# Book of Abstracts

# 12th International Meeting On Atomic and Molecular Physics and Chemistry



# June 11–14, 2023
# Innsbruck, Austria

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# Preface

IMAMPC is an annual event that has been held for the first time in Madrid in 2010. Other previous meeting took place in Rennes (2011), Pisa (2012), Lille (2013), Salamanca (2014), Birmingham (2015), Le Havre (2016), Torun (2017), Berlin (2018), again in Madrid (2019), and in Prague (2022). This interdisciplinary meeting is a great opportunity for researchers in the early stage of their scientific careers to promote their research by sharing their innovative ideas and high-quality research results. Four world-class researchers will set the scene by highlighting the state of the art in their field and sharing with us their vision on its evolution. The conference is mainly focused on atomic and molecular physics and chemistry, both experimentally and theoretically. This year's special attention will be dedicated to:

- Electronic structure and spectroscopy of molecules
- Macromolecules and nanostructures
- Chemical reactivity in the gas phase and at the gas/surface interface
- Cold atoms and molecules

The meeting this year is divided into five oral sessions and one poster session, which present in total four keynote talks, twenty invited talks, sixteen hot topics, and forty posters.

# Program

| | Sunday 11th June | Monday 12th June | Tuesday 13th June | Wednesday 14th June |
|---|---|---|---|---|
| **Chair** | | **Milan Ončák, Olga Lushchikova** | **Martin Beyer** | **Jennifer Meyer** |
| 8:00-8:45 | | *Registration @ conference site (theological faculty)* | | |
| 8:45-9:00 | | *Opening words* | | |
| 9:00-9:15 | | Helen Fielding | Juraj Fedor | Piero Ferrari |
| 9:15-9:30 | | Helen Fielding | Juraj Fedor | Piero Ferrari |
| 9:30-9:45 | | Helen Fielding | Juraj Fedor | Piero Ferrari |
| 9:45-10:00 | | Alice Green | Lucas Schwob | Dariusz Grzegorz Piekarski |
| 10:00-10:15 | | Alice Green | Rico Mayro Tanyag | Robin Bernhardt |
| 10:15-10:30 | | Till Jahnke | Eva Muchová | Vesna Erić |
| 10:30-10:45 | | Till Jahnke | Eva Muchová | Risnita Vicky Listyarini |
| 10:45-11:15 | | *Coffee Break + Stretching* | *Coffee Break + Stretching* | *Coffee Break + Stretching* |
| 11:15-11:30 | | Kasra Amini | Leo Sala | Jakub Kubečka |
| 11:30-11:45 | | Kasra Amini | Leo Sala | Jakub Kubečka |
| 11:45-12:00 | | Laura McCaslin | Hanns Christian Schewe | Štěpán Sršeň |
| 12:00-12:15 | | Laura McCaslin | Evangelos Miliordos | Loren Ban |
| 12:15-12:30 | | Antonio Prlj | Fatemeh Keshavarz | Loren Ban |
| 12:30-12:45 | | Antonio Prlj | Rafał Szabla | Michael Hütter |
| 12:45-14:30 | | *Lunch @ Hotel Innsbruck* | *Lunch @ Hotel Innsbruck* | *Lunch @ Hotel Innsbruck* |
| **Chair** | | **Laura McCaslin** | | **Dariusz Grzegorz Piekarski** |
| 14:30-15:15 | Lab visits @ the Institute of Ion Pyhsics and Applied Physics, Technikerstraße 25 starting at 15:00 | Claire Vallance | Free afternoon | Tomás González Lezana |
| 15:15-15:30 | | Shazia Farooq | | Elisabeth Gruber |
| 15:30-15:45 | | Sebastian Louis Jackson | | Katrin Erath-Dulitz |
| 15:45-16:00 | | Gianmarco Vanuzzo | | Katrin Erath-Dulitz |
| 16:00-16:30 | | Jennifer Meyer | | Sérgio Domingos |
| 16:30-17:00 | | *Coffee Break + Stretching* | | *Coffee Break + Stretching* |
| 17:00-17:15 | *Registration @ Hotel Innsbruck* | Loïse Attal | | *Poster and Hot Topic Awards* |
| 17:15-17:45 | *Registration @ Hotel Innsbruck* | Jiaye Jin | | M. Celina Bermúdez |
| 17:45-18:15 | *Welcome Reception* | Edit Mátyus | | Helgi Rafn Hróðmarsson |
| 18:15-18:45 | *Welcome Reception* | Jörg Meyer | | Martín Taccone |
| 18:45-18:50 | *Welcome Reception* | *Flash Poster Presentations* | *Conference Dinner @ Restaurant 1809 on the Bergisel* | Closing |
| 18:50-19:15 | *Welcome Reception* | *Flash Poster Presentations* | *Conference Dinner @ Restaurant 1809 on the Bergisel* | |
| 19:15-22:00 | *Welcome Reception* | *Poster Session* | *Conference Dinner @ Restaurant 1809 on the Bergisel* | |

# List of Contributions

## *Hot Topic Talks*

*Poster*

# Keynote Talks

# UV photoelectron spectroscopy of aqueous solutions

Helen Fielding

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Ultraviolet (UV) photoelectron spectroscopy provides a direct way of measuring valence electronic structure; however, its application to aqueous solutions has been hampered by a lack of quantitative understanding of how inelastic scattering of low energy (<5 eV) electrons in liquid water distorts the measured electron kinetic energy distributions. We have recently developed a method for retrieving true UV photoelectron spectra of aqueous solutions [1]. Its application will be demonstrated for liquid water and organic chromophores [1, 2]. We will also demonstrate how complementary UV liquid-jet photoelectron spectroscopy and femtosecond transient absorption spectroscopy measurements reveal the mechanism of photooxidation of aqueous phenolate [3].
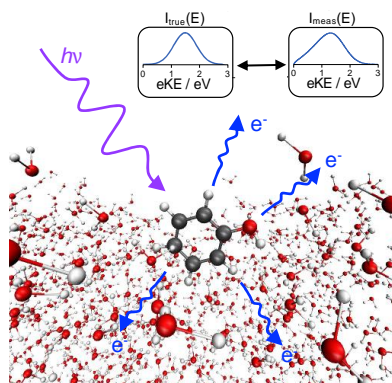


**References:**

[1] Scholz, M.S., et al., Accurate vertical ionization energy of water and retrieval of true ultraviolet photoelectron spectra of aqueous solutions. J. Phys. Chem. Lett., 2022. **13**: p. 6889-6895.

[2] Tau, O., et al., Liquid-microjet Photoelectron Spectroscopy of the Green Fluorescent Protein Chromophore. Nature Commun., 2022. 13: p. 507.

[3] Robertson, K., et al., Wavelength dependent mechanism of phenolate photooxidation in aqueous solution. Chem. Sci., 2023. **14**: p. 3257-3264.

# Multi-mass velocity-map imaging: a new toolkit for studying photoinduced and electron-induced chemical processes

Claire Vallance

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Multi-mass velocity-map imaging (VMI) enables measurement of complete scattering distributions for all products of a photoinduced or electron-induced chemical event [1], and is becoming established as a promising method for probing the dynamics of a variety of gas-phase processes. In addition to efficient measurement of the scattering distributions for individual reaction products, multi-mass imaging data sets also contain information on correlations between the scattering distributions of different reaction products, accessible via a technique known as covariance mapping [2].  Covariance mapping is already providing greatly enhanced insight into reaction mechanisms, including those involving multiple steps (see Figure 1) [3,4].   When coupled with Coulomb-explosion imaging it is also able to provide direct information on molecular structure on the femtosecond timescale [5], opening up the tantalizing prospect of recording real-time 'molecular movies' of chemical dynamics.  As these new methods become established within the reaction dynamics community, they promise new mechanistic insights into chemistry relevant to fields ranging from atmospheric chemistry and astrochemistry through to synthetic organic photochemistry and biology.

After a brief introduction to multi-mass imaging and covariance mapping, we will illustrate a number of different applications of these new techniques through a series of short case studies.
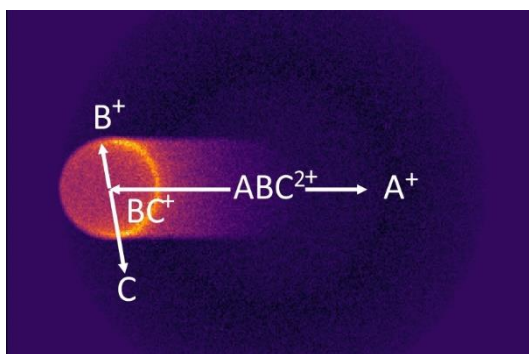


*Figure 1. Disentangling multi-step dissociation mechanisms via multi-mass covariance-map imaging.*

**References:**

[1]  Vallance, C., *Chem. Comm. volume 55*, 6336, 2019
[2]  Vallance, C. et al, *Journal of Physical Chemistry A volume 125*, 1117, 2021
[3]  Lee, J. W. L. et al, *Nature Communications volume 12*, 6107, 2021
[4]  Koeckert, H. et al., *Molecular Physics volume 119*, e1811909, 2021
[5]  Slater, C. S. et al., *Physical Review A volume 89*, 011401(R), 2014

# Dynamics of nuclear motion revealed by electron scattering

Juraj Fedor

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One of the central questions in AMO physics is to specify how the atomic nuclei move, for example, upon a vertical excitation by an external trigger. In my talk, I will provide an overview of experiments in which the nuclear motion is triggered and probed by collisions of molecules with free electrons.

The interaction time of an electron with the kinetic energy in the chemical range (units of eV) is, in the direct scattering regime, typically too short for any nuclear dynamics to proceed. The situation dramatically changes if quasi-bound states embedded in continuum are formed in the collision. Such states – electronic resonances and virtual states – have often autodetachment lifetime comparable with the timescale of nuclear motion. Probing various decay channels of the continuum states thus provides information about the nuclear dynamics.

Historically, majority of such experiments have been performed on gas-phase targets. I will briefly discuss some of the effects revealed this way, for example an extremely non-Born-Oppenheimer dynamics of the vibronic coupling through continuum [1], vibrational autodetachment mediated by a presence of dipole-bound states [2], or the symmetry control of the bond cleavage [3].

In the second part of the talk, I will discuss recent developments in using the same approach (electron scattering) in combination with a liquid microjet technique in order to probe the dynamics in the liquid phase.

**References:**

[1]  J. Dvořák et al., *Phys. Rev. Lett.* 129, 013401, 2022
[2]  C. S. Anstöter et al., *Phys. Rev. Lett.* 124, 203401, 2020
[3]  R. Kumar et al., *J. Phys. Chem. Lett.* 13, 11136, 2022

# Searching for snowballs in doped helium clusters

Tomás González-Lezana

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Helium droplets are an ideal environment for spectroscopic investigations of different species at low temperature. From a fundamental point of view these clusters also constitute a fantastic opportunity to investigate the interactions between the helium atoms and the atoms, ions and molecules embedded inside the droplet. In this seminar I will review some of the results obtained by our group at the Instituto de Física Fundamental -CSIC- in our studies along the years of helium droplets doped with a series of species ranging from atoms to large molecules as coronene $C_{24}H_{12}$. [1-4]

In recent years, we have collaborated with the experimental group of Prof. Paul Scheier at Innsbruck University searching for helium "snowballs" (solid-like ordered structures) surrounding different atomic ions [5-7]. For Ca2+ we have observed up to four of such closed shells around the ion. In particular, we have reported the detection for 74 He atoms of the largest structure found up to date [8].
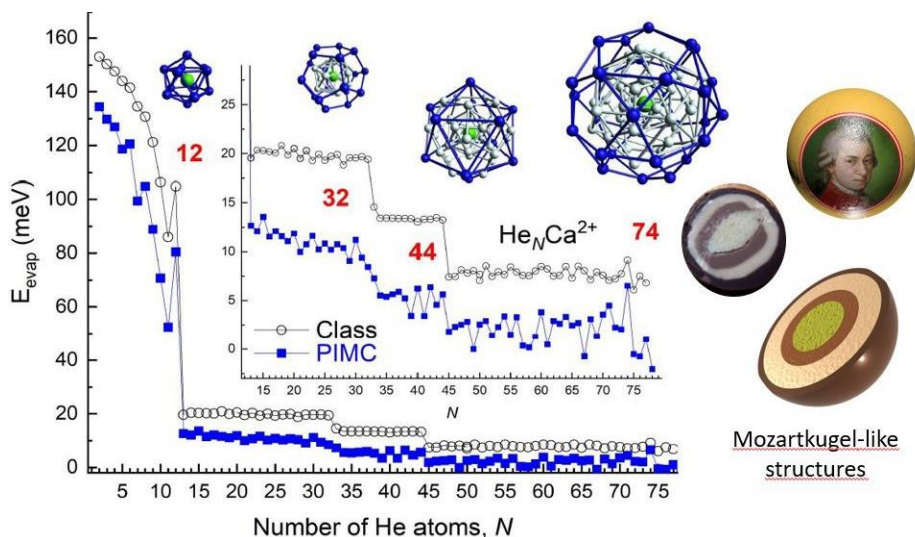


*Figure 1. Evaporation energies as a function of the number of helium atoms*

**References:**

[1]  R. Rodríguez-Cantano *et al. J. Chem. Phys.* **143** 224306 (2015)
[2]  R. Rodríguez-Cantano *et al. J. Chem. Phys.***146** 034302 (2017)
[3]  R. Rodríguez-Cantano *et al. Int. Rev. Phys. Chem.* **35** 37 (2016)
[4]  T. González-Lezana *et al. Int. Rev. Phys. Chem.* **39** (4) 465-516 (2020)
[5]  M. Rastogi *et al. Phys. Chem. Chem. Phys.* **28** 25569-25576 (2018)
[6]  R. Pérez de Tudela *et al. J. Chem. Phys.***150** 154304 (2019)
[7]  E. Zunzunegui-Bru *et al. Phys. Chem. Chem. Phys.***24** 2004-2014 (2022)
[8]  E. Zunzunegui-Bru *et. al. J. Phys. Chem. Lett.* **14** (13) 3126-3131 (2023)

# Invited Talks

# X-ray spectroscopic signature of ultrafast hydrogen transfer dynamics in acetylacetone

A. E. Green [1,2], P. Chakraborty [3], E. G. Champenois [1], J. Wang [1], T. Driver [1], LCLS LV29 experiment collaboration, J. P. Cryan[1], T. J. Martinez[1], N. H. List [3], T. J. A. Wolf [1]

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[2]*European XFEL, Germany*
[3]*KTH Royal Institute of Technology, Sweden*
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To study breakdowns in the Born-Oppenheimer approximation and the associated coupled electronic and nuclear dynamics, which are ubiquitous across photochemistry, suitable ultrafast experimental probes are required. Recent developments in ultrafast X-ray sources, driven by breakthroughs in laboratory-based high-harmonic generation and free-electron lasers (FELs), have enabled novel site-specific spectroscopic probes based on transitions involving inner-shell orbitals [1]. Here, we present results from a FEL-based ultrafast O K-edge X-ray absorption study on dynamics of gas-phase UV-photoexcited acetylacetone.



Acetylacetone (shown in Figure 1a) can be considered a model system for studying ultrafast excited-state hydrogen transfer. Absorption in the UV prompts excitation to the $S_2$ (of $\pi\pi^*$ character) state from the enol form. Theory predicts rapid passage from the Franck-Condon region to the $S_1$ ($n\pi^*$) state via a conical intersection and concurrent hydrogen transfer between the two oxygen sites. Utilizing the site-selectivity of our X-ray spectroscopic probe, we observe signatures of these ultrafast coupled electronic- nuclear dynamics through evolving energies of inner-shell transitions involving the two oxygen sites (Figure 1b), in addition to changes on longer timescales associated with intersystem crossing to the $T_1(\pi\pi^*)$ state. The observed spectral evolution is qualitatively similar to that predicted in the related malonaldehyde molecule [2]. To extract these spectra with high energy resolution, we use spectral-domain ghost imaging ('spooktroscopy') methods [3], capitalizing on the inherent stochastic nature of the FEL X-ray pulses.

These results help demonstrate how time-resolved X-ray absorption spectroscopy is a powerful tool in site- selectively probing the non-adiabatic dynamics at the heart of organic photochemistry, particularly in light of the ongoing technical breakthroughs in high-repetition FELs.
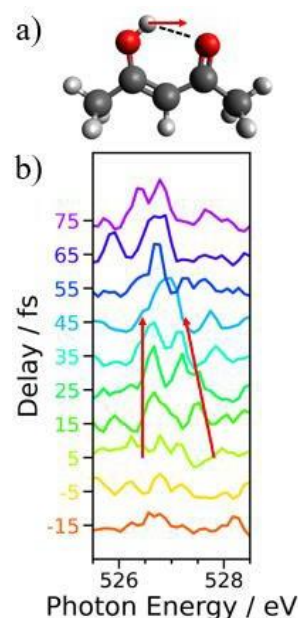
*Fig. 1 a) Structure of acetylacetone, b) Time-resolved X-ray absorption spectra for <100 fs UV – X-ray delay. Red arrows indicate the H motion in a) and the resultant spectroscopic shifts in b).*

**References:**

[1]  T. J. A. Wolf *et al.*, *Nat. Comm.*, *8*, 29, 2017.
[2]  N. H. List *et al.*, *Chem. Sci.*, *11*, 4180, 2020.
[3]  T. Driver *et al.*, *Phys. Chem. Chem. Phys.*, *22*, 2704, 2020.

# Towards molecular movies made with synchrotrons and X-ray free-electron lasers

Till Jahnke

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Capturing "movies" of the dynamic occurring within molecules, for example as a chemical reaction is in progress, has been a powerful motivator in various fields of fundamental sciences over the past few decades. More recently, experimental methods have emerged that incorporate the coincident detection of individual particles to examine the properties of single molecules in the gas phase.

Techniques such as Coulomb explosion imaging utilize extremely short and intense light pulses to disintegrate molecules, enabling the deduction of the original molecular structure based on the fragmentation pattern. Additionally, photoelectron diffraction imaging utilizes the interference pattern of electrons ejected from molecules to glean similar information.

