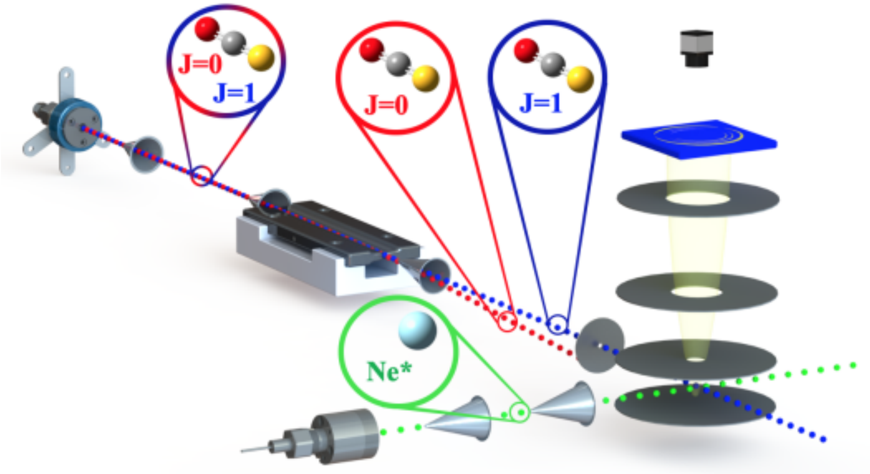

Figure 1: Schematic of a new crossed-molecular-beam setup featuring an electrostatically deflected molecular beam for studying reactions of state- and conformationally selected strong-field-seeking molecules [8].

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Quantum mechanical Mean Square Displacement

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1. Introduction

Colliding, but otherwise freely moving classical particles will undergo a zig-zag motion in the xy-plane (elastic collisions are supposed, see Figure 1, one dimensional motion will be considered here as a mild simplification).

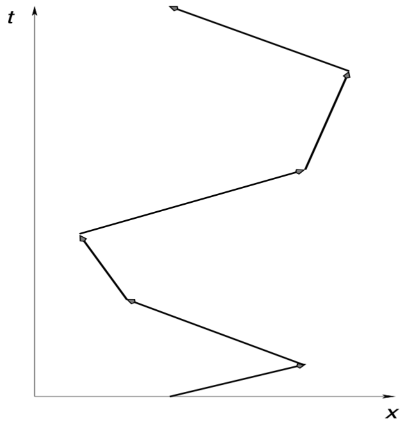

Figure 1: Typical zig-zag trajectory of a particle moving in a 1D space, schematic.

For times much shorter than typical collision times t_c, particles travel, under frictionless conditions, at constant velocity v: $x(t) = x(0) + vt$. The mean square displacement (MSD) $\delta_x^2(t) = \langle (x(t) - x(0))^2 \rangle$ of particles can be evaluated from the statistical distribution of initial states $x(0)$ and $v(0) = v$. If thermal conditions are considered

$$\delta_x^2(t) \;=\; \langle v^2 t^2 \rangle = \langle v^2 \rangle \; t^2 = \frac{k_\mathrm{B} T}{m} \, t^2 \tag{1}$$

at least for times $0 \le t \le t_\mathrm{c}$. T is the temperature, k_B is the Boltzmann constant and m is the particle's mass. The expression in Eq. (1) is a characteristic feature of *ballistic* motion.

For particles moving under the action of frictional forces the MSD is given by the Einstein equation [1]:

$$\delta_x^2(t) = 2\,n_\mathrm{f}\,D\,t \tag{2}$$

$$D = \frac{k_\mathrm{B}\,T}{m\,\gamma} \tag{3}$$

Here, D is the diffusion coefficient; γ is the friction coefficient and $n_\mathrm{f} = 1$ for a 1D system, and 3 for a 3D system.

The expression in Eq. (2) is a characteristic feature of *Brownian* diffusion.

What are the corresponding quantum mechanical results?

2. Quantum mechanical definitions of the MSD

The MSD of a thermalized quantum particle has been evaluated in previous work [2–5] as the time dependent quantity

$$\delta_x^2(t) = \mathrm{Tr}(\hat{\rho}^{(T)}\,(\hat{x}(t) - \hat{x}(0))^2) \tag{4}$$

In this definition, $\hat{x}(t) = \hat{U}^\dagger(t)\hat{x}(0)\hat{U}(t)$ is the particle's time dependent position operator in the Heisenberg representation and $\hat{\rho}^{(T)}$ is its thermal equilibrium density operator.

In the present work we shall critically assess this definition and show that it leads to a contradictory result [6], if the Liouville-von-Neumann equation for the time dependent operators or the Heisenberg equations of motion are considered.

Furthermore, we shall propose a different, general quantum mechanical definition of the MSD based on the concept of an initial *thermal wave packet* [7]

$$|\psi^{(T)}(0)\rangle \equiv \sum_n \frac{\mathrm{e}^{-\beta\,E_n/2 + \mathrm{i}\,\theta_n}}{\sqrt{Q}}\,|\phi_n\rangle \tag{5}$$

where the quantities $0 \le \theta_n \le 2\pi$ are random angles, E_n and $|\phi_n\rangle$ $(n = 1, 2, \ldots)$ are eigenvalues and eigenstates of the system's Hamiltonian $\hat{H}$, which without lack of generality are supposedly countable, and Q is the canonical partition function; $\beta = 1/(k_\mathrm{B}\,T)$.

3. Key result

An interesting result from the definition proposed in ref. 6 is the MSD of a free particle of mass m moving without collisions ($t_c \to \infty$):

$$\delta_x^2(t) = \frac{\hbar}{m}\left(\sqrt{t^2 + {t_\mathrm{T}}^2} - t_\mathrm{T}\right) \tag{6}$$

Such particles are dubbed *ideal* in ref. 6, and the evolution is depicted in Figure 2.

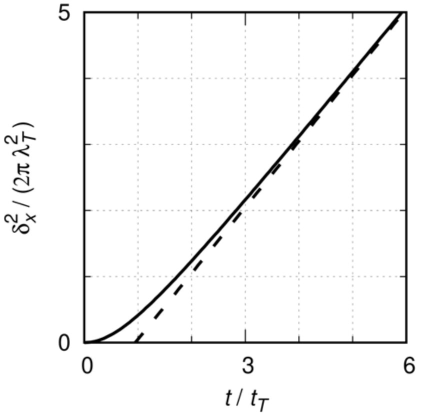

Figure 2: Quantum dynamical time evolution of the mean square displacement $\delta_x^2(t)$ for an ideal particle of mass m at temperature T according to Eq. (6) in the natural units $\lambda_\mathrm{T} = \hbar/\sqrt{2\pi\, m\, k_\mathrm{B} T}$ and $t_\mathrm{T} = \hbar/k_\mathrm{B}T$; for $t \lesssim t_\mathrm{T}$, the motion is ballistic with $\delta_x^2(t) = k_\mathrm{B}T/(2\,m)\ t^2$; for $t_\mathrm{T} \ll t$, the motion resembles Brownian diffusion $\delta_x^2(t) = 2D_\mathrm{q}\,t$; the quantity $D_\mathrm{q} = \hbar/(2m)$ is half the slope of the interrupted line.

This result is intriguing for two reasons. First, it states that the MSD of a single, freely moving quantum particle bears, at asymptotic times, an essential feature of Brownian diffusion, despite the absence of friction. Secondly, the classically expected ballistic behaviour is observed qualitatively only in the initial phase of the time evolution of the MSD; quantitatively, the initial MSD is only half the classical value, however.

4. Conclusions

The quantum mechanical formulation of the mean square displacement has not been thoroughly investigated so far. Previous definitions are problematic, as they lead to contradictions. A new definition [6] shows an interesting, yet intriguing result, which does not seem to have a classical counterpart.

Acknowledgment

This work receives financial support from the Agence Nationale de la Recherche (ANR) under the project acronym QDDA. Generous support from the Centre National de la Recherche Scientifique (CNRS) and the University of Strasbourg is also acknowledged. The author thanks Peter Saalfrank, Salvador Miret-Artés, Jörn Manz, Fabien Gatti, Jean-Christophe Tremblay, Lorenz Cederbaum and Emmanuel Fromager for many fruitful discussions.

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Is an efficient intermolecular energy transfer from vibrations to electronic motion possible?

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In this work we investigate the possibility of intermolecular vibrational energy transfer to electronic motion. Energy transfer of all kinds is of central importance for chemical reactivity and has been widely studied both experimentally and theoretically over many years including the transfer between the two kinds of energies, vibrational and electronic. The studies of the latter are, however, carried out in the framework of collisions where the collision complex formed and/or nonadiabatic coupling give rise to the transfer. Here, we concentrate on intermolecular vibrational energy transfer to electronic motion in weakly bound molecules, i.e., at internuclear distances at which they do not have a chemical bond and nonadiabatic coupling is negligible. We shall see that the transfer can be highly efficient.

If time is left, intermolecular vibrational energy transfer between weakly bound molecules is also addressed. Here, most of the studies were done for describing resonant vibrational energy transfer in the condensed phase. Very recently, it has been noticed that if the lifetime of the vibrationally excited molecule is much longer than that of its neighbor, efficient non-resonant vibrational energy transfer can take place.

Mechanisms of Photochemical Hydrogen Evolution on Hydrated Metal Ions

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Microhydrated metal ions are very suitable systems for precise (photo)chemical investigations. Using small, well-defined ions, we might understand their structure, hydration-dependent reactivity or spectral properties to an unanticipated level of detail. Comparing different hydrated metals, trends in the periodic table might be elucidated.

In the present contribution, we compare mechanisms of photochemical hydrogen evolution in Mg^+, V^+, Al^+ and Zn^+.[1–3] On the experimental side, we used Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry to select the ions that were subsequently irradiated in a broad spectral range from IR to UV. A wide range of quantum chemical methods, including Equation of Motion Coupled Cluster (EOM-CC) technique and multi-reference calculations, was employed to rationalize the observations and propose photochemical mechanisms.

For the investigated metals, we observe complicated photochemical behavior that includes switches of electronic states near conical intersections, intersystem crossings and electron transfer. For the vanadium cation hydrated with one water molecule, the multitude of electronic states (194 states within 3 eV when including spin-orbit coupling) underlines the challenging nature of transition metals as photochemical agents. Finally, we show that the mechanism of photochemical hydrogen evolution is fundamentally different compared to the situation in the electronic ground state – the photon is not only a source of energy, it re-defines the ion chemistry.

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Simulating the Molecular response to Photoionisation

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Introduction

One of the most direct responses of a molecule to light is ionisation. This can be used as a probe of the electronic structure of the molecule, as well as a probe for following its time-evolution after photo-excitation as the ionisation energy is dependent on the molecular geometry. In this contribution, we will look at three different ways in which simulations of photoionisation can be used to understand molecular properties.

1. Continuous Source Photo-electron Spectrum of Cyclobutadiene

Cyclobutadiene (C_4H_4) is the classic anti-aromatic molecule, with a π-system containing 4-electrons. As a result it is not stable, and not as highly symmetrical as aromatic molecules such as benzene. In a recent experiment by the Fisher group (Würzburg), cyclobutadiene was created in-situ using photolysis and the photoelectron spectrum was recorded. A simulation of the spectrum was then used to prove that the spectrum was indeed from cyclobutadiene and to investigate the natural dynamics of the molecule [1].

The simulation used wavepacket dynamics with a model Hamiltonian [2] to treat all the vibrational modes and the manifold of electronic states, both of the neutral and the cation, involved in the ionisation. The vibrations activated by the ionisation were found to be strongly coupled due to (Jahn-Teller) vibronic coupling and it could be shown that the molecule can easily transform between rectangular structures.

2. Nano-second Pulse 1+1Resonant Photo-emission Spectrum of Phenol

Rather than direct ionisation, electron photo-emission can be obtained indirectly by first exciting a bound state, before a second photon is absorbed that leads to ionisation. Such 1+1 spectroscopy experiments can be used to give information about the excited neutral electronic state, often as a pre-cursor to a time-resolved experiment. A still unanswered question is what happens during the two-step ionisation? If the excitation uses a single nano-second laser pulse, does the excited molecule initially relax before ionisation takes place, or does the ionisation take place as a single resonant process?

