ABSTRACT BOOK

STEREODYNAMICS2022

30 OCTOBER TO 4 NOVEMBER

RETHYMNON, Crete, Greece

Welcome note

Welcome note

Dear Colleagues and Friends,

It is with great pleasure that I welcome you all to Stereodyanmics 2022 in Rethymno, after a 4-year pause due to the pandemic. I wish you a fruitful and pleasant stay!

October 2022

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Organization

Local Organizers

Dr. Peter Rakitzis, IESL-FORTH & Univ. of Crete, (Greece)
Dr. Petros Samartzis, IESL-FORTH (Greece)
Dr. von Klitzing Wolf, IESL-FORTH (Greece)
Dr. Paris Tzallas, IESL-FORTH (Greece)
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Dr. Peter Rakitzis (Greece)
Dr. Niloufar Shafizadeh (France)
Dr. Steven Stolte (Netherlands)
Dr. Oleg Vasyutinskii (Russia)
Dr. Xueming Yang (China)

Sunday 30 October

18:00–20:00 Welcome reception and registration

Monday 31 October

8:45–9:00	Introduction

Chirality

Chair	**Ivan Powis**
9:00–9:30 **Invited**	**Sandra Eibenberger-Arias** *Rotational state control of chiral molecules.*
9:30–10:00 **Invited**	**Greta Koumarianou** *Gas-phase chirality detection in cryogenic buffer gas cells.*
10:00–10:30 **Invited**	**Ron Naaman** *Chirality and the Electron Spin- The answer to the mystery of oxygen based life.*
10:30–11:00	Coffee break
Chair	**Wes Campbell**
11:00–11:30 **Invited**	**Ivan Powis** *Examination of Intermediate Rydberg States, their Alignment, and Vibronic Dynamics using Resonance Enhanced Multiphoton Photoelectron Circular Dichroism.*
11:30–12:00 **Invited**	**Bernard Pons** *Using time-resolved photoelectron circular dichroism to probe the dynamics of photo-excited chiral molecules.*
12:00–12:20 **Hot Topic**	**Tzu Ling Chen** *Cavity Enhancement of the Circular Dichroism in Non-reciprocal Organic Thin Film Embedded Microcavities.*
12:30 –14:00	Lunch

Mixed Session

Chair	**Helen Chadwick**
15:00–15:30 **Invited**	**Wes Campbell** *Prospects for optical cycling of large, gas-phase, organic molecules.*
15:30–15:50 **Hot Topic**	**Dmitriy Borodin** *NH3 Oxidation on Platinum -- A new mechanism in surface chemistry?*

15:50–16:10 **Hot Topic**	**Baruch Margulis** *Tomography of Feshbach resonance states.*
16:10–16:40 **Invited**	**Laurent Bonnet** *Semiclassical analysis of classical reactive scattering results.*
16:40 – 17:10	Coffee break

Controlled Beams

Chair	**Andriana Tsikritea**
17:10–17:40 **Invited**	**Jolijn Onvlee** *Towards controlled reactive collisions.*
17:40–18:00 **Hot Topic**	**Gil Alexandrowicz** *Coherently manipulating the rotational projection states of ground state hydrogen molecules; from state-resolved molecule-surface scattering experiments towards gas-phase collisions.*
18:00–18:20 **Hot Topic**	**Helen Chadwick** *Stopping molecular rotation using coherent ultra-low-energy magnetic manipulations.*
18:30 – 20:00	Dinner
20:00 – 22:00	Poster session

Tuesday 1 November

Cold Beams

Chair	**Gil Alexandrowicz**
9:00– 9:30 **Invited**	**Frédéric Merkt** *Cold ion chemistry within the orbit of a highly excited Rydberg electron.*
9:30– 10:00 **Invited**	**Sebastian Trippel** *Ultrafast dynamics in microsolvated biomolecular model systems.*
10:00– 10:20 **Hot Topic**	**Andriana Tsikritea** *Probing ion−molecule reactions within the environment of* *Coulomb crystals.*
10:20 – 10:50	Coffee break
Chair	**Jolijn Onvlee**

10:50– 11:20 **Invited**	**Daniel Horke** *Enhancing the chemical sensitivity of gas-phase ultrafast photochemistry*.
11:20– 11:50 **Invited**	**Heather Lewandowski** *Cold Ion-Molecule Reactions Relevant to Astrochemistry.*
11:50– 12:20 **Invited**	**Andreas Osterwalder** *A Travelling Wave Guide as a band-pass velocity filter for Neutral Polar Molecules.*
12:30 – 14:00	Lunch

Reaction Dynamics

Chair	**Richard N. Zare**
15:00– 15:30 **Invited**	**Dora Papp** *Vibrational-, rotational- and stereo-specificity in the dynamics of atom + ethane and N/P-centered SN2 reactions.*
15:30– 15:50 **Invited**	**Morgane Vacher** *Simulations of photo-induced reaction dynamics upon excitation of azobenzene and ionization of ethylene.*
15:50– 16:10 **Hot Topic**	**Gianmarco Vanuzzo** *Crossed beam studies of O and N reactions with small aromatics: the effect of the attack site on the dynamics.*
16:10 – 16:30	Coffee break

Surface Dynamics

Chair	**Arthur Suits**
16:30– 17:00 **Invited**	**Matthew Costen** *Stereodynamics of Scattering of OH at the Gas-Liquid Interface.*
17:00– 17:30 **Invited**	**Ralf Engels** *How to produce polarized Hydrogen/Deuterium Molecules in single Hyperfine Substates.*
17:30– 18:00 **Invited**	**Alec Wodtke** *Tunneling dynamics of up-side down CO on surfaces.*
18:30 – 20:00	Dinner
20:00 – 22:00	Poster session

Wednesday 2 November

Dissociation Dynamics	
Chair	**Theo Kitsopoulos**
9:00– 9:30 **Invited**	**Arthur Suits** *How Far Can a Radical Roam? Quantum Aspects of Roaming Radical Reactions.*
9:30– 9:50 **Hot Topic**	**Chow-Shing Lam** *Probing ultrafast structural dynamics through covariance imaging of laser-induced Coulomb explosions.*
9:50– 10:20 **Invited**	**Oleg Vasyutinskii** *Mechanisms of orbital orientation and alignment in photolysis of polyatomic molecules: the role of geometric phase.*
10:20 – 10:50	Coffee break
Ultrafast processes	
Chair	**Sebastian Trippel**
10:50– 11:10 **Invited**	**Nektarios Papadogiannis** *Ultrafast and coherent multispectral diffraction imaging in the Extreme Ultraviolet.*
11:10– 11:40 **Invited**	**Markus Büscher** *Spin physics in relativistic plasmas: tools and prospects.*
11:40– 12:00 **Hot Topic**	**Francoise Remacle** *Exploiting electronic entanglement for steering stereoselective bond forming in molecules pumped by ultrashort optical pulses.*
12:00 – 13:00	Lunch
13:00 – 22:00	Excursion and Conference dinner

Thursday 3 November

Exotic Stereodynamics

Chair	**Markus Büscher**
9:00– 9:30 **Invited**	**Benoît Darquié** *High-resolution spectroscopy of cold molecules for precision measurements and tests of fundamental physics.*
9:30– 10:00 **Invited**	**Anastasia Borschevsky** *Testing the Standard Model with Molecules.*
10:00– 10:20 **Hot Topic**	**Boy Lankhaar** *Stereodynamics in the Interstellar Medium.*
10:20 – 10:50	Coffee break

Cold/Controlled Stereodynamics

Chair	**Andreas Osterwalder**
10:50– 11:20 **Invited**	**Javier Aoiz** *Stereodynamical effects in cold energy collisions.*
11:20– 11:40 **Hot Topic**	**Junwen Zou** *Probing van der Waals interactions between Rydberg atoms and polar molecules by FRET at temperatures below 100 mK.*
11:40– 12:10 **Invited**	**Richard N. Zare** *Cold Collision Stereodynamics.*
12:30 – 14:00	Lunch + Stereodynamics board meeting

Mixed Session

Chair	**Sebastian Trippel**
15:00– 15:20 **Hot Topic**	**Niloufar Shafizadeh** *Small ligand binding to heme from first principles.*
15:20– 15:40 **Hot Topic**	**Dominik Stemer** *Liquid-Phase Photoelectron Circular Dichroism.*
15:40– 16:00 **Invited**	**Ioannis Kominis** *Quantum Sensing with Atoms and Living Systems.*
16:00 – 16:40	Coffee Break

Ions

Chair	**Niloufar Shafizadeh**
16:40– 17:00 **Hot Topic**	**Tobias Sixt** *Mechanistic insights into the chemi-ionization of lithium atoms by highly excited helium atoms.*
17:00– 17:20 **Hot Topic**	**Sang Kyu Kim** *Chemical Dynamics of Nonvalence-Bound State of the Molecule Anions.*
17:20 – 17:40 **Hot Topic**	**Jannik Lübke** *Electric-field control of biological macromolecules and the recording of "molecular movies".*
17:40 – 18:20	Break
Chair	**Raphy Levine**
18:20 – 19:20	**Bernstein Award Winner Presentation** **Tanya Zelevinsky** *Photodissociation and high-precision spectroscopy of trapped ultracold molecules.*
19:20 – 21:30	Dinner

Friday 4 November

Quantum Chemistry/Dynamics

Chair	**David Chandler**
8:30– 8:50 **Hot Topic**	**Foudhil Bouakline** *On the role of nuclear permutation symmetry in quantum molecular dynamics.*
8:50– 9:10 **Hot Topic**	**Pei-Ling Luo** *Microsecond time-resolved dual-comb spectroscopy for kinetic and product studies of gas-phase reactions.*
9:10– 9:40 **Hot Topic**	**Martin Fournier** *NO(A)-He and NO(A)-Ne steric scattering experiments.*
9:40 – 10:00	Coffee break

Dynamics

Chair	**Heather Lewandowski**

10:00– 10:20 **Hot Topic**	**Mengxu Jiang** *Multiphoton breakdown of acetylene; Formation of organic building block fragments.*
10:20– 10:40 **Invited**	**David Chandler** *New Applications of Velocity-Mapped Ion and Electron Imaging.*
10:40	Closing remarks

Poster List

P.1 Time-resolved Coulomb explosion imaging of inner-shell excited state dynamics in CH_2I_2 and CH_2BrI
Castellani Maria Elena

P.2 Inelastic collision dynamics of oriented NO(X) molecules
Featherstone Josh

P.3 Investigation of the interaction of formic acid with flat and stepped palladium surfaces
Fingerhut Jan

P.4 Novel developments in optimizing radiation-gas jet interactions by micro-fabricated nozzles
Janssen Maurce

P.5 Cavity Enhanced Absorption Spectroscopy in Atomic Iodine at 1315nm: first measurement of the E2 component
Katsoprinakis Georgios

P.6 Recombination of hydrogen atoms at metal surfaces - A step towards predictive surface chemistry
Kitsopoulos Theofanis

P.7 Selection and control of (bio)nanoparticles with electric fields
Kupper Jochen

P.8 Studying rotational-state and conformational effects in chemi-ionisation reactions
Mizhra Amit

P.9 Quantum-logic control of complex molecular ions for applications in molecular and chemical physics
Paliwal Prerna

P.10 Vector-Model semiclassical wavefunction: the quantitative pictorial description of angular momentum addition and transformation
Rakitzis Peter

P.11 Wavelength- and Intensity-Dependence of Strong Field Ionization and Fragmentation Dynamics of Argon-dimer
Sen Arnab

P.12 How water changes the photophysics of small model chromophores
Trippel Sebastian

P.13 Conformationally-selected ions for reactions with conformationally-selected molecules
Xu Lei

P.14 Cavity enhanced chiral optical rotation
Xygkis Michail

P.15 Ultrahigh-density spin-polarized hydrogen from the photodissociation of hydrogen halides
Xygkis Michail

Rotational state control of chiral molecules

Sandra Eibenberger-Arias
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

I report on the recent exploration of novel spectroscopic schemes in order to overcome previous limitations in the transfer efficiency of enantiomer-specific state transfer (ESST).

The ESST method was recently developed using tailored microwave fields [1,2]. It allows to populate or depopulate a rotational state of a chosen enantiomer, providing a way of quantum-controlled chiral separation.

By combining optical methods [3] with microwave spectroscopy, we developed a new spectroscopic scheme that generates maximum population difference between initial and final rotational levels and enhances the sensitivity of the detection method [4]. Our scheme enables a quantitative comparison between experiment and theory for the transfer efficiency of enantiomer-specific state transfer involving the absolute ground state level. Straightforward extensions will allow to create a molecular beam with an enantiomer-pure rotational level, holding great prospects for future spectroscopic and scattering studies.