The presentation will provide an overview of these experimental methods and showcase several instances of recent studies carried out at the European X-ray free-electron laser using a COLTRIMS reaction microscope [1,2].

Synchrotron light sources supply light pulses that, in essence, are too extensive to satisfy the conditions needed to film molecular activities. However, there are strategies to work around this limitation by leveraging data obtained from coincidence measurements. The presentation will also highlight examples of such molecular movies created using synchrotron light.

**References:**

[1] J. Ullrich et al., Rep. Prog. Phys. 66, 1463(2003).
[2] T. Jahnke et al., JESRP 141, 229(2004)

# High repetition rate ultrafast electron diffraction

Fernando Rodríguez Díaz, Mark Mero,, <u>Kasra Amini</u>

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Light can initiate numerous chemical reactions, which may be beneficial (*e.g.*, in the process of vision) or harmful (*e.g.*, causing mutations which may lead to cancer). So far, knowledge of the reaction mechanisms and accompanying structural changes in these processes is still not well understood. The evolution of these photo-induced processes is determined by sub-Ångström changes in the position of atoms within an excited molecule evolving on a timescale as fast as a few hundred femtoseconds (fs). So far, ultrafast electron diffraction (UED) [1,2] is often employed to directly image the structural dynamics of photo-induced picosecond gas-phase reactions in real-time with picometre and <300-fs spatiotemporal resolution [3]. However, the temporal resolution of state- of-the-art gas-phase UED setups, often operating at <1-kHz, is insufficient to time-resolve rapidly evolving photo-induced processes (*e.g.*, <350-fs complete timescale of photoisomerization which plays a crucial role in vision [4]). The limited temporal resolution is due to the severe space-charge dispersion experienced in electron pulses containing $10^4$ to $10^5$ electrons. Here, we present a new high repetition rate UED setup that will be capable of performing time-resolved measurements of photochemical reactions in gas-phase molecules with 50-fs temporal resolution, going beyond the current state-of-the-art in non-relativistic and relativistic UED. This is made possible by operating below the severe space-charge dispersion regime using electron pulses containing very few electrons ($<10^3$) but with sufficient electron flux ($>10^7$ electrons/s) thanks to the high repetition rate of our system. Preliminary results from the commissioning of the initial stages of this UED setup are presented (see Fig. 1) with the implementation of radiofrequency-compressed electron pulses [5] and the timing corrections [6,3] often associated with a non-relativistic gas-phase UED setup.
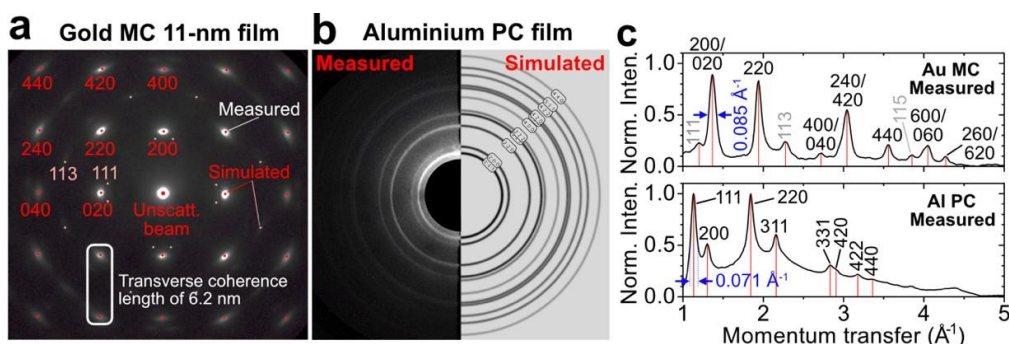


*Fig. 1 (a-b) Electron diffraction of a 70-keV electron beam containing 400 electrons on a gold monocrystalline (MC) 11-nm film (a) and aluminium polycrystalline (PC) film (b) with a 200-µm aperture placed in front of the samples. In (a), the measured diffraction signal (white) and simulated Bragg spots calculated with CrystalMaker® (red/pink circles) are shown. (c) Measured reciprocal- space 1D distribution extracted from (a-b). Crystal planes corresponding to simulated electron diffraction signals are labelled (vertical red lines). The real-space resolution is <14.4-pm.*

**References:**

[1] H. Ihee *et al.*, *Science* **291**, 458 (2001).
[2] K. Amini *et al.*, *Adv. At. Mol. Phys.* **69**, 163 (2020).
[3] D. Filippetto *et al.*, *Rev. Mod. Phys.* **94**, 045004 (2022).
[4] J. K. Yu *et al.*, *J. Am. Chem. Soc.* **142**, 20680 (2020).
[5] T. van Oudheusden *et al.*, *Phys. Rev. Lett.* **105**, 264801 (2010).
[6] M. R. Otto *et al.*, *Struct. Dyn.* **4**, 051101 (2017).

# Predicting excited state charge transfer of donor-acceptor complexes using ground state orbital analysis: from molecular clusters to co-crystals

Laura M. McCaslin

*Sandia National Laboratories*

The structure and properties of donor-acceptor complexes have been widely studied for over 70 years. Crystalline semiconducting materials made up of stoichiometric ratios of organic donor and acceptor molecules, which we call donor-acceptor co-crystals, have long been synthesized and characterized. There has been a recent resurgence of interest in these materials due to their unique, tunable photophysical properties suitable for integration into next-generation optoelectronic devices. When donor and acceptor molecules interact, they form non-covalent bonds deemed charge transfer interactions due to electron density moving from the donor to the acceptor. Identifying donor-acceptor materials that exhibit desired properties is challenging, due to the vast dimensionality of chemical space. For this reason, scientists have developed modern high-throughput screening and machine learning methods to find candidate materials for further experimental study. These screening methods often rely on properties of donor-acceptor dimers such as orbital energies, structural parameters, and vibrational frequencies to predict properties of solid-state materials. One of the greatest challenges that these procedures face is the prediction of photophysical properties of molecular materials, as the calculation of electronic excited states, even in donor-acceptor dimer models, can be prohibitively expensive. Here we present systematic studies of the relationships between orbital structure and excited state charge-transfer in donor-acceptor dimer complexes. We find that the degree of similarity between an isolated donor molecule's highest occupied molecular orbital (HOMO) and the HOMO of a donor-acceptor dimer is predictive of the degree of charge transfer in the excited state characterized by the HOMO $\rightarrow$ LUMO transition (generally $S_1$). This relationship is also true between an isolated acceptor's lowest occupied molecular orbital (LUMO) and the LUMO of a donor-acceptor dimer. The similarity between isolated and complexed orbitals is computed as the integral overlap. This relationship reveals a metric for predicting an excited state property of a complex (charge transfer in the $S_1$ state) based on ground state orbital analysis alone. We deem this analysis a discovery of *orbital structure*-function relationships for predictive materials characterization.

# Influence of ground-state distributions on calculation of photolysis observables

Antonio Prlj[1], Daniel Hollas[2], Basile F. E. Curchod[2]

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Nonadiabatic molecular dynamics offers a powerful tool to study the excited-state dynamics of molecular systems beyond the Born-Oppenheimer approximation. The key to any nonadiabatic dynamics simulation is the definition of the initial conditions, ideally representing the initial molecular quantum state of the system of interest. We provide a detailed analysis of how initial conditions may influence the calculation of experimental observables by focusing on the photochemistry of methylhydroperoxide, the simplest and the most abundant organic peroxide in the atmosphere. Following our protocol for the determination of photolysis observables of transient atmospheric molecules,[1] we investigate the outcomes of trajectory surface hopping simulations for distinct sets of initial conditions sampled from different approximate quantum distributions: harmonic Wigner distribution and ab initio molecular dynamics using a quantum thermostat. We show how the choice of initial conditions critically affects photoabsorption cross-sections, photolysis quantum yields, and translational kinetic energy maps, in particular when low-frequency normal modes are coupled to the photophysics of a molecule.[2,3]

**References:**

[1]  Prlj, L. M. Ibele, E. Marsili, B. F. E. Curchod, *J. Phys. Chem. Lett. 11*, 5418 (2020).
[2]  Prlj, E. Marsili, L. Hutton, D. Hollas, D. Shchepanovska, D. R. Glowacki, P. Slavíček, B. F. E. Curchod, *ACS Earth Space Chem. 6*, 207 (2022).
[3]  Prlj, D. Hollas, B. F. E. Curchod, *submitted*

# Dynamics of the oxygen atom transfer reaction between carbon dioxide and group V cations.

M. Meta[1], M. Huber[1], A. Ayasli[2], T. Michaelsen[2], M. Určák[2], R. Wester[2], J. Meyer[1]

[1]*Fachbereich Chemie und Forschungszentrum Optimas, RPTU Kaiserslautern-Landau, Erwin-Schrödinger Str. 52, 67663 Kaiserslautern, Germany*
[2]*Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25/3, 6020 Innsbruck, Austria*
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Reaction dynamics open a window into the fundamental process of elementary reactions, that is into the reactive collision. Understanding chemistry at this level will help us to derive detailed structure reactivity relations with the final aim at controlling chemical reactivity using a bottom-up approach. We probe reactive collisions in the gas phase to investigate these atomistic dynamics using a combination of crossed beams and velocity map imaging (VMI) to record experimental angle and energy differential cross sections. [1].

We apply the method of crossed beam velocity map imaging to reactions between transition metal ions and small molecules, like methane and carbon dioxide. In a first study, we investigate the oxygen atom transfer (OAT) reaction between a transition metal cation and carbon dioxide $M^+$ + $CO_2 \rightarrow MO^+$ + CO with the transition metal being one of the group V elements (Nb, Ta). These four-atom reactions present model systems for multi-state reactivity often found in transition metal ion chemistry. The reactions are spin forbidden in the ground state of the cation but allowed in the first electronically excited state [2-5]. Further, several electronic states of the product cation $MO^+$ are accessible. We recorded energy dependent velocity map images of the $MO^+$ product ion at relative collision energies up to 2eV. At the highest investigated collision energy, direct dynamics can be seen. The product ion velocity distributions show indirect dynamics to be dominant even at high collision energy. Additional collision energy is preferentially partitioned into internal excitation leading to a near constant kinetic energy release which is a signature of a bottleneck along the reaction coordinate. We compare our recent results on niobium with those of the heavier tantalum.

**References:**

[1]  J. Meyer, R. Wester, *Annu. Rev. Phys. Chem.* 2017, *68*, 333
[2]  R. Wesendrup, H. Schwarz, *Angew. Chem. Int. Ed.* 1995, *34*, 2033
[3]  G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* 2006, *110*, 1232
[4]  N. Levin, J. T. Margraf, J. Lengyel, K. Reuter, M. Tschurl, U. Heiz, *Phys. Chem. Chem. Phys.* 2022, *24*, 2623
[5]  M.R. Sievers, P.B. Armentrout, *Int. J. Mass Spectrom.* 1998, *179/180*, 103

# Probing the vibrational wave packet dynamics of mass-selected neutral metal clusters

Jiaye Jin, Max Grellmann, and Knut R. Asmis

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Metal clusters possess remarkable photoelectric and catalytic properties, making them subject of current research. The studies on metal clusters isolated in the gas phase do not only provide detailed information on their intrinsic properties, like geometric and electronic structure, molecular vibrations, bonding energies and time scales for internal energy redistribution in the absence of a perturbing environment, but also represent ideal model systems for benchmarking modern quantum chemistry methods. However, obtaining vibrations on neutral metal clusters remain challenging, due to difficulties in mass-selecting neutral clusters and a lack of easily accessible and widely wavelength-tunable far infrared light sources.

Here, we report our recent results on vibrational wave packet dynamics for mass-selected neutral metal clusters that allow us to access detailed vibrational information in the far-IR spectral region as well as in the femtosecond time domain. For this purpose, we combine femtosecond pump-probe spectroscopy with the negative-neutral-positive (NeNePo) excitation sheme and using a cryogenice ion-trap tandem mass spectrometer.[1,2] A femtosecond pump pulse is used to produce a vibrational wave packet on the neutral gourd electronic state by photodetachment from the corresponding mass-selected cold anionic cluster. The vibrational wave packet dynamics are probed using a second femtosecond pulse, which ionizes the neutral cluster. The mass-selected cation as a function of the delay time between two pulses yields the fs-NeNePo spectrum. The obtained transient spectra are fruitful for investigating the vibrations of metal-metal bond on a particular potential energy surface (PES) as well as the energy flow in metal clusters on a femtosecond or picosecond (ps) time scale.

**References:**

[1]  S. Wolf, G. Sommerer, S. Rutz, E. Schreiber, T. Leisner, L. Wöste, Phys. Rev Lett. 74, 4177 (1995)
[2]  J. Jin, M. Grellmann, K. R. Asmis, Phys. Chem. Chem. Phys. (2023)

# Towards a relativistic QED for atomic and molecular bound states

<u>E. Mátyus</u>, D. Ferenc, P. Jeszenszki, Á. Margócsy

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Relativistic quantum electrodynamics developments are presented with the aim of developing (the practical applicability of) the fundamental theory of molecular matter in relation with precision spectroscopy experiments. Interactions in atomic and molecular systems are dominated by electromagnetic forces and the theoretical framework must be in the quantum regime. The physical theory for the combination of quantum mechanics and electromagnetism, quantum electrodynamics has been 'established' by the mid-twentieth century, primarily as a scattering theory. To describe atoms and molecules, it is important to compute bound states. In the non-relativistic quantum mechanics framework, bound states can be computed to high precision using robust and general methodologies by solving *wave equations.* With the sight of the development of a computational quantum electrodynamics framework for atomic and molecular matter, the field theoretic Bethe–Salpeter wave equation expressed in space-time coordinates, its exact equal-time variant and emergence of a relativistic wave equation is re- viewed. An explicitly correlated variational framework for solving this relativistic wave equation is presented, which allows to converge the energy within a (sub-)parts-per-billion (ppb) relative precision. These variational relativistic computations have extensively been tested with respect to the traditional perturbative framework, *i.e.,* expansion of the total energy about the non-relativistic reference with respect to the $a$ fine structure constant, which currently provides benchmark theoretical values for precision spectroscopy of atoms and molecules with the smallest $Z$ nuclear charge numbers. To have results useful for precision spectroscopy from a variational relativistic approach, it is necessary to account also for pair, retardation, and radiative corrections to high precision. Ongoing work and open challenges are discussed based on the equal-time Bethe–Salpeter equation and a high-precision, variational relativistic wave function.

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# Bonding nature between noble gases and small gold clusters

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Noble gases are usually seen as utterly inert, likewise gold, which is typically conceived as the noblest of all metals. While one may expect that noble gases bind to gold via dispersion interactions only, strong bonds can be formed between noble gas atoms and small gold clusters [1]. In this contribution, we present combined mass spectrometry, infrared spectroscopy, and density functional theory calculations to address the bonding nature between $Au_n^+$ ($n \leq 4$) clusters and three noble gas atoms: Ar, Kr, and Xe. We unambiguously determine the geometries and quantitatively uncover the bonding nature in $Au_nNg_m^+$ (Ng = Ar, Kr, Xe) complexes [2]. Furthermore, we show a unique feature of the $AuXe_3^+$ complex, where the $Au^+$ ion leads to the stabilization of a Xe-Xe interaction going beyond purely dispersive [3]. As a consequence, $AuXe_3^+$ adopts a linear structure, in which two Xe atoms form a direct bond, instead of an expected geometry in which three Xe atoms coordinate directly with a central $Au^+$ ion [4].
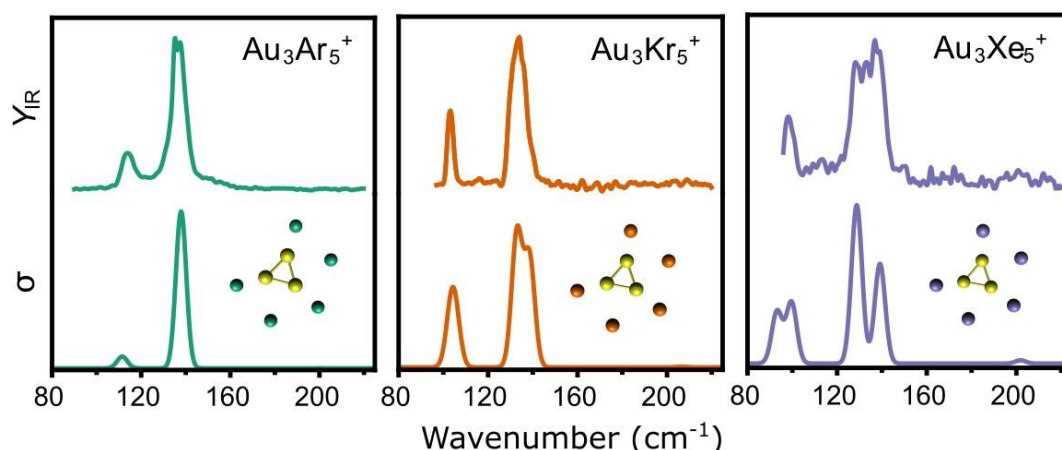


*Figure 1. Experimental (top of each panel) and calculated (bottom) infrared spectra of $Au_3Ng_5^+$. Each cluster geometry appears as an inset, with Au (yellow), Ar (green), Kr (orange), and Xe (purple).*

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# X-ray induced electron dynamics in water: theoretical modelling