Wavepacket dynamics simulations are being performed to answer this question, comparing to 1+1 photo-emission spectra of phenol recorded by the Fielding group (UCL) [3,4]. These again use a vibronic model Hamiltonian, but this time include the excitation pulse explicitly, and accounting for the kinetic energy of the outgoing electron. Simulations seem to indicate that the dominant process is the resonant ionisation.

3. Attosecond Pulse Electronic Wavepacket Creation in Propriolic Acid

The computational machinery used to simulate the photoemission described above can be used to simulate a range of experiments which involve laser pulses. A recent study looks at the formation of electronic wavepackets and the subsequent electron and nuclear dynamics. An electronic wavepacket can be formed by photo-ionisation as a superposition of ion states that provide a localised electron (hole). In some situations, for example propriolic acid, coupling between states due to electron correlation can then lead to charge migration, the spontaneous motion of the hole across the molecular framework [5].

Questions of interest to these systems are how the nuclei couple to the electron wavepacket, and how their motion interacts with the electron motion. An additional question is how the initial pulse can control the composition of the electron wavepacket and thus the subsequent dynamics. In a set of simulations using a single ultrashort laser pulse, as well as pairs of pulses, it has been shown that it is possible to use interference effects to change the wavepacket composition and extend the coherence lifetime of the system.

Summary

Quantum Dynamics simulations can model, and thus help understand, molecular behaviour after ionisation. In particular, explicit inclusion of the ionising pulse provides a useful tool to support a range of different experiments.

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High resolution photoelectron spectroscopy of vibrationally excited anions

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Photoelectron spectroscopy (PES) of negative ions is a powerful tool for investigating the electronic and vibrational structure of free radicals, clusters, transition states, and other chemical species of interest. In our laboratory, we have developed slow electron velocity map imaging of cryogenically cooled anions (cryo-SEVI) as a high resolution variant of PES, yield electron kinetic energy resolution as high as 1-2 cm^{-1} for complex molecular species. Recently, we have incorporated infrared pre-excitation of negative ions into this experiment, which enables measurement of the photoelectron spectrum of vibrationally excited anions. As a result, one can access neutral vibrational levels and, more generally, regions of the neutral potential energy surface that are inaccessible from the anion ground vibrational state. Moreover, this method can be used as an IR-action spectroscopy technique to locate vibrational frequencies of negative ions without "tagging". Results will be presented for the hydroxide anion OH^- and the vinoxide anion $C_2H_3O^-$.

Reactive scattering of ion molecule reactions for disentangling chemical reactivity

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Reaction dynamics open a window into the fundamental process of a elementary reactions, namely the reactive collision. Understanding chemistry at this level will help us to derive detailed structure reactivity relations with the final aim at controlling chemical reactivity in a bottom up approach. Alternative reaction channels are common in chemical synthesis leading to unwanted side products and lower yield of the desired the product. One of the most studied competition in physical organic chemistry is the one between bimolecular nucleophlic substitution S_N2 and elimination E2 due to the importance of both mechanisms in chemical synthesis. We used crossed beams in combination with 3D velocity map imaging to investigate the competition in a set of gas phase experiments [1-3]. The challenge of disentangling these reaction pathways lies in the fact, that the same ionic product is formed which requires methods beyond standard mass spectrometry.

We investigated the competition for an archetypal test reaction in physical organic chemistry: $F^- + CH_3CH_2Cl$ by measuring energy and angle differential cross sections at the Innsbruck crossed beam experiment [4]. Together with quasi classical trajectory simulations from the group of Group Czako, we were able to disentangle the atomistic dynamics of the S_N2 and E2 reaction pathways as a function of collision energy [3]. We found an excellent agreement between experiment and theory, which allowed us to assign atomistic mechanisms to individual scattering signatures and found the reactions to become dominantly direct with increasing collision energy.

In the second part, we will report on a new crossed beam 3D velocity map imaging experiment in Kaiserslautern is dedicated to metal ion molecule reactions. Goals and recent progress toward understanding gas phase reaction dynamics of transition metal ions with small molecules will be presented together with first results on scattering experiments of the tantalum cation Ta^+ with small molecules.

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Quantum state tomography of Feshbach resonances in molecular ion collisions via electron-ion coincidence spectroscopy

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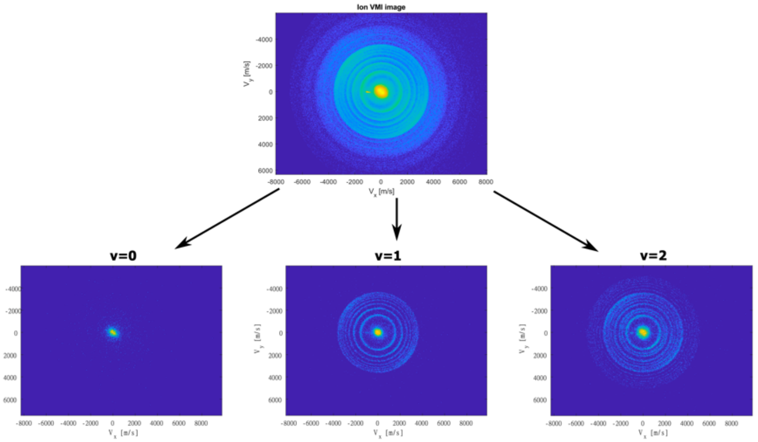
During collisions coupling between relative and internal atomic and molecular degrees of freedom leads to the formation of Feshbach resonances. The large phase space volume that particles explore in this metastable scattering state supports interference between many different quantum pathways that include inelastic and reactive processes.

We present a new method that allows us to measure simultaneously all the quantum channels for Feshbach resonances that appear in collisions between vibrationally excited H_2^+ ion and noble gas atoms. Our quantum state mapping is based on ion-electron coincidence velocity map imaging spectroscopy.

$$Ne + H_2^+(v = 0,1,2,3,4 \ldots)$$



$$Ne + H_2^+(v = 0) \qquad Ne + H_2^+(v = 1) \qquad Ne + H_2^+(v = 2)$$

$$Ne + H_2^+(v = 0, j) \qquad Ne + H_2^+(v = 1, j')$$

$$Ne + H_2^+(v = 0, j'')$$

Isomers effect in ion-molecule reactions of astrochemical relevance

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Ion-induced processes have long been regarded as playing a pivotal role in the synthesis of molecular species in the interstellar medium, as well as in the atmospheres of planets and their satellites. During the processes of star formations, leading from a dense and cold cloud to a fully developed planetary system, reactions of ions (as well as radicals) have been invoked as intermediate steps in the build-up of complex organic molecules (COMs) which can act as building blocks in the formation of prebiotic molecules and could be eventually delivered to planetary surfaces by impacts with comets and asteroids [1].

Thanks to the advances in telescope sensitivities and spatial resolutions, increasingly complex ions have been recently detected [2], and with such an increase in complexity the role of isomers becomes crucial. As isomers have different spectroscopic and chemical properties and, in many cases, isomerization barriers are too high to be overcome under interstellar conditions, they have to be treated as different species with distinctive chemical reactivities in astrochemical models.

This contribution focuses on two intriguing N-containing ions: the methanimine radical cation $H_2CNH^{+\bullet}$ and its isomer aminomethylene $HCNH_2^{+\bullet}$. Having a radical character, in addition to the charge, they are expected to react with saturated and unsaturated hydrocarbons via bondforming reactions, thus contributing to chain elongation processes in Titan's atmosphere [3]. By exploiting photoionization of appropriate neutral precursors via VUV synchrotron radiation, an efficient method to form both isomers in a selective way is proposed and results will be presented on their reactivity with CH_4 [4], C_2H_4 [5], C_2H_2 [6] as well as other larger hydrocarbons and nitriles.

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Spectroscopy in Cold Ion Traps

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Spectroscopy in cold ion traps is one of the brilliant techniques invented by Dieter Gerlich already in the early 1990s. I joined his group in 1994 in order to apply this technique to measure spectra of molecular ions such as CH_5^+ and other peculiar systems for which experimental spectra are difficult to record and their interpretation is also not possible with standard models. This was hard enough a problem to catch Dieter's interest and we collaborated since, until he sadly passed away in 2020. I am dedicating this presentation to the memory of Dieter Gerlich who was one of the most influential people to our community as a whole and to this conference series in particular. It is impossible to address all the techniques he developed and pushed to the ultimate experimental limit. Therefore, I will concentrate on spectroscopy in cold ion traps.

The tool box of action spectroscopy grew tremendously over the last 20 years, [1] also thanks to strong activities of Dieter in several laboratories around the globe. Apart from our first experiments in Chemnitz until the early 2000s [2] the method was exported to Heidelberg, where high-resolution spectra of H_3^+ were recorded [3]. Also, the group of John Maier in Basel benefitted tremendously from the further development of light induced reactions (LIR) driven by Dieter and John's team in Basel [4]. One of the peaks of this development was the recording of the first gas-phase near infrared spectrum of C_{60}^+. These laboratory spectra led to the identification of C_{60}^+ as one of the carriers of the diffuse interstellar bands, absorption features observed towards reddened stars. This was one of the break-throughs made possible by the superb skills and knowledge of Dieter. He also helped the developments in Tom Rizzo's laboratory in Lausanne. Dieter was also proud of collaborating with Jana Roithova, first in Prague, then in Nijmegen, where she together with Dieter uses parts of commercial tandem mass spectrometers with a cold ion trap to record infrared spectra of molecules relevant to organic chemistry [5]. Thanks to the cold trapping environment a correlation of the recorded spectra with the predicted spectra based on quantum chemical structure calculations is much more definitive than in traditional methods such as infrared multiple photon dissociation (IRMPD) spectroscopy. Many interesting ions have been studied during the ten years of their collaboration. Likewise Dieter was instrumental in the development of the Berlin trap by Otto Dopfer [6]

The technique was also imported by Roland Wester who applied it to mainly anions of astrophysical but also general interest. Here, the detachment of the extra electron on the molecule leads to a measurable signal. High-resolution spectra of OD^- [7] and NH_2^- have been recorded. It has been pointed out by Dieter from the very beginning of action spectroscopy in traps, that spectroscopy is only one possible application using LIR techniques but that it is also possible to study collisional processes where the initial state of the ionic partner is prepared by the excitation process. This has been nicely demonstrated by the Wester group through inelastic scattering of OH^- + He, to just name one example.

In Cologne we concentrated on applying LIR to astrophysical relevant ions such as H_3^+ and its isotopic siblings, CH_3^+, CH^+, C_3H^+ and many others. Some of theses species were identified in space based on these laboratory measurements. In the beginning, mainly the excitation of a molecular vibration was used to promote an otherwise hindered reaction. This approach could be used to record vibrational spectra in medium resolution where, e.g., the light from the free electron laser (FELIX, Nijmegen) allows to cover a very wide spectral range. But, also rotationally resolved infrared spectra became available with the use of narrow bandwidth cw-OPO systems and QCLs.

In recent years the technique of vibrational excitation was “only” used as a detector for addressing a specific ion. Double resonance experiments where microwave, Millimeter- or submm-waves are used to change the population of the rotational states of the ion ensemble in the trap. As a result of this double resonance approach, pure rotational spectra in very high resolution opened yet another door for action spectroscopy.