[1] S. Eibenberger, J. Doyle, D. Patterson, Phys. Rev. Lett. 118, 123002 (2017)
[2] C. Pérez, A. L. Steber, S. R. Domingos, A. Krin, D. Schmitz, M. Schnell, Angew. Chem. Int. Ed. 56, 12512 (2017)
[3] A. O. Hernandez-Castillo, J. Bischoff, J. H. Lee, J. Langenhan, M. Karra, G. Meijer, and S. Eibenberger-Arias, Phys. Chem. Chem. Phys. 23, 7048-7056 (2021)
[4] J. H. Lee, J. Bischoff, A. O. Hernandez-Castillo, B. Sartakov, G. Meijer, and S. Eibenberger-Arias, Phys. Rev. Lett. 128, 173001 (2022)

Return

Gas-phase chirality detection in cryogenic buffer gas cells

G. Koumarianou

Chirality is a property of polyatomic molecules; they possess two versions called enantiomers that are non-superimposable mirror images. Current research focuses on answering two fundamental questions associated with chirality: 1) the origins of homochirality, and 2) measuring the energy difference between enantiomers due to parity violation. The answer to these questions, together with the understanding of its role in biological processes, its potential use as a signature of life in other planets, and its role in drug design, calls for sophisticated experimental tools able to determine precisely the ratio of enantiomers in complex chemical samples. This requires progress in both sensitivity and resolution of current scientific methods. I will discuss our recent experimental results on broadband phase-sensitive spectroscopy for acquiring "chiral" spectra of unknown mixtures and new developments on studying weak chiral effects in the gas phase.

Return

Chirality and the Electron Spin- The answer to the mystery of oxygen based life.

Ron Naaman
Dep. of Chemical and Biological Physics
Weizmann Institute, Rehovot 76100, Israel

Oxygen based life require processes that are spin forbidden, like photosynthesis and respiration. This is a result of the oxygen being in a triplet ground. It was assumed that nature overcomes the spin related barrier for this reaction, by spin orbit coupling induced by metal ions in the enzymes related to these processes. However, it became apparent that some of the enzymes involved do not contain cofactors.

Based on the chiral induced spin selectivity (CISS) effect, we explored the possibility that oxygen related processes occur efficiently due to the spin polarization of the electrons being transferred. Our experiments show that when the electrons being transferred are transmitted through chiral molecules, they are spin polarized and as a result the reactions can occur on the triplet electronic potential surface with no need for spin orbit coupling. The spin alignment also eliminate the production of by products like hydrogen peroxide.

Abstract Chirality is a property of polyatomic molecules; they possess two versions called enantiomers that are non-superimposable mirror images. Current research focuses on answering two fundamental questions associated with chirality: 1) the origins of homochirality, and 2) measuring the energy difference between enantiomers due to parity violation. The answer to these questions, together with the understanding of its role in biological processes, its potential use as a signature of life in other planets, and its role in drug design, calls for sophisticated experimental tools able to determine precisely the ratio of enantiomers in complex chemical samples. This requires progress in both sensitivity and resolution of current scientific methods. I will discuss our recent experimental results on broadband phase-sensitive spectroscopy for acquiring “chiral” spectra of unknown mixtures and new developments on studying weak chiral effects in the gas phase.

Return

Examination of Intermediate Rydberg States, their Alignment, and Vibronic Dynamics using Resonance Enhanced Multiphoton Photoelectron Circular Dichroism.

Ivan Powis
School of Chemistry, University of Nottingham, NG7 2RD UK

Photoelectron circular dichroism (PECD) – an asymmetry in the forward-backward photoelectron angular distributions (PADs) -- has been recorded with state-state vibrational level resolution using S-(+)-fenchone enantiomers and picosecond laser (2+1) resonance enhanced multiphoton ionization (REMPI) via 3*s* and $3p_{x,y,z}$ Rydberg intermediate states. Comparisons with single photon VUV absorption spectra are used to clarify the spectroscopic identification of the REMPI excitation channels and two-photon excitation circular-linear dichroism ratio measurements provide additional corroboration. The 3*p* state decays to the 3*s* state on a picosecond timescale so that, above the 3*p* Rydberg excitation threshold, ionization of vibrationally hot 3*s* states competes with direct $3p^{-1}$ ionization. Complex vibronic dynamics of the $3p \rightarrow 3s$ internal conversion weaken the Rydberg $\Delta v=0$ propensity rule in both the $3p^{-1}$ and $3s^{-1}$ ionization channels. Large variations of the forward-backward chiral asymmetry factors are observed between $\Delta v=0$ and $\Delta v>0$ vibrational transitions, including complete reversal of the preferred direction for photoelectron emission in the laboratory frame, associated to the vibronic dynamics.

A quantitative two-step theoretical model that includes state-specific, two-photon alignment of the Rydberg intermediate state and its subsequent one-photon chiral photoionization dynamics is used to model the three chiral PAD harmonic terms (b_1, b_3, b_5) in the net 3-photon PADs, seeking to develop appreciation and understanding of how the intermediate state influences vibronically selected REMPI-PECD asymmetries. Conversely, the question of what PECD measurements can reveal about the identity and dynamics of the intermediate state can start to be be addressed.

Return

Using time-resolved photoelectron circular dichroism to probe the dynamics of photo-excited chiral molecules

B. Pons
CELIA, University of Bordeaux (France)

Photoionization of randomly oriented chiral molecules by circularly polarized photons leads to an asymmetric photoelectron momentum distribution with respect to the light propagation axis[1-3]. This forward/backward asymmetry, known as PhotoElectron Circular Dichroism (PECD), is highly sensitive to structural and electronic molecular properties, being able to distinguish enantiomers, isomers, vibrational excitation as well as molecular orbitals from which ionization proceeds[4,5]. These observations identified time-resolved (TR)-PECD as a promising candidate for tracking the transient properties of chiral systems at short timescales.

In TR-PECD, a pump pulse launches a wavepacket in electronic state(s) and the subsequent dynamics are pictured by the time-dependency of the PECD resulting from photoionization by a delayed probe pulse. This will be first illustrated at the Conference through the observation of the relaxation dynamics of fenchone and camphor molecules photo-excited in their 3s electronic Rydberg state. We will show how TR-PECD enables to reveal strong isomerism effects which barely show up in the time-resolved photoelectron spectra[6,7]. After this, we will consider methyl-lactate molecules and a newly developed light source providing linearly polarized few-femtosecond UV pulses[8]. Such intrinsically broadband pulses enable to launch a coherent electronic wavepacket among Rydberg states. Electronic beatings initiated by this coherent superposition result in oscillations of the charge density which can be used for chiroptical switching: the net photoelectron current from the initially isotropic sample, imaged by PECD, can be reversed on a sub-10 fs timescale without any structural rearrangement[9].

[1] B. Ritchie, Phys. Rev. A **13**, 1411 (1976)
[2] I. Powis, J. Chem. Phys. **112**, 301 (2000)
[3] N. Böwering *et al*, Phys. Rev. Lett. **86**, 1187 (2001)
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[6] A Comby *et al*, JPCL **7**, 4514 (2016)
[7] V. Blanchet *et al*, PCCP **23**, 25612 (2021)
[8] M. Galli *et al*, Optics Letters **44**, 1308 (2019)
[9] V. Wanie *et al*, submitted (2022)

Return

Cavity Enhancement of the Circular Dichroism in Non-reciprocal Organic Thin Film Embedded Microcavities

T. Chen[1,2], K. A. Parrish[1], J. Rasch[1], A. H. Salij[3], A. Dhavamani[4], F. Zinna[5], M. S. Arnold[3], R. Tempelaar[3], L. D. Bari[5], R. H. Goldsmith[1],
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Controlling optical chirality is essential in broad applications of molecular and bio-sensing and quantum information science. An optical cavity is a straightforward way to amplify chirality in a compact size by directly increasing the light-matter interaction path. However, achieving this control in a cavity has been a challenge because of the reciprocal properties of molecular chirality, which results in a null effect of the optical chirality when the light goes back and forth in a round-trip. Here, we present a new way to achieve this goal. Taking the advantage of the newly developed non-reciprocal chiral organic thin film PTPO, the chirality is preserved upon reflection from a mirror. Consequently, the chiral properties are amplified in a planar microcavity.

The non-reciprocal feature of the PTPO originates from their chiral conjugated phenylene bis-thiophenylpropynone groups which are able to self-assemble into ordered structures during the deposition process. In this work, we built a broadband spectrometer using a white light source to characterize the chiroptical properties of the thin film and PTPO embedded planar microcavities. The non-reciprocal features of the PTPO are clearly observed with the opposite signal of the circular dichroism (CD) spectra when flipping the light incident directions.

An enhancement of chiroptical properties is observed in a planar microcavity, containing the PTPO (thickness 50 nm ~ 200 nm) sandwiched between two dichroic coated mirrors. Having the cavity finesse of ~37 and cavity thickness ~300 nm, 8-15 times amplification of the CD is detected, which shows a great agreement with our prediction. In addition, our studies on the CD dependence of the incident angle and beam size can be compared to the theoretical model, which will help to evaluate the controllability of the optical chirality and further the possibilities of the chiral polariton.

Return

Prospects for optical cycling of large, gas-phase, organic molecules

Wesley C. Campbell[1], Guanming Lao[1], Guo-Zhu Zhu[1], Claire E. Dickerson[1], Benjamin L. Augenbraun[2], Anastassia N. Alexandrova[1], Justin R. Caram[1], Eric R. Hudson[1]
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[2] Harvard University, Cambridge, MA USA

An optical cycling transition in a molecule is an electronic transition in which the upper state preferentially decays back to the original rovibrational state (or states) from which it was excited. Because the laser-induced fluorescence can be repeated many times with a nearly deterministic final internal state, these transitions are useful for laser-driven applications such as Doppler cooling and quantum state preparation and detection of single molecules (i.e. quantum technology applications). I will discuss recent progress toward endowing molecules as large as polycyclic arenes with optical cycling centers [1] and how this progress may continue even when the species involved are so large that rotational lines are no longer optically resolved [2].

[1] Kłos, J.; Kotochigova, *S. Phys. Rev. Research* **2020**, *2*, 013384. Ivanov, M.V. *et al., J. Phys. Chem. Lett.* **2020**, *11*, 6670. Dickerson, C.E.; Guo, H. *et al., Phys. Rev. Lett.* **2021**, *126*, 123002. Zhu, G.-Z. *et al.*, *Nat. Chem.* **2022** *14*, DOI: 10.1038/s41557-022-00998-x. Mitra, D. *et al., J. Phys. Chem. Lett.* **2022**, *13*, 7029.
[2] Campbell, W.C. and Augenbraun, B.L. *J. Mol. Spectrosc.* **2022**, *385*, 111596.

Return

NH_3 Oxidation on Platinum – A new mechanism in surface chemistry?

Dmitriy Borodin[1,2], Oihana Galparsoro[2], Igor Rahinov[3] , Jan Fingerhut[1], Michael Schwarzer[1], Stefan Hörandl[1], Daniel J. Auerbach[2], Sascha Kandratsenka[2], Dirk Schwarzer[2], Hua Guo[4], Theofanis N. Kitsopoulos[1,2] and Alec M. Wodtke[1,2]

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[2]*Department of Dynamics at Surfaces, Max Planck Institute for Natural Sciences, Am Fassberg 11, 37077 Goettingen, Germany*
[3]*Department of Natural Sciences, The Open University of Israel, 4353701 Raanana, Israel*
[4]*Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, USA*

In the Ostwald process ammonia is catalytically oxidized to nitric oxide (NO), which is needed for the production of artificial fertilizer. Under industrial conditions, it is believed that the overall product formation rate is (gas-to-catalyst) transport limited[1], making a detailed study of the surface reaction mechanism *in-operando* very challenging. However, understanding the surface reaction mechanism and being able to characterize the underlying elementary rate constants is highly important to predict and control the selectivity of NO over the formation of unwanted side products like N_2 and N_2O.

In this work we study the kinetics of NH_3 oxidation at well-defined single crystal Platinum surfaces under ultrahigh vacuum conditions. We employ the Velocity Resolved Kinetics method[2] which combines molecular beam surface scattering and ion imaging techniques for precise measurement of thermal surface reaction rates. To understand the oxidation mechanism we require to determine many elementary rate constant such as sticking coefficients, desorption and diffusion coefficients. By slowly increasing the complexity of the studied system we make use of a “ladder principle” which allows us one after another to characterize many elementary constants. This way we already characterized the active-site specific interaction of ammonia on Pt[3] and we managed to characterize the non-reactive interaction between NH_3 and the adsorbed O-atoms[4].