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Charge transfer is in the heart of fundamental processes in nature; in many cases it takes only femtoseconds and it is often mediated by electrons. In this work, we investigated the X-ray-induced electron dynamics between the solvated isoelectronic cations ($Na^+$, $Mg^{2+}$, and $Al^{3+}$) and water. The ions represent systems with varying strength of interaction with the environment; the interaction ranges from ion-dipole to coordination bonding. Experimentally, the X-rays excite 1s electrons of the cations into unoccupied levels and the wave packet within femtoseconds evolves into delocalized state over the neighboring water molecules. The timescale was measured by the core-hole clock method and it varies for different cations reflecting the strength of the interactions. From the theoretical perspective, the process involves modelling of core-excited states in liquids and modelling of subsequent two- electron Auger decay. Modelling of the electron dynamics itself is extremely challenging for the highly-excited states in liquids but will be a matter of further study.
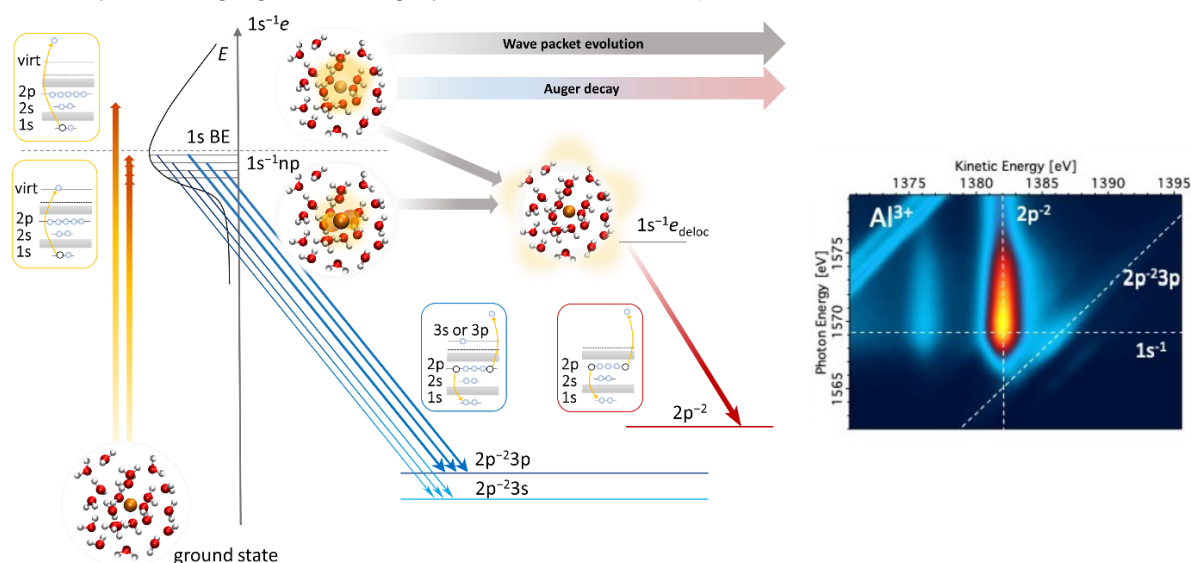
*Figure: Schematic representation of the X-ray initiated processes. Orange arrows show core excitation/ionization, grey arrow shows wave packet evolution, and blue and red array shows Auger decay. Excitation of the 1s electron yields a partially delocalized wave packet. After excitation, the wave packet evolves towards stationary states and in parallel, the core hole undergoes the Auger decay.*

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# Probing DNA radiosensitization in solution using DNA nanotechnology

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Fabrication of nanostructures from DNA has led to interesting applications, especially in constructing frameworks for guided assemblies of inorganic nanoparticles for sensing, and even biomolecules and drugs for pharmaceutics [1]. In our laboratory, we use DNA origami (DO) nanostructures formed by folding long single-stranded DNA scaffolds using shorter complementary staple strands. These nanostructures offer addressable sites that allow for the immobilization of various components within precise nanometric spacings, which is ideal for exploring distance-dependent mechanisms at the nanoscale [2]. We then link DNA sequences of interest on DO nanoplatforms and examine their response to ionizing radiation relevant to cancer radiotherapy. We have already shown the structural stability of bare DO in solution over a wide dose window under ionizing radiation, demonstrating their potential for use as substrates in irradiation experiments [3]. We then investigated the radiosensitization of DNA by halogenated nucleosides using DO nanoframe supports (Fig. 1), on which strand breaks can be observed through Atomic Force Microscopy (AFM), as well as by Real-Time Polymerase Chain Reaction (RT-PCR). Enhancement of total and double-strand breaks can vary depending on the type of incorporated halogenated nucleoside, and the damage is also felt by an unsensitized neighboring strand placed ~10 nm away [4]. By exploring these damage mechanisms, we could generate some insights into the improvement of existing radiotherapeutic modalities dedicated to enhancing DNA damage in tumor cells. Preliminary results on ion-beam-induced damage to DO will also be presented as well as potential applications for DO as a carrier for possible radiosensitizers in more complex/biological environments.
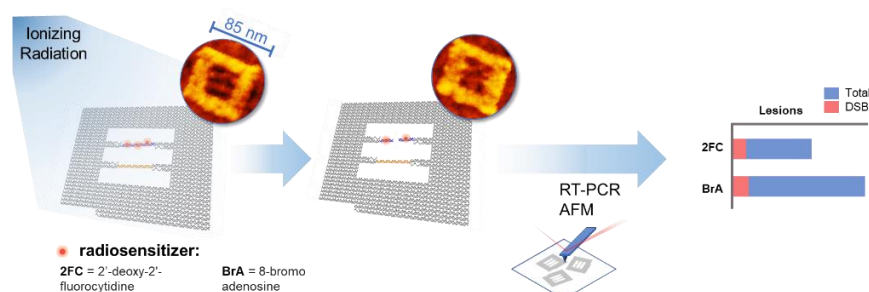


*Figure 1. Scheme of irradiation experiments on a DO nanoframe with parallel strands of interest in its aperture [4]. This allows for direct comparison between sensitized and unsensitized DNA strands.*

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# New insights into the volume isotope effect of ice Ih from polarizable many-body potentials

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In crystalline phases of water nuclear quantum effects manifest themselves quite prominently in macroscopic thermodynamic properties, like for example density change at low temperatures [1] upon substitution of a light by a heavier isotope or phase transition enthalpies [2]. The former is called the volume isotope effect (VIE). In most materials, substitution with a heavier isotope results in a smaller volume at temperatures approaching the absolute zero. Handwavingly, in a classical picture, this can be rationalized by the smaller vibrational amplitude ascribed to a heavier nucleus experiencing the same chemical interaction potential at the same temperature. In contrast, the volume of the $D_2O$ isotopologue of ice Ih is 0.1% larger than its $H_2O$ counterpart, which is called anomalous VIE. Earlier computational studies established a link to the zero-point energy of intra- and intermolecular vibrational modes (phonons). However, even the most elaborate force fields developed from basic principles yielded a normal VIE in clear contradiction to experiments. Furthermore, DFT calculations with various exchange-correlation functionals have been struggling to get close to the experimental data. This made it difficult to determine which contributions to the interaction potential result in what effects on the different types of phonon modes and impossible to identify which of them are responsible for this subtle effect.

Motivated by recent high-precision neutron diffraction experiments [3], here we present a computational study based on the quasi-harmonic approximation [4]. We focus on recently developed polarizable many body potentials [5,6] and find that one of them, MB-pol [6], yields the anomalous VIE in good agreement with the most recent high-resolution neutron diffraction measurements – better than many density functionals. We further scrutinize the interaction potentials by decomposing the zero-point pressure into contributions from different vibrational mode groups. This allows us to confirm the remarkable performance of MB-pol by comparing to a hitherto unconsidered "independent" benchmark value for the intramolecular stretching modes of $H_2O$ ice Ih obtained from Raman spectroscopy data. According to MB-pol, the librational and stretching are the most important phonon modes responsible for the anomalous VIE, mitigated by short-range three- body effects. This prediction is experimentally verifiable. Our study thus goes one step further towards a deeper understanding of hydrogen-bonding in this most ubiquitous and important system.

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# Theoretical insights into anion-binding organocatalysis: fine-tuning of enantioselectivity

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Asymmetric anion-binding catalysis[1] has become a powerful synthetic tool in recent years. However, only a limited number of catalyst's motifs are available i.e. based on chiral bidentate N-H and, more recently, O-H hydrogen-donor catalysts such as thioureas[2] and silanediols,[3] respectively. Additionally, while anion-binding offers high flexibility and tunability, the non- covalent interactions involved are experimentally more difficult to control compared to the covalent approaches, especially looking at the C-H binding.[4] Therefore, theoretical approaches are necessary to tune the many-body reactions in a way to strengthens or activates the given type of binding mode.[5] The first example of enantioselective (*ee*) activity of the Iodo-TetrakisTriazoles was recently shown.[6] In the next step, we have investigated the possibility of tuning the *ee* introducing additional halogen bond (XB) interactions between the reactants and catalyst. An extensive analysis of the transition state structures, energetics, and wave function analysis of the catalytic systems has been performed based on quantum chemical calculations for the two enantioselective routes ((*S*) and (*R*)). We found cooperative XB interactions with additional stabilization effects that drove the reaction pathway towards the (*S*)-product formation with a very good 66% *ee*. Excellent agreement with the experiments has been found and further optimization of the reaction allows us to achieve the exceptional 90% *ee*.[7]

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# Quantum chemical modelling of atmospheric molecular clusters enhanced by machine learning

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Formation of atmospheric molecular clusters and their subsequent growth into secondary aerosol particles have a pronounced impact on our global climate. Due to small cluster sizes and low cluster concentrations, it is very difficult to measure the initial steps of new particle formation or even explain its molecular mechanism. To investigate this phenomenon, we applied quantum chemical calculations to study the cluster thermodynamic stabilities. The collision probabilities are obtained via kinetic gas theory and cluster population dynamics are applied to study the particle formation mechanism (see Figure 1). Many previous studies have already used this methodology and revealed the importance of many binary systems (e.g., sulfuric acid–ammonia, sulfuric acid–methylamine) in atmospheric new particle formation. We also use this traditional multi- level, funnel, configurational-sampling approach.[1]
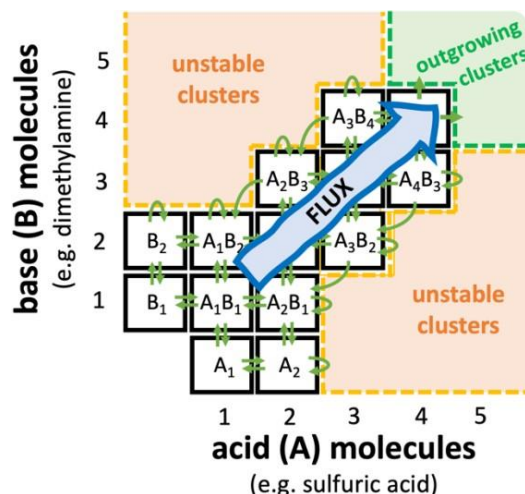


*Figure 1. Typical scheme for cluster population dynamics. Monomers A and B are combined into clusters which eventually grow towards aerosol particles.*
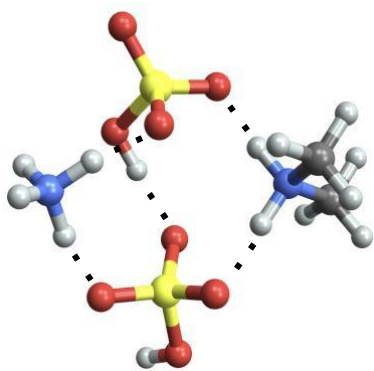


*Figure 2. Example of a SA$_2$AM$_1$DMA$_1$ cluster.*

However, we augmented this procedure with machine-learning (ML) step which reduces the number of the required computationally demanding quantum chemistry calculations. In this presentation, we discuss newly benchmarked quantum chemistry methods for molecular clusters formation [2] and the potential enhancements due to utilization of ML techniques.[3] For example, utilizing ML immensely accelerated the whole configurational sampling process and allowed us to examine significantly more (316) different clusters of the atmospherically relevant clusters composed of sulfuric acid and up to five different base molecules: ammonia AM, dimethylamine DMA, trimethylamine TMA, methylamine MA, and ethylenediamine EDA. See, for instance, the SA$_2$AM$_1$DMA$_1$ cluster in Figure 2. We reveal the atmospheric role of the individual bases and their synergy with other base molecules within (multi-component) sulfuric acid–multi-base new particle formation.

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# Photoemission from droplets and particles

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Droplets and particles emerged as promising systems to investigate light-matter interactions on the nano- and micrometer scale [1]. While molecules in their interior are essentially in a bulk environment, high surface-to-volume ratio allows surface-specific properties to emerge. In addition, their finite size requires considering often invaluable effects of optical confinement. Following photoemission of electrons and ions from these finite-sized samples, therefore offers an exciting route to better understanding of electronic processes in condensed phase.

In this talk, I will describe a versatile photoelectron imaging setup that can be used to study liquid droplets, as well as solid particles in a submicrometer size regime (100 nm to a few μm in diameter). The setup implements techniques from aerosol science to prepare a droplet beam in vacuum, whose physical properties (i.e. size and charge) can be controlled and characterized [2]. Together with a velocity-map imaging spectrometer and ultrafast laser pulses ranging from infrared to extreme ultraviolet, the setup allows for time-resolved investigations of electronic processes in various condensed phase samples.

I will present a few examples that highlight the importance of interfaces and finite size for electronic processes in droplets [3,4].
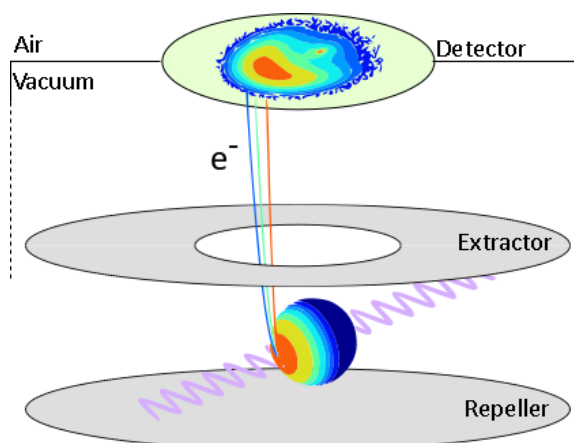


*Figure 1. Sketch of a typical photoelectron imaging experiment on droplets.*

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# Infrared action spectroscopy of ions embedded in helium nanodroplets

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Infrared (IR) action spectroscopy of mass-selected ions is a powerful gas-phase method for the structural determination of biomolecular ions and complexes. The most used technique for this purpose, Infrared Multiphoton Dissociation (IRMPD) suffers from bandwidth broeading mainly associated with the multiphoton absorption process. With this, the obtained spectral resolution is often not high enough to fully resolve vibrational features and be able to distinguished between similar conformers. Infrared action spectroscopy of ions embedded in liquid helium droplets (HeDrop), instead, has the advantage of analyzing the molecular ions at the equilibrium temperature of the He droplet ($\approx 0.4$ K), greatly reducing the spectral congestion. Moreover, because in a superfluid state, the helium droplet exhibit a very high thermal conductivity, allowing a rapid cooling of the dopant ion after light absorption. These unique properties allows us to obtain highly-resolved IR spectra.[1]

Here we show some results on the structure of the deprotonated formic acid trimer in helium nanodroplets. In this case, the lowest energy structure predicted by theory does not match the experimental spectra, and it is most likely related with either the kinetics and dynamics of the complex formation or its interaction with the helium environment.[2] Moreover, a comparison between the IRMPD and HeDrop IR spectra of protonated crown ethers will be shown, along with theoretical calculations. In here, the highly-resolved HeDrop IR allows us to account or discard the coexistence of more than one conformer in the gas phase, at experimental conditions.

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# Beyond structure-solving with rotational spectroscopy: new molecular libraries, new methods, new challenges

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Rotational spectroscopy has in recent years emerged as an outstanding tool for molecular structure elucidation, enabling novel exploratory approaches with unprecedented tracing capabilities. The enhanced sensitivity and broadband capabilities of chirped-pulse Fourier transform microwave spectroscopy [1] unlocked investigations into increasingly intricate molecular species [2], including notable examples such as artificial molecular motors [3]. Leveraging the inherently narrow line widths of rotational transitions, microwave spectra are unique molecular fingerprints, facilitating unambiguous determination of precise three-dimensional structures and even enabling identification and quantification of enantiomers through recently developed strategies [4-6]. In this contribution, we will discuss recent findings showcasing the wide-ranging applications of rotationally resolved spectroscopy in the realm of molecular structure elucidation and beyond.

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# Detection of new molecules in space by rotational spectroscopy: analysis of indole

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Most of the chemical species identified in the interstellar medium (ISM) or circumstellar envelopes (CSE), about 290 species, have been detected by rotational spectroscopy. Earth observatories, like the IRAM 30 m or the 40 m Yebes radiotelescopes, detect the spectral emission of the chemical species present in the objects of the ISM or CSE in the millimeter frequency ranges (around 75-300 GHz). Those spectra contain transitions from all the chemical species in space, hence, if the rotational spectra of each individual specie is not known, the identification of individual species is almost impossible. Our goal in the laboratory consists of providing the experimental spectroscopic parameters (rotational constants and conformational behavior) to be able to identify the chemical species in the space.

In the molecular cloud TMC-1 (Taurus Molecular Cloud) several complex organic molecules (COMs) have been detected, between them, the first aromatic species, like: eg. benzonitrile, indene… [1]). These detections contribute with essential information to the question of the presence of the PAHs (polycyclic aromatic hydrocarbons) in the space.

Indole is a PAH (see Figure 1) whose structure is relatively close to indene or cyanoindene, both detected in TMC-1. The rotational spectra of indole is known up to 60 GHz [2] but to be able to search for this species in the space a precise set of rotational parameters and a wide frequency range are required. In the Physical Chemistry department of the University of Valladolid, we have now available a broadband chirped pulsed rotation spectrometer covering the 75-110GHz frequency range. In the present talk, I will introduce the spectroscopic

**Fig. 1** *Structure of Indole*

fundamentals and the work about molecules of astronomical interest that we are working on in the group, with special attention to the analysis of the rotational spectrum of indole up to 110GHz. More than 400 transitions for indole will be included in a global analysis that will allow to search this species in molecular clouds like TMC-1 in the space.