Dieter’s attention was caught again when complexes of molecular ions with He became available in traps as cold as 4 K or even lower. This was a development he strongly pushed in the Basel and Prague laboratories. In a collaboration with Dieter we studied the pre-dissociation of the He-H_3^+ complex in our COLtrap instrument, first in high-resolution. When adding a He atom to H_3^+ the simple infrared spectrum of H_3^+ which consists of a handful of lines because only a few states of this light ion are populated in the cold trap, the spectrum of the complex is composed of hundreds of lines where no clear structure is helping the assignment of the spectrum. Medium resolution studies with a pulsed IR OPO system finally were used to find the lowest ro-vibrational lines of the many bands of this very floppy complex. High level electronic structure calculations of the potential energy surface by Harding, Lipparini and Gauss were the input for the computation of the vibrational-rotation-tunneling (VRT) states of the He-H_3^+ complex by van der Avoird. These calculations enabled an assignment of many experimental lines. In a first approach we reconstructed the energy term diagram of the lowest energy states of this floppy system just based on the experimental lines and compared this with the results of our theoretical collaborators. In contrast to the full spectrum these term diagrams have a clear and simple structure which can even be explained by the model of a diatom between the He atom and the H_3^+ subunit.

This pure spectroscopic result was only of minor interest to Dieter. He was most interested in understanding and assigning the lines of highest energy where short life-times lead to the broadening of the observed lines. It is most likely that these transitions excite the complex to states which are very close to the dissociation limit of the van der Waals stretching vibration. These dissociative states are connected to the continuum states of the collision system He + H_3^+. This is the situation where a molecule is destroyed (dissociation) or formed (incoming collision). Understanding this process is one of the most exciting questions in molecular physics. Searching for the nature of these resonance states was a large motivation by Dieter and it is a task for us in the future where we continue and try to follow his path.

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Planarization of non-planar aromatic hydrocarbons: Dehydrogenation *versus* hydrogenation

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Besides their interest for potential organic electronic devices, 2D chiral crystallization of carbohelicenes on metal surfaces is of paramount importance for light sensors or for electron-spin filters. We report the 2D chiral crystallization of 2,2'-bispentahelicene (bis[5]H, Fig. 1) on Au(111) and its thermally-induced cyclodehydrogenation, as studied with scanning tunneling microscopy (STM). The low coverage deposition of bis[5]helicenes on Au(111) kept at 400 K, leads to formation of heterochiral zigzag chains of the *(M,M)-* and *(P,P)-*enantiomers growing along the herringbone reconstruction pattern. In the closed-packed monolayer, both enantiomers self-assemble into a racemate phase and rotational and mirror domains are observed. Due to its strong steric overcrowding in its adsorbate state, the *(P,M)-*meso form was not observed Upon annealing the substrate to approximately 670 K and subsequent cooling to 50 K, the characteristic twisted shape of the bis[5]helicenes with protrusions is no longer observed and two-dimensional homochiral

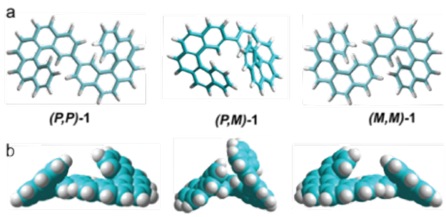


Figure 1. Diastereomers of bis[5]H.

domains of planar coronocoronene molecular species can be distinguished (Fig. 2). The transformation from helical to planar chiral molecules via dehydrogenation and loss of eight hydrogen atoms are confirmed by secondary ion mass spectrometry (ToF-SIMS). STM measurements at 7 K confirm the formation of 2D homochiral conglomerate domains of planar S_p- and R_p-coronocoronene (Fig. 2).

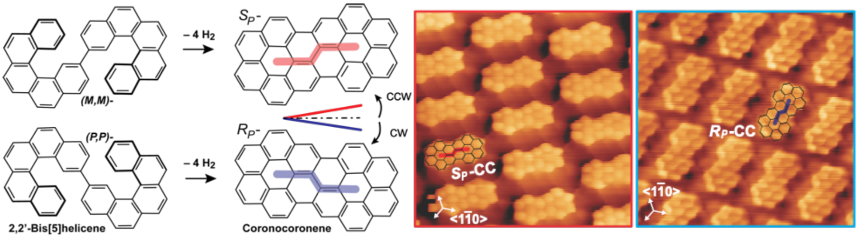


Figure 2. Cyclodehydrogenation bis[5]helicene proceeds stereoselectively to planar coronocoronene which is chiral if confined onto a surface. The planar product assembles upon cooling into homochiral domaines.

The modification of a Cu(100) surface with molecules of the buckybowl pentaindenocorannulene (PIC) has been studied by means of STM, carbon monoxide-modified noncontact atomic force microscopy (nc-AFM), ToF-SIMS, and quantum chemical calculations. Two different adsorbate modes are identified, in which the majority is oriented such that the bowl cavity points away from the surface and the convex side is partially immersed into a four-atom vacancy in the Cu(100) surface. A minority is oriented such that the convex side points away from the surface with the five benzo tabs oriented basically parallel to the surface.

Thermal annealing leads to hydrogenation and planarization of the molecules in two steps under specific C−C bond cleavage (Fig. 3) The benzo tabs of the convex side up species serve as a hydrogen source. The final product has an open-shell electron structure that is quenched on the surface.

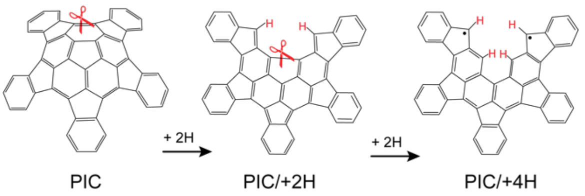
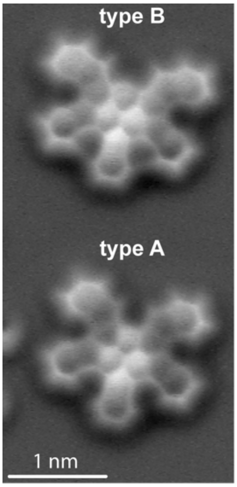


Figure 3. Planarzation of PIC by hydrogenation and C–C bond cleavage. nc-AFM and ToF-SIMS confirm this on-surface chemistry.



Femtosecond photoexcitation dynamics of atoms and molecules inside helium nanodroplets

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Superfluid Helium nanodroplets offer fascinating opportunities for spectroscopic studies of atoms, molecules and aggregates because of their low temperature of 0.4 K and the high degree of control in loading the droplets. Systems investigated with frequency-domain spectroscopy include charge and energy transfer in tailor-made or weakly bound aggregates, and the investigation of solvent influence in a growing microsolvation environment. Here, we present the development of helium droplets for time-domain studies, aiming at a broad application of these nano-cryo-reactors to investigate the dynamics of photophysical and photochemical processes in real time.

In a first step, we were able to observe the photoexcitation dynamics of a single atom (In) solvated inside a droplet with femtosecond time-resolved photoelectron spectroscopy [1,2]. This experiment yields three important findings: (i) it demonstrates that photoelectrons are a good observable for ultrafast processes inside helium droplets, (ii) it enabled a characterization of the response of superfluid He to photoexcitation of solvated atoms/molecules and, (iii) it showed that these processes can be modeled with time-dependent helium density functional theory simulations.

In a second step, we investigated the helium influence on coherent nuclear dynamics by exciting a vibrational wave packet (WP) in dimer molecules (In2) [3]. Very surprisingly, we find that the coherent WP signal can be observed for tens of picoseconds, demonstrating that the perturbation imposed by this quantum liquid can be lower by a factor of 10-100 compared to any other solvent.

Finally, in a recent effort to characterize the propagation of free electrons within the helium nanodroplets, we were able to demonstrate laser-assisted electron scattering, an energy transfer process between strong laser fields and free electrons, for the first time in the condensed phase [4].

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Hot Topic Papers

Estimation of the Water Binding Energy in Hydrated Carbonate Ions Using Blackbody Infrared Radiative Dissociation Kinetics and Master Equation Modelling

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Blackbody infrared radiative dissociation (BIRD) is the dissociation of molecules in a low pressure environment due to surrounding blackbody radiation. As blackbody radiation depends on temperature, also the resulting dissociation channels show a strong temperature dependence. Here, BIRD of $CO_3^{\bullet-}(H_2O)_{1,2}$ is investigated. The ions are trapped in a FT-ICR mass spectrometer, mass selected and their BIRD induced fragmentation is recorded at temperatures in the range from 250 K to 330 K.

Dissociation rates can be modelled with Master Equation Modelling (MEM), considering three processes, namely absorption and emission of photons (leading to changes in the energy content of the molecule), and dissociation of molecules above a certain energy level. To describe the process, we consider not only the isomer with the lowest energy, but also other local minima.

Precise experimental measurements of BIRD kinetics at different temperatures and the multiple-well approach for Master Equation Modelling are combined, providing water binding energies of the investigated clusters. These energies are consistent with ab initio calculations. Comparison with the use of a single-well-MEM approach shows that the multiple well approach is better suited for the description of the BIRD process of hydrated carbonate ions.

Unravelling the molecular organic signature of aerosol particles: Coupling of a thermaloptical carbon analyser (TOCA) to an improved laser photo-ionization mass spectrometer

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Carbonaceous material in airborne particulate matter (PM) is of interest due its adverse health effects and its climate impact. PM fractions often are charcterized by sum parameters (organic carbon, OC and elemental carbon, EC contnet). In this context thermal-optical carbon analysis (TOCA) is a key technique in air quality monitoring, atmospheric research and combustion science. In the framework of air quality program such as the Interagency Monitoring of Protected Visual Environments (IMRPOVE) network, fine particulate matter (PM2.5) is collected on quartz fiber filters at multiple sites and analysed to obtain the content of particulate organic and elemental carbon (OC, EC). Different OC ractions an be analyzed in the TOCA process by stepwise heating of the PM loaded filter samples (used steps in the IMRPOVE protocol: OC1 - 120 °C, OC2 - 250°C, OC3 - 450°C, OC4 - 550°C). The yield of information from a TOCA can be extended beyond OC and EC fraction by evolved gas analysis (EGA) techniques, such as photoionisation time-offlight mass spectrometry (PI-TOFMS) (Grabowsky et al., 2011; Diab et al., 2015, Miersch et al. 2019a/b). For example, health-relevant polycyclic aromatic hydrocarbons (PAH) can be detected and quantified by resonanceenhanced multiphoton ionization (REMPI) TOFMS simultaneously to OC and EC (Miersch et al., 2019a). We present current results of the TOA-PIMS approach on PM samples from wood combustion and ship emissions. Furthermore, concepts and results of an improved TOCAbased instrument (Figure 1) for EGA-analyzing filter samples are discussed.