Preliminary analysis of our reaction data suggests that the role of NH_3 diffusion on the Pt surface in highly relevant for the overall NO formation rate. We believe that the activation of NH_3 only happens if the molecule adsorbs in close coordination to the step-edge, which makes this reaction highly regioselective. This situation is very untypical for the standard view on how surface reactions proceed, where it is believed that reactants adsorb anywhere on the catalyst and quickly diffuse to the active site in order to react[5,6].

References

[1] Haas *et al*, *Chem. Eng. Sci.* **260**, 117832 (2022).
[2] Neugebohren *et al*, *Nature* **558**, 280 (2018).
[3] D. Borodin *et al*, *J. Am. Chem. Soc.* **143**, 18305 (2021).
[4] D. Borodin *et al*, *submitted* (2022).
[5] G. Ertl, *Angew. Chem. Int. Ed.* **47**, 3524 (2008).
[6] Henß *et al*, *Science* **363**, 715 (2019).

Return

Tomography of Feshbach resonance states

Baruch Margulis[1], Karl Horn[2], Daniel Reich[2], Meenu Upadhyay[3],
Markus Meuwly[3], Christiane Koch[2] and Edvardas Narevicius[1]
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Quantum phenomena that lead to the formation of long-lived collision complexes, such as scattering resonances, play a central role in the outcome of cold molecular collisions. These resonances are fundamental probes of the fine details of internuclear interactions and serve as a benchmark for current computational methods.

Here we present a joint experimental and theoretical study where we are able to generate and investigate the multi-channel decay of a Feshbach resonance state with quantum state-to-state resolution. Our method is based on the coincidence detection of electron/ion momenta in Penning ionization collisions between metastable noble gas atoms and neutral molecules. At the ionization step of the dynamics, the molecular ion-neutral atom system is generated in a specific Feshbach resonance state which is identified by the kinetic energy of the ejected electron. The kinetic energy of the product ions provides information about the decay of each resonance state to a manifold of states labeled by the molecular ion's final vibrational state. Here, in a single measurement, we obtain both the energy and the composition at the continuum of each resonance state. We obtain several tens of quantum numbers per measurement without laser detection schemes.

The experimental results pose a formidable challenge to current computational methods. We show that Feshbach state tomography allows us to probe both the short-range interactions that are responsible for rovibrational and reactive dynamics as well as the long-range part of the potential affecting the energy location of resonances states.

We also present an experimental scheme for control of tomography of the Feshbach states, which is based on the initial constraint of total angular momentum at the Ionization step of the dynamics. The latter is motivated by our recent observation of a partial wave resonance at the lowest state of relative angular momentum.

Return

Semiclassical analysis of classical reactive scattering results

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Data on chemical reactions measurable in crossed molecular beam experiments are deduced from *S*-matrix elements, which are the probability amplitudes to go from a given quantum state of the reagents to a given quantum state of the products. By expressing *S*-matrix elements in terms of Feynman propagator and substituting the latter by the semiclassical van Vleck-Gutzwiller propagator, one can obtain these elements from classical trajectory calculations.[1,2] This approach can then be used as a guide to modify the statistical weights assigned to classical trajectories in the standard analysis of classical trajectory outcomes.[3-6] This strategy is briefly outlined and then applied to two processes, H2/Pd(111) nonactivated sticking,[3,4] and the D + H+ 3 reaction.[5]

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Return

Towards controlled reactive collisions

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One of the important goals in physical chemistry is to get a complete understanding of chemical reactions and the underlying dynamics on a molecular level. Investigating collisions and reactions between individual molecules and atoms in the gas-phase using the crossed molecular beam technique is a well-known approach for this. We use the combination of Zeeman deceleration and Velocity Map Imaging in our crossed-beam setup in order to study these molecular encounters in extremely high detail [1]. The decelerator produces beams of paramagnetic species with a well-defined and tunable velocity, narrow velocity spreads, and a high quantum-state purity, while Velocity Map Imaging in combination with near-threshold ionization enables us to accurately probe the velocity vectors of the scattered products. This powerful combination of techniques enables scattering experiments with extraordinary resolution, thereby unveiling fine details of molecular collisions, such as diffraction oscillations and scattering resonances.

So far, we used this experimental approach to investigate *inelastic* collisions, for instance between carbon atoms and helium atoms [2] or hydrogen molecules. Recently, we started examining *reactive* scattering processes. By measuring the collision-energy dependence of state-to-state differential cross sections, we aim to provide an extremely sensitive test for potential energy surfaces and scattering calculations used to describe the molecular reaction dynamics.

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Coherently manipulating the rotational projection states of ground state hydrogen molecules; from state-resolved molecule-surface scattering experiments towards gas-phase collisions.

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To study how stereodynamic effects influence the outcome of a collision, it is desirable to be able to manipulate the rotational orientation projection states (m_J) of a molecule in a controlled way. Whilst various techniques have been developed to control and study stereodynamics in molecular beams of polar molecules, photo-excited molecules and paramagnetic molecules, achieving this for closed-shell ground state molecules is challenging. A magnetic manipulation technique has been shown to overcome this limitation, and allows the m_J (and nuclear spin projection, m_I) states of ground-state hydrogen molecules to be controlled and measured [1].

In this talk the method for coherently manipulating m_J states will be explained, emphasising the difference between this type of control and trajectory bending state-selection experiments. A surface scattering application of the magnetic manipulation technique will be presented where the scattering matrix, which describes how the magnitude and phase of the wave function components change during a molecule surface collision, has been extracted from the experimental interference pattern [2]. We will also present a recent extension of the experimental magnetic manipulation setup which allows us to study the direct beam in a state-resolved way. This extension allows us to verify the coherent control scheme for different molecular beams, and also paves the way for developing similar magnetic control schemes for gas phase collision experiments, first proof of concept results will be presented.

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Return

Stopping molecular rotation using coherent ultra-low-energy magnetic manipulations.

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The most detailed insights into collisions at a molecular level are provided by quantum state resolved experiments, as they remove the averaging over the many degrees of freedom that can influence the outcome of the collision. One quantum state that was particularly difficult to control for ground state molecules is the rotational orientation projection (m_J) state, restricting stereodynamic collision studies to particular molecules where control techniques have been developed.

In this talk, we will present a recent study of the rotationally inelastic scattering of D_2 from a Cu(111) surface[1]. A magnetic manipulation technique[2] was used to coherently control both the m_J, and m_I (nuclear spin) projection states of the molecules when they arrived at the surface. The probability that a D_2 molecule, originally in the rotational state $J = 2$, will be de-excited into a non-rotating state after a molecule-surface collision, was shown to depend on the quantum super-position state of the impinging molecule. This effectively means that an energy perturbation on the order of peV changed the probability the molecule lost 22 meV of rotational energy in the collision. The results from state of the art calculations predict that only molecules in the $m_J = 0$ state of $J = 2$ undergo this rotationally inelastic transition when D_2 scatters from Cu(111), but this does not reproduce the experimental data, illustrating the importance of these results as benchmarks for the development of accurate modelling of molecule-surface interactions.

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Cold ion chemistry within the orbit of a highly excited Rydberg electron

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The study of ion-molecule reactions at low collision energies (Ecoll) below Ecoll=kB =10 K, or low temperatures, is experimentally challenging because stray electric fields in the reaction volume heat up the ion samples. A potential difference of 1 mV across a reaction region of 1 cm accelerates the ions to 1 meV, which corresponds to heating them up to about 12 K. To overcome this problem and study ion-molecule reactions below 10 K, we have developed a new method, in which the ion molecule reaction takes place within the orbit of a Rydberg electron at high values of the principal quantum number n. In high-n Rydberg states, the Rydberg electron only very weakly interacts with the ion core, so that it does not significantly influence the ion-molecule reaction taking place within its orbit but shields the ion from heating by stray electric fields. Instead of studying exothermic and barrier-free ion-molecule reactions of the type I+ 1 +M1 !I+ 2 +M2; (1) we study the reactions I_1 +M1 !I_2 +M2; (2) in which I_1 and I_2 represent atoms or molecules in high Rydberg states with ion cores I+1 and I+2 , respectively and M1 and M2 are neutral molecules. To reach very low collision energies, we use chip-based Rydberg-Stark decelerators and deflectors to merge cold supersonic beams of I_1 and M1 and to vary their relative velocities [1]. Monitoring the product yield as a function of the relative mean velocity of the two beams, we obtain the relative reaction cross sections as a function of the collision energy. At collision energies (Ecoll=kB) below 1 K, we find that the reaction rate coefficients deviate from those estimated with Langevin-type capture models [2-5]. The talk will present general aspects of this new method as well as the results of studies of the reactions of H+2 and He+ (I+1) with neutral molecules such as N2, H2, CH3F, NH3, NO and CH4 (M1) at very low collision energies and will discuss the observed low-temperature behavior in terms of the electric dipole and quadrupole moments of M1. Our latest efforts at detecting the theoretically predicted [6-9] factor-of-two quantum enhancement of the Langevin rate coefficient at collision energies close to zero will be summarized.

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Ultrafast dynamics in microsolvated biomolecular model systems

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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-light-induced 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.

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Probing ion−molecule reactions within the environment of Coulomb crystals

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Laser-cooled Ca^+ ions, confined in a linear Paul trap, can be used as a cold framework to undertake reactions between sympathetically cooled ions and polar neutrals. In this way, charge transfer reactions between rare gas ions (Xe^+, Kr^+ or Ar^+) and thermal polar molecules (NH_3, ND_3, H_2O or D_2O) have been studied within Coulomb crystals [1-3]. Accompanying the experimental measurements, *ab initio* calculations have shown that the most favourable approach for the water and Kr^+ collisions is when the negative end of the dipole in the neutral reactant approaches the ion [3]. For the ammonia charge transfer reaction systems, no crossing point has been identified between the reactant and product potential energy surfaces—making the reaction mechanism much more challenging to predict [1-2].

To further our understanding of how charge transfer occurs in these reaction systems, the properties of the neutral reactants can be controlled and varied experimentally. We employ supersonic beams of ammonia neutrals, to investigate the effect of the rotational state distribution and the velocity of the ammonia beam on the charge transfer reactions. Building on recent work where the orientation of a buffer gas-cooled and electrostatically guided ammonia beam was measured and manipulated [4], we discuss the prospect of exerting even more control over the properties of the neutral reactants in future studies.

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Enhancing the chemical sensitivity of gas-phase ultrafast photochemistry

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Time-resolved photoelectron spectroscopy has emerged as one of the premier tools to study the complex coupled motion of electrons and nuclei that underlies ultrafast photochemical processes. The chemical sensitivity of the approach has so far, however, been limited to whatever molecular ensemble was produced during the sample evaporation and entrainment into a molecular beam. The incorporation of isomer-selected beams, produced via electrostatic selection, allows us to increase this chemical sensitivity and directly investigate the influence of intramolecular interactions on the ultrafast photochemistry. We will report on our efforts of merging these two approaches and show first results of conformer-dependent dynamics in aryl halides.

A further limitation to studying entire reaction pathways, from reactants through intermediates to products, is the requirement of sufficiently energetic photons to ionize all species involved. This frequently leads to situations where ground state species, such as final products or stable intermediates, are not observed. The advent of high-flux high-harmonic generation sources now allows us to circumvent these problems by using XUV-pulses as a global probe. We demonstrate this approach and follow the dynamics of dissociating CS_2 molecules across the entire reaction pathway upon excitation. We show that, despite being more rapid, the singlet dissociation is the minor product and that triplet state products dominate the final yield. Extending this to larger systems, we will show first results of recent UV-pump XUV-probe studies of acetaldehyde photodissociation with the aim to unravel the competing direct and roaming dissociation channels.

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Cold Ion-Molecule Reactions Relevant to Astrochemistry

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Laboratory measurements of cold ion-molecule reactions contribute to the understanding of dynamics and kinetics in the interstellar medium and planetary atmospheres. To be able to explore these reactions, we trap ions at cold temperatures and react them with neutral molecules in an isolated environment. The products and branching ratios of these reactions are measured with high resolution using a time-of-flight mass spectrometer. Recently, we studied two reactions of interstellar importance CCl^+ + CH_3CN (acetonitrile)[1] and CCl^+ + C_6H_6 (benzene) [2]). Isotopologue substitution and quantum chemical calculations aided in identifying the resulting products and reaction pathways. Both reactions may contribute to the buildup of cyclic carbocations in the interstellar medium. The CCl^+ + benzene reaction, in particular, demonstrates potential as a participant in the growth of larger aromatics that are present in the interstellar medium.