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# Photodissociation and photoionization in space: from the ISM to exoplanetary atmospheres: recent updates to the Leiden VUV cross section database

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VUV photons are important drivers of chemical processes in space. Thus, it is important to accurately characterize and constrain photorates in different radiation fields. This is done by utilizing photodissociation and photoionization cross sections of individual atoms and molecules which have been available in the Leiden VUV Photodissocation and Photoionization cross section database.[1]

Experimental and theoretical advances in the past decade or so have allowed multiple new cross sections to be obtained, particularly photoionization cross sections of radicals. The database is hereby updated by including these more recent cross sections and is also expanded with several astronomically relevant species.[2]

The cross sections have been used to calculate photodissociation and photoionization rates in several different radiation fields as well as from cosmic ray induced VUV fluxes. The reduction of rates in shielded regions has also been calculated as a function of dust, molecular and atomic hydrogen, atomic carbon, and self-shielding column densities. The relative importance of these shielding types is molecule/atom dependent, as well as the assumed dust absorbance. All the data are publicly available from the Leiden VUV cross section database.[1]

The Leiden VUV cross section database has been updated with 14 new astrophysically relevant molecular species and 16 updates to previous entries. During this presentation I will give a brief introduction to cross sections, particularly the measurements of photoionization cross sections of radicals, the calculation of photorates, shielding, and current/future challenges.

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# Control of chemi-ionization by quantum-state preparation

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

As a first step towards co-trapping of Li and metastable He, my group at the University of Freiburg has studied and controlled the chemi-ionization of ultracold Li by He in the metastable $2^1S_0$ and $2^3S_1$ states. We have observed a strong suppression (enhancement) of chemi-ionization for non-spin-conserving (spin-conserving) reaction channels after all-optical electron-spin-state preparation of both atomic species [1]. The ionization rate also decreases when Li is laser-excited to the $2^2P_{1/2,3/2}$ states [2] and when He is laser-excited to the $2^3P_{0,1,2}$ states [3], respectively. In this talk, I will explain the underlying mechanisms.

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# Hot Topic Talks

# Revolutionizing velocity map imaging with timepix3 technology

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Velocity map imaging (VMI) is a powerful technique for studying the dynamics of molecules and processes in the gas phase. However, conventional VMI detectors such as CMOS-based cameras or delay line detectors have limitations in terms of temporal and spatial resolution and the number of particles that can be detected. Timepix3 technology offers a revolutionary solution to these challenges, providing sub-nanosecond time resolution, excellent spatial resolution, and the ability to detect a large number of particles in real-time. With the help of Timepix3, it is possible to extract detailed information regarding particle dynamics, such as energy, velocity, and position.

I will discuss the advantages of Timepix3 technology for VMI experiments [1][2][3] and show how it has enabled us to gain insights into molecular dynamics. We will describe the design and implementation of different VMI setup, which uses Timepix3 detectors, and present experimental results demonstrating this technology. I will show how Timepix3 has enabled us to detect rare events that were previously difficult to observe and gain information about molecular dynamics.

Our results show how Timepix3 technology has the potential to revolutionize the VMI industry by enabling high-resolution and real-time imaging of atomic and molecular processes. Timepix3 technology will help us understand the underlying physical and chemical mechanisms that control these processes and will create new possibilities for the development of innovative applications in a wide range of scientific fields.

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# Ultrashort, deep-ultraviolet pulses by resonant dispersive wave emission from hollow capillary fibres for time-resolved photoelectron imaging

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We exploit the phenomenon of resonant dispersive wave (RDW) emission in gas-filled hollow capillary fibres to realise time-resolved photoelectron imaging (TRPEI) measurements with an extremely short temporal resolution of just 10 and 11 fs at central pump wavelengths of 250 and 280 nm, respectively. This first demonstration of the application of RDW pulses to spectroscopy represents an advance in the current state of the art for ultrafast photoelectron imaging. We also present an initial TRPEI measurement investigating the excited-state photochemical dynamics operating in the N-methylpyrrolidine molecule. Looking forward, we present work in progress on upgrading our system to higher UV conversion efficiencies and shorter temporal durations.
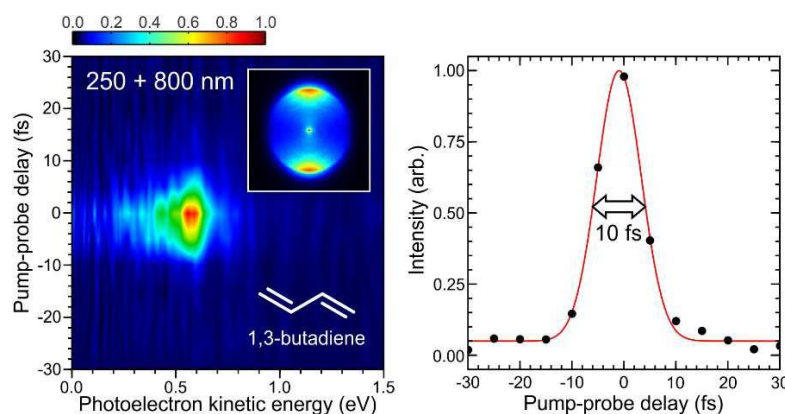


*Figure 1. Left: Time-dependent photoelectron spectrum of 1,3-butadiene obtained using a 250 + 800 nm, 1 + 3' ionization scheme. A photoelectron image obtained close to zero pump–probe delay is inset. Right: The energy integrated photoelectron transient with a Gaussian fit is shown in red with the temporal full-width half-maximum labelled.*

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# Crossed-beam and theoretical studies of the multichannel nonadiabatic reaction O($^3$P) + 1,2-butadiene

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Reactions between unsaturated hydrocarbons (UHs) and $^3$P oxygen atoms are crucial elementary steps in detailed combustion mechanisms. These reactions involve a range of energetically open and competing product channels, some of which can only occur through intersystem crossing (ISC) from triplet to singlet potential energy surfaces (PESs). While the overall kinetics of many of these reactions have been extensively studied, there is much less knowledge about the primary products' identity and their branching fractions (BFs), particularly at combustion temperatures. The most effective way to address this issue is to combine crossed-molecular-beam (CMB) experiments with universal, soft ionization, mass-spectrometric detection and time-of-flight analysis to high-level ab initio electronic structure calculations of triplet/singlet PESs and RRKM/Master Equation computations of product BFs, including ISC.[1-6] This method has recently been demonstrated to be successful in studying O($^3$P) reactions with simple UHs (such as alkynes, alkenes, and dienes) containing two [1], three [2-4], and four [5,6] carbon atoms. Here, we extend the combined CMB/theoretical approach to 1,2-butadiene (methylallene), the next member of the diene series with four C atoms, to investigate how the product distribution, branching fractions, and ISC change as the molecular complexity increases. By analyzing product angular and velocity distributions obtained from measurements at different masses, we have identified primary products from *nine* competing channels arising from both triplet and singlet PESs. Notably, CO+$C_3H_6$ (propene) was found to be the main reaction channel (BF=0.49) and occurs via ISC, whereas $CH_3$+$CH_2CCHO$ (BF=0.14) is the second most important one and occurs on the triplet PES. Interestingly, these two reaction channels play a crucial role as they cause chain termination in combustion systems, unlike radical-forming channels (overall BF=0.37) which instead lead to chain propagation. We found that the extent of ISC is 70%. Comparison of the experimental BFs with theoretical ones shows good agreement. These results are expected to be highly beneficial in developing more accurate combustion models.

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# A system-bath model to investigate the interaction of a molecule with its environment

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Addressing the dynamics of molecular systems coupled to an environment is a challenging task, especially when considering finite-size environments that can be affected by their interactions with the smaller system. In such cases, the usual open quantum system methods and approximations might fail as they assume that the environment (or "bath") is infinite, always at thermodynamical equilibrium, and not perturbed by the system [1]. In particular, they do not take into account the fact that finite environments can be heated by the excitation of the system and evolve out of equilibrium. For example, such situations may occur when studying molecules in clusters or matrices [2], or when probing small molecules trapped in fullerenes [3] or clathrates [4].

In this context, we are developing a new theoretical model based on a system-bath approach where we consider a one-dimensional system (*e.g.* one vibrational mode) interacting with a large harmonic bath (~100-1000 modes). The system and its coupling to individual bath modes are treated as rigorously as possible but the bath part of the Hamiltonian is simplified with its modes being replaced by a ladder of effective quantum energy states which describes the energy stored in the bath. This model allows us to study the relaxation dynamics of the system at finite temperature and to analyze the response of the bath to the system's excitation. In this contribution, we will present the first results obtained by using this method on a system taken from [5], where an O-H stretching mode interacts with a "surface" modeled by a set of 40 to 800 harmonic oscillators.
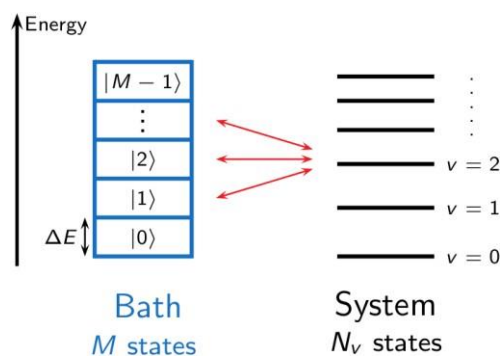


*Figure 1. Schematic view of our model with the vibrational levels of the system (in black), the effective states of the bath (in blue) and the coupling between the two (in red).*

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# Using X-ray action spectroscopy to probe the protonation site of gas-phase biomolecular ions.

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Over the past decades, biomolecules such as peptides and proteins have been investigated in the gas phase using state-of-the-art mass spectrometric techniques combined with electrospray ionization sources. In order to obtain new insights into the electronic and structural properties of such biomolecules, X-ray action spectroscopy experiments, which are based on the resonant photoexcitation of core electrons, have been carried out at synchrotron facilities, which offer a broad photon energy range and a high photon flux and tunability. It has been successfully used to unravel different aspects of the photodissociation of peptides and to probe conformational features of proteins. It is a current question to which extent the resonant photoabsorption are sensitive toward effects of conformational isomerism, tautomerism, intramolecular interactions, and (de)protonation, in gas- phase biomolecular ions. In particular, in the biological medium, the charge states of molecules such as peptides, proteins, and nucleic acids, plays a significant role as they influence conformation and reactivity. Within the physiological pH range, an important mechanism altering the charge state is the protonation and deprotonation of specific chemical groups. Improving our understanding of biological processes and of the structure-function relationship requires us to localize the (de)protonation sites in biomolecules.

Here, we explored the ability of X-ray action spectroscopy to probe the protonation site and resolve specific electronic transitions at the nitrogen and oxygen K-edges. We first investigated the protonated 4-amino benzoic acid, which protonation can occur at either the carboxylic or amino group. In order to map the electronic transitions of the different protonation sites in peptides, we studied, experimentally and theoretically, the following tailored peptides: Gly-Gly-Gly-Gly-Xxx where Xxx is the basic residue Arginine, Histidine or Lysine (protonated side chain, non-protonated N-terminus), Pro-Gly-Gly-Gl-Gly, Gly-Gly-Gly-Gly-Gly (protonation on N-terminus), Ac-Gly-Gly-Gly-Gly-Gly (backbone protonation) and Gly-Gly-Gly (controversy protonation site). The experiments have been performed at the P04 soft X-ray beamline of the PETRA III synchrotron (DESY, Hamburg, Germany) and at the UE52_PGM Ion trap beamline of the BESSY II synchrotron (HZB, Berlin, Germany).

# X-ray imaging of nanostructures in superfluid helium droplets

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A self-bound superfluid helium droplet is an extremely cold and frictionless medium for growing metastable and self-organized dopant nanostructures. Their visualization offers an opportunity to identify different structure formation regimes and dissect the mechanisms driving their assembly. Using X-ray coherent diffractive imaging, three regimes have been distinguished: vortex-free aggregation, vortex-induced aggregation, and cluster network formation [1,3]. In this contribution, we point out that the regime boundaries depend on the droplet size and the number of dopants, and on how the droplet's rotational state influences the types of structure formed. Additionally, the transition between the vortex-free and vortex-induced aggregation was discovered to occur when the droplet contains about $10^8$ atoms; only partially affected by how the droplets are generated [3]. These results not only present a means of controlling structure formation in superfluid helium droplets, but they also lay the foundation for imaging the assembly of nanostructures with different intermolecular forces for future studies.

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# The naphthalene radical anion in the context of birch reduction: when solvation is the key

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The naphthalene radical anion is widely used as a reducing agent in the synthesis of organic, inorganic and organometallic chemistry [1]. Moreover, it is a molecular anion pertinent to several organic reactions, including the Birch reduction processes. Beyond organic chemistry, it is an intriguing subject to study solvation phenomena: in the gas phase, the species appears as a metastable shape resonance, while upon solvation in the liquid phase, it remains stable.

Here, we approach the system by conducting liquid jet (LJ) experiments in combination with photo-electron spectroscopy (PES) to determine the complex electronic structure of neutral naphthalene as well as the naphthalene radical anion dissolved in tetrahydrofuran (THF). We employ recently developed techniques for the accurate determination of vertical ionization energies (VIEs) [2,3]. Firstly, this enables us to characterized the changes of the electronic structure of the valence band between the neutral and the anionic species. Secondly, we can also quantify the magnitude of changes in the electron affinity which directly reflects the lower stability and the higher reactivity of anionic species compared to the neutral one.

To complement this study, we performed molecular dynamics simulations of these solutions to understand the complex electronic structure. We find that the inclusion of the solvent is crucial and indeed leads to stability of the anion. Moreover, the theoretical models enable comparisons to other aromatic hydrocarbons and their anionic species. Thus, we discuss general implications on the formation, stability and reactivity of aromatic radical anions in solution – especially the benzene radical anion [4] – defining the crucial intermediate in a Birch reduction process.

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# Molecules with diffuse electrons mimick atoms and disclose novel materials for catalysis and quantum computing

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We present electronic structure and chemical reactivity information for ground and excited electronic states of metal ammonia complexes. These complexes (called solvated electron precursors or simply SEPs) have the unique feature to accommodate bound diffuse electrons in their ground state. They are present in concentrated metal ammonia solutions, where the solvated valence electrons of the metal orbit around the positively charged metal ammonia skeleton. For example, $Li(NH_3)_4$ has a $Li(NH_3)_4^+$ core and one peripheral electron. Our state-of-the-art ab initio wavefunction and density functional theory calculations show that the diffuse electrons populate a hydrogenic shell model but with the nuclear or jellium shell energy order: 1s, 1p, 1d, 2s, 2p, 1f, 2d [1]. We demonstrate that transition metal ammonia complexes retain electrons in both their inner-d shell and the peripheral orbitals [2]. In addition, two such complexes can bind together like two hydrogen atoms producing molecular hydrogen and form σ, σ*, π, π* orbitals identical to traditional diatomic molecules [3]. The formation of dimers and polymers is confirmed experimentally in saturated lithium ammonia solutions which turn to the so-called liquid or expanded metals. For the first time, we propose the bridging of two SEPs by replacing ammonia ligands with diamines or hydrocarbon chains. For small chains the two diffuse electrons couple into a closed-shell singlet, but for longer chains the two electrons prefer a triplet spin configuration. The spin coupling can be adjusted by the chain length and by decorating the chain with functional groups [4]. We finally demonstrated that SEPs can capture, reduce, and convert $CO_2$ to industrial platform chemicals simultaneously avoiding additional catalysts [5]. Based on these results, we proposed the existence of novel 2d- and 3d-materials composed of SEPs linked together with hydrocarbon chains, which can potentially serve both as redox catalysts and quantum computing materials. The electronic band structure for such materials is reported and explained.

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# Can molecular docking simulation accelerate material discovery?

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Molecular docking describes how two molecules bind to each other. It can be studied using complex microscopy and spectroscopy techniques [1] or molecular docking simulation (MDS) [2], which can treat many molecules at the same time with low computational cost. MDS is now a mature tool for biomolecules, speeding up drug discovery. Interestingly, the same concept could also revolutionize materials sciences. However, only few studies have used MDS to study binding to non-biological materials, such as ref. [3]. The main reason is that MDS has been developed for biomolecules and limitations are expected when the present MDS versions are applied to other materials, such as metal-organic frameworks (MOFs) which contain both organic and inorganic building units. Regardless, our assessment of MDS performance for studying gas uptake and drug delivery by MOFs shows that the current MDS software can surprisingly predict binding mechanisms well. However, it has serious shortcomings that must be addressed to reliably speed up material discovery. A major shortcoming is the lack of a universal forcefield representing all categories of materials and its implementation in the current MDS software.

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# Nonadiabatic dynamics reveals the limitations of Marcus theory for electron transfer

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Marcus theory is one of the simplest and yet most prominent models used for understanding the mechanistic aspects and kinetics of various electron transfer reactions [1]. It relates the electron transfer rate constant to quantities, which are relatively easy to calculate for most molecular systems, such as the driving force ($\Delta G$) of the reaction and the reorganization energy ($\lambda$). Consequently, it is broadly applied to elucidate charge transfer processes occurring on the surfaces of ground as well as excited electronic states of various organic and inorganic donor-acceptor molecular systems, such as organic chromophores [2], cationic metal centers or stacked DNA bases [3]. Nevertheless the inherent assumptions of Marcus theory make it applicable to two-state equilibrium systems with well-behaved harmonic potential energy surfaces and constant electronic coupling. In this talk, I will present our latest results from nonadiabatic molecular dynamics simulations, which allow us to elucidate the details of photoinduced electron transfer between two stacked tautomers of the adenine DNA base. These results uncover the abundance of various electron transfer mechanisms in this seemingly simple donor-acceptor system, most of which cannot be reproduced with Marcus theory. We also thoroughly evaluate the results obtained from kinetic modelling based on the Marcus approach with calculations of potential energy surfaces, fragment charge differences and electronic couplings along the reaction path.
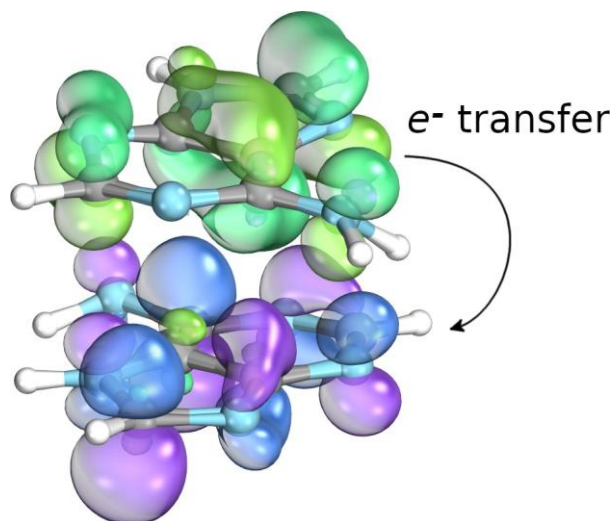


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# Structural disorder as the origin of optical properties and spectral dynamics in squaraine nano–aggregates

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Transition dipole interactions and exciton delocalization often lead to drastic, but from an application perspective favorable, changes in the optical and optoelectronic properties of ordered dye molecule systems. In aggregates of dyes with strong transition dipole moments, Coulomb interaction between transition dipole moments can yield large spectral shifts and broadening in the absorption spectra, as well as enhancing or quenching of fluorescent emission.[1] This relatively simple model yields two archetypes of aggregates, namely J– and H–aggregate, which offer a decent explanation for the optical properties of many aggregates. However, not all molecular aggregates can be categorized so easily and the structure-property relations cannot always be resolved straightforwardly. An intriguing example is given by a class of squaraine dyes.