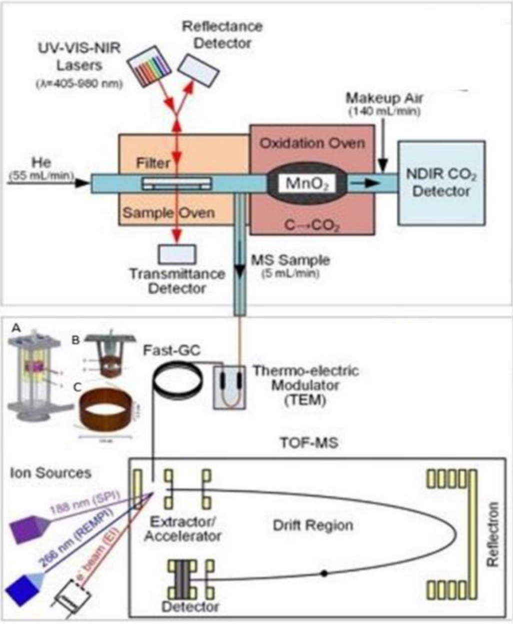

Figure 1: Coupling of the EI/PI-TOF mass spectrometer to the TOCA instrument with the optional fastGC unit (A optical heater, B column holder with halogen lamp for heating, C GC-column)

On the one hand quasi-simultaneous EI and PI (REMPI or SPI) detection by high-resolution TOFMS, enabling detection of PAH and the oxidation state of organic PM similar to the high-resolution AMS approach, is described. A quadrupole mass spectrometry (qMS) approach with electron ionization (EI) and a thermal fragmentation oven was privously introduced by Riggio et al. (2018) to provide quantitative results on organic matter, nitrate, and sulfate, aiming to transfer fragmentation tables from online aerosol mass spectrometry (AMS, Canagaratna et al., 2007) to offline filter analysis. However, no information on elemental composition and finally carbon oxidation state can be derived because the qMS cannot provide sufficient mass resolution to distinguish between key isobaric ions, such as C3H7+ and C2H3O+ and m/z 43. In this work EGA from TOCA was done via on-line sampling from a modified TOCA quartz oven. Ions were generated by an electron gun for EI and a KrF laser with 248 nm radiation for REMPI. Detection of the ions was performed by a Reflectron-TOFMS with a mass resolution of ~2,800 at m/z 43. The benefits of this instrument are demonstrated on different combustion aerosols from engines and wood stove as well as laboratory-aged wood combustion emission and ambient PM2.5 samples. For the example of fresh and aged spruce combustion emissions (Figure 2), a decrease in hydrocarbon-like fragments (e.g. C3H7+) can be observed, whereas ions of oxygenates (e.g.C2H3O+ and CO2+) as well as NO2+ as fragment of nitrate noticeably increased by atmospheric ageing. The sufficiently high mass resolution thus allows separation of many hydrocarbon- and oxygenate-isobars. Simultaneously, the selective REMPI detection of PAH addresses indicates the PAH and this indirectly the carcinogenicity of the organic aerosol (Miersch et al., 2019b)

Elucidating the structural deformation of CO_2 induced by Cu based clusters

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Copper-based materials are among the most promising catalysts for CO_2 utilization.[1] However, CO_2 conversion is still inefficient and requires high-energy input resulting in even more CO_2 emissions. Therefore, the molecular level understanding of CO_2 interacting with copper is crucial for the design of more efficient catalysts. In our study, we mimic the active site of the catalyst with copper clusters to study how they affect the structure of CO_2. Negatively and positively charged clusters are produced in a laser ablation source, react with CO_2 in a flow-reaction tube, and are studied by IR multiple-photon dissociation spectroscopy as illustrated in Figure 1. Size dependent activation and dissociation was observed for carbon doped Cu_n^- (Figure 2), while Cu_n^+ do not have any effect on the CO_2 structure independent of their size[2].

As a next step, we implement He superfluid nanodroplets as nano-reactors to study the reaction of CO_2 with both bare and metal doped Cu-clusters. In this way, even the subtle changes in the CO_2 structure could be recognized by high-resolution photo fragmentation spectroscopy of He tagged ions.

This work was supported by the Dutch Research Council (NOW) and Austrian Science Fund FWF (project M 3229).

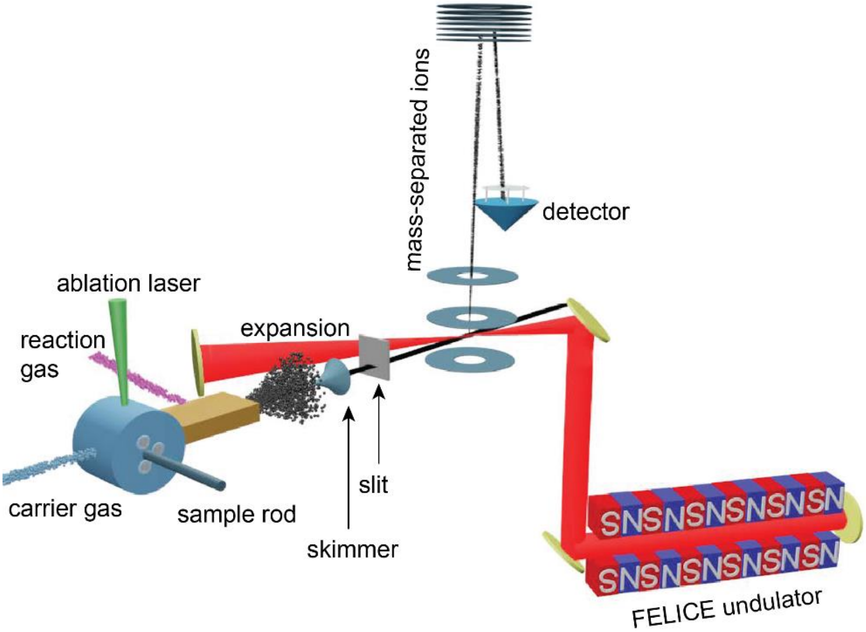

Figure 1: Schematic representation of the experimental instrument.

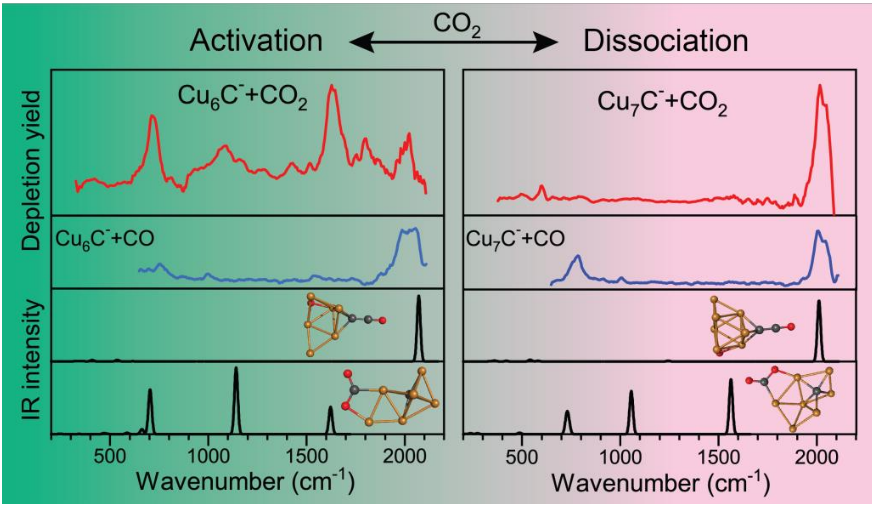

Figure 2: IRMPD spectra of CCu_6^- and CCu_7^- reacted with CO_2 (red) and CO (blue), and calculated spectra (black) of activated and dissociated complex.

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Interstellar methanol: the challenge of reactivity under astrophysical conditions

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Abstract

The presence of clouds of methanol in the InterStellar Medium (ISM) has been confirmed recently by the ALMA (Atacama Large Millimeter Array) telescope [1]. The high abundance of this organic molecule despite being exposed constantly to the energetic radiation present in the ISM, is a challenging question. Indeed, radiation impact can lead to dissociation molecules, and at the same time can also open up opportunities for the formation of more complex organic molecules, such as dimethyl ether [2]. It is likely that the very high abundance of protons in the ISM is mirroring the presence of small protonated methanol clusters $H^+(CH_3OH)_n$, and that this can also account for the production of other species detected.

The Molecular-Cluster Irradiation Device (DIAM) [3] [4], set-up at the Institut de Physique des 2 Infinis de Lyon is devoted to perform experiments under conditions that reproduce some aspects of interstellar, circumstellar or planetary atmospheric environments. In order to investigate the occurrence and competition of various fragmentation and intramolecular processes, as evaporation, dissociation, or formation of further complex organic molecules (COMs), we have performed single collision experiments of 8-keV mass-selected protonated methanol clusters with an argon atom. It is interesting to note that the protonated

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[1] International joint thesis supervision: University of Lyon and University of Innsbruck

dimethyl ether can be seen within DIAM as a result of a water loss reaction from an excited protonated methanol cluster ion. The associated velocity distribution of the eliminated water molecules, elucidating the dynamics of this reaction, has been measured here with the COINTOF (Correlated Ion and Neutral Time Of Flight) mass spectrometry technique combined with velocity-map imaging [5].

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Ultrafast dynamics in microsolvated bimolecules

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Interactions between proteins and their solvent environment can be studied in a bottom-up approach using hydrogen-bonded chromophore-solvent clusters. The ultrafast dynamics following UV-lightinduced electronic excitation of the chromophores, potential radiation-damage, and their dependence on solvation are important open questions. The microsolvation effect is challenging to study due to the inherent mix of the produced gas-phase aggregates. We used the deflector to spatially separate different molecular species in combination with pump-probe velocity-map-imaging experiments, including applications of 3D "cameras" based on Timepix3. We demonstrated that this powerful experimental approach reveals intimate details, e.g., on the radiation damage of pyrrole-water as well as on the UV-induced dynamics in the near-UV-absorbing prototypical biomolecular indole-water system. We determined the time-dependent appearance of the different reaction products and disentangled the occurring ultrafast processes. This novel approach ensures that the reactants are well-known and that detailed characteristics of the specific reaction products are accessible – paving the way for the complete chemical-reactivity experiment.

Femtosecond time-resolved alignment dynamics of alkali dimers on helium nanodroplets

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Alkali dimers, Ak_2, residing on the surface of helium nanodroplets, are doubly ionized by an intense fs laser pulse leading to Coulomb explosion into two Ak^+ fragment ions. We show that the kinetic energy of these fragment ions can be used to identify if the dimers were initially populated in the $X^1\Sigma_g^+$ ground state or in the lowest-lying triplet state a $^3\Sigma_g^+$. We use the quantum-state-sensitive detection to investigate state-specific properties, such as rotational and vibrational dynamics.

The work presented here focuses on the time-dependent alignment of Li_2, Na_2, K_2, and Rb_2 on He nanodroplet surfaces. The dimers are set into rotation by an 800 fs alignment pulse and their instantaneous spatial orientation is measured by Coulomb explosion with an intense delayed 50 fs probe pulse. We recorded the emission direction of the atomic aragment ions through velocity map imaging. The measured alignment traces, obtained by scanning the delay between the alignment and the probe pules, show distinct periodic features that differ qualitatively from that expected for freely rotating gas phase molecules. Comparison to theoretical models suggest that this modified behavior stems from the orientation-dependent interaction of the dimer with the droplet surface.

For the Na and K dimers, the calculated alignment dynamics agree well with the experimental results and are close to those calculated for 2-dimensional rotation of the dimers in a plane.

Measurement of the quantum tunneling reaction $H_2 + D^- \rightarrow HD + H^-$

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Hydrogen is the most abundant element in the universe, and collisions of hydrogen and its charged forms are important in the chemistry and evolution of the interstellar medium. Additionally, binary collisions of atomic with molecular hydrogen belong to the most fundamental molecular systems and are simple enough to be theoretically investigated using first-principle methods, providing suitable benchmark systems for quantum calculations.

The rate of the tunneling reaction $H_2 + D^- \rightarrow HD + H^-$, for which the collision complex is closely related to the H_3^- anion, has been calculated but has lacked verification. Here we present high-sensitivity measurements of the reaction rate carried out in a cryogenic 22-pole ion trap. We model the effect of a high-energy tail in the velocity distribution to investigate its influence on the reaction rate. Our measured value agrees with quantum tunneling calculations, serving as a benchmark for molecular theory.

Recent progress in theoretical description of excitation and dissociative processes in collisions of electrons with molecular ions

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Abstract

The article gives a short overview of recent progress in successful theoretical description of various processes taken place in collisions of electrons with molecular ions at energies below a few eV: dissociative recombination, rotational, vibrational, and electronic excitation of the ions, molecular photoionization. The theory based on first principles only (and, sometimes, heavy numerical calculations) is now able to give reliable cross sections for these processes for ions up having up to approximately 10 atoms. The progress in the theoretical description of the processes is crucial for various applications, where molecular plasma is involved.

1. Introduction

Molecular plasma is used in many applications and modern technologies and present in many environments, such as interstellar medium, planetary and stellar atmospheres, plasma etching, plasma depollution, near walls in tokamaks and many others. Understanding microscopic processes taking place in molecular plasma and knowing corresponding cross sections and rate coefficients is crucial for reliable plasma modeling to understand those environments or control technological processes. One important family of processes is processes taking place in collisions of electrons with molecular ions. In recent years, there have been a significant progress in theoretical description of many such processes: dissociative recombination (DR), rotational (RE), vibrational (VE), and electronic excitation. Theory is now able to produce accurate cross sections for these reactions using first principles only. This article discusses very briefly the progress.