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A Travelling Wave Guide as a band-pass velocity filter for Neutral Polar Molecules

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The resolution in a merged beam experiment depends critically on the velocity spread of the reactants. This defines the range of collision energies probed in any measurement which determines, in particular, the lowest attainable energy when the central velocities of the two beams are the same. Studies from the past years mostly used reactions where charged products were formed. This has the distinct advantage that products which were formed outside the detection region or prior to and after a short extraction pulse were deflected away and not recorded [1,2]. In this way, a resolution was obtained that was significantly better than what would be given by the original velocity spreads of the individual supersonic expansions. This advantage is lost when probing reactions that form neutral products. While also in this case the product can be extracted from a well-defined volume, the previous type of discrimination no longer works: as soon as the packets from the two supersonic expansions overlap they also start to react, and the neutral products are not easily removed from the beam but instead accumulate and are all detected. Unless the two packets move at precisely the same speed, the total relative-velocity distribution becomes a convolution of the two individual distributions. As a consequence, it is critical to perform such experiments using packets with the initial translational temperatures as low as possible. To overcome this problematic situation a new device is proposed to obtain the desired velocity selection: A Travelling Wave Guide for neutral polar molecules. A hexapole guide is segmented in several short elements that are periodically switched on only when molecules with the desired velocity are inside, reminiscent of earlier experiments that used curved velocity filters built from 2-4 segments [3,4]. In that way, the velocity spread of each reactant is significantly reduced, thus increasing the energy resolution of merged beam experiments also in the case of neutral product formation.

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Vibrational-, rotational- and stereo-specificity in the dynamics of atom + ethane and N/P-centered S_N2 reactions

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We develop full-dimensional analytical potential energy surfaces using the ROBOSURFER program package [1], which surfaces allow the accurate quasi-classical dynamical investigations of polyatomic reactive systems. We study the dynamics of the F/Cl + $C_2H_6 \rightarrow$ HF/HCl + C_2H_5 reactions [2,3] and obtain excellent agreement with experiments, this way solving a 25-year-old contradiction for the latter reaction regarding the rotational-state distribution of the HCl product [3]. Vibrational and rotational mode-specificity is also investigated for atom + ethane reactions [4,5,6]. We also study N- and P-centered ion + molecule reactions, namely the F^- + NH_2Cl/PH_2Cl systems, resulting in Cl^- + NH_2F/PH_2F (S_N2 path) and HF + $NHCl^-$/$PHCl^-$ (proton-transfer) products. We find that stereo-specificity, taken for granted at C-centered S_N2-reactions, is undermined in the N-centered case due to the newly-discovered multi-inversion mechanism [7], whereas at P center it is somewhat restored, however, only at low collision energies [8].

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Simulations of photo-induced reaction dynamics upon excitation of azobenzene and ionization of ethylene

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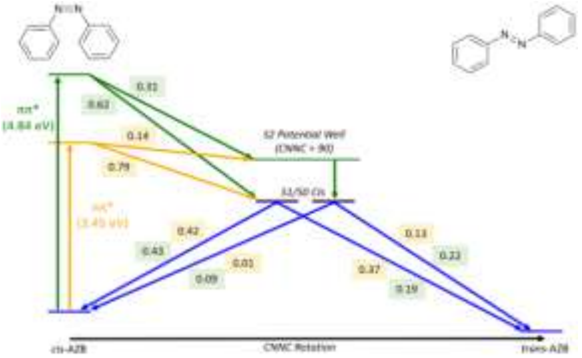
Computer simulations are a key complement to experiments in the laboratory, providing great details of a molecular process than can be observed experimentally. For instance, ab initio molecular dynamics simulations are often key to the understanding of the mechanism, rate and yield of chemical reactions. In this talk, I will present simulations of photochemical and attochemical reactions [1]. In the first part, I will focus on simulations of the cis-to-trans photo-isomerisation of azobenzene, after excitation to the nπ* and ππ* states [2]. A reduction of photoisomerisation quantum yield of 0.10 on exciting to the higher energy ππ* state compared to the lower energy nπ* state is obtained, in close agreement with the most recent experimental values [3]. By direct comparison of both excitations, we have found that the explanation for the decrease in quantum yield is not the same as for the reduction observed in the trans-to-cis photoisomerization (Figure 1, left). In the second part of my talk, I will discuss the dynamics induced in ethylene following ionization by an extreme ultraviolet attosecond pulse train [4]. We have found that isotope labelling can be an efficient tool in attochemistry to identify the relevant nuclear coordinates controlling the relaxation dynamics (Figure 1, right).



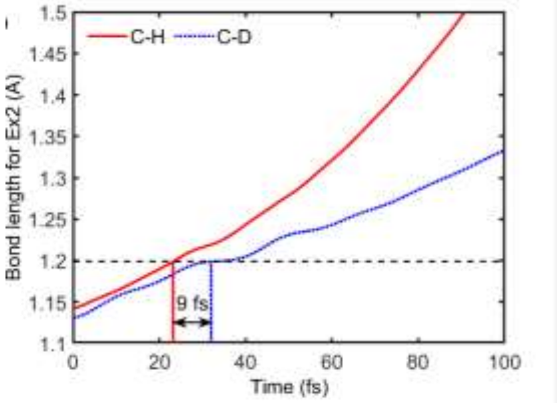


Figure 1. (Left) Major relaxation pathways in the cis-to-trans photoisomerization of azobenzene; (Right) Temporal evolution of the C-H bond upon ionization and excitation of ethylene and its deuterated counterpart.

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Crossed beam studies of O and N reactions with small aromatics: the effect of the attack site on the dynamics

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Given the importance of aromatic compounds in numerous contexts ranging from atmospheric pollution to combustion chemistry and astrochemistry, we have started a systematic investigation of the reactions of atomic oxygen and nitrogen with small aromatic compounds, namely benzene, toluene and pyridine, in our laboratory. These compounds are quite common in the above-mentioned environments and can also be considered simple prototypes for polycyclic aromatic hydrocarbons (PAHs) and nitrogen-containing polycyclic aromatic hydrocarbons (PANHs).
We have employed the crossed molecular beam technique with mass spectrometric detection to identify the reaction mechanism and the branching fractions of the possible reaction products [1]. The interpretation of our experimental results has been supported by dedicated electronic structure calculations of the relevant potential energy surfaces and statistical estimates of product branching fractions (see, for instance, [2-5]). Remarkably, according to our experimental results the presence of a nitrogen atom in the aromatic ring increases the probability of a ring contraction and non-aromatic products are preferentially formed in the reactions involving pyridine with respect to the reaction involving benzene ([2] and in preparation). This can be rationalized by considering the different reactivity of the *ortho*-, *meta*-, *para*- and even *ipso*- approach in the case of pyridine. On the contrary, the presence of a methyl group attached to the aromatic ring allows preservation of the aromaticity of the products in the reaction of nitrogen and oxygen atoms with toluene compared to the case of benzene where ring contraction has also been observed [3-6].

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Stereodynamics of Scattering of OH at the Gas-Liquid Interface

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Gas-Liquid interfaces, and the heterogeneous processes that occur at them, have been the subject of much less experimental and theoretical study than the gas-phase or gas-solid interface. Relatively little is known about the structure of liquid surfaces, and the interplay between the surface structure and the elementary chemical processes resulting from gas-liquid interaction. In recent years, new experimental techniques and theoretical methodologies have begun to provide detailed understanding in this area

We have developed a gas-liquid scattering apparatus with planar-laser-induced fluorescence imaging of the real-space scattering distribution. Combined with a pulsed supersonic DC discharge source of OH, we have used this apparatus to study the dynamics of the inelastic collisions of OH radicals with inert liquid surfaces, namely perfluoropolyether, and reactive hydrocarbon surfaces, namely squalane (saturated) and, squalene (unsaturated).

Analysis of images taken in a time-series that spans before and after collision reveals that the OH radicals are scattered from all 3 liquids, and for both normal and 45° incident angles, with a predominately superthermal speed distribution, with no strong evidence for a substantial thermalized component. Angular scattering distributions are determined from both time-series and single-time images for each incident angle, each liquid and as a function of OH rotational state. Significant anisotropy is observed in the scattering for 45° incident angle, with the scattering angle distribution varying as a function of liquid and final N'. We discuss the observed differences in scattering dynamics in the context of the inelastic and reactive processes occurring at the three liquids.

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How to produce polarized Hydrogen/Deuterium Molecules in single Hyperfine Substates

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Polarized atomic beam sources (ABS's), modified versions of the Rabi apparatus, are used in nuclear physics either to produce nuclear polarized protons/deuterons to be accelerated further or to feed polarized targets. Thus, the spin dependence of the nuclear forces can be investigated directly. Due to the relatively small flux of about 10^{17} atoms/s the density of the gas jet is less than 10^{12} atoms/cm^2. To increase this density up to 10^{14} polarized atoms/cm^2 T-shaped storage cells are an important tool and used since many years at different accelerators.

One problem of this technique is the reactivity of the hydrogen radicals, because during chemical reactions usually a large fraction of the polarization will be lost. To investigate this processes and how to avoid them, especially the recombination into molecules, a dedicated apparatus was built at the research center Jülich. The exchangeable storage cells are mounted inside a superconducting solenoid to produce a magnetic field up to 1 T and to cool the cell to temperatures down to 100 - 40 K. After the recombination of the polarized atoms on different surface materials, the molecules are ionized and electrostatically accelerated to 1-2 keV. The ions in the beam are then filtered by a Wien filter before they reach the Lamb-shift polarimeter, where the occupation numbers of the nucleons with different spin orientations are determined. In this way it was possible to produce H_2, D_2 and even HD molecules and their ions in dedicated hyperfine-substates with polarization values up to P=0.8. In parallel, it is possible to measure the coupling constants between the nuclear spins and the rotational magnetic moment or the shift of the rotation axis between H_2/D_2 and HD. Possible future projects might be the collection of the polarized molecules as ice for further use as polarized fuel in fusion reactors or the measurement of the Breit-Rabi diagram of H_2^+, D_2^+ or HD^+ ions.

Return

Tunneling dynamics of up-side down CO on surfaces

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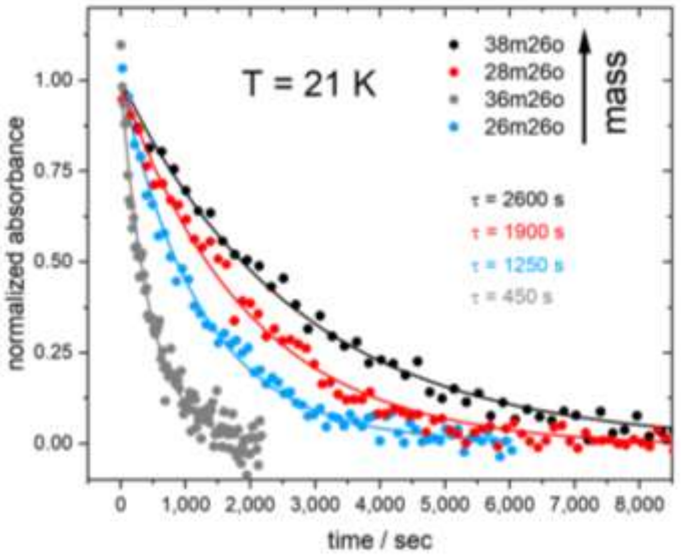
Superconducting nanowire single-photon detectors (SNSPDs) provide sufficient sensitivity to enable laser induced fluorescence (LIF) experiments in the mid-infrared, an exciting technical development for studying molecule-surface interactions. In this talk, I will present results of experiments on the vibrational dynamics of monolayers and multilayers of solid CO adsorbed at the surface of a NaCl crystal that provide observations of quantum state resolved dynamics. When, for example, a pulsed ns laser excites CO to its v=1 state, a monochromator equipped with an SNSPD detects wavelength- and time-resolved mid-infrared emission from CO vibrational states up to v=27 that are produced by vibration-vibration (V-V) energy transfer. Kinetic Monte Carlo (kMC) simulations show that vibrational energy collects in a few CO molecules at the expense of those up to eight lattice sites away. The excited CO molecules relax by a mechanism resembling Sommerfeld's theory of ground waves important to radio wave propagation, losing their energy to NaCl lattice-vibrations via the electromagnetic near-field. This is a weak coupling limit, where the potential energy surface is not needed to describe the relaxation process.