In contrast to regular J- and H-aggregates, squaraine aggregates often carry broad absorption spectra containing both J– and H–like features which are favorable for organic photovoltaics.[2] However, the detailed aggregation mechanism and the assignment of the optical features are currently still under debate.[3] In this work[4], we provide solid evidence that both the red- and blue-shifted peaks come from the same disordered nanoscale aggregate structure using steady state and ultrafast transient absorption spectroscopy on aggregated rigid n–butyl anilino squaraines. Upon femtosecond light pulse excitation of the aggregated thin film, a transient absorption spectrum substantially deviating from a simple bleaching of steady state absorption spectrum emerges. Both the steady state and transient absorption spectra can be explained considering only transition dipole moment interaction together with structural disorder of the aggregate. Our results disclose the aggregate structure and the origin of red- and blue-shifted peaks as well as the absence of photoluminescence in squaraine thin films, underlining the importance of disorder for the optical properties of molecular aggregates.

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# Spectral signatures unravel molecular origin of the efficient energy transfer in supramolecular aggregates

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Chlorosomes from green sulfur bacteria are supramolecular aggregates ac- claimed for the most efficient light capture and energy transfer among natural light-harvesting antennas. To unravel the molecular origin behind these unique properties, we described the excitonic landscape based on the atomistic structure indicating its dependence on slow and fast nuclear degrees of freedom, especially the presence of hydrogen bonding. [1,2] Good agreement of the simulated absorption and two-dimensional electronic spectra with the experimental measurements [3] validates our model. Further analysis revealed the importance of the interplay of exciton delocalization over hundreds of molecules and molecular fluctuations for establishing the robustness of the energy transfer process on the sub-picosecond time scale. Our study confirms the utility of the combined efforts of the theory and experiments [4] for unraveling the structure-property relationships in nanostructures and anticipating novel designs for applications.

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# Storage and diffusion of carbon dioxide in the metal organic framework MOF-5 - a semi empirical molecular dynamics study

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In the past two decades, novel porous materials called metal-organic frameworks (MOFs) have attracted increasing attention because of their manifold properties. Due to their high porosity, MOFs are very well known for exceptional gas storage applications, e.g. $CO_2$ [1]. MOF-5 belongs to the family of isoreticular metal-organic frameworks (IRMOFs) that consist of $Zn_4O^{6+}$ clusters linked by 1,4-benzenedicarboxylate (BDC) [2, 3]. Because of the large number of atoms in the unit cell a description based on density functional theory (DFT) proves too demanding while more efficient empirical potentials models (i.e. chemical force fields) are often times not sufficiently accurate to model the complex host-guest interaction. To overcome this limitation, an alternative semi-empirical approach using a set of approximations and extensive parametrisation of interactions called Density Functional Tight Binding (DFTB) [4, 5] was applied in this work to study $CO_2$ in the MOF-5 host. Calculations of pristine MOF-5 yielded very good agreement with experimental data in terms of X- ray diffraction patterns as well as mechanical properties such as the negative thermal expansion coefficient ($\alpha$) and the bulk modulus (K). In addition a different loadings of $CO_2$ were introduced and the associated self-diffusion coefficient ($D_s$) and activation energy ($E_a$) were investigated. The results show very good agreement with other experimental and theoretical investigations. This study provides a detailed insight into the capability of the semi-empirical DFTB approach in the molecular dynamics simulation studies of these challenging guest@host systems.

Keywords: Density Functional Tight Binding, molecular dynamics, metal-organic frameworks, $CO_2$ storage.

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# Master equation modeling of water dissociation in small ions: $Ag^+(H_2O)_n$, $n$ = 4–6

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Due to their complex electronic structure, resulting in a wide range of chemical and physical properties, noncovalent metal ion complexes have been extensively studied for their role in numerous catalytic processers in biology and industry. A gas phase model system can yield important insight in these processes by providing a fundamental and quantitative description of the involved interactions. Here we studied the solvated silver cation $Ag^+(H_2O)_n$, $n$=4–6, using Master Equation Modeling (MEM) to calculate Blackbody Infrared Radiative Dissociation (BIRD) rates and compared them to previously measured experimental ones [1].

The physical properties of these clusters result in the presence of multiple low-lying populated isomers, which pose a significant challenge in obtaining accurate energetics from MEM. To identify and accurately consider these isomers within the MEM framework, we utilized our own implementation of a Genetic Algorithm (GA) as a global optimization search strategy, in tandem with a recently developed multiple-well approach for MEM [2]. Our findings demonstrate the necessity of considering multiple isomers for precise energetics prediction. Furthermore, we investigated two different models to describe transitional modes within the RRKM framework for dissociation, as employed in MEM. Namely we compared rigid activated complex (RAC) RRKM with the phase space limit (PSL) and found that the PSL model aligns better with the experimental rates, supporting the notion of weakly bound ligands. To gain further insight into ligand movement away from equilibrium positions and the potential for isomerization, we conducted classical molecular dynamics simulations.

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# Quantum machine learning gets excited: bridging the gap between ground and excited-state applications

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Machine learning has infiltrated various fields of science including computational and quantum chemistry. Unfortunately, the efficiency of machine learning algorithms for excited states and spectroscopy is far behind the ground-state applications.[1] This is due to the high complexity of reference electronic-structure calculations, subtle dependencies among densities of states and mainly because the modelled properties are not smooth functions of geometrical coordinates in the vicinity of state crossings and conical intersections. We proposed several data-based approaches how to overcome these limitations allowing us to efficiently model excited-state and spectroscopic properties both in the configuration and in the chemical space.

Adiabatic states, as we get them from electronic-structure codes, are usually not smooth in the whole configuration space as they form conical intersections. Therefore, it is advantageous to switch to a smooth diabatic basis. Unfortunately, diabatization is also an outstanding problem. We use machine learning to correct for deficiencies of a property-based diabatization scheme which provides us in return with smooth properties that can be easily trained. We need only a small amount of training data and we observe the increase in prediction accuracy by up to two orders of magnitude.

Another approach how to tackle the inefficiency of spectroscopic modelling is the reduction of the number of geometries representing the nuclear density. We proposed a data-based approach combining a fast exploratory electronic-structure method with simulated annealing to select a representative subset of geometries with minimal loss of accuracy.[2] This way, we can speed up the simulations by an order of magnitude. We demonstrate here the performance on electronic spectra simulations based on the nuclear ensemble method.

There are additional obstacles in the chemical compound space, that is, when learning across different chemical species. Modern molecular representations and machine learning models are usually designed using contributions from atomic environments and assume some kind of additivity. Such an approach is advantageous for extensive or local properties such as molecular energy or atomic forces, but it is suboptimal for global intensive properties such as transition and excited-state properties. We propose new representations and kernels more suitable for these properties.

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# Messenger spectroscopy of phthalocyanine cations isolated in the gas-phase and solvated in water

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The increasing interest in using photoactive organic molecules in solar energy conversion systems, as photocatalysts and as photosensitizers in photodynamic therapy, requests a deep understanding of the photophysical and photochemical properties of the underlying molecular system, and how the natural environment influences them. The combination of mass spectrometry with laser spectroscopy and methods to isolate organic molecules in a cryogenic environment enable to study the geometry, the electronic as well as the photodynamical properties of molecules in a well-defined environment.

In this contribution, we present spectroscopic investigations of phthalocyanine cations isolated in the gas-phase as well as solvated in water in the UV/Vis wavelength range. Phthalocyanine and its metallic derivatives are aromatic, macrocyclic, organic compounds with a porphyrin like structure similar to biologically relevant molecules like heme and chlorophyll. They can be used as model systems to investigate spectroscopic properties of the mentioned biomolecules, which need a more sensitive handling in comparison to the robust phthalocyanine.

The measurements are performed by using a newly developed setup, which allows the efficient formation of He-tagged molecular (cluster) ions, which are perfectly suitable for messenger spectroscopy [1]. Phthalocyanine as well as phthalocyanine-water cluster cations are seeded in multiply-charged HNDs [2], then gently liberated from the He-matrix, mass-per-charge selected and eventually irradiated by the laser beam. The photofragments are detected in a time-of-flight mass- spectrometer [3] and are used to deduce the absorption spectra. We will present recent results obtained for phthalocyanine and phthalocyanine-water cluster ions by using this technique and discuss the benefits of the novel method.

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# Poster

# Populating non-stationary molecular vibrational states using laser pulses

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We simulate laser control of ro-vibrational populations in molecules. This constitutes first steps towards the final aim to modify the outcome of molecular reactions in the direction of bond-selected chemistry using non-stationary vibrational states.

Focusing on the small molecule of acetylene ($C_2H_2$), we take advantage of the global spectroscopic Hamiltonian for the ground electronic state built from the extensive high resolution spectroscopy studies on the molecule. In addition, transition dipole moments obtained from intensities, and effects of the (inelastic) collisions parametrized from line broadenings using the relaxation matrix [1] provide together all structural parameters to simulate laser-induced dynamics. This approach, based on an effective Hamiltonian outperforms today's *ab initio* computations both in terms of accuracy and computational cost, however, is limited to a few small molecules. With such accuracy, the Hamiltonian permits to study the inside machinery of theoretical pulse shaping [2] for laser quantum control.

The photodissociation of $CO_2$ into C and $O_2$ was found to proceed largely via a transition state pathway in the ground electronic state [3]: the molecule bends until it forms a ring intermediate, followed by a linear COO structure that eventually splits into C and $O_2$. Furthermore, evidence was found that a roaming pathway in an excited electronic state also leads to these products, with a mechanism that avoids the transition state [4]: one CO bond is partially cleaved, with the now-distant oxygen roaming the remaining CO fragment until it finds a reactive site on the other oxygen atom. Zhou *et al.* [4] were able to experimentally achieve the photodissociation of $CO_2$ into $C + O_2$ with a yield of $5 \pm 2\%$ using a vacuum ultraviolet laser. We investigated the roaming potential energy surface in the excited state and identified the dissociative reaction pathway.

In a second time, we aim to increase the photodissociation rate of $CO_2$ into $C + O_2$ by starting from a different initial vibrational state to maximize the overlap with the vibrational excited states. Using the newly developed methods for the PES fitting [5], we can include the potential in MCTDH to investigate the dissociative mechanism and identify an eventual control strategy.

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# Proton transfer in the pyrrole-water system: relaxation after double ionization

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Relaxation processes after electron excitation or ionization in hydrogen-bonded systems are of intense interest, particularly in liquid water and then also in biologically relevant systems.[1-3] Understanding the primary relaxation processes accompanying, for example, radiotherapy is essential to understanding its effect on living organisms. Radiation with energies in the lower hundreds of electrons eV is capable of ionizing valence and internal valence electrons, creating highly unstable radical cations that relax through one of many, often competing, relaxation channels.

This poster presents a detailed study of relaxation processes in the pyrrole-water system after its double ionization by fast electrons, with the focus on the proton transfer state dependency and rates. In the doubly ionized state, the system can be prepared by either direct double ionization or by subsequent processes after ionization of the inner electrons. The pathways by which a doubly charged cluster decays a with charge localized on one of the molecules or a charge delocalized between the two units was investigated by quantum chemistry methods, utilizing a new quantum chemical code BAGEL containing a highly efficient implementation of multireference methods.[4] The investigation was based on the experimental data obtained from Dr. Xueguang Ren's team.
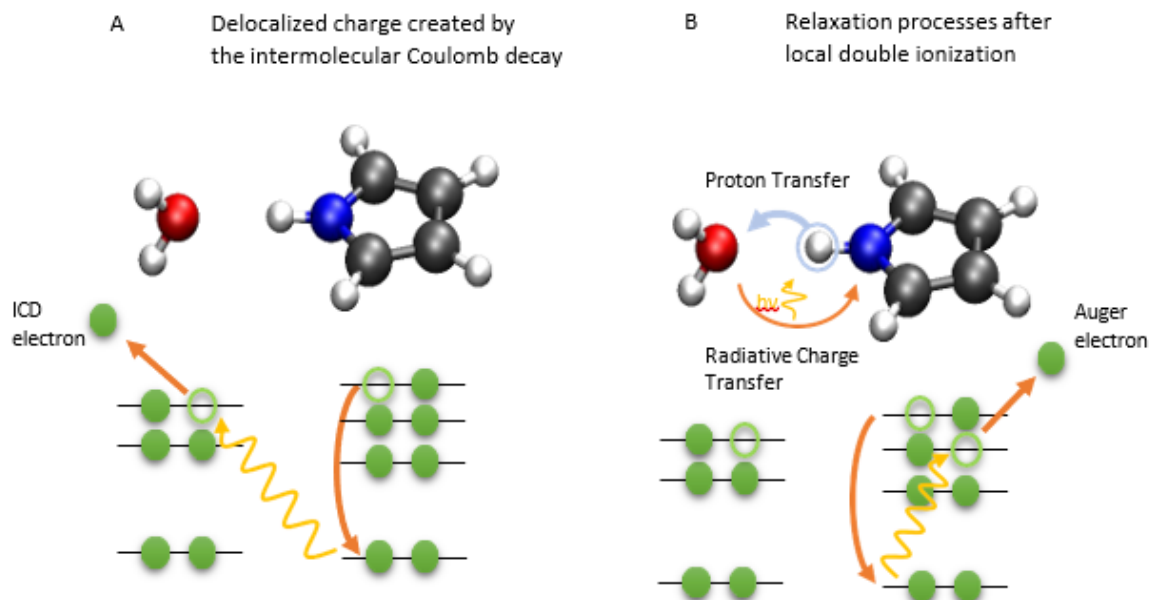


*Figure: Schematic depiction of several relaxation processes. A: Intermocelular Coulombic Decay. B: a local Auger-Meitner effect as a source of doubly ionized molecule followed by two charge redistribution processes: Proton Transfer and Radiative Charge Transfer*

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# Radical processes in gas phase involving demethylation of methoxy group

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Many naturally occurring phenolic compounds can scavenge free radicals, usually they possess hydroxy and methoxy groups attached to their primary structure. Available published papers are mainly focused on the antioxidant activity of these molecules attributed to the presence of hydroxyl groups, but they do not anticipate the active role of methoxy groups in overall radical scavenging activity [1, 2]. Some experimental reports suggest that oxidation of guaiacyl moiety leads to the formation of catechol or *ortho*-quinone [3, 4]. Therefore, we decided to study primary radical processes contributing to guaiacol (as a model compound) degradation in gas phase. These radical processes can lead to formation of structures capable of scavenging free radicals.

Theoretical calculations of total enthalpies were performed using Gaussian 16 [5] program package. From obtained total enthalpies we calculated individual reaction enthalpies of relevant mechanisms of guaiacol oxidation. Next, based on the results (see Fig. 1) we calculated methoxy group demethylation reaction enthalpies of substituted anisoles. We have chosen 15 substituents including various electron-donating and electron-withdrawing groups. These results may lead to a better understanding of the role of the methoxy groups in naturally occurring compounds.
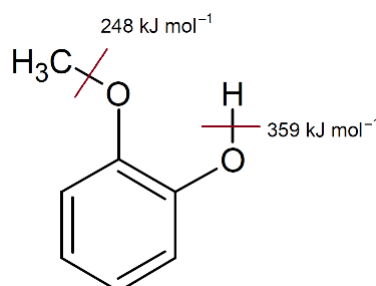


*Fig. 1 Bond dissociation enthalpies in guaiacol*

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# Dissociative electron attachment to thiazole and 2-bromo-5-nitrothiazole

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In the modern treatment of tumors, one important problem is that a characteristic of solid tumors is the presence of areas of low oxygen content (hypoxia). Hypoxic cells often promote tumor metastasis and exhibit resistance to radiotherapy and chemotherapy [1]. Concomitant adjuvant radiotherapy and chemotherapy using radiosensitizers could play a key role in solid tumors by sensitizing them to enhance the lethal effect of radiation injury. Over the past few decades, many radiosensitizers have been proposed in an attempt to overcome hypoxia [2]. Despite intensive research to find effective radiosensitizers, open questions remain about their underlying mechanisms of action.