2. Dissociative recombination

For diatomic molecules, theory can represent the process of dissociative recombination at the level of individual rotational and vibrational states of the target molecule. Probably, the most successful case is the theoretical description of DR in the two-electron system of the HeH^+ ion [1]. The theoretical approach combines the quantum defect matrix obtained in electron-scattering calculations with the UK R-matrix code, energy-dependent rovibrational frame transformation, vibrational wave functions (discrete and continuum) of HeH^+ computed using the complex-scaling method. Obtained theoretical cross section reproduces in detail the experimental data from the Cryogenic Storage Ring, including multiple resonances.

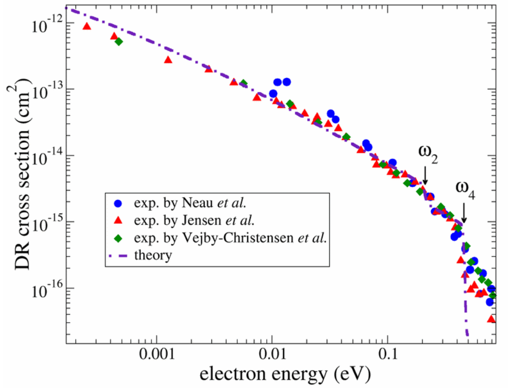

Fig. 1: Theoretical and experimental cross section for DR in H_3O^+ *. For details, see Ref.* [2] .

The theoretical approach described above can give wave functions of the electron-ion system in their full dimensionality: rotational, vibrational, and electronic. if needed, the wave functions can explicitly be written as functions of these coordinates. Such a detailed approach is not technically feasible for polyatomic ions. Studying the DR in the simplest polyatomic ion H_3^+, we have developed a simplified approach to compute overall cross sections for the DR and VE in polyatomic ions. The approach is also based on first principles and have been tested on several molecular ions. Figure 1 shows a comparison of available experimental DR cross sections obtained for H_3O^+ with the theoretical one, obtained using the simplified approach. As one can see, the agreement is very good. The approach can be used for closed-shell molecular ions having up to roughly 10 atoms. Figure 2 demonstrates the results obtained for the NH_2CHOH^+ ion.

The simplified approach was developed in a series of studies (see [3,4] and references therein). It is easy to implement. The DR cross section in this approach is obtained from the derivative of the scattering matrix with respect to normal-coordinate displacements. A typical calculation of the DR cross section is made in two steps: (a) a determination of normal mode frequencies and coordinates, which can be performed, for example, using Molpro or Gaussian and (b) calculation of geometry-fixed scattering matrices for electron-ion for two geometries per normal mode. It should noted that the approach is applicable only for energies below the excitation energies of the vibrational modes of a given molecular ion, i.e. in practice it works for scattering energies below approximately 0.2-0.3 eV.

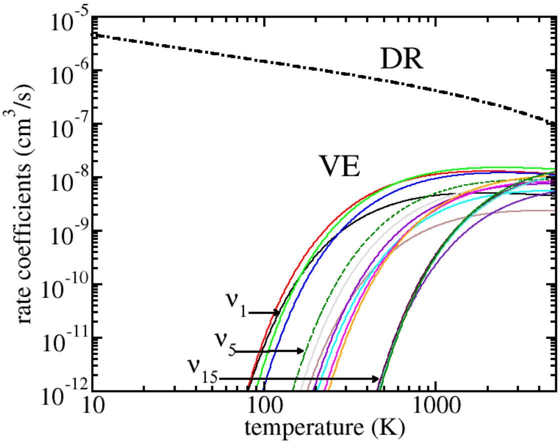

Fig. 2: Theoretical rate coefficients for the DR and VE processes in NH_2CHOH^+*. The number of VE curves corresponds to the number of vibrational modes in the molecule. For details, see Ref. [4].*

2. Vibrational excitation

Cross sections for vibrational excitation and de-excitation can be calculated in both, full (for diatomic ions) and simplified (polyatomic ions) approaches. The calculation in the simplified approach is particularly simple: One uses the same derivatives of the scattering matrix, mentioned above. Figure 2 shows rate coefficients obtained from VE cross sections of the NH_2CHOH^+ ion for all 15 modes of the ion. Because of its simplicity, the approach was implemented and included into the Quantemol package of *ab initio* electron-scattering codes and can now be used by non-experienced users. Here, we also note that the approach is applicable only for relatively low scattering energies: below the energy of excitation of two quanta of the same mode.

3. Rotational excitation

Within the fully-quantum approach, cross sections for rotational excitation are obtained directly from the complete scattering matrix represented in the basis of asymptotic rovibronic channels. Cross sections for rotational excitation of polyatomic ions can be computed using the rotational frame transformation and the approximation of the rigid rotor. Very briefly, for such calculations the following is needed. (a) The geometry-fixed scattering matrix obtained, typically, by *ab initio* methods for the geometry of equilibrium of the target ion. For example, the UK R-matrix code can be used to obtain the fixed-geometry scattering matrix.

(b) The rotational constant of the molecular ion and – if the ion is an asymmetric-top rotor – rotational wave functions of the ion, represented by coefficients of expansion over Wigner functions. Using this information, the scattering matrix for purely-rotational transitions is constructed. If needed, the lowest vibrational levels in the normal-mode approximation, described above, could be included into the treatment, extending it to rovibrational transitions.

4. Summary

Diatomic and small polyatomic ions: Theory can now give quite reliable cross sections and rate coefficients for state-to-state rovibronic excitation and DR of closed-shell molecular ions. The approach could also be adapted to the ions with low-energy excited states (and radicals) as it was recently demonstrated for the DR and VE of the CH^+ ion. Such ions were known to be difficult to treat theoretically using previous theoretical methods.

One significant problem persists in the theoretical description of electron-molecular ion collisions at low energies (<10 eV): There is no uniform approach for evaluation of branching ratios in DR products. A time-dependent method developed by Ann Orel is essential the only one available for polyatomic ions, but it is limited due to the reduced-conditionality approximation. In addition, it is quite labor intensive.

Acknowledgements

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Multidimensional nonlocal dynamics in resonant electron molecule collisions – application to $e^{-}+CO_2$

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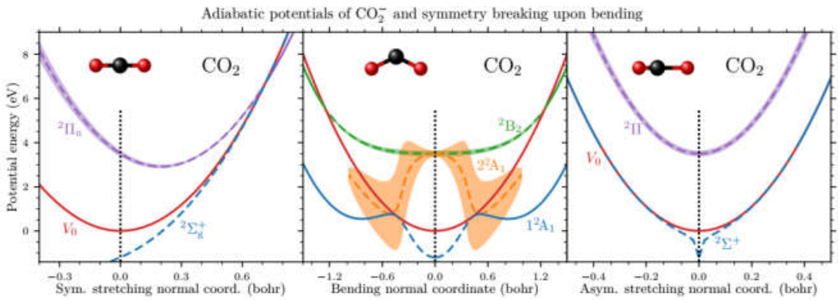
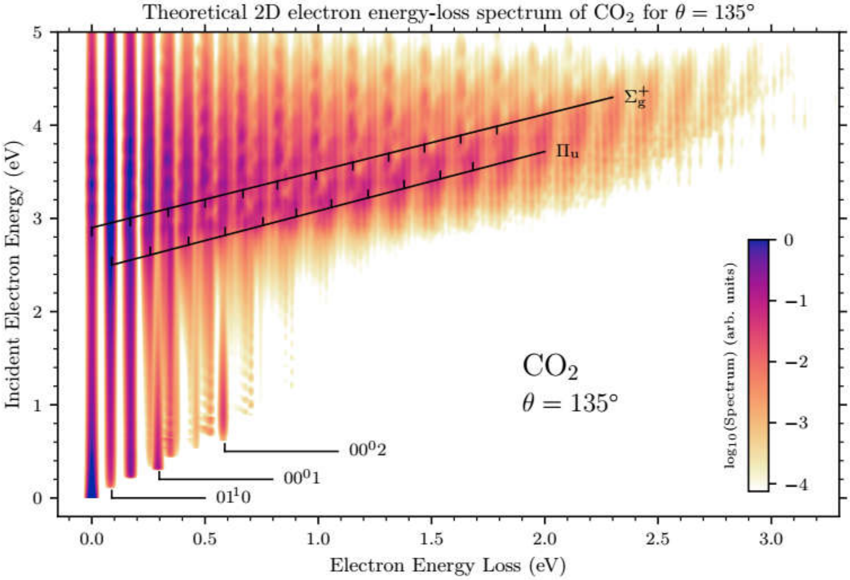
We formulate theory of vibronic dynamics of three interacting metastable states in linear molecule and apply it to resonant vibrational excitation of CO2 molecule. The model includes the Renner-Teller Π-state dublet interaction with Σ virtual state. We fit the model parameters to R-matrix fixed-nuclei electron scattering data for large set of molecular geometries. Finally we perform the calculation of the dynamics withing the model including all four vibrational degrees of freedom and apply it to recently measured electron-loss spectra. The calculation captures all essential features of the spectra and provides interpretation for surprisingly narrow structures appearing at high electron energy losses.

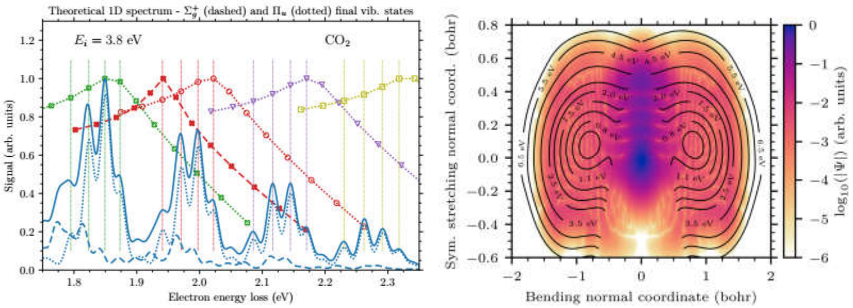

Adiabatic potentials of CO_2^- and symmetry breaking upon bending

We have constructed a nonlocal discrete state in continuum model for description of the vibrational excitation process in $e^{-} + CO_2$ for the electron energy starting from the threshold to the region around 3.8eV shape resonance. The model was constructed on the basis of fixed-nuclei scattering eigephase sums obtained with the UK R-matrix codes for large set of molecular geometries. The nonlocal model contains three discrete states. Two describing Renner-Teller Π_u dublet and one additional state corresponding to the virtual state of Σ_g symmetry. All states can become bound upon deformation of the molecule as pointed out by Sommerfeld et al. [1], and the model with ambition to describe deeply inelastic vibrational excitation must contain them all. The previous attempt to describe the nonadiabatic Renner-Teller coupling between the resonance states in the dublet employed the local complex potential approximation [2]. We extended the nonlocal approach of Estrada et al. [3] and included three discrete states vibronically coupled through all four vibrational degrees of freedom. The vibronic model reflects the symmetry group of the molecule, which makes the fitting procedure for the parameters of the model from the fixed-nuclei scattering data feasible. The dynamics is solved by expanding the Schrodinger equation projected on the electronic discrete states in the basis of harmonic vibrational modes of the neutral molecule. The effective Hamiltonian for the nonlocal dynamics is thus sparse matrix and the Schrodinger equation can efficiently be solved by matrix iteration methods in Krylov subspaces [4]

The final model contains coupling to all continuum partial waves with angular momentum l=0,1. The model can thus describe differential cross sections for vibrational excitation into all vibrational states of Σ_g^+, Σ_u^+, Π_g, Π_u, Δ_g symmetries. We calculated all individual cross sections and we also organized them in simulated 2D electron energy loss spectrum [5].



The final data are discussed and analysed using decomposition of the dynamics into irreducible representations and by looking of their sensitivity to model modifications. We also present 2D sections through scattering wave functions.



Finally we also compare the results with new measurements of differential cross sections with high electron energy resolution [6] and propose interpretation of narrowing of spectral features at high energy losses.

Acknowledgement: The work has been supported by grant 19-205224S form Czech national grant foundation GAČR and by student grant GAUK 552120.