Condensed phase isomerization through tunneling gateways. CO bound by its O-atom to a NaCl (100) surface isomerizes by tunneling through a barrier to the more stable C-bound form.Note that $^{13}C^{16}O$ (grey, m=29) tunnels faster than $^{12}C^{16}O$ (blue, m=28), which is faster than $^{12}C^{18}O$ (red, m=30), which is faster than $^{13}C^{18}O$ (black, m=31). The peculiar mass dependence indicates the importance tunneling

At high resolution, we observe new lines appearing in the infrared emission spectra, showing that CO vibrational energy converts "the right-side up" where CO is bound by its C-atom to the surface to an "up-side down" metastable isomer. Flipping back involves thermally activated tunneling, exhibiting a large isotope effect, where the lightest isotope is not the fastest tunneller. This is explained by a quantum rate theory of isomerization involving tunneling gateways. Near resonant states, localized on opposite sides of the isomerization barrier are coupled by collisions with a phonon bath. This represents an alternative to traditional tunneling pictures like Instanton and WKB, which are based on a continuum scattering picture that is not valid in condensed phases.

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How Far Can a Radical Roam? Quantum Aspects of Roaming Radical Reactions

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Roaming reactions, first identified in formaldehyde dissociation twenty years ago, feature near dissociation to radical fragments followed by reorientation at long range then intramolecular abstraction. These roaming reactions have now been identified in many systems and are now recognized as a common feature of chemical dynamics. Nearly all treatments of roaming have employed classical methods, and these have been largely consistent with experimental results. We will show evidence of quantum roaming resonances in new systematic measurements of formaldehyde photodissociation at the radical threshold and far above it. These are threshold resonances but embedded in dense continua 4 eV above available product channels. The results suggest that such resonances may occur just below the energies at which new channels open for H+HCO, permitting the system to roam to very long range. Owing to the limited state density in HCO, such new channels appear rather infrequently, suggesting that roaming is often confined to shorter range than seen in classical simulations. Implications for roaming in other systems will be explored.

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Probing ultrafast structural dynamics through covariance imaging of laser-induced Coulomb explosions

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Recording the real-time nuclear positions in molecules during structural transformations, has been a long-standing dream in the study of molecular dynamics. Filming ‘molecular movie’ to visualize the photo-induced structural change of molecules is of fundamental interest in understanding the essence of photochemistry, but the required timescale naturally poses formidable challenges [1]. The advent of ultrafast techniques has been trailblazing to elucidate transient evolution of electronic structure accompanied with changing molecular geometry, yet limited to provide definitive pictures anticipated.

Coulomb explosion imaging (CEI) with coincidence detection have been ranked as the most promising movie-making approach by accumulating snapshots of the photochemical process. Through the correlated measurement of multiple charged fragments, which are unambiguously assigned to a single origin, unparalleled structural details in the molecular frame can be deduced. However, this methodology is restricted to low-count rate regime (<1 per laser shot) to avoid false coincidences. Instead, covariance imaging circumvents this constraint by measurement of the joint variability of velocity distributions from two fragments in each laser shot to determine the correlations at high count rate, immensely expedites data acquisition [2].

In this work, nitrobenzene and its methyl- substituted derivatives have been selected to demonstrate the multitude of promising aspects of time-resolved covariance CEI technique. They permit prototypical study for nitro-aromatic compounds, a class which sees wide applications in the field of photoswitches, photolabile protecting groups and NO-donors in vasodilators [3]. Pump-probe covariance CEI studies identify co-fragments and reveal the UV-excitation dynamics in terms of total kinetic energy release. The torsional-dynamic effect of the nitro group on the NO-loss channel, which is a nonadiabatic process complicated by intramolecular rearrangement can be evaluated and conclusive remarks can be made by comparisons with results from time-resolved photoelectron imaging from ref. [4].

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Return

Mechanisms of orbital orientation and alignment in photolysis of polyatomic molecules: the role of geometric phase

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Quantum interference between multiple pathways in molecular photodissociation often results in angular momentum polarization of atomic products and this can give deep insight into fundamental physical processes. For dissociation of diatomic molecules, the resulting orbital polarization is fully understood and consistent with quantum mechanical theory. For polyatomic molecules, however, coherent photofragment orbital polarization is frequently observed but so far has eluded theoretical explanation, and physical insight is lacking.

In this talk we present recent experimental observations of new effects of orbital orientation and alignment of $O(^1D_2)$ atoms produced in photodissociation of ozone within the Hartley band at 266 nm. In particular, we present a direct determination of photofragment alignment produced by circularly polarized light in photolysis of a planar polyatomic molecule. The alignment directly depends on the helicity of the photolysis light and arises via a mechanism involving coherent excitation of two mutually perpendicular in-plane transition dipole moment components.

We show that a key aspect of understanding coherent orbital polarization in dissociation of polyatomic molecules is a recognition that this polarization directly manifests geometric phase effects, and a model we develop incorporating these effects qualitatively accounts for fundamental aspects of ozone photodissocation seen in many experiments. We show this geometric phase effect permits the existence of coherent polarization in cases where it would otherwise vanish, and cancels it in some cases where it might otherwise exist. The model accounts for measurements in ozone that have hitherto defied explanation, and represents a step toward a deeper understanding of coherent electronic excitation in polyatomic molecules and a new role of the geometric phase.

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Ultrafast and coherent multispectral diffraction imaging in the Extreme Ultraviolet

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The rapid evolution of ultrafast laser pulse technology and laser-matter interaction science has resulted in the development of different secondary light sources in the XUV and soft X-ray region of the EM spectrum. Among them the femtosecond laser high harmonic generation in atomic gases has been extensively studied. These XUV semi-coherent ultrafast pulses consist of a comb with frequencies of odd integer multiples of the laser frequency. This light source is an ideal tool for table-top ultrafast coherent diffraction imaging of matter in the nanoscale. Furthermore, multispectral imaging in the visible part of the EM spectrum and longer wavelengths up to thermal infrared is a well-established technique with several applications. In this work we will present a table-top XUV diffraction ultrafast imaging system able to operate in a multispectral mode in the nanoscale. The extension of multispectral imaging to the soft x-ray region of the spectrum in combination with the ultrafast capabilities offered by laser high harmonic pulses could be a valuable tool for real time photochemistry. Future applications of such small-wavelength ultrafast multispectral imaging, combined with femtosecond time-resolved measurements, may allow to assess unexplored areas of science, such as imaging of chemicals at their absorption edges~~;~~.

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Spin physics in relativistic plasmas: tools and prospects

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High-density hyperpolarized atomic or molecular targets – where either the electron or nuclear spins are aligned – have found numerous new areas of applications. A prominent example are laser-generated highly relativistic plasmas that can be used for the acceleration of polarized particle beams to multi-MeV energies, or to optimize fusion energy generation with polarized fuel. This may come as a surprise since the kinetic energies of the plasma particles are many orders larger than the energy differences of the spin states. However, in some cases, the polarization lifetimes can become sufficiently long to be useful for the above-mentioned applications [1].

In my talk I will present our polarized targets (based on HCl molecules for electrons and protons, DBr for deuterons, as well as ^{3}He where the spin is basically carried by a neutron) that we developed for use at PW-class laser facilities. We carried out a pioneering measurement at the Phelix laser of GSI Darmstadt, accelerating $^3\mathrm{He}^{2+}$ ions from a polarized gas jet with a density of a few 10^{19} cm^{-3} [2] and measuring their degree of polarization with a newly developed polarimeter [3]. In the next years we will extend these measurements by using a composite ^{3}He-Deuteron gas target where both nuclear species are polarized with the goal to achieve a proof-of-principle demonstration of the expected polarization enhancement of the fusion rates.

We have also carried out numerical studies – partially on supercomputers – to predict the properties of plasma-accelerated electron [4] and proton [5] beams. All these simulations predict high particle fluxes and multi-MeV energies at high degrees of polarization (typically 50%, depending on the 'starting' polarization in the target). This illustrates the high strategic relevance worldwide of polarized targets for the development of next generation's particle accelerators.

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Exploiting electronic entanglement for steering stereoselective bond forming in molecules pumped by ultrashort optical pulses

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Short attosecond (as) or few femtoseconds (fs) pulses have a broad energy bandwidth which allows exciting a superposition of several electronic states in neutral molecules and molecular cations. The nature of the states excited (valence, Rydberg) can be controlled by tuning the pulse parameters. This opens the way to novel avenues for control by engineering of electronic coherences between selected electronic states to steer charge migration and the stereo selective localization the electronic density on its purely electronic time scale.[1] As the nuclei begin to move, the electronic and nuclear motions are entangled and the engineered electronic coherences can be usefully exploited for steering the vibronic density through the network of non adiabatic interactions to specific products.[2, 3]

In order to design control schemes built on a stereoselective photoexcitation of electronic coherences, we analyze the time evolution of the entanglement between nuclear and electronic degrees of freedom using singular valued decomposition (SVD) of the wave function.[4] At each time step, the wave function is thereby written as a superposition of singular states weighted by their corresponding singular values ordered by their decreasing magnitude. Each singular state is a product of a component that depends only on the nuclear degrees of freedom and a component depending on the electronic coordinates. This singular state is a separable wave function. When more than one singular state is necessary for describing the wave function, it is entangled. This analysis gives valuable insights on how the entanglement of the initial state governs its subsequent modulation by the nuclear motion on coupled electronic states. It is the initial entanglement that can be controlled by the excitation pulse.

We first compare the entangled electron-nuclei dynamics in two diatomic molecules, LiH and N_2, excited by short 2fs UV pulses.[4] If time permits, we will also report preliminary results on the time evolution of the entanglement in the ultrafast structural rearrangement of the methane cation ionized to a superposition of its three lowest electronic states.[2]

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High-resolution spectroscopy of cold molecules for precision measurements and tests of fundamental physics

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There is an increasing demand for precise molecular spectroscopy, in particular in the mid-infrared fingerprint window, whether it be for modelling our atmosphere, interpreting astrophysical spectra or testing fundamental physics.

I will present our efforts towards building new-generation mid-infrared spectrometers specifically designed for precision vibrational spectroscopy of complex polyatomic molecules in the gas phase. This includes amongst other things producing gases of polyatomic species cooled to a few kelvins in cryogenic buffer-gas cells [1] and developing frequency stabilised quantum cascade lasers calibrated to some of the world's best frequency standards [2]. The proposed technologies are at the forefront of cold molecule research and frequency metrology and have allowed us to measure absolute frequencies of a variety of species of atmospheric, astrophysical or fundamental interest with record up to 12-digit accuracies [2,3].

This opens possibilities for using polyatomic molecules to improve tests of fundamental physics and precision measurements in general. I will for instance present our ongoing work towards testing the parity symmetry in cold chiral molecules using precise mid-infrared spectroscopy, *i.e.* by measuring the tiny energy difference between enantiomers induced by electroweak interactions [4].

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Testing the Standard Model with Molecules

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Search for violation of fundamental symmetries provides a unique opportunity for testing the Standard Model. Atomic and molecular experiments offer a low energy and comparatively inexpensive alternative to high energy accelerator research in this field. As the observable effects (such as parity violation, PV) are expected to be very small, highly sensitive systems and extremely precise measurements are required for the success of such measurements.

An important task of theoretical research is to identify optimal molecular and atomic systems for measurements and to understand the mechanisms behind the enhanced sensitivity, which is strongly dependent on the electronic structure. Thus, accurate computational methods are needed in order to provide reliable predictions rather than estimates, and to obtain the various parameters that are required for the interpretation of the experiments.

I will present the results of our recent investigations of molecules in the context of search for parity violating effects. A short overview of the theoretical methods will be provided, but the talk will focus on showcasing the different types of systems (diatomic and chiral molecules) that are promising candidates for experiments that aim to test the Standard Model and perhaps detect new physical phenomena.

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Stereodynamics in the Interstellar Medium

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Molecules in the interstellar medium (ISM) occur in molecular clouds or in the circumstellar envelopes of evolved stars. Here, temperatures are of the order of 10s of Kelvin and number are typically 10000 particles per cubic centimeter. Additionally, and importantly, magnetic fields permeate the ISM, with a strength upwards of 10-100 microGauss. Under these conditions, and under the influence of an anisotropic radiation field, which is abundantly present in the ISM, molecules (such as CO, CS, or SiO) will align themselves with respect to the magnetic field, and consequently emit partially polarized (of some percents) radiation that astronomers use to trace the magnetic field direction in astrophysical regions. Molecular spectral line polarization observations are one of the most robust methods that astronomers can use to detect magnetic fields in astrophysical regions. Information on magnetic fields is valuable, as they are of vital importance to understand accretion and outflow processes in both star forming regions and circumstellar envelopes of evolved stars.