We have studied the electron attachment induced fragmentation of thiazole and its derivative 2-bromo-5-nitrothiazole. These molecules are five-membered heterocyclic compounds, see Figure 1. We report that thiazole and 2-bromo-5-nitrothiazole are efficiently decomposed by low-energy electrons with kinetic energies 0-14 eV via single or multiple bond-cleavages. This behavior is beneficial to our understanding of the physicochemical properties of thiazole and 2-bromo-5-nitrothiazole, which is very important for the synthesis of related drugs and the potential application of radiosensitizers.
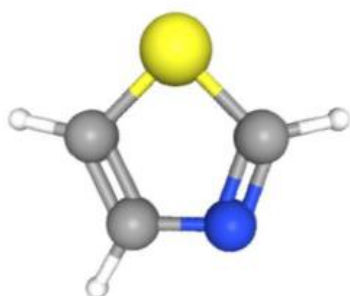


Thiazole
$C_3H_3NS$
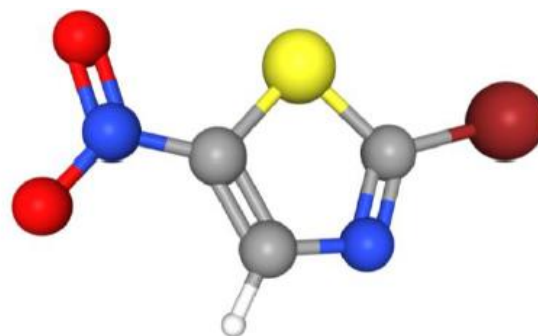
2-Bromo-5-Nitrothiazole
$C_3HBrN_2O_2S$

*Figure 1. Chemical structure of thiazole and 2-bromo-5-nitrothiazole*

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# Molecular aggregation and phase behavior in aqueous solutions

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The concept of hydrophobicity or hydrophilicity decisively contributes to understanding solubility and phase behavior in aqueous mixtures. Water dissolves polar molecules well, but nonpolar liquids do not mix with water. This "like dissolves like" rule does not always work. For example, methane, which is hydrophobic, is rarely soluble in water, while a considerable amount of methane is soluble under high pressure. Recently, we proposed a distinct molecular aggregation behavior in aqueous mixtures [1], which is associated with the formation of self-associated aggregates and spatially extended aggregates. Some dissolved molecules tend to self-associate to minimize the interaction with water, while others form spatially extended aggregates by interacting with water significantly. Based upon molecular dynamic simulation and graph theory, this aggregation feature was found in salt solution [1], osmolyte solution [1] and alcohol-water mixtures [2-4]. Computational studies in various aqueous solutions are presented to quantitatively investigate the solute aggregation and water H-bond network and to clarify the relationship between molecular aggregation and phase behavior in binary liquid system [5].
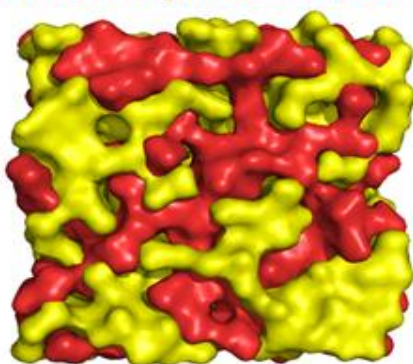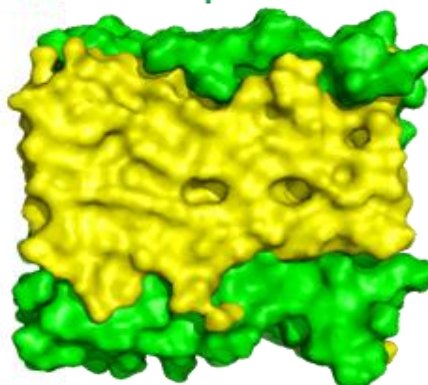


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# Excited state photodissociation of cationic and anionic caesium iodide clusters

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Charge-transfer processes, particularly in hydrated iodide and salt clusters, depend sensitively on the chemical environment and number of water molecules solvated around the iodide ion. Studying such charge-transfer behaviour is ideally suited to gas-phase clusters, whereby the size and chemical composition, along with number of water molecules, can be controlled. For example, when hydrated iodide interacts with ultraviolet light, the electron fully separates from the iodine ion, forming a solvated electron. Charge-transfer transitions are also observed in ionic systems such as metal-halide clusters. To understand these charge-transfer processes at a molecular level, laser spectroscopic measurements in the ultraviolet and visible region are utilised and, initially, focussed on the ionic salt systems. Electrospray ionization is employed producing salt clusters, which can then be stored in the cell of a Fourier transform ion cyclotron resonance mass spectrometer. Laser systems using optical parametric oscillators are implemented, providing intense tuneable laser light in the 225 – 2600 nm region. For each size-selected salt cluster, evaporation of stoichiometric and non-stoichiometric fragments are recorded, elucidating photochemical pathways connected to charge-transfer transitions. These evaporation channels are revealed by mass spectrometry, whereby an electronic absorption spectrum can be generated in each case, in addition to wavelength-specific photochemistry. These experiments are complemented with simulated spectra generated using quantum chemical calculations. Unanswered questions such as where the charge is located, and where it moves to within the cluster, along with whether the charge is localised to one atom, are yet to be fully understood. Isolating size-selected hydrated iodide alongside a systematic series of salt clusters and exploring their photochemistry offers a targeted approach to tackle such questions. Studying these systems not only provides fundamental insight into charge-transfer mechanisms in cluster physics, but also offers a laboratory model system for a molecular level understanding of reactions occurring during marine aerosol ageing or radiation-induced cell damage.

# Determination of spectroscopic constants from rovibrational configuration interaction calculations

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Molecular (ro)vibrational spectra from microwave, millimeter wave, and infrared spectroscopy are usually represented by rotational and centrifugal distortion constants. These spectroscopic constants are derived from and usually computed by perturbation theory. In experimental studies, transition line lists from spectroscopic experiments are taken as references for fitting an effective Hamiltonian, turning the constants into fit parameters. These constants (or parameters) concisely grasp the essence of a spectrum and, thus, are indispensable when communicating spectroscopic results. While "experimental" spectroscopic constants are derived by fitting, their ab initio calculation is often based on vibrational perturbation theory (VPT). However, it is well-established that variational approaches, e.g., rovibrational configuration interaction (RVCI), are superior in calculating rovibrational states. Thus, spectroscopic constants from RVCI are desirable. We here present a parameter fitting (PFIT) procedure [1], using RVCI [2] calculated rovibrational states and transitions as a reference for fitting Watson's A- or S-reduced Hamiltonian including up to sextic centrifugal distortion [3, 4]. Our procedure becomes very efficient based on an educated parameter guess from VPT. Benchmarks on small asymmetric top molecules (water, hydrogen sulfide, formaldehyde, and thioformaldehyde) show very good agreement with experimentally derived spectroscopic constants [1]. The procedure has recently been applied to derive spectroscopic constants for the astrochemical-relevant species propynal [5].

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# Joint experimental and theoretical investigation of excited state vibrational coherences in mn single molecule magnets

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Single molecule magnets (SMM) are typically large poly-metallic molecules with two degenerate magnetic ground states that retain magnetisation under a so-called "blocking temperature". In d-metal molecules, the blocking temperature is very low, rendering most industrial applications impossible. The lowest blocking temperature is observed in the Mn12 complex that retains magnetisation for months below 2K [1]. Magnetic recording using femtosecond laser pulses has recently been achieved in some dielectric media, showing potential for ultrafast data storage applications. Light control of magnetisation represents a great challenge in the field of data storage as it opens the way for larger and more compact storage arrays. Yet, SMMs remain largely unexplored using ultrafast techniques.
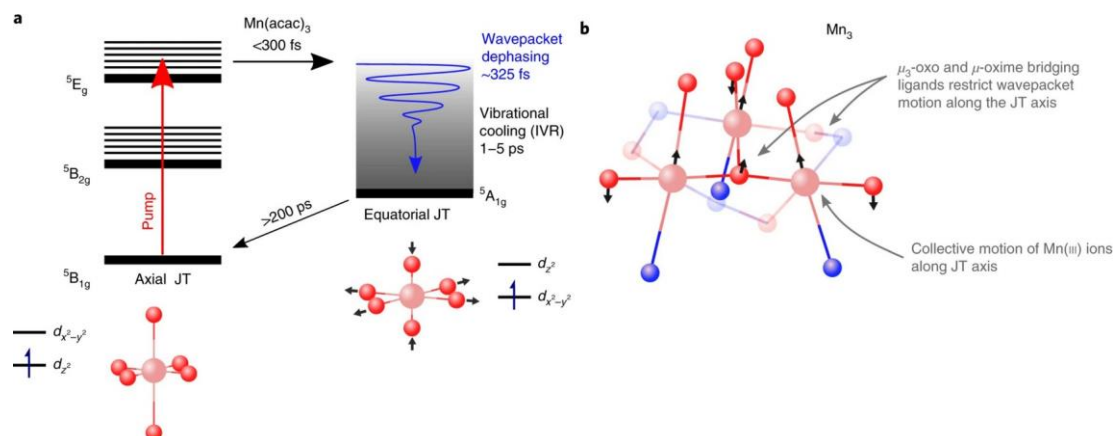


In this work [2,3], we investigate the photophysics and excited-state relaxation of a series of Mn(III) SMM, whose magnetic anisotropy is closely related to the Jahn–Teller distortion. Ultrafast transient absorption spectroscopy in solution reveals oscillations superimposed on the decay traces due to a vibrational wavepacket (WP). A joint experimental and theoretical study on Mn monomers allows to shine light on the origin of the vibrational coherences observed experimentally on the larger Mn3 complex. It is shown to emanate from the μ3-oxo-bridge effectively constraining the WP motions along the Jahn-Teller axis. Our results provide new possibilities for optical control of the magnetisation in SMMs and open up new molecular-design challenges to control the WP behaviour in the excited state of SMMs.

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# Messenger spectroscopy of astrophysically relevant ions with a novel experimental setup

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We present a newly designed setup that enables the spectroscopic investigation of (molecular) ions in the gas-phase by using the loss of weakly-bound helium atoms as a messenger for light absorption. In our setup, the molecules of interest are picked up by the traversing beam of highly, positively or negatively charged helium nanodroplets (HNDs) [1]. Inside the HDNs, the molecules are ionized via charge transfer or Penning ionization. Collisions of the doped HNDs with room-temperature helium gas atoms lead to shrinking of the droplets' helium matrix, resulting in the extraction of helium-tagged dopant ions from the HND. A subsequent quadrupole mass filter enables the selection of the ions by their mass-to-charge ratio. Finally, the mass-selected, helium-tagged ions are merged with the beam of a tunable laser in order to investigate them by laser spectroscopy. The absorption of light by the helium-tagged ion leads to the evaporation of the attached helium atoms and the formation of the bare ion as photofragment which is detected in a time-of-flight mass spectrometer. The feature to select a precursor ion species with the quadrupole allows us to measure the absorption spectrum by recording the photofragment and not only the depletion of the precursor ions. As the photofragments arise from almost no background, the spectra gained with this method exhibit a better signal-to-noise ratio which is especially beneficial when recording absorption spectra with small absorption cross sections.

The charged HNDs represent a perfect environment to simulate the conditions in interstellar space, hence one research focus of our group is to search for possible carriers of the so-called diffuse interstellar bands (DIBs). To test the new setup, we have for example successfully reproduced the NIR spectrum of the fullerene ions $C_{70}^+$ and $C_{60}^+$ - of which the latter is the only confirmed carrier of the DIBs to date [2]. Currently, we work on performing spectroscopy of $C_{60}$ analogues such as multiply charged $C_{60}$, $C_{60}H^+$ and [$C_{60}$-metal]$^+$ ions as they were considered to be potential carriers of the DIBs [3, 4]. In our contribution, the test measurements of $C_{70}^+/C_{60}^+$ and the first results of the measurements of the $C_{60}$ analogues are presented.

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# A genetic algorithm combined with graph-based machine learning clustering for exploring molecular structures

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There is a demand for large sets of molecular structures to compare them with experimental data in order to gain understanding of fundamental chemical phenomena. Here, we present a novel approach that integrates a genetic algorithm (GA, see e.g. Ref. [1]) with a graph-based machine learning algorithm for discovery and clustering of chemical structures.

We generate the initial population by randomly distributing the specified atoms in a box. One cycle starts by optimizing the structures employing a comparably fast quantum chemical method, for example the semi-empirical PM6 method. Afterwards, we select the best structures based on the minimal energy, which currently acts as our fitness criteria, and we remove duplicates. In the next two steps, we apply the genetic operators for recombination and mutation. Here we work with probabilistic processes that are typical for genetic algorithms. The structures to be combined are either selected randomly or chosen according to their fitness. The mutation techniques include exchanging the position of two atoms, reordering the position coordinates as well as rotating an atom around the structure centre.

In many practical cases, a large part of the chemical space needs to be explored. Therefore, a large genetic diversity is needed in the genetic algorithm. To achieve this, we want to cluster the structures and select the structures not only according to their fitness, but also according to the structure category they belong to. In essence, we want to obtain structures from many different groups. Methodologically, we detect all bonds between the atoms utilizing distance rules [2] to create an undirected graph for each structure representing the bonds between the atoms. Next, we explore two different concepts: we either identify isomorphic graphs or use an unsupervised machine learning procedure to cluster the graphs.

So far, our GA implementation [3] has been used for finding structures of $C_{120}^+$ and explaining the experimentally observed vibrational features. Additionally, the GA has been employed to discover structures of $Ag(H_2O)_n$, $n$ = 4–6 to perform multi-well master equation modelling on the water dissociation of these clusters.

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# Searching for the origin of magic numbers amongst sodium chloride clusters

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As one of the main components of sea salt aerosols, sodium chloride clusters are involved in many atmospheric processes such as cloud formation and photochemical as well as chemical reactions, significantly affecting the climate on earth [1]. Thus, investigating sodium chloride clusters is of particular interest regarding science and politics. According to previous studies [2,3], the cluster size significantly affects properties like stability or reactivity of the clusters. Of particular interest are so called "magic clusters", having an outstandingly high stability and cubic geometries, resembling the sodium chloride crystal lattice. The smallest magic clusters include singly charged anions $(NaCl)_xCl^-$ and cations $(NaCl)_xNa^+$ with $x = 4, 13, 22$.

In order to understand this size dependency, quantum chemical calculations are performed, yielding geometries and binding energies of neutral $(NaCl)_x$, anionic $(NaCl)_xCl^-$ and cationic $(NaCl)_xNa^+$ clusters up to $x = 8$. Contradicting previous theoretical studies [4], the binding energy of NaCl units

or the respective ion ($Na^+$ or $Cl^-$) to the smallest anionic and cationic magic cluster with $x = 4$ is lower than that of the neighboring cluster sizes, raising the question on the origin of the high stability of these magic clusters.

To answer this question, sustained off-resonance irradiation collision-induced dissociation (SORI CID) experiments are performed inside the ion cyclotron resonance (ICR) cell of a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS), equipped with an electrospray ionization (ESI) source. It can be shown that the dominant loss channels are the loss of neutral cluster sizes $(NaCl)_x$ with an even number of sodium chloride units ($x = 2, 4, \ldots$), even when the magic anionic or cationic cluster with $x = 4$ can be reached via the loss of a neutral cluster size containing an odd number of sodium chloride units ($x = 1, 3, \ldots$). The calculated binding energies of the neutral cluster sizes $(NaCl)_x$ with even $x$ are higher than these with odd $x$, matching the experimental results. As an additional support of the experiments, the density of states and RRKM rates are calculated for the anionic and cationic magic cluster with $x = 4$ and the neighboring cluster sizes with $x = 3$ and $x = 5$, yielding an explanation for the high stability of the magic clusters.

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# Role of quantum confinement of charge carriers on the photoluminescence quenching of quantum dots-dye assemblies

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We study the photoluminescence (PL) quenching of $CuInS_2$/ZnS (CIS) and InP/ZnS (InP) core/shell QDs induced by dye adsorption. Steady-state and time-resolved Stern-Volmer analysis show that (i) quenching is generally more pronounced in CIS-dye assemblies as compared to InP-dye assemblies and (ii) dynamic quenching is dominating in all QD-dye assemblies with only a minor contribution from static quenching. We correlate these observations with the relatively weak (664 meV) and strong (1194 meV) confinement potentials for the conduction band electron of CIS and InP QDs respectively. The larger amplitude of the electronic part of the exciton wavefunction near the dye binding sites in CIS QDs compared to that in InP QDs favor photoexcited charge trapping in the former case. Furthermore, due to the shorter excited state lifetime of InP QDs (37 ns) in comparison to that of CIS QDs (290 ns), pico to nanosecond charge trapping processes influence the measured lifetime of InP- dye dye assembly, thus increasing the relative weight of dynamic quenching in the total quenching process.

# A dark charge-transfer state mediates vibronically coherent energy transfer in nadh (nicotinamide adenine dinucleotide) dimer.

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The co-enzyme NADH displays a sub-100fs energy transfer process upon excitation of adenosine moiety[1,2]. We uncover that this ultrafast process is mediated through a low-lying charge-transfer state coupled to the bright states of the two chromophores. The time-evolution of the system modelled through multidimensional wavepacket dynamics[3] demonstrate that the population transfer is a vibronically coherent event channeled through activated molecular vibrations. The structural heterogeneity of this flexible dimer alongwith the effect of solvent environment has stark effects on the energetics of the charge-transfer state and the relaxation pathways adopted by the system.
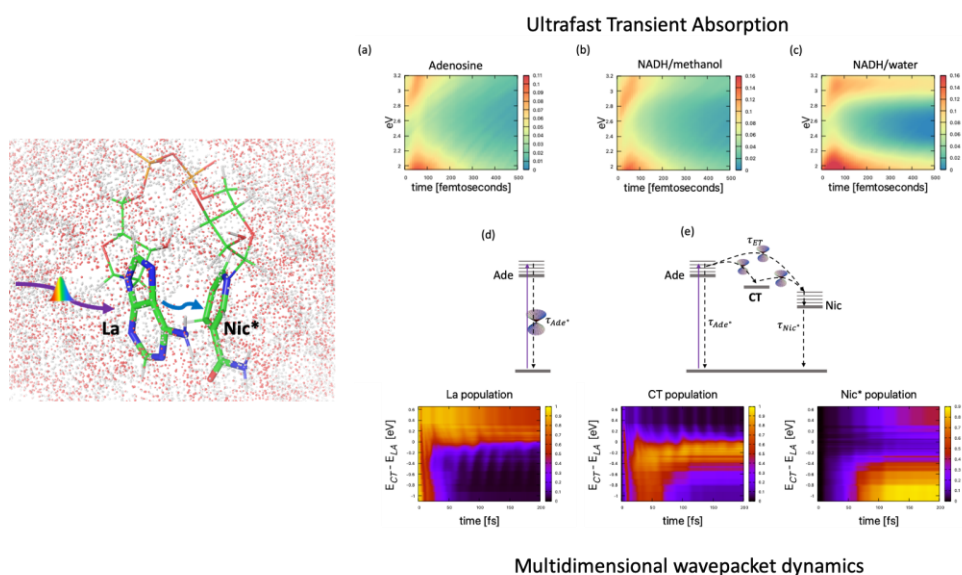
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# Photochemistry and spectroscopy of hydrated zinc clusters $Zn_m^+(H_2O)_n$, $m = 1,2$, $n \leq 8$

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Gas phase hydrated singly charged zinc clusters $Zn_m^+(H_2O)_n$, $m = 1,2$, $n \leq 8$ are hydrated metal ions which allow to study elementary processes in a highly detailed manner. They are perfect systems for which hydrogen evolution or catalytic properties can be expected, as found previously for the electronically similar $Mg^+(H_2O)_n$ [1] where hydrogen evolution was observed in a wide wavelength range. The change of the excitation energy in dependence of the cluster size is also of great interest, giving further insights on the type of bonding for the different isomers and the respective electronic properties, in particular the coordination number.