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Test of the spectator role of the Rydberg electron in the He(n) + CO reaction and effects of the CO dipole and quadrupole moments on the reaction-rate coefficients at low collision energies

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Rydberg atoms have large electric dipole moments and therefore their translational motion can be easily manipulated by inhomogeneous electric fields [1–3]. We deflect a beam of He Rydberg atoms using a Rydberg-Stark surface deflector and accelerator and merge it with a beam of ground-state CO molecules to study the $He^+ + CO \rightarrow C^+ + O + He$ reaction. In the experiment, we exploit the facts that the Rydberg electron prevents the heating up of the ions by stray electric fields and that it hardly affects the ion-molecule reaction taking place within its orbit [4–8], in accordance with the independent particle model of Rydberg collisions [9,10]. We detect the C^+ product of the reaction as a function of the velocity of the He(n) atoms. In this way, we can adjust the collision energy of the reaction and probe the range between 0 and ~25 K k_B.

In the first part of our investigation, we tested the spectator role of the Rydberg electron by measuring the distribution of principal quantum numbers of the He(n) reactants and the C(n') products using pulsed-field ionization [11]. We find that the distributions are affected by spontaneous emission and blackbody-radiation-induced transitions, but not by the ion-molecule reaction, which in turn indicates that the Rydberg electron does not influence the ion-molecule reaction. In the second part, we carried out an investigation of the effect of the dipole and quadrupole moments of CO on the reaction rates at low collision energies. In particular, we observe a 30% decrease in the product formation at the lowest collision energies (below ~ 5 K k_B) and attribute it to the negative quadrupole moment of CO on the basis of calculated state-dependent capture-rate coefficients.

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Spin-state-controlled Penning collisions between metastable helium atoms and ground-state lithium atoms

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

As a first step towards co-trapping, we study quantum-state-controlled Penning collisions between metastable helium atoms (He*) and ultracold lithium atoms (Li) in order to investigate efficient ways of controlling the outcome of such ionizing collisions. For this, we have combined a supersonic-beam source for He* with a magneto-optical trap (MOT) for Li [1]. In order to distinguish in between the contributions of He(2^3S_1) and He(2^1S_0) to the reaction rate, we deplete the population of He* atoms in the 2^1S_0 state using a novel optical-excitation scheme [2]. Furthermore, we use laser-optical pumping to prepare both He(2^3S_1) and Li($2^2S_{1/2}$) in selected magnetic sub-levels prior to the collision [3].

In this contribution, we demonstrate the efficient control of He(2^3S_1)-Li($2^2S_{1/2}$) Penning ionization by spin-state preparation. Our results imply a strong suppression (enhancement) of Penning-ionizing collisions for non-spin-conserving (spin-conserving) reaction channels. Our results are in good agreement with a model based on spin angular momentum coupling of the prepared atomic states to the molecular reaction channels. Small deviations from the model indicate the contribution of quartet states to the reaction rate, which is in violation of spin-conservation rules.

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Survival of rotational alignment in H2 scattering from Si(100)

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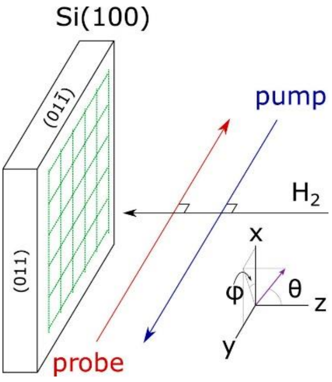
We report a state-prepared, state-resolved study of rotational scattering of a diatomic molecule from a solid surface. Specifically, H_2 molecules with 80 meV kinetic energy are rotationally aligned in the $j = 3$ rotational state via stimulated Raman pumping and then scattered from a Si(100) surface at normal incidence. The rotational alignment of the scattered molecules is determined by measuring, for both the incident and scattered molecules, the ionization yield of a probe laser, tuned to selectively ionize molecules in the $j = 3$ rotation level, as the probe laser polarization is rotated. The measurement is performed for two initial rotational alignments: a “helicoptering” alignment with the bonds constrained to lie primarily parallel to the surface and a “cartwheeling” alignment with the bonds lying primarily normal to the surface. For both initial alignments, the modulation of the probe ionization yield with laser polarization for the scattered molecules is pronounced, although significantly weaker than the modulation measured for the incident molecules. This indicates a significant modification but not a complete elimination of the initial alignment. The modulation is found to be stronger for the scattered molecules originating in the cartwheeling alignment than for the helicoptering alignment. These results contribute toward an improved understanding of the role of rotational motion in molecule–surface dynamics.



References:

Christopher Reilly, Andrew Hutchison, and Greg O. Sitz, "Survival of rotational alignment in H2 scattering from Si(100)", *J. Chem. Phys.* **155**, 174705 (2021) https://doi.org/10.1063/5.0068518

Recombination of hydrogen atoms at metal surfaces – A step towards predictive surface chemistry

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Transition state theory (TST) is the leading tool for the description of chemical reaction rates. Predictive surface chemistry is limited by the inaccuracy of electronic structure theory and simplifications within TST. For reactions at metal surfaces, which are so important to heterogeneous catalysis, there are few tests of its accuracy against elementary rate constants from experiments. This is mostly because highly accurate experimental data is absent. For example, previously reported rate constants for hydrogen atom recombination at Pt(111) have uncertainties of 3 orders of magnitude. Here, we report accurate experimental rate constants for hydrogen atom recombination on Pt(111) and Pt(332) derived from the Velocity Resolved Kinetics[1] method. We introduce a TST-based model which reproduces experiments with no adjustable parameters over a broad temperature range. The model's key to success is a fully quantum mechanical entropy for the adsorbed H atoms. We extended our modelling efforts to other single crystal metal surfaces and catalytic nanoparticles and find a general applicability for the prediction of hydrogen atom recombination rates and adsorbate entropies.

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Cryo kinetics and cryo spectroscopy of N2 adsorbates on the surfaces of transition metal clusters

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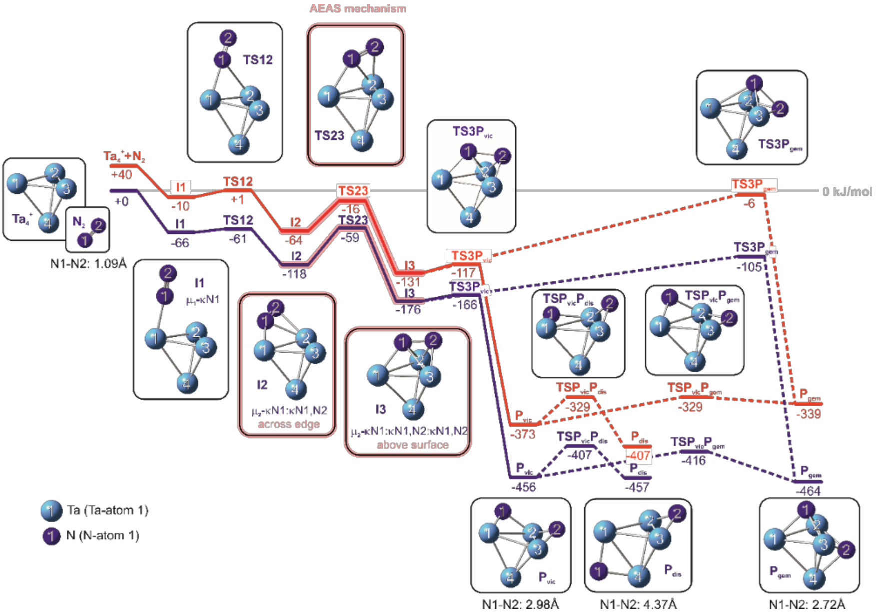
It has shown that IR spectroscopy of isolated transition metal complexes reveals valuable information on structures and activation pathways of attached adsorbate molecules, and it proved beneficial to apply cryogenic ion storage trap techniques as well as various photonic pumping and detection schemes.
This presentation reports on conceptual investigations of small molecules such as N2 and H2, when interacting with size selected transition metal clusters and complexes.



Case studies comprise transition metal clusters of Cobalt[1], Nickel[2-4], Ruthenium[5], Rhodium[6,7], Tantal[8], Iron[9,10], as well as some alloy clusters[11,12]. Rather than covering the conducted research at length, the presentation aims to provide for glimpses on some findings of particular interest, and on their interpretation. The applied methodology[13] encompasses cryo kinetics under single collision conditions, various schemes of IR spectroscopies, as well as synchrotron based magnetic characterizations, all of which receive verification by dedicated quantum chemical modelling at various DFT levels.
The conducted research is knowledge driven but provides for outreach towards various applications, and major parts of the presentation cover most recent work published and to be published alike.

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Real-space imaging of anisotropic charge of σ-hole by means of Kelvin probe force microscopy

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An anisotropic charge distribution on individual atoms, such as e.g. σ-hole, may strongly affect material and structural properties of systems. Nevertheless, subatomic resolution of such anisotropic charge distributions represents a long-standing experimental challenge. In particular, the existence of the σ-hole on halogen atoms has been demonstrated only indirectly through determination of crystal structures of organic molecules containing halogens or via theoretical calculations. Nevertheless, its direct experimental visualization has not been reported yet. We demonstrate that Kelvin probe force microscopy, with a properly functionalized probe, can reach subatomic resolution imaging the σ-hole, see Figure 1, as well as a quadrupolar charge of carbon monoxide molecule [1]. This achievement opens new way to characterize biological and chemical systems where anisotropic atomic charges play decisive role.

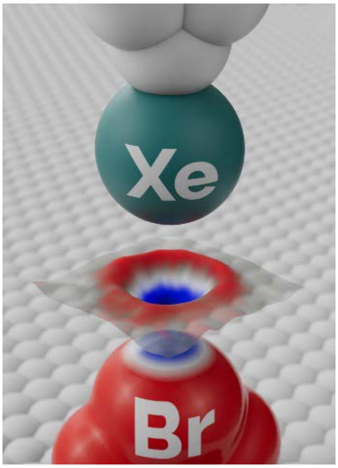

Fig. 1 *Schematic view showing the principle of the experiment that made it possible to visualize the sigma-hole on a bromine (Br) atom in a molecule using a specially modified tip of a scanning microscope functionalized with a single xenon (Xe) atom. Top: schematic view of the tip of the scanning microscope with single xenon (Xe) atom. Center: an experimental illustration of the sigma-hole acquired by means of a scanning microscope using the Kelvin probe principle. Bottom: electrostatic potential map depicting the sigma-hole*

(inhomogeneous atomic charge distribution on a bromine atom), which is formed by a positive charge on top of the atom (blue crown) surrounded by a negative electron plume (red field).

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H atom scattering from a van der Waals surface.

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Recently, detailed theoretical and experimental investigations of energy transfer between hydrogen atoms and late fcc transition metal (111) surfaces have been made and on the basis of these experiments, it was possible to clarify the role of electron-hole pair excitation during the scattering process. [1-4] However, those investigative efforts excluded metals that crystalise in other crystal structures and surface facets as well as insulators, because the theoretical methods in those investigations are based on Effective Medium Theory (EMT) [5], a theory that has been formulated to describe fcc metals and their alloys. Here, I demonstrate that EMT can also be successfully used to describe the interactions between atomic hydrogen and solid xenon. The fitted potential has an RMSE smaller than 30 meV and MD simulations are capable to reproduce experimental recorded energy loss distributions extraordinarily well. [6] MD simulations performed a simple Lennard-Jones potential fail to describe the experiment.

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Contributed Papers

Posters

Quantum dissipation driven by electron transfer within a single molecule investigated with force atomic microscopy

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Intramolecular charge transfer processes play an important role in many biological, chemical and physical processes including photosynthesis, redox chemical reactions and electron transfer in molecular electronics. These charge transfer processes are frequently influenced by the dynamics of their molecular or atomic environments, and they are accompanied with energy dissipation into this environment. The detailed understanding of such processes is fundamental for their control and possible exploitation in future technological applications. Most of the experimental studies of the intramolecular charge transfer processes so far have been carried out using time-resolved optical spectroscopies onlarge molecular ensembles. This hampers detailed understanding of the charge transfer on the single molecular level.