Interpreting polarization signals from molecular spectral lines for their magnetic field information, requires accurate modeling of the stereodynamics of interstellar molecules. In this talk, I present recent progress that has been made in this regard. First, I discuss recent developments of radiative transfer techniques, that may be used to characterize molecular alignment in complex astrophysical regions such as circumstellar disks, outflows or galaxy nuclei. Second, I discuss conditions in the interstellar medium under which directional collisions, leading subsequently to collision-induced alignment, occur. Collision-induced alignment of molecular ions in the ISM is predicted theoretically, and the observational confirmation of this effect would be the first direct confirmation of the process of ‘ambipolar diffusion’: a process that is ubiquitous in astrophysics, has importance to theories of star-formation and turbulent cloud thermodynamics, but has never been directly detected and characterized.

In the talk I will lay emphasis on the molecular physics surrounding these topics. I will point out where stereodynamical modeling of interstellar molecules would benefit from improved theoretical and experimental characterization of the stereodynamics of collisional processes that occur in the ISM.

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Stereodynamical effects in cold energy collisions

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The last decade has witnessed extraordinary advances in the exploration of inelastic and reactive collisions at cold (<1 K) and ultra-cold (< 1 mK) energies, to the point that our understanding of these processes has experienced a stunning. At these collision energies, scattering is contributed by few partial waves whose manifestation in the integral and differential cross sections can be singled out thus making possible to isolate and detect resonances, which are ubiquitous in most of the studied processes. One such elementary molecular process is the inelastic rotation–translation energy exchange. In particular, the regime near 1 K has also been the focus of a series of experiments by Zare and coworkers [1-3] in which rotational quenching of HD and D_2 by He, D_2 and He has been reported. The experiment involves coexpansion of the molecular species in a supersonic beam combined with selection of the initial alignment of the molecular rotational angular momentum through Stark-induced adiabatic Raman Passage (SARP). The SARP method allows stereodynamical control of the collision process by selecting a given projection (m_j) of the molecular rotational angular momentum j on the relative collision velocity vector or preparing a molecular state.

In our recent work we have applied theoretical methods to describe the stereodynamics of inelastic and reactive collisions in the cold energy regime. In my talk I will show some examples of how the stereodynamics of cold molecule-molecule collisions can be used to achieve exquisite control of the collision outcome. Specifically, I will address the issue of how scattering resonances are affected by the polarization of the collision partners and the extent of control that can be achieved by a suitable preparation of internuclear axis/rotational angular momenta vectors at cold collision energies and how the integral and differential cross sections are influenced. It will be shown that low energy resonances can be dramatically affected by some specific preparations and in some cases completely suppressed. In addition, I will present the simulation [4-6] of the results of the SARP experiments [1-3] and it will be shown that the theoretical approach is necessary for a full interpretation of the experimental results. [6]

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Probing van der Waals interactions between Rydberg atoms and polar molecules by FRET at temperatures below 100 mK

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Collisions at low translational temperatures between atoms in Rydberg states with large electric dipole transition moments, and polar ground-state molecules represent an ideal setting to study Förster resonance energy transfer (FRET) between electronic and nuclear degrees of freedom [1-4]. Here we report intrabeam collision experiments with ground-state NH_3 molecules, and He atoms in triplet Rydberg states with principal quantum numbers, n, between 38 and 40. The pulsed supersonic beams used in this work were formed of NH_3 seeded in He at a ratio of 1:99. The Rydberg-Rydberg transitions studied here were tuned into resonances with the NH_3 inversion intervals using electric fields up to 8 V/cm. FRET resonance widths as low as 100 ± 20 MHz were observed. These results from binary interaction were at mean center-of-mass collision speeds of 19.3 ± 2.6 m/s (i.e., $E_{\mathrm{coll}}/k_B = 73 \pm 20$ mK). The measured resonance widths are strongly Rydberg-state dependent and are broadened by van der Waals interactions in stronger fields when the atoms are more strongly polarized. This has been inferred by comparison of the experimental data with the results of numerical calculations of the Stark shift and static dipole-dipole interactions. These results are of importance to the implementation of proposed schemes for cooling, coherent control, and sensing that exploit Rydberg-atom-polar-molecule interactions [5-8].

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Cold Collision Stereodynamics

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Scattering experiments probing a dynamical resonance with complete control of both the internal and external degrees of freedom provide invaluable data elucidating the long-range anisotropic forces so important to chemistry. Completely alignment-controlled diatom-diatom scattering experiments have been greatly anticipated by theoreticians and experimentalists alike. They are considered one of the holy grails of scattering studies. In this presentation based on the work in my research group of Mr. Haowen Zhao, Dr. William E. Perreault, and Dr. Nandini Mukherjee, we demonstrate nearly complete control on the internal and external degrees of freedom of both collision partners, thus gaining control of collision geometry at the most fundamental quantum level.

We prepared D_2 molecules in the ($v = 2$, $j = 2$) state in a supersonically expanded pure beam of D_2, and we studied the cold rotationally inelastic scattering process:

$$D_2(v = 2, j = 2) + D_2(v = 2, j = 2) \rightarrow D_2(v = 2, j = 2) + D_2(v = 2, j = 0).$$

By aligning the bond axes of both D_2 colliding partners either parallel or perpendicular to the approach direction, we observed a dramatic difference in the response of their scattering rate to the collision temperature, revealing the strong anisotropy of the long-range quadrupole-quadrupole interaction. In fact, the anisotropic effect is so dramatic that the inelastic scattering can be very nearly switched off by aligning both bond axes parallel to the collision velocity. These experimental results are made possible by introducing a new pump-probe technique, which enables us to control the collision temperature. This technique utilizes a laser-based gating mechanism that relies on state preparation and delayed state detection with nanosecond laser pulses. By combining alignment and temperature control, we could simultaneously locate and fingerprint a resonance experimentally. The nearly complete control that we have achieved has important implications in cold and ultracold four-center collision processes.

If time permits, another experiment will be described by the same research team in which we coherently couple two bond axis orientations of $D_2(v = 2, j = 2)$ to form what we call a biaxial state. This biaxial state acts as two slits that generate two indistinguishable quantum mechanical pathways connecting initial and final states of the colliding system. The interference disappears when we decouple the two orientations of the bond axis by separately constructing the uniaxial states of D_2. This result unequivocally establishes the double-slit action of the biaxial state. This preparation of a quantum-entangled biaxial state opens new possibilities in the coherent control of molecular collisions.

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Small ligand binding to heme from first principles

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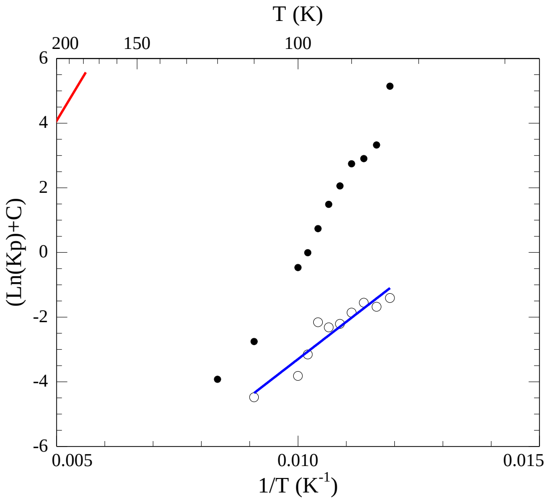
Small ligand binding (O_2 CO NO, H_2O) to heme in hemoproteins is a strongly stereospecific process. This is stem from orbital considerations in the Iron atom-molecule interactions. Due to the complexity of the Fe atom electronic structure the energetics of this bond is insufficiently known, although it determines the binding of these ligands.

We shall present an overview of gas phase investigation of heme-ligand binding via the Vant'Hoff equation and high level calculations.

As in nature the degree of oxidation of iron plays an important role in the binding of small molecules to hemoproteins, we measured the binding energies of ferrous and feric heme with different ligand. We have also characterized the critical influence of the water molecule on the reaction of ligadation of heme.



Van't Hoff plots of ln (K_p(T)) + C *versus 1/T for* $[Fe^{II}\text{-hemeH}(O_2)]^+$ *(full circles and linear fit in red) and* $[Fe^{III}\text{-heme}(O_2)]^+$ *(open circles and linear fit in blue),*

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Liquid-Phase Photoelectron Circular Dichroism

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Photoelectron circular dichroism (PECD) — the forward-backward asymmetry in photoemission from chiral molecules photoionized by circularly polarized light — is an exquisitely sensitive experimental probe, capable of determining enantiomeric excess and electronic and molecular structures in chiral samples.[1] Although the use of PECD to study chiral biomolecules under physiologically relevant conditions promises to reveal otherwise inaccessible interactions, for example the nature of chirality transfer between the chiral solute and the solvent shell, PECD has until now been exclusively demonstrated in the gas phase. PECD is a threshold effect, with magnitude increasing as photoelectron kinetic energy decreases. Conversely, scattering of photoelectrons in the liquid phase becomes increasingly significant at low kinetic energies (< 10 eV), thereby leading to unavoidable convolution of PECD signal with the secondary electron background in the kinetic energy region of most interest.[2] Despite these challenges, we have recently successfully measured core-level PECD in neat liquid fenchone,[3] and in aqueous solutions of alanine, under both neutral and basic conditions. These results constitute the first measurements of PECD in the liquid phase. Here, we will present experimental results, discuss the recent developments that have enabled these measurements,[4] and highlight opportunities and challenges in the burgeoning field of liquid-phase PECD.

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Quantum Sensing with Atoms and Living Systems

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In this talk we will address two different yet interrelated directions of research. We will first discuss recent progress in quantum sensing and metrology, in particular magnetometry, with hot atomic vapors. We will then draw analogies with quantum sensing using living systems. Biological systems have long been assumed to be a hostile environment for quantum coherent effects. Contrary to the conventional wisdom, we have shown that the radical-pair mechanism of spin chemistry offers a fruitful playground for applying tools and concepts from quantum information science in biological systems. Magnetic quantum sensing with radical-pairs offers the first concrete paradigm of quantum biology.

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Mechanistic insights into the chemi-ionization of lithium atoms by highly excited helium atoms

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Ultracold trapped mixtures of different atomic species are the starting point for the production 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, chemi-ionizing collisions must be efficiently suppressed.

As a first step towards co-trapping, we study quantum-state-controlled chemi-ionizing collisions between highly excited, metastable helium atoms (He*) and ground-state lithium atoms (Li) in order to investigate efficient ways of controlling the outcome of this process. 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 in the 2^1S_0 level 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 some experiments, we also use laser excitation to populate the $2^3P_{1/2,\,3/2}$ levels in Li and the 2^3P_2 level in He, respectively.

In this contribution, I will 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 a quartet state to the reaction rate, which is in violation of spin-conservation rules [4].

In addition, I will also provide details on recent experiments in which we have reacted Li($2^2S_{1/2}$) with He(2^3S_1) and He(2^3P_2), respectively. In contrast to our previous results on collisions of He(2^3S_1) with Li($2^2S_{1/2}$) and Li($2^2P_{1/2,\,3/2}$) [5], we observe only a small change in the reaction rate upon laser excitation of He*. This makes us conclude that the He*-Li chemi-ionization process is dominated by electron exchange, i.e., the interaction between the valence electron of Li and the electron core hole in He.

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Return

Chemical Dynamics of Nonvalence-Bound State of the Molecule Anions

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Non-valence bound state (NBS) of the anion is ubiquitous in nature and plays the essential role of the doorway into anion physics and chemistry. Here, we developed the technique for the investigation of the state-specific chemical dynamics of the metastable NBS of various chemical systems; the picosecond time-resolved pump-probe spectroscopy on the cryogenically cooled anions using the velocity-map electron imaging gives the mode-dependent dynamic behavior of the NBS in terms of the autodetachment and/or concomitant fragmentation reactions. Deprotonated closed-shell anions such as the phenoxide or halogen-substituted phenoxides, for example, have been generated by the home-made electrospray apparatus before they are mass-selected and collimated into the cryogenically cooled trap. Anion packet was extracted to the velocity-map imaging electrodes where the laser pulses were given. The autodetachment rate of the NBS has been precisely measured in a state-specific way for various chemical systems involving the phenoxide, 4-cyanophenoxide, or *o*- (*m*- or *p*-) halogen substituted phenoxides. Fermi's golden rule is found to be extremely helpful for the rational explanation of the experiment whereas the more sophisticated theoretical model is definitely desirable for the more quantitative analysis. For iodophenoxides, the C-I bond rupture (giving the I^- fragment at the asymptotic limit) has been found to be mediated by Feshbach resonances of the NBS, providing the foremost evidence for the dynamic doorway role of the NBS in the anion chemistry and physics.