Zinc water clusters along with their electronic structure were investigated in a Fourier-Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer by means of Infrared Multiple Photon Dissociation (IRMPD) and UV/Vis spectroscopy. Decomposition is initiated through vibrational excitation of (a)symmetric O–H stretching, as well as electronic transitions using tunable laser systems. Experiments are supported by quantum chemical calculations.

Structural properties of the systems were already analyzed in Ref. [2,3], which show for $Zn^+(H_2O)_n$ a triply coordinated structure for $n > 3$, whereas the $Zn_2^+(H_2O)_n$ isomers are mostly found in an asymmetric structure where water only coordinates to one of the two zinc atoms. Currently, we are examining the electronic properties, potential energy surfaces, and the fragmentation patterns of the clusters via UV spectroscopy and *ab initio* calculations including multi-reference treatment.

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# Transparent superhydrophilic silicate glass surfaces for antifogging applications

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Fogging of various glass surfaces is a highly undesirable phenomenon that significantly impairs optical transmittance when a cold surface is in contact with warm and humid air [1]. Superhydrophilic or superhydrophobic surfaces must be designed and used to prevent glass fogging [2-5]. This work demonstrates inductively coupled plasma reactive ion etching of silicate glass in the mixture of $CF_4$ and $O_2$ gases with the aim of rendering the glass surface superhydrophilic and antifogging. Two-dimensional arrays of submicrometer-sized pillars and pits were formed on the glass surface by etching through the masks fabricated by electron beam lithography. The average roughness of the textured glass surface increased more than 20 times. The effect of both fabricated textures on the optical transmittance of the glass was small. The optical transmittance decreased only by 1 - 1.5 % in the visible light range and by 2 - 3 % in the near-infrared range. Both textures were suitable to impart superhydrophilicity to the silicate glass surface and ensured at least 85 - 90 % optical transmittance during real-time fogging tests. However, preference should be given to the pillar-like texture, which ensured minimal changes in the optical transmittance and was beneficial for the formation of a continuous water layer.

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# On the wavelength-dependent photochemistry of the atmospheric molecule CF$_3$COCl

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Kasha-Vavilov's rule postulates that photochemical reactivity depends only weakly on the excitation wavelength. However, there are exceptions to that rule and examples of wavelength-dependent photochemistry are well known. [1,2,3] The wavelength control of photochemistry usually results from ultrafast dynamics following the excitation to different electronic states. Here, we investigate the atmospheric molecule CF$_3$COCl which exhibits an unusual case of wavelength-dependent photochemistry within one electronic state. CF$_3$COCl is an important molecule in our atmosphere, formed from tropospheric photo-oxidative degradation of hydrochlorofluorocarbons and brominated species. The presence of these molecules in our atmosphere has increased in the last decades, and understanding their possible sink through photolysis and photoproducts is of first importance. Upon excitation, the CF$_3$COCl releases Cl and CO fragments whose quantum yields depend on the excitation wavelength. [4] We describe a new consecutive mechanism of photodissociation where the immediate release of Cl from the excited state is followed by a slower ground-state dissociation of the CO fragment. The CO release is subject to an activation barrier in the ground state and is controlled by the excess internal energy via the excitation wavelength. Therefore, a selective release of CO along with Cl can be achieved. Furthermore, the release mechanism and kinetic energy of the Cl fragments can be modulated by excitation to different electronic states. The mechanism behind the photon- energy dependence was revealed by combining mapping of the potential energy surfaces and non- adiabatic *ab initio* molecular dynamics. These findings are complementary to recent velocity map imaging experiments performed in the Cluster Dynamics Group (Vinklárek I. S., Rakovský J., Mukhopadhyay D. P. and Fárník M.) at J. Heyrovský Institute of Physical Chemistry. Taken together, they provide a comprehensive view of the mechanism of the title reaction.

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# Diffuse Interstellar Bands carriers: Fe⁺(H₂O) complex as a very promising candidate

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Iron is the most abundant metal the universe and plays a leading role in the field of organic prosthetic group of proteins and biochemistry, making iron as a potentially crucial for understanding interstellar processes, the evolution of interstellar dust and interstellar medium (ISM) composition. Despite the presumable gas-phase presence of iron in the ISM due to its very high abundance in the galaxy and its initial release from stars to the ISM in gaseous state, its difficult detection in the interstellar gas-phase to date may be due to depletion of iron hidden in interstellar dust. Nevertheless, although ISM observations show iron to be severely depleted, it is highly expected to find iron-containing gas-phase molecular species in the ISM. Here we present a high-resolved (0.1 nm resolution) photodissociation spectrum of Fe⁺(H₂O) in the region 410–680 nm measured in a blackbody radiation field (ca. 80 K) in the cell of a Fourier-Transform Ion Cyclotron Resonance mass spectrometer. The experimental results have been supported by multi-reference quantum chemical calculations including spin-orbit coupling reveal several low-lying excited states, which are significantly populated at typical blackbody radiation temperatures of 50 K in interstellar clouds. The spectrum is dominated by two broad bands, with sharp features emerging on top. Such features are observed especially in the regions around 443 nm, 480 nm, and 630 nm, where prominent diffuse interstellar bands (DIBs) are known. The features match the width of some known DIBs, but are shifted by several nm from their position. Both broad, structureless and structured bands are observed, suggesting excitations to bound excited states, with possible second photon absorption inducing dissociation of the water molecule. While we could not assign any known DIB to Fe⁺(H₂O), this work shows that iron complexes exhibit properties that make them very promising candidates for DIB carriers.
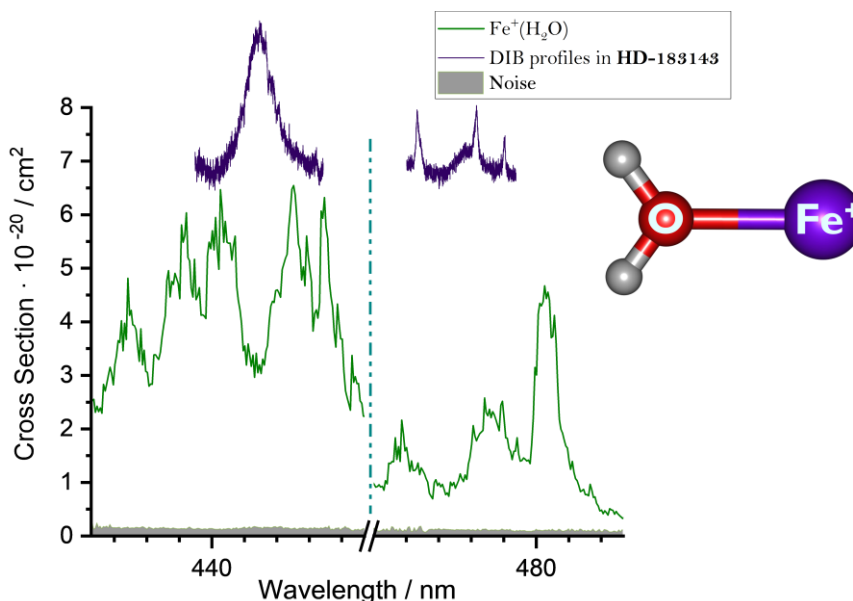


*Figure 1. Measured photodissociation spectrum of Fe⁺(H₂O) vs. observed DIB profiles in HD 183143*

# Spectroscopy of cationic $C_{60}$ clusters in the mid-infrared

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We have investigated the absorption spectra of $C_{60}^+$ and its smallest oligomer $C_{120}^+$ in the mid-infrared range [1]. Absorption spectra were recorded experimentally by helium messenger spectroscopy using superfluid helium nanodroplets to create helium tagged cationic species. An optical absorption spectrum of $C_{60}^+$ had been recorded previously [2]. The observed spectral range is extended in this study. Our experimental findings are compared with calculated vibrational spectra for the cationic monomer and dimer. For the $C_{120}^+$ ion different structures are investigated by theory. Also, low lying electronically excited states have been identified in the theoretical studies, which account for broad absorption features starting above 2200 cm$^{-1}$ for $C_{60}^+$ and showing onset below 2000 cm-1 for $C_{120}^+$.

The absorption spectra in the mid-infrared for the cationic $C_{60}$ trimer and tetramer show features that are very similar to the spectrum of $C_{120}^+$.
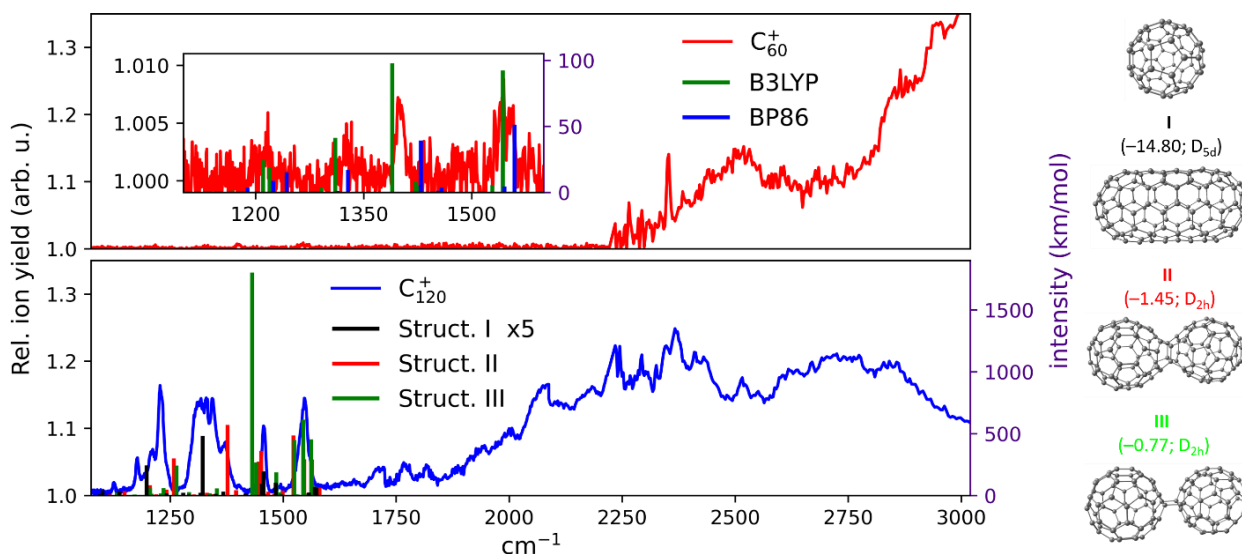


*Figure 1. Absorption spectra of $C_{60+}$ (top panel) and $C_{120+}$ (bottom panel) with calculated vibrational spectra at the B3LYP+D3/def2SVP (scaled by 0.96) and BP86+D3/def2SVP (unscaled) level of theory for $C_{60+}$ and P86+D3/def2SVP (unscaled) level of theory for $C_{120+}$ for three different structures shown on the right with their respective point group symmetries and formation energies.*

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# Modelling surface reactions and reconstruction using nanoreactors

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Depending on the complexity of the potential energy surface, molecular dynamics simulations are performed for time intervals of about nanoseconds (*ab initio* molecular dynamics) to fractions of milliseconds (force fields). However, some reactions may take hours or years to complete in reality. One way of modelling such reactions computationally utilises nanoreactors, which simulate the reactions at extreme pressures and temperatures, with subsequent analysis of the reaction pathways to find the respective local minima and transition states using different methods, such as Nudged Elastic Bands (NEB). An example of this kind of reaction are sintering reactions, specifically for MgO-crystals.

My presented work revolves around the process of using nanoreactors as a model for chemical reactions. Specifically, I will present the insight obtained from modeling $MgO$-$H_2O$ reactions under high temperatures and pressures, as well as the process of modelling transition states using a NEB method. The accuracy of the method is discussed via benchmarks for small molecules, such as $NH_3$ and $PH_3$, and I present some predicted energy barriers for idealised surface reactions.

The final goal is to simulate energy barriers for realistic MgO-surface reactions, which is currently a work in progress. The obtained results for idealised surface reactions suggest that this method works for predicting the transition path for surface dissociation of MgO crystals.

# Indirect interatomic Coulombic decay induced by photoelectron impact excitation in large pure He nanodroplets

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Ionization of matter by energetic radiation generally causes complex secondary reactions which are hard to decipher. Using high-resolution electron spectroscopy, we report here on observation of an indirect interatomic ionization secondary process—Interatomic Coulombic Decay (ICD) [1]—in large He droplets irradiated with one single XUV photon of energy $h\nu \geq 44.4$ eV. It is mainly based on the formation of two excited He atoms. While the first excited atom is formed just via impact excitation driven by the primary photoelectron, the second excited atom is a result of the friction-induced slowdown of the electron through electron-atom collisions. The eventual re-capture of the electron by the original residual ion forms the second excited atom. The correlated decay—ICD—of the pair of excited atoms produces a very unusual and characteristic ICD electron signal (See Fig. 1). We find that this ICD becomes the dominant process of electron emission in nearly the entire XUV range in droplets with radius $\geq 40$ nm. It likely plays an important role in other dense systems exposed to ionization radiation as well, including biological matter.
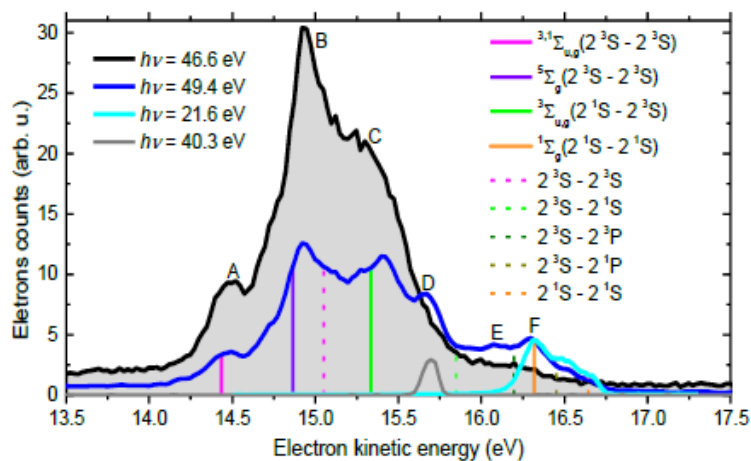


*Figure 1. High-resolution ICD electron spectra of He droplets recorded for different hν's. The dashed and solid lines indicate expected electron energies for ICD involving two He\*'s and metastable dimer of two He\*'s. The cyan line is a reference spectrum measured at hν =21.6 eV. The gray line is a He photoline recorded at hν = 40.3 eV used for calibration purposes.*

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# $CO_2$ activation by Cu clusters in superfluid helium nano-droplets

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Copper-based materials are among the most promising catalysts for $CO_2$ utilization. However, $CO_2$ conversion is still inefficient and requires high-energy input resulting in even more $CO_2$ emissions. Therefore, the molecular-level understanding of $CO_2$ interaction with copper is crucial for the design of more efficient catalysts. In our study, we mimic the catalyst's active site with copper clusters to study how they affect the structure of $CO_2$.

Previously, the structure of cationic Cu clusters and its role in $CO_2$ hydrogenation has been extensively studied by IR multiple-photon dissociation spectroscopy using a free-electron laser, FELIX.[1, 2] The clusters were formed using a laser ablation source, resulting in the log-normal distribution of the cluster sizes limiting the choice of the studied cluster sizes.

In the present study, we demonstrate the possibility of forming singly charged clusters via the pickup of dopant metal into multiply charged superfluid helium nano-droplets (mc-HNDs).[3] This method allows the formation of cluster size distribution narrower than Poisson, which is much narrower than conventional gas-phase methods allow.[4] Simulation of the experimental data helped us to understand, what is the underlying mechanism of the cluster formation, and which parameters are responsible for the cluster size distribution and selection of the most abundant cluster size.

As a next step, we implement mc-HNDs as ultracold (0.4 K) nano-reactors to study the reaction of $Cu_n^{+/-}$ with $CO_2$. Here, we start with the verification of the cluster structure using He as a probe molecule.[5] Then, $Cu_n^{+/-}$ are reacted with $CO_2$ and structure, fragmentation patterns and energies are investigated by means of collision-induced dissociation and photo-fragmentation spectroscopy of He-tagged ions. Formation of clusters in ms-HNDs allows a substantial signal intensity stable over a long-time range of the desired cluster size and makes it possible to perform He tagging of negatively charged ions, which is impossible otherwise.

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# Photochemistry of pyruvate in sodium chloride cluster cations

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Around 70% of the globe is covered by the ocean. Marine aerosol is therefore one of the most important naturally occurring aerosol systems. It influences the climate through direct and indirect interaction with solar radiation as well as through the effects caused by the aerosols serving as cloud condensation nuclei. Alkali halide clusters are used as a laboratory model for marine aerosol, because a main constituent of marine aerosol is inorganic salts like sodium chloride. Doping these alkali halide clusters with organic acids mimics the organic components of marine aerosol, which can consist of hydrocarbons such as acids, lipids or terpenes. When exposed to sunlight, photochemical processes can be induced in these organic materials, leading to highly reactive species such as $OH^\cdot$ radicals. The reason for choosing pyruvic acid as the organic substance for this work is its abundance and importance as an alphacarboxylic acid in the atmosphere. Earlier work in our group addressed the photochemistry of glyoxylate embedded in sodium chloride clusters [1]. The irradiation of these clusters resulted not only in the production of stoichiometric fragments, but also non-stoichiometric fragments could be observed, resulting from a C-C bond cleavage of the acid. One of these non- stoichiometric fragments was a $CO_2^{\cdot-}$ radical anion, which was stabilized by the salt environment. This showed that glyoxylate can act as a natural source of this elusive radical anion. In this work, the question was addressed if glyoxylate is a unique case, or if this mechanism can be found in other acids.