Here we build upon the recent progress in scanning probe microscopy, and demonstrate the control of mixed valence state. We report observation of single electron transfer between two ferrocene redox centers within a single molecule and the detection of energy dissipation associated with the single electron transfer.

We demonstrate that we can indeed use AFM to create and probe mixedvalence state of a molecule. The sensitivity of AFM to the mixed-valence state is tightly related to electron transfer between different redox centers within a single molecule, induced by the oscillating probe of the microscope (see Fig. 1).

AFM allows us to detect underlying energy dissipation to the environment. The back action of single electron tunneling between two redox centers on an oscillating scanning probe allows us to determine both the average switching rate and dissipated energy as a function of temperature.

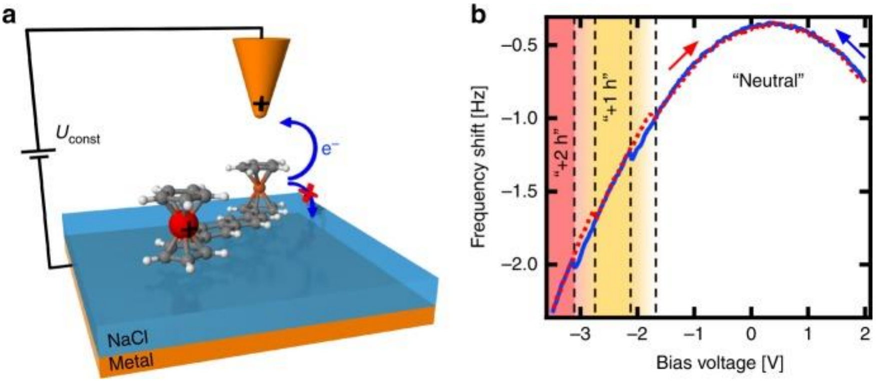

Fig. 1. Charging of the molecule.

a Schematic view of the experimental setup, showing the definition of the sample voltage U, transport of electrons into the tip as well as within an adsorbed molecule. Thick layer of NaCl prevents tunneling current between bisFc molecules and the metallic substrate.

b Charging parabola (blue solid line) taken above a bisFc molecule. Jumps in the parabola denote the extraction of an electron from the bisFc molecule, which bringsthe molecule to the once (U = −2.1 V) and twice (U = −3.1 V) positively charged states (light orange and light red regions). Discharging parabola (red dotted line) jumps are shifted in comparison with charging ones, creating hysteresis of charging. Jumps in parabola denote insertion of an electron to the bisFc molecule, which brings the molecule to the once positively charged (U = −2.8 V) and neutral states (U = −1.8 V).

Conformational effects in chemi-ionisation reactions in the gas phase

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Conformers are the dominant isomers of complex molecules. The conformation of a molecule can have pronounced effects on its chemical reactivity. However, because they often interconvert into one another under ambient conditions, individual molecular conformations are difficult to isolate. Consequently, only sparse experimental data exists on the chemical properties of distinct conformers [1]. Over the past years, we have developed experimental methods to study conformational effects in ion-molecule reactions under single-collision conditions [2,3]. Extending our methodology to neutral reactions, we have recently built a new crossed-molecular-beam setup equipped with an electrostatic deflector which enables the spatial separation of different conformers or individual rotational states of molecules based on their effective dipole moments. The products of chemical reactions of the separated conformers are monitored by time-of-flight mass spectrometry (TOF-MS) and velocity-mapped ion imaging (VMI) [4]. As a first application of this new method, rotational-state and conformationally specific chemiionisation reactions of carbonyl sulfide (OCS) and hydroquinone with metastable neon atoms were investigated. Pronounced state- and conformation-specific effects on the product branching ratios of both reactions were observed. Our result suggests that OCS molecules in the rotational ground state $j = 0$ are a factor of 2.5 more reactive for dissociative ionisation than Penning ionisation compared to the $j = 1$ state. Similarly, cis-hydroquinone shows a stronger propensity for dissociative ionization in comparison to Penning ionisation than transhydroquinone. Moreover, in a collaboration with the Korean Advanced Institute of Science and Technology (KAIST), we are currently undertaking a comparative study of the photochemistry, photoionisation and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene as a prototypical system. These investigations aim to gain a comprehensive understanding of the role of molecular conformations in unimolecular and bimolecular reactivity.

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Dissociative Electron Attachment Studies with Nitro-heterocyclic aromatics compounds

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Nitro-heterocyclic aromatic compounds are bio-relevant molecules and have a wide range of applications in the medical industry. Due to their specific toxicity, which is defined by their reduction to the biologically active form in the lack of oxygen, these compounds play a crucial role in targeting the hypoxic tumor cell during cancer treatment [1, 2]. The basic mechanism is attributed to the reduction of the nitro group by nitro reductases, producing the electrophilic intermediates nitroso and hydroxylamine, which are capable of binding to DNA and other biomolecules in microorganisms.

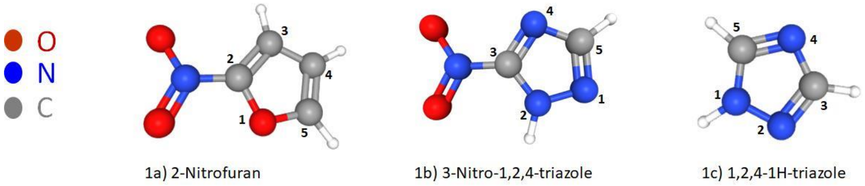

Figure 1. The schematic representation of molecules, 2-nitrofuran, 3-Nitro-1,2,4-triazole, and 1 2,4-1H-Trizole, are shown respectively.

In the present project, we studied the formation of anions following electron attachment to nitroheterocyclic compounds in the gas phase. By using crossed electron/molecular beams experiments with mass spectrometric detection of the anions, we studied 2-Nitrofuran, 3-Nitro-1,2,4-triazole, and 1H- 1,2,4-triazole molecules (see Fig. 1a, 1b, and 1c respectively), the nitrofurans containing a furan ring with a nitro group attached. Both dissociative electron attachment (DEA) and non-dissociative electron attachment were observed. The obtained results of electron attachment to 2-Nitrofuran (C4H3NO3), which is considered as a potential radiosensitizer candidate for application in radiotherapy, indicate that low-energy electrons with kinetic energies of 0–12 eV effectively decompose the molecule and leads to a large variety of charged fragments and radicals with NO2 – as the most abundant fragment anion. The experimental study was supported by thermochemical threshold calculations [3].

This work was supported by the FWF, Vienna (P30332)

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Complex Formation in Three-Body Reactions of Cl^- with H_2

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Dihydrogen halide clusters are the subject of various theoretical and experimental studies [1]. In their anionic state they are weakly bound complexes and can provide insight into dynamical processes in chemical reactions. Here we report the three-body reaction rate of Cl^- with H_2 forming the $Cl^-(H_2)$ complex, as well as the temperature dependence of this reaction in the range of 10 – 26K [2]. Furthermore, we observe the back-reaction with an unexpected dependence to the third power of the density. Comparisons of the experiment in a 22-pole rod and a newly installed 16-pole wire trap [3] are presented and show that the ions reach lower temperature in the 16-pole trap.
We have recently also observed a three-body process in the reaction of C_2^- with two H_2 which leads to the product C_2H^-. In the future we plan on expanding the research of three-body reactions at low temperatures. One focus will be the influence of the nuclear spin state of hydrogen on three-body reaction rates.

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Proton Transfer From ArH^+ to Methanol and Acetone

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Proton transfer reactions (PTR) from H_3O^+ are widely used to monitor organic compounds in the atmosphere.[1] To utilize PTR for high purity gas analysis, proton donors with small proton affinities, such as ArH^+ and N_2H^+, are necessary to quantify impurities like CO, CO_2, H_2O, as well as hydrocarbons. In an effort to record proton transfer rates to molecules relevant in gas analysis, unexpectedly complex reaction profiles for ArH^+ with methanol and acetone were observed.
Experiments on PTRs of ArH^+ to acetone were performed on a 4.7 T FT-ICR-MS, which revealed formation of $C_2H_3O^+$, $C_3H_5^+$, and protonated formaldehyde in addition to protonated acetone. Methanol forms, apart from $CH_3OH_2^+$, protonated formaldehyde. In a secondary reaction, protonated dimethyl ether is formed. Quantum chemical calculations reveal the most probable reaction pathways.

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Conformationally-selected ions for reactions with conformationally-selected molecules

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

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Selection and control of (bio)nanoparticles with electric fields

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Single-particle imaging (SPI) experiments at free-electron lasers (FELs) promise high-resolutionimaging of the structure and dynamics of nanoparticles and macromolecules. Guiding sample particles into the focus of an FEL, diffraction patterns of individual particles can be collected. Sufficient amounts of patterns of identical nanoparticles are needed to overcome the inherently small signal-to-noise ratio and reconstruct the underlying 3D structure. Size-optimized delivery of identical nanoparticles is key to efficient and successful SPI experiments. Here, we present approaches for the production of purified high-density beams of a broad variety of biological nanoparticles. We establish control through electric fields, aiming at charge state or conformational state selectivity. This is especially relevant for soft biological samples, such as proteins or protein complexes, which in uncontrolled environment are prone to structural instability

Low-energy reactive collisions of all stable molecular hydrogen isotopologues: branching ratios, deviation from Langevin behavior and kinetic energy analysis of the products.

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The study of low-temperature collisions between small molecules, molecular hydrogen in particular, is crucial to understand the chemistry of interstellar clouds, characterized by temperatures typically in the 3 K to 60 K range. These studies can also be used to test theoretical predictions about the reaction rates, and the product branching ratios and kinetic-energy distributions [1]. The ion-molecule capture rates are well described by the semi-classical Langevin theory at high to moderate energy, but deviations at low energies are predicted, and experimentally observed [1,2,3].

Low-energy collisions of molecules with ions are difficult to study directly because stray fields heat the ions up. This difficulty is circumvented by replacing the ions with the corresponding parent neutral molecule in highly excited Rydberg states. The Rydberg electron, very far from the core and loosely bound, shields the ion core from external fields while having negligible impact on its reactions with neutral molecules located within the Rydberg-electron orbit [3,4]. To reach low collision energies, velocity-tunable supersonic beams of the reactants are merged.

The Rydberg states are produced in one of the two beams by photoexcitation in the presence of an electric field and subsequently velocity selected and deflected using a curved chip-based surfaceelectrode deflector [5]. This deflector allows us to merge the Rydberg molecular beam with a supersonic beam of the ground-state neutral molecules. The relative and absolute axial velocity of the reactants can also be varied by adjusting the velocity selected by the deflector, by adjusting the delays between the openings of the valves, and by changing their temperatures. The fact that the longitudinal velocity spread of the molecular beams rapidly evolve into a spatial dispersion enables a high collisionenergy resolution and studies at collision energies below 1 K, where the reaction rates are enhanced relative to the Langevin capture rate for a pure ion-induced dipole interaction [1,2].

We report on experimental studies of low-energy ion-molecule reactions between the neutral molecules H_2, HD, and D_2 and the molecular ions H_2^+, HD^+, D_2^+. Differences resulting from nuclear-spin symmetry were investigated by exchanging natural H_2 with enriched para H_2. The entirety of studied reaction systems allow systematic quantitative studies on the enhancement effect for systems of different reduced masses and rotational-state occupations of the ground-state reactant and could be explained by ion-quadrupole interaction and quantum-capture contributions. The studies also allow the determination of the branching ratios to test simple theoretical models, a combinatorial approach, a model describing the reactions as H-, H+-, D-, and D+-transfer processes, and a statistical model relating the reaction rate coefficients to the translational and rovibrational state densities of the product channels.