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Selection and control of (bio)nanoparticle species with electric fields

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In single-particle diffractive imaging (SPI), individual gas-phase macromolecules are successively exposed to coherent x-ray pulses from free-electron lasers [1]. In this concept, the individual diffraction patterns are recorded, classified according to the particle's orientation, and combined into a diffraction volume, which can be inverted to retrieve the three-dimensional molecular structure of the sample molecules [2]. While impressive results were obtained over the last years, two major experimental bottlenecks are the structural heterogeneity of the macromolecules and their weak scattering resulting in tiny signal-to-noise ratios for the single-molecule-diffraction signal.

Here, we present electric-field-based approaches to sample purification [3]. Charge-state distributions on particles of varying size and from different aerosolization techniques are disentangled, biological macromolecules are separated according to their charge state, and considerations for deflecting and separating neutral macromolecular conformers are presented. These approaches are suitability for SPI experiments and provide experimental means to diffract of a series of homogeneous sample molecules and to average patterns until signal is above noise [4]. This extension of sample-control mechanisms to biological macromolecules and nanoparticles paves the way toward the recording of high-resolution "molecular movies" of biological macromolecules in the gas phase, similar to recent results for gold nanoparticles [5].

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Photodissociation and high-precision spectroscopy with trapped ultracold molecules

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Precise control of the internal and motional quantum states of diatomic molecules enables new insightful measurements. We apply this control to strontium dimers that are synthesized at ultracold temperatures and trapped in an optical lattice. This allows us to observe key features of ultracold chemistry by inducing and imaging the photodissociation process. These striking features include matter-wave interference of coherently created reaction products as well as tunneling through reaction barriers. By applying small magnetic fields, we can predictably control the reaction. Furthermore, by tuning the kinetic energy of the fragments we observe a transition from the distinctly quantum mechanical to the quasiclassical chemistry regime. In parallel, vibrational spectroscopy of the bound molecules can be used to build new frequency standards, test molecular QED and search for new physics. We demonstrate the most precise and accurate molecular spectroscopy, with systematic effects characterized to the 14th digit of precision, enabled by carefully designing the optical lattice trap to preserve coherence between molecular states.

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On the role of nuclear permutation symmetry in quantum molecular dynamics

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Permutation symmetry of identical particles is a central pillar of quantum mechanics. The corresponding spin−statistics theorem stipulates that the total wavefunction of a quantum system, such as an atom or a molecule, must be antisymmetric under permutation of two indistinguishable fermions, and symmetric under exchange of two identical bosons. In the former case, the identical particles have half-integral spin and obey Fermi−Dirac statistics, whereas in the latter case, they have integral spin and obey Bose−Einstein statistics.

As regards molecules, this symmetry requirement applies to electrons and identical nuclei alike. For electrons, obeying the related Pauli exclusion principle is a prerequisite for any electronic structure theory. Using Slater determinants as bases for the electronic states, this precondition is automatically fullfilled, and implemented in all numerical programs of computational chemistry. However, the same cannot be said about the identical nuclei of a molecular system. Indeed, nuclear permutation symmetry is often overlooked in quantum molecular dynamics calculations, whether their focus is on electronic or nuclear motion. Due to the so−called curse of dimensionality, most of these computations rely on reduced descriptions of the dynamics, which include only presumably relevant molecular degrees of freedom, and neglect all the remaining ones—considered as spectators to the dynamical process under study. These reduced theoretical models do not generally obey nuclear−spin statistics, and usually give rise to misleading pictures of iconic molecular processes.

In this contribution, I will present well known textbook examples of dynamical molecular processes whose reduced descriptions contravene the principle of the indistinguishability of identical nuclei. The latter include tunneling dynamics in symmetric double-well achiral molecules [1], as in umbrella inversion of ammonia [2], electronic Kekulé dynamics in the benzene molecule [3], and coupled electron-nuclear motion in the dihydrogen molecular cation [4]. To obey nuclear−spin statistics, the descriptions of these processes require the inclusion of some seemingly irrelevant molecular degrees of freedom. This has important consequences on molecular motion, particularly on dynamical localization of the molecular subdensities. The main object of the dispute between these reduced and fully−symmetrized descriptions of the dynamics is whether nuclear permutations allow localization of the electronic, vibrational, or even rotational density on a specific molecular substructure (or configuration) rather than on another one, which is exactly equivalent (indistinguishable). Understanding this issue has far-reaching implications for the description, imaging and control of other molecular processes, as well as for the interpretation of many femtosecond pump−probe experiments.

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Return

Microsecond time-resolved dual-comb spectroscopy for kinetic and product studies of gas-phase reactions

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Time-resolved infrared spectroscopy with both temporal and spectral resolutions offers great opportunities to explore the transient intermediates and kinetics of chemical reactions. Dual-comb spectroscopy, a multi-heterodyne Fourier transform spectroscopic technique relying on two frequency combs with slightly different repetition rates, enables high-resolution and rapid spectral measurements. Here, a new approach to kinetic and product studies of the gas-phase reactions by means of mid-infrared microsecond-time-resolved dual-comb spectroscopy will be reported. The mid-infrared dual-comb sources are constructed based on electro-optic frequency comb and the difference frequency generation techniques. By employing two sets of dual-comb laser sources with central wavelengths respectively near 3 and 8 μm, multiple species such as the simplest Criegee intermediate (CH_2OO), formaldehyde (CH_2O), hydroxyl (OH) and hydroperoxy (HO_2) radicals can be simultaneously probed upon on flash photolysis of the $CH_2I_2/O_2/N_2$ gas mixtures. The concentration of each observed reaction molecule can be determined based on its rotationally resolved infrared absorption spectra. The detection limit for each molecule can be obtained down to 10^{11}~10^{12} molecules cm^{-3} by coupling the dual-comb sources into a multi-pass reaction cell. In addition to quantitative analysis of the high-resolution time-resolved dual-comb spectra, the kinetics and product yields of the gas-phase reactions involving the simplest Criegee intermediate (CH_2OO) are also investigated under varied experimental conditions.

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NO(A)-He and NO(A)-Ne steric scattering experiments

M. Fournier

We report the first experimental measurement of state-to-state ***k*-*j*-*k’*** correlations in rotationally inelastic scattering.

In a crossed-beam VMI experiment, we prepare electronically excited NO ($A^2\Sigma^+$, N = 4, j = 3.5). The polarization of that preparation laser allows control of the rotation vector ***j***, preparing an alignment of ***j*** relative to the collision vector ***k***. Rotationally inelastic collisions with either He or Ne produce NO (A, N’=0-3 and 5-14). These are probed by saturated 1+1’ REMPI, which is insensitive to the product rotational alignment. We measure state-selected velocity-mapped images for both in-plane (Horizontal, H) and out-of-plane (Vertical, V) preparation laser polarizations. The final images contain ***k*-*j*-*k’*** correlations. The images are fitted to determine the polarization dependent differential cross sections that describe these correlations, which are compared to quantum scattering calculations performed on *ab initio* potential energy surfaces. We observe strong ***k*-*j*-*k’*** correlations that vary with final N’ state, consistent with the QS calculations. Representing the results as the respective differential cross sections for limiting ‘propellor’, ‘cartwheel’ and ‘frisbee’ alignments of ***j*** provides physical insight into the observed scattering dynamics

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Multiphoton breakdown of acetylene; Formation of organic building block fragments

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Mass resolved REMPI spectra and electron and ion velocity map images were recorded for REMPI of acetylene in case of two-photon resonant excitations to low lying 3p and 4p Rydberg states. Combined data analysis of ion signal intensities, electron and ion kinetic energy release spectra and angular distributions revealed multiphoto-fragmentation processes in terms of photodissociation and photoionization channels to form the molecular ion, $C_2H_2^+$ and the fragment species H^+, C^+, CH^+, CH_2^+, C_2^+ and C_2H^+. The ratio of fragment ion formation over the parent ion formation increases with excitation energy. To a large extent the multiphoton-fragmentation involves initial breakdown of the molecule into ground and excited state neutral fragments by two-, three- and four- photon dissociation processes prior to multiphoton ionization. The three-photon dissociation processes via superexcited molecular state(s) are found to be most important and electronically excited fragment species play a significant role in the overall multiphoton-fragmentation. Furthermore, the data was indicative of an involvement of secondary photodissociation processes, energetics of fragment species as well as state interactions. The question, whether acetylene could be an important source of building block fragments for formation of organic molecules in interstellar space is addressed.

Return

New Applications of Velocity-Mapped Ion and Electron Imaging

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Velocity Mapped Ion Imaging has given one the ability to measure the quantum-state-resolved differential cross section as a function of laser properties, such as intensity and polarization, of both unimolecular and bimolecular gas phase processes. This has enabled the measurement of the alignment and orientation of molecules and atoms as a function of their speed and direction. Here I will discuss and show new applications of the velocity mapped ion imaging that promise to provide this information for surface reactions. Nascent molecules that are the product of a catalytic reaction on a surface are state-selectively ionized and spatially imaged after being velocity filtered in order to allow one to measure the nascent angular distribution of the fragments as they leave a surface as a function of the location from which they were ejected from the surface with micron resolution. In addition, I will discuss a new apparatus for imaging secondary electrons from a surface, utilizing a modified commercial secondary electron microscope, in order to measure the energy and angular distribution of the ejected secondary electrons. This technique can now provide quantitative information about the ejected electrons as function of position and time from a surface and has the promise, after further developments, on reaction at surfaces with nm spatial resolution and picosecond time resolution.

Return

Time-resolved Coulomb explosion imaging of inner-shell excited state dynamics in CH_2I_2 and CH_2BrI

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The invention of Free Electron Lasers (FELs) has opened the door to the real-time observation of photochemical reactions driven by core-to-valence transitions.[1-3] As the electronic states populated following Auger-Meitner decay of these core-excited state may only be accessible via site-selective excitation schemes, FEL-based experiments are rather unique in their findings. A recent transient absorption study on CH_2I_2, following $4d_{5/2} \rightarrow \sigma$ C-I^* excitation via a XUV pump – XUV scheme,[3] show that, before its decay on a ~100 fs timescale, the molecular cation isomerizes to a transient iso-species (CH_2-I-I^+),[4] as previously hinted in a study using a similar excitation scheme in a one-color setup using synchrotron radiation.[5]

We have studied the multi-channel photochemistry of CH_2I_2 and CH_2BrI using Time-Resolved-Coulomb Explosion Imaging (TR-CEI)[6,7] at the SACLA XFEL in Japan. In TR-CEI, a molecule is stripped of its outer electrons through excitation with an intense laser pulse at a range of different delays, producing a variety of small cationic fragments. By measuring the relative momenta of these fragments, one can obtain information on the nuclear geometry of the molecule of interest at the point of ionization. In our experiment, CH_2I_2 and CH_2BrI molecules were pumped by a 50.4eV FEL pulse to initiate $4d_{5/2} \rightarrow \sigma$ C-I^* core-to-valence excitations, and then Coulombically exploded using the intense 800 nm output of a synchronized optical laser. The fragments were imaged using a three-dimensional Velocity Map Imaging (VMI) spectrometer,[8] and their correlations evaluated through covariance analysis methods.[9-11] Through these experiments, we aim to obtain information on the isomerization and photodissociation reactions in both CH_2I_2 and CH_2BrI following site-selective inner shell excitation. Moreover, through comparison of the two molecules, we aspire to gain a better understanding of how molecular structure affects the reaction dynamics observed.

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Poster Session

Inelastic collision dynamics of oriented NO(X) molecules

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Examining the scattering dynamics of oriented NO molecules with a combined experimental and theoretical approach allows one to benchmark how well theory reflects reality. By orienting the NO molecule before collisions different regions of the potential energy surface and their associated collision pathways can be examined, such as side-on or end-on collisions [1-3]. An examination of simple collision partners, such as rare gasses, allows for an excellent starting point to examine the foundations of quasi-classical and quantum mechanical theory techniques, and how such techniques hold up in unique environments, such as "cold" collisions (NO + He) [4]. Expanding the scope to larger collision partners, such as ND_3 or CH_3I, pushes these foundations of molecular dynamics, introducing new considerations such as the orientation and internal energy levels of the collision partner, and truly assesses the accuracy and applicability of the theory. However, to test such collisions, the initial states of the collision partner must now be selected similar to that of the NO, to reduce the complexity of the experimental data allowing for easier comparison to the theory. This requires the construction of a double hexapole secondary beamline to allow for selecting various initial states of the collision partner, as seen previously in the literature, for example with collisions of He with ND_3 [5].