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Investigation of the interaction of formic acid with flat and stepped palladium surfaces

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Understanding heterogeneous catalysis is based on knowing the energetic stability of adsorbed reactants, intermediates, and products as well as the energetic barriers separating them. Formic acid (HCOOH) for example is a potential hydrogen carrier and its decomposition on transition metals such as platinum or palladium is important to derive insights into the development of direct formic acid fuel cells. While the HCOOH chemistry was investigated especially under oxidative conditions[1], less attention has been paid to oxygen lean conditions which are more representative to industrial applications. The decomposition on the bare metal surface has been mostly covered by theoretical studies[2], but critical comparison to experimental rates are rare.

Here, we investigate the interaction of formic acid with atomically flat and stepped palladium surfaces by using Velocity-Resolved Kinetics (VRK)[3]. We obtain accurate rates for formic acid desorption as well as CO_2 formation. Substitution of the C-end hydrogen with deuterium guides us to the key intermediates participating in the decomposition process. We identify key intermediates and quantify reaction barriers with support of DFT calculations. Our results indicate that step sites increase the conversion of formic acid to CO_2 and H_2.

Furthermore, formic acid decomposition also yields the formation of hyperthermal CO_2. This dynamic component has only been observed for CO oxidation before while we clearly discard a contribution of this reaction to our results. However, the formation of hyperthermal CO_2 might be intermediate and/or site selective.

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Towards Elementary Rate Constants of Water Formation from the Reaction of Hydrogen and Oxygen on Palladium

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Even though the interaction of hydrogen and oxygen adsorbed on single crystal palladium surfaces has been studied in great detail,[1] there is still uncertainty about the elementary chemical processes which govern the catalytic action.

The mechanism of water formation is studied under ultra-high vacuum conditions by either dosing the oxygen atom covered surface with a temporally narrow molecular pulse of H2 (30 μs) or by dosing the hydrogen atom covered surface with a pulse of O2. The transient kinetics of water formation is obtained by applying the velocity resolved kinetics[2] method, which allows for direct measurement of the reactive flux.

Both experiments lead to fundamentally different kinetic behavior. Using the tools of rigorous kinetic modeling and advanced application of transition state theory allows for extraction of elementary energetic parameters. These can be used directly for testing density functional theory calculations.

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Low-energy electron dissociation of esters of 2′-Deoxycytidine 3’,5′-diphosphate and 2′- Deoxycytidine 5′-monophosphate

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The ionization of water caused by interaction of high-energy radiation with living cells results in the creation of highly reactive oxygen species (ROS), which can react with DNA, and also in the production of a large number of secondary low-energy electrons (LEEs), with an energy distribution peaking around 10 eV. LEEs may contribute to DNA damage in this energy range by inducing primarily single- and double-strand breaks via dissociative electron attachment (DEA) [1,2]. When a molecule resonantly captures an electron, a transient negative ion (TNI) is formed, which can decay into anionic fragments and neutral radicals [1,3]. Thus, the action of LEEs seems to be decisive for radiation damage to biological systems [4]. According to Berdys et al. [5] low energy resonances of 2’-deoycytidine (dC) may lead to dC decomposition via electron transfer from the initial π* radical anion to the σ* orbital of the C3’-O or C5’-O bond . It has been suggested that low energy DEA reactions may result in SSBs in DNA, either through direct electron attachment to the phosphodiester backbone and cleavage of the C–O bond between the sugar and the phosphate moiety or through initial electron capture by DNA base followed by the transfer of the excess electron to the DNA backbone [5-7]. In the current study, we investigated DEA to the ethyl esters of 2′-deoxycytidine 3’,5′- diphosphate (dCDP) (molecular mass 499 u) and 2′-deoxycytidine 5′-monophosphate (dCMP) (molecular mass 363 u), using a crossed electron-molecular beam system coupled with a quadrupole mass spectrometer. The sample vapour was introduced in the interaction region of a hemispherical electron monochromator (HEM) via a 1 mm stainless-steel capillary and crosses an electron beam. The HEM was used to form an electron beam with an energy resolution of 120 meV at full width at half maximum (FWHM) and an incident electron current of 10–30nA. A weak electrostatic field extracted the formed anions to the quadrupole mass spectrometer (QMS). They were analysed in the QMS based on their mass-to-charge ratio. Subsequently, the mass-separated anions were detected using a channeltron-type secondary electron multiplier set to single pulse counting. The ion yields depict the intensity of a given mass-separated anion in a function of incident electron energy. At ~0eV, the electron energy scale and resolution were determined by monitoring the well-known resonances for the formation of SF6– from SF6 and Cl– from CCl4. Finally, electrons passing through the interaction region were collected using a Faraday plate, and the obtained current was measured with a picoammeter.

We observed 8 fragment anions, which indicate that low-energy electrons with kinetic energies ranging from 0 to 12eV decompose heavily the studied esters. The current findings show that in the esterified nucleotides, low energy electron attachment causes the break of the CX’-O bond not only via electron localization on the phosphate unit, but also on cytosine which confirms electron-transfer mechanisms of electron-induced DNA strand breaks.

This work was partially supported by the FWF (P30332, I 5390).

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

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The combination of crossed beams with kinematically complete velocity map imaging is a powerful tool to obtain experimental insight into reaction dynamics. The obtained differential cross sections can be linked to atomistic reaction mechanisms. We are investigating reactive scattering of CH_3I with atomic oxygen anions. Energy dependent experiments ranging from 0.4 eV to 2 eV relative collision energy revealed four reaction pathways with different atomistic mechanisms. Here we report recent results on the reaction of a radical anion reaction: O^- reacting with CH_3I. We discuss energy-dependent differential cross sections and branching ratios for four observed, competing reaction pathways.

Spectroscopy and vibrational state control of C_2^- in a cryogenic wire trap

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Control of the motion and internal states of molecular anions plays an important role in many fields such as cold chemistry, astrochemistry and high-resolution spectroscopy. Anions are commonly cooled via collisions with neutral atoms, which thermalize with a cryostat attaining temperatures of about 4 K[1]. To overcome this limit, it was proposed to sympathetically cool anions via laser cooling of the molecular anion C_2^- [2]. This, in addition to its potential role in forming carbon chain anions in the interstellar medium, makes C_2^- an important molecule in anion research.

In this contribution we present a newly developed 16-pole cryogenic radio frequency wire trap for spectroscopic and kinetic studies of molecular anions.

We studied transitions between the electronic ground state and second excited state of C_2^- using a cw diode laser and are able to resolve spin-rotation splitting. Also measurements where the amount of molecules in the first vibrational state of C_2^- are tuned via cold collisions with H_2 are presented.

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Disentangling the relationship between S_N2 and E2 reactions in ethyl halides

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The bimolecular nucleophilic substitution reaction (S_N2) and bimolecular elimination reaction (E2) are two essential reaction types in organic chemistry. [1] As both reactions lead to the same ionic product, it is inherently difficult to distinguish between them solely with experimental approaches. In an attempt to overcome this experimental deficiency, we measured the reaction of fluoride with iodoethane and its fully β-carbon-fluorinated counterpart. This leads to the complete suppression of the E2 pathway. Here, we report the results of the reactions in the gas phase at four collision energies between 0.4 and 2 eV. For these measurements, we employed a crossed molecular beam setup combined with a velocity map imaging spectrometer. The obtained energy and angle differential cross sections can reveal a mechanistic understanding of reaction dynamics on an atomic level [2], especially in cooperation with state-of-the-art theory. [3] In the present experiment we observe an increased signal in the proton transfer channel and at higher collision energies the formation of CF_2CI^-. Both reaction pathways originate from an attack on a α-carbon hydrogen. In CH_3CH_2I this would most likely lead to a hydrogen migration along the C-C bond and a subsequent E2 breakup.

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Experimental setup towards High-Resolution Ion-Molecule Crossed Beam Imaging

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Detailed insight into the dynamics of elementary reactions in the gas phase can be obtained from crossed-beam reactive scattering experiments. Crossed beam combined with velocity map imaging (VMI), angle and energy differential cross sections can be obtained [1][2]. In this contribution, we present the design plan and relevant simulations for an experimental setup to investigate ion molecule reactions with higher precision than previously attainable. The ions will be created by laser ionization so that they are mostly in the vibrational ground state[3]. In addition, according to our simulation, a proper shaping of the ionization volume and a very weak acceleration of the ions play a crucial role in deciding the ion beam energy resolution. The beam is overlapped withthe beam of neutral molecules and the collision products are collected by theVMI spectrometer. We also plan a coincidence detection of both the ionic and neutral products after the reaction, which will be further implemented by a laser ionization scheme. With our new setup, we plan to study fundamental astrophysically significant reactions such as $H_2^+ + H_2 \rightarrow H_3^+ + H$.

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Impact of an impurity on the thermalization of water nanodroplets

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Abstract

A large number of molecules are present in the earth atmosphere and some of them are key to aerosol formation in the atmosphere. The concentration of some of these organic molecules, such as pyridine, has recently increased significantly [1, 2, 3, and 4] due to human activities and therefore may contribute significantly to a change in atmospheric aerosol formation. Pyridine (C_5H_5N) is a hydrophobic molecule and the pyridinium-water clusters are thus of interest since water plays a key role in the aerosol nucleation [5, 6].

The Molecular-Cluster Irradiation Device (DIAM) at the *Institut de Physique des 2 Infinis de Lyon* is dedicated to the study of out-of-equilibrium mass- and energy- selected molecular cluster ions [7, 8]. The evaporation of water molecules from out-of-equilibrium pyridinium-water cluster ions is studied here using the correlated ion and neutral time-of-flight mass spectrometer technique (COINTOF) in combination with a velocity-map imaging (VMI) method [9]. The role of the pyridium versus hydronium ion in such water nanodroplets is investigated in the present

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study. The results highlight the importance of the ion-molecule interactions in the thermalization process, a question that is of interest for atmospheric and biological phenomena especially when water is involved.

Keywords :
Pyridinium, water clusters, out-of-equilibrium dynamics, aerosol formation.

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Metal cluster matter-wave interferometry

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Vienna's Long-Baseline Universal Matter-wave Interferometer (LUMI) has successfully demonstrated interference of massive molecules consisting of up to 2000 atoms and with masses up to 28.000 amu [1]. LUMI's high force sensitivity has also been used to sense electronic, optical, magnetic and structural properties of a very diverse class of particles. For example, measuring the diamagnetic susceptibility of barium and strontium [2] or the polarizability of fullerenes with improved accuracy to previous measurements [3]. Most recently we have used a magnetic gradient field to measure interferometrically the phase shifts of cesium and rubidium atoms according to their hyperfine structure.

Upgrading our interferometer to an all-optical setup using three 266 nm UV-lasers as beam splitters will allow us to exploit a wide range of metal clusters. In addition, we are working on the preparation of a stable metal cluster beam using a magnetron sputtering aggregation source. We are currently investigating beam characteristics such as the velocity distribution, divergence and temperature, but also internal cluster properties. First measurements of depletion efficiencies, optical absorption cross-sections and velocity distributions were carried out for different size-selected metal clusters. Considering our requirements, we found Hafnium and Yttrium to be promising candidates. I will show our preliminary results and explain how we will proceed to use them in our matter-wave interferometer.

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π*/σ* coupling in DEA velocity map imaging of unsaturated chlorohydrocarbons

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We report on a velocity map imaging study of Cl^- anions resulting from the dissociative electron attachment to four unsaturated chlorohydrocarbons. In all four molecules, this process is mediated by the formation of the lowest shape resonance. The choice of the molecules was motivated by the different character of this resonance. In the planar compounds chlorobenzene and vinyl chloride, it is a π^* resonance, which is not dissociative along the C-Cl bond without distortion of the planar geometry. In the nonplanar compounds benzyl chloride and allyl chloride, the shape resonance has a mixed π^*-σ^* character and is directly dissociative without the need for any additional distortion.

Our motivation was to find out whether the dissociation-allowing nuclear motion has a common imprint in the resulting fragment angular distributions. In spite of the expected similarities between the two classes of compounds, the resulting images are quite different for all four molecules. We interpret the results, especially the imprints of the bending dynamics, with the aid of a single-electronic-state model in the axial recoil approximation. [1]

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