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Return

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 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. The decomposition on the bare metal surface has been mostly covered by theoretical studies [1], 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) [2]. We obtain accurate rates for CO_2 formation for four different isotopologues of formic acid (HCOOH, HCOOD, DCOOH and DCOOD). 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 can form CO on the stepped palladium at surface temperatures around 673 K. While, the rate of CO formation seems to be desorption limited, the presence of a CO forming pathway indicates the presence of a carboxyl-intermediate which was proposed for the water-gas-shift reaction [3] before but has not been reported experimentally yet.

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Return

Novel developments in optimizing radiation-gas jet interactions by micro-fabricated nozzles

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Recent years have witnessed the development of advanced experimental techniques that strongly rely on the ability to bring molecular/material systems of interest into the gas phase for further applications. Many of these advanced applications employ techniques that are pulsed in nature and are often based on photonic instrumentations like for example high-repetition rate (ultrafast) lasers, Free-Electron-Laser or Synchrotron radiation. Efficient use and analysis of molecular/material samples - sometimes only available in minute quantities- thus imposes the further requirement that samples ideally are brought in a pulsed way into the gas phase.

In many applications the specifics of the nozzle exit determine the detailed characteristics of the supersonic flow like density, internal temperature, geometry of expansion. For many current and future applications, it is highly desirable to match the geometry of the expansion to the typical geometry of a (focused) radiation beam (laser, FEL or Synchrotron). This will make it possible to have an optimal density and use of precious samples in the application and therefore optimal sensitivity.

Here we report on recent developments, in close collaboration with the University of Twente, the Netherlands, where we microfabricate specially designed de Laval type micronozzles, with throat dimensions below 10 micrometer, using lithography and Deep-Reactive-Ion-Etching (DRIE). These micronozzles can be used both in a pulsed expansion produced by e.g. a piezo-operated cantilever pulsed valve [1] or in a continuous gas expansion. An example of the latter application of these micronozzles is the novel micro-Gas Chromatograph chiral-Mass Spectrometer, that is currently under development by a public-private consortium [2].

[1] www.amsterdampiezovalve.com

[2] Project microGC- chiralMS, financially supported by the European Fund for Regional Development and OPOost (EFRO-00949, 2020-2023), by MassSpecpecD BV, Qmicro by Sensirion, Radboud University, University of Twente and Saxion University of Applied Sciences; see also www.massspecpecd.com

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Cavity-Enhanced Absorption Spectroscopy in atomic iodine at 1315nm: first measurement of the quadrupole (E2) components

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The $5^2P_{3/2} \rightarrow {}^2P_{1/2}$ forbidden magnetic-dipole (M1) transition in atomic iodine at 1315 nm is a potential testbed for low-energy studies of Parity Non-Conservation (PNC) via optical rotation experiments in atomic systems. We use a cavity-enhanced absorption spectroscopy (CEAS) scheme, and high atomic iodine densities produced by photodissociation of molecular iodine at 532 nm, to measure the $F = 4 \rightarrow F' = 2$ and $F = 1 \rightarrow F' = 3$ pure electric-quadrupole (E2) hyperfine components of this transition, which will be useful in studying the anapole moment component of PNC. We report on the first ever measurements of the E2 components, and of the ratio $\chi = E2/M1$ of the electric quadrupole to magnetic dipole matrix elements.

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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[1-4].

Here, we report accurate experimental rate constants for hydrogen atom recombination on Pt(111) and Pt(332) derived from the Velocity Resolved Kinetics[5] method (VRK). VRK combines molecular beam-surface scattering with out-of-plane ion imaging of reaction products, which enables independent determination of reaction kinetics and dynamics. We also 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 partition function for the adsorbed H atoms. It accounts for nuclear quantum effects, associated with the light mass of the atom, and electronic quantum effects, associated with the hydrogen atoms electron spin. We note that conventional models for adsorbate partition functions like Harmonic Approximation or Complete Potential Energy Sampling[6] introduce errors of more than one order of magnitude between 300 and 1000 K.

Our modelling efforts are extended to other single crystal metal surfaces and catalytic nanoparticles and we find a general applicability for the model prediction of hydrogen atom recombination rates and adsorbate entropies.

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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-resolution- imaging 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. Suf- ficient 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 environments are prone to structural instability.

[1] https://www.controlled-molecule-imaging.org

Return

Studying rotational-state and conformational effects in chemi-ionisation reactions

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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]. We have recently built a new crossed-molecular-beam setup to extend our methodology to neutral-neutral reactions [4]. This setup is 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.

As the first application of this new method, rotational-state-dependent chemi-ionisation reactions of carbonyl sulfide (OCS) with metastable neon atoms were investigated. A pronounced state-specific effect on the product branching ratio was 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 [4,5]. Moreover, for heavier molecules, the disentanglement of conformational and rotational-state effects can be difficult to analyse due to the involvement of several rotational states [5]. Choosing conformers that can be chemically separated and have high interconversion barriers could disentangle the conformational and rotational state dependencies. Therefore, we chose to study the chemi-ionisation reaction of 1,2-dibromoethylene (DBE), the conformers of which can be chemically separated [6,7]. Additionally, in a collaboration with the Korean Advanced Institute of Science and Technology (KAIST), we are also currently undertaking a comparative study of the photochemistry, photoionization, and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene (DBE) as a prototypical system [8]. These investigations aim to gain a comprehensive understanding of the role of molecular conformations in unimolecular and bimolecular reactivity.

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Return

Quantum-logic control of complex molecular ions for applications in molecular and chemical physics

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Over the past years, the coherent manipulation of single isolated quantum systems such as atoms, ions, superconducting circuits, and quantum dots has advanced greatly and yielded important applications in the fields of quantum metrology, quantum sensing, and quantum computing. Recently, extending and applying quantum technologies to molecules has become one of the prime goals of the quantum physics community. However, their complex internal structure and lack of cycling transitions makes it difficult to cool, control and manipulate them. In our lab, we co-trap a single molecular ion together with an atomic ion which acts as a *coolant* to cool the molecule translationally as well as a *messenger* for the internal state identification of the molecule without destroying it. The information of the complex molecular ion is mapped onto an easily addressable atomic ion from where it is read out. We will highlight the quantum-non-demolition detection of the rovibrational state of single nitrogen ions which is a crucial step towards their coherent manipulation[1]. We will also show how this method allows us to go beyond the state-of-the-art and prepare molecular ions in well-defined hyperfine-Zeeman states[2]. We will discuss the extension of our technique to polyatomic ions to lay the foundations for the exploration of their spectroscopy and molecular dynamics.

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Return

Vector-Model semiclassical wavefunction: the quantitative pictorial description of angular momentum addition and transformation

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We propose the Vector Model Wavefunction and:
1) Show it is an asymptotic solution of the angular momentum operators
2) Give geometrical interpretation to semiclassical expressions for Clebsch-Gordan coefficients and Wigner D-matrices.
The VM wavefunction offers a direct geometrical interpretation of semiclassical equations of C-G coefficients and D matrices, and excellent approximation of the exact QM expressions, showing that the VM wavefunction gives a compelling picture of angular momentum coupling and rotation, even down to $j = 1/2$.

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Wavelength- and Intensity-Dependence of Strong Field Ionization and Fragmentation Dynamics of Argon-dimer

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In the presence of an intense laser field molecules ionized via different ionization mechanism depending on the intensity and the wavelength of the laser field [1]. Following ionization, molecules will eventually dissociate into several ionic fragments. The fragmentation dynamics is often affected by the presence of the laser field, which coupled the electronic and nuclear motion making the investigation of the ionization dynamics of molecules in intense laser fields very challenging. For rare-gas dimers, which are loosely bound by attractive van der Waals force and have electrons localized at their nucleus [2], ionization by intense laser field mostly site specific, making rare-gas dimers a very attractive system for the study of their interaction with strong laser field [3,4,5]. In particular, rare-gas dimers in interaction with intense laser fields provide an important playground for the investigation of interatomic relaxation mechanism such as Interatomic Coulombic Decay (ICD) [6], Electron Transfer Mediated Decay (ETMD) [7], Charge Resonance Enhanced Ionization (CREI) [8,9] and Radiative Charge Transfer (RCT) [10] processes. In this work, we have used a velocity map imaging spectrometer to study the wavelength- and intensity-dependence of the strong field ionization and fragmentation dynamics of Argon-dimer. We show, that the fragmentation dynamics of Argon-dimer via Dissociation and Coulomb Explosion (CE) channels show a strong dependence on the wavelength and intensity of the laser field, which is observed through angular distribution and the kinetic energy spectrum of the ionic fragments.

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How water changes the photophysics of small model chromophores

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The properties of atoms and molecules are strongly dependent on their environment, with hydrogen bonds, in particular, playing an important role in chemistry and biochemistry. It is therefore of great interest to bridge the gap between single molecules and molecules in solvation.

In our group, we focus on experimental studies of small, model-chromophore dynamics including one-to-one clusters of a (bio)molecule with a single water molecule attached in the gas phase, as well as liquid-phase studies [1]. We have investigated indole and pyrrole, which are both relevant for the photophysics of tryptophan, the most strongly near-UV absorbing amino acid. Here, we present results on the UV-induced dynamics of indole-water$_1$ and pyrrole-water$_1$ clusters, probed by IR and x-ray laser sources both in our lab and at larger facilities such as LCLS and the European XFEL. Recent progress on our newly-developed transportable endstations (COMO and eCOMO) for experiments at large-scale facilities will also be shown, including the use of time- and position-sensitive detection schemes provided by Timepix3 cameras [2]. Furthermore, Mid-infrared pump IR-probe experiments on indole-water$_1$ will be presented [3], including efforts to use laser-induced electron diffraction to probe and track photo-induced dynamics [4]. Finally, we discuss our theoretical results aiming to study molecular dynamics using x-ray diffraction off laser-aligned molecules in the gas phase [5].

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Conformationally-selected ions for reactions with conformationally-selected molecules

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The different effective dipole moments allow for the spatial separation of conformational isomers employing electrostatic deflection to investigate their individual reactivities [1]. An attractive application of conformationally selected molecules in the gas phase is the study of ionic Diels-Alder reactions (polar cycloadditions), which constitute essential synthetic routes for cyclic molecules. However, their mechanistic details and conformational selectivities are still poorly understood. A recent pioneering study of the conformer-specific polar cycloaddition of dibromobutadiene (DBB) with trapped propene ions has shown that both the *gauche* and *s-trans* conformers of DBB display capture-limited reaction rates [2]. Furthermore, 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 an electrostatically deflected molecular beam containing the two separated conformers at a static target of propene ions embedded within a Coulomb crystal of laser-cooled calcium ions. In order to gain further control over the reaction partners, we now also wish to select the ionic reactant's conformational isomer. Here, we discuss the generation of conformationally selected ionic targets of *meta*-aminostyrene (mAS) to enable the study of fully conformationally selected ion-molecule reactions. Following a detailed study of the isomer-selective ionization of the two different *m*-aminostyrene conformers [3], we individually load them into a Coulomb crystal to determine their stability in such an environment for subsequent reaction studies.

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Cavity enhanced chiral optical rotation

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Chiral sensing plays a crucial role in numerous fields of science and industry. The measurement of weak chiral signals is limited by spurious birefringence, as well as slow and imperfect background subtraction procedures. We present a novel *chiral cavity-enhanced polarimeter* (*CCP*), an optical instrument in which the sensing light traverses the chiral sample multiple times, thus amplifying the weak chiral optical rotation signal by the number of cavity round-trips (typically > 100). The hallmark of this technique is the implementation of rapid signal reversals, which eliminate the need for background subtractions, and enable absolute chiral measurements even in noisy environments, resulting in greatly enhanced sensitivities (~0.02 mdeg $Hz^{-1/2}$), relative to commercial instruments (~5 mdeg $Hz^{-1/2}$).

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Ultrahigh-density spin-polarized hydrogen isotopes from the photodissociation of hydrogen halides: new applications for laser-ion acceleration, magnetometry, and polarized nuclear fusion

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Recently, our group produced spin-polarized hydrogen (SPH) atoms at densities of at least 10^{19} cm^{-3} from the photodissociation of hydrogen halide molecules with circularly polarized UV light and measured them via magnetization-quantum beats with a pickup coil. These densities are approximately 7 orders of magnitude higher than those produced using conventional methods, opening up new fields of application, such as ultrafast magnetometry, the production of polarized MeV and GeV particle beams, such as electron beams with intensities approximately 10x higher than current sources, the study of polarized nuclear fusion, for which the reaction cross sections of D–T and D–He reactions are expected to increase by 50% for fully polarized nuclear spins and the production of various nuclear-spin-polarized molecules, through SPH reactions, on nanosecond timescales, for pump-probe ESR/NMR detection with signal enhancement.

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