The experiments were conducted on a 9.4T FT-ICR mass spectrometer equipped with an electrospray ionization source. Using a tunable OPO laser system, action spectroscopy was performed. Photodissociation spectra for five different cluster sizes were measured in the wavelength region of 210 - 400 nm. All of the clusters show absorptions in the ranges of 210 - 260 nm, as well as in the actinic region, which is the environmentally relevant range of 290 - 400 nm. Two cluster sizes showed the same non-stoichiometric fragmentation process concerning the C-C bond cleavage of the acid, as it was found in the previous study. However, for both studies the photodissociation cross sections of those non-stoichiometric fragments are around two orders of magnitude lower than the ones found for the stoichiometric fragments. Usually the photolysis of pyruvic acid is the dominant degradation process in the atmosphere, and also for pyruvate in the gas phase the photolysis has been observed [2,3]. In the present experiments, only traces for such a process were found. This suggests that the salt environment might suppress the photolysis of pyruvate by providing additional relaxation pathways, leading to almost purely stoichiometric fragmentation.

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# Cu(II) complexes with flavonoids: formation, antioxidant action and DNA intercalation

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Flavonoids are polyphenolic compounds naturally occurring in plants. Their primary function is the protection against UV radiation and reactive oxygen species (ROS) [1]. In the presented work, antioxidant and DNA-intercalating properties of Cu(II)-flavonoid complexes are investigated using molecular spectroscopy, DFT methods and molecular docking. The studied set consists of four flavonoids: apigenin, fisetin, kaempferol, and luteolin, see Figure 1. UV-Vis spectroscopy confirmed the formation of Cu(II)-flavonoid complexes in different metal:ligand ratios (i.e., 1:1 and 1:2) [2, 3]. The ABTS test showed that the presence of Cu(II) ion improves the antioxidant activity of parent flavonoids [4, 5]. Molecular docking studies confirmed the ability of the studied Cu(II)-flavonoid complexes to interact with DNA molecule via intercalation [2, 3]. This suggests potential application of these compounds as perspective DNA-damaging agents.



*a*) apigenin    *b*) fisetin    *c*) kaempferol    *d*) luteolin
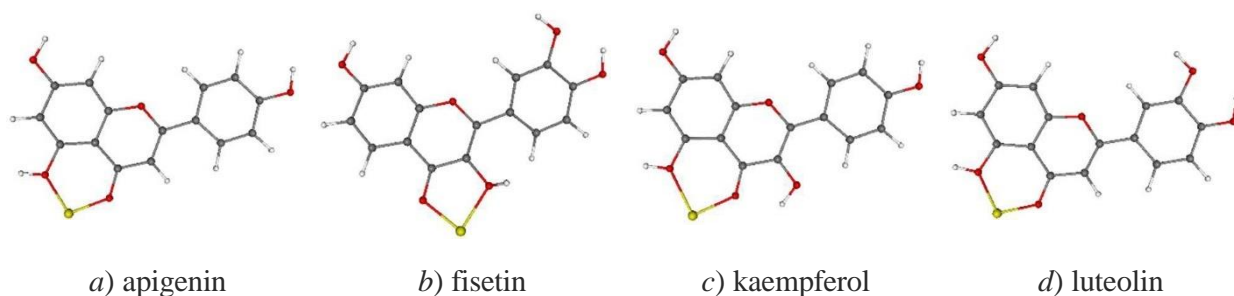
*Figure 1. Scheme of the studied Cu(II)-flavonoid complexes*

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# Molecular simulations of salts hydrates

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Classical molecular simulations have become an important tool for studying electrolyte solutions under various thermodynamic conditions. Such simulations are based on microscopic models, force fields, whose use is limited by their ability to reasonably predict solubility of the electrolyte studied and thus avoid spurious precipitation and ion clustering. Previous simulation studies have often focused on the solubility of anhydrous crystalline salts, but virtually never on crystalline hydrates, except for hydrohalite, $NaCl \cdot 2H_2O$ [1, 2], despite there are at least 23 experimentally known different hydrates that can precipitate from alkali-halide solutions.

This work attempts to fill this gap in hydrate simulation studies by systematically investigating the ability of the best force fields selected to qualitatively capture the stability of the individual phases of various alkali-halide hydrates and to quantitatively predict their lattice parameters. First, we show that the nonpolarizable force fields studied often fail to model hydrates containing the $Li^+$ cations, whereas the polarizable force fields recently refined in our group [3, 4] are able to model all the hydrates except for $LiCl \cdot H_2O$. Second, we further refine our FFs for $Li^+$ to yield stable $LiCl \cdot H_2O$. Third, our simulations clarify the positions of the $Li^+$ cations in the beta phases of $LiBr \cdot H_2O$ and $LiI \cdot H_2O$, whose distributions were previously described only as stochastic [5]. As a byproduct, a simple and reliable simulation methodology suitable also for complex polarizable models and nonorthorhombic crystal lattices is proposed and tested, based on simulations of finite crystals floating in vacuum.

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# Ring-polymer molecular dynamics simulations and machine-learning assisted study of the reaction path bifurcation mechanism: application to the Diels-Alder intramolecular cycloaddition

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The bifurcation mechanisms for the unimolecular Diels-Alder cycloaddition of the system, which has cyclobutadiene part and butadiene moiety, have been studied using molecular dynamics simulations and machine-learning analysis. Scheme 1 shows the two reaction systems. The bifurcation reactions of both systems lead to [4+2]- and [2+2]-products via the ambimodal transition states. The main products for Reaction No. **1** and No. **2** have been predicted as [2+2]- and [4+2]-products, respectively, using the only statistical information such as the potential energy surfaces (PESs). [1, 2] In this study, from the ambimodal transition states, three molecular dynamics simulations called ring-polymer molecular dynamics (RPMD), classical MD and quasi-classical trajectory (QCT) methods at 298 and 10 K have been performed to clarify the reaction mechanisms associated with the branching dynamics and discuss the importance of the quantized vibrational modes and thermal fluctuation for the bifurcation phenomena. While the branching fraction of three simulations at both temperatures were quite similar, the molecular motions of the system during the dynamics for QCT simulation especially at 10 K have larger magnitude than the motions for other methods due to the zero-point energy leakage problem of QCT method. Supervised machine-learning analysis identified the significant importance in the transition state features. The displacements and momenta of the lowest and 2nd lowest vibrational modes at the ambimodal transition states affected the bifurcation processes.
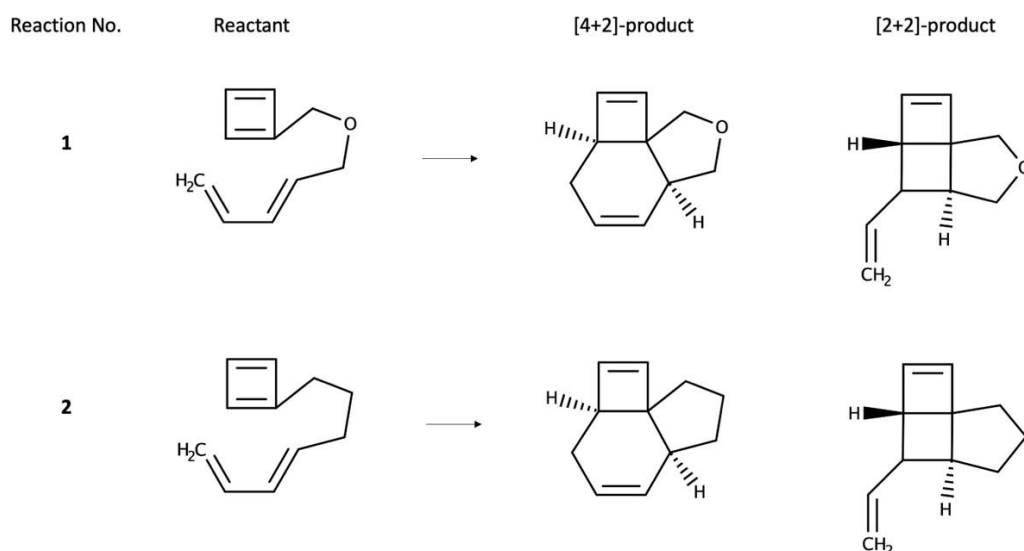
*Scheme 1. Reactants and products for [4+2]- and [2+2]-products for Reaction No. 1 and No. 2*

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# Computational chemistry in exploring the photostability of prebiotically plausible isomers of adenosine

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Photostability is considered one of the key selection factors for the chemical evolution of biomolecular building blocks on the young Earth [1]. Computational chemistry methods can be employed as a useful tool allowing for its exploration by analyzing the topography and accessibility of conical intersections (the crossing of excited state and ground state potential energy surfaces) in considered chromophores [2].

The comparison of the excited state lifetimes of biological nucleobases and their non-biological derivatives reveals remarkably higher photostability of the former ones [3]. My research aimed to comparatively assess the photostability of two isomers of adenosine possibly formed on primordial Earth through a prebiotic synthesis published in 2020 by Xu et al. [4]. Interestingly, while one of them became a molecular building block for DNA, the second one does not exhibit a biological relevance. It is still not clear, what advantage does the biological adenosine have. I propose that exploring the photostability of these molecules may provide the answer to this question.

The major outcome of my investigations are cross-sections of the potential energy surfaces for the excited states. They revealed that the conical intersection is less accessible for the non-biological isomer of adenosine, which suggests its longer lifetime and lower photostability. The results were confirmed experimentally by femtosecond transient absorption spectroscopy measurements.

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# Sampling internal coordinate sets for optimal representation of molecular vibration

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Normal modes in Cartesian coordinates are widely appreciated by spectroscopists to bridge theory with experiments. Arising from the harmonic approximation in solving the vibrational Schrödinger equation, normal modes are versatile and uniquely derivable for molecules and crystals. As normal modes dissect the molecular vibration in descriptive vibrational degrees of freedom, they give rise to notations for assigning observations from spectroscopic experiments [1,2]. However, the use of Cartesian coordinates for normal modes comes with crucial drawbacks that can only be overcome by defining normal modes in terms of changes in internal degrees of freedom, i.e., internal coordinates. Considering vibrational notations, the Cartesian normal modes give a poor basis for defining vibrations with a widely delocalized character. Furthermore, in computations beyond the harmonic approximation, expansions of potential energy surfaces w.r.t. normal modes play a significant role to access more accurate solutions of the vibrational Schrödinger equation. These expansions, however, show a beneficiary convergence only for semi-rigid molecules. Similar expansions in internal coordinates are desirable to treat more flexible systems [3,4,5].

We have implemented a toolkit, named NOMODECO, to automatically perform a normal mode decomposition for a given molecular geometry and a corresponding Hessian. The procedure presented here is based on a normal mode decomposition scheme introduced by Boatz and Gordon [6]. In contrast to the set of Cartesian normal coordinates as a unique result of the vibrational Schrödinger equation in the harmonic approximation, the choice of internal coordinates of a molecule is not unique and multiple sets can be found for one system. Based on our straight-forward normal mode decomposition scheme, we here provide a tool that samples internal coordinate sets to find an optimal set for representing molecular vibrations [7].

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# Staying in shape: investigating the S∴π interaction that stabilize folded proteins by using advanced light sources

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In their natural environment, for example in our bodies, proteins are usually folded, which is what gives them their biological function. Non-covalent interactions within the protein are important for their folded geometry. Sulfur containing functional groups are capable to build specific non-covalent interactions with nearby polar functional groups. Morgan et al. evidenced in the late 1970s a strong interaction between sulfur and aromatic groups of amino-acid sidechains [1]. Based on recent protein database analyses, methionine (Met) is preferentially found near aromatic amino-acids, especially tyrosine (Tyr) and tryptophan (Trp) [2]. The studied proteins have been shown to stabilize their structure by S∴π interactions. A good approach for a detailed experimental characterization of this non-covalent interaction is to perform experiments, in a well-defined and isolated state, in the gas phase. By using an electrospray ionization (ESI) source, biomolecules such as proteins or peptides are converted from a non-volatile solution to an isolated charged molecule in the gas phase. In combination with advanced light sources such as synchrotron light and free-electron lasers, insights into the electronic and structural properties of these biomolecules can be obtained by performing mass spectrometry based-action spectroscopy experiments.

The aim of this work is to experimentally characterize the properties of the S∴π interactions in tailored-made peptides using action spectroscopy in the UV, vacuum ultraviolet (VUV) and soft X-ray range to provide new insights into various aspects of the photodissociation of the peptides. With that we are able to evaluate fragmentation channels as fingerprints of the S∴π interaction.

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# Temperature dependent single molecule force spectroscopy of ester bonds

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Force spectroscopy of chemical bonds involves the stretching of single molecule chains between a surface and cantilever using an atomic force microscope (AFM) to assess their mechanical stability. There are two techniques available to obtain information about the chemical bond: overstretching the bond, which causes immediate rupture, or clamping the bond at a pre-set clamp force and measuring the bond's lifetime. In this study, the latter technique was used to directly measure the rupture kinetics of an ester bond.

To achieve this, diamond-like carbon (DLC) coated surfaces and cantilevers were functionalized with undecanoic acid, creating acid anchors. Polyethylene glycol (PEG) was stretched between the anchors, forming a molecule chain during the approach over ester bonds, which break under mechanical stress via hydrolysis. The experiment was performed at different temperatures, pH values, and clamp forces. The observed lifetimes of the molecule chains were used to extract rate constants, which were then processed further in an Arrhenius diagram. This allowed us to extract the activation energy required for bond rupture, yielding information about the rupture mechanism involved.
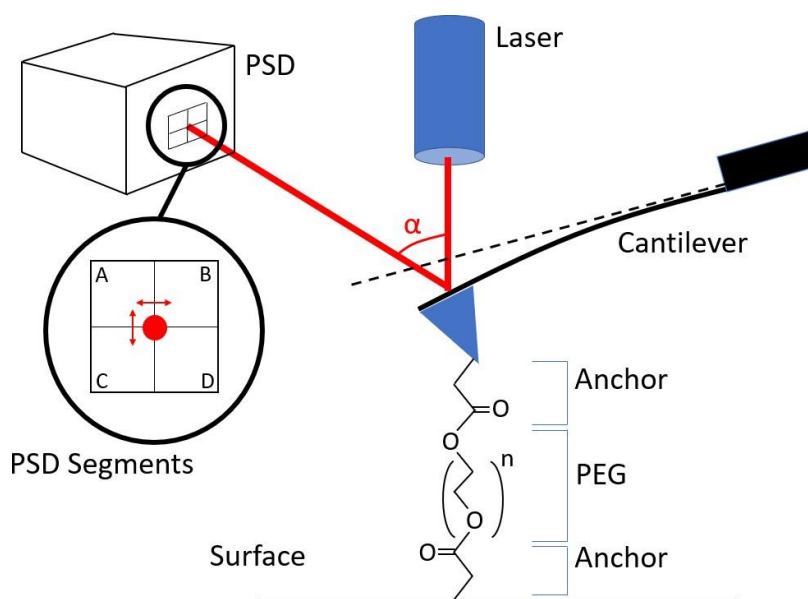
# Activation of CO$_2$ on size-selected copper clusters

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Global urbanisation and industrialisation undoubtedly led to the crucial problem of global warming due to the accumulation of various greenhouse gases. Among these, the atmospheric concentration of CO$_2$ has increased drastically, with still rising levels, as its anthropogenic origin is stemming mainly from fossil fuel combustion. Consequently, research has been conducted to recycle CO$_2$ into valuable chemicals, where, as a first step, the reactions typically rely on the activation of CO$_2$ through a catalyst. The industrial conversion of CO$_2$ to methanol is commonly achieved at elevated temperatures and pressures through a Cu/ZnO/Al$_2$O$_3$ catalyst [1]. Besides this, several other catalysts for the hydrogenation of CO$_2$ to methanol have been investigated, where overall, copper based catalysts prove to be the most efficient ones. As this efficiency is influenced by the structural and electronic properties of the catalyst, studies suggest that the doping of the catalytic substrates with size-selected Cu clusters can enhance the catalytic activity [2]. Hence, detailed insight into the fundamental reaction steps of hydrogenation of CO$_2$ over Cu clusters on a molecular level is necessary to optimise any industrial processes.

In this sense, IR spectra offer the possibility to investigate the structures resulting from adsorption of CO$_2$ on cationic or anionic Cu$_n$ clusters. Previous studies suggest that CO$_2$ is physisorbed on cationic copper clusters (Cu$_n^+$, with $n$ = 4-7) and show no signs of activation or reduction [3]. However, several studies on anionic metal clusters, such as experimental IR spectra of carbon doped Cu clusters (C$_m$Cu$_n^-$, with $m$ = 1-2, $n$ = 3-10) [4] suggest a strong size dependent activation and dissociation of CO$_2$.

In this work, we want to investigate the reactions and structural properties of CO$_2$ on pure anionic Cu$_n$ clusters via IR spectroscopy. To do so, we utilise superfluid helium nanodroplets as an ultra-cold and inert reaction matrix for the formation of Cu$_n^-$ clusters and adsorption of CO$_2$, where additional He attachment serves as a non-perturbing messenger for high-resolution IRMPD spectra.

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# Photochemistry of hydrated Fe⁺ complexes using IR, UV, and DFT calculations

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Photochemical hydrogen evolution at metal centres features a rich variety of reaction pathways. Here, we study metal water complexes and their structures, with a focus on their photochemical properties. The structures of hydrated iron complexes, $Fe^+(H_2O)_n$, $n = 3$–$20$, were analyzed using mass spectrometry with a Fourier transform ion cyclotron resonance (FT-ICR) experimental setup in combination with spectroscopy techniques in the IR and UV range and density functional theory (DFT) calculations. We focus on the $H_2O$ bending region at $1500$–$1700$ $cm^{-1}$ and OH stretching region at $2200$-$4000$ $cm^{-1}$, as well as UV/VIS spectra, to determine the structure of the hydrated $Fe^+$ clusters. A previous study reported that the Fe+ ions are two-coordinated for $n = 3$-$8$.[1] We extended the cluster size to $n = 3$–$20$, and found that the coordination number of two is predicted as the lowest energy structure for all studied clusters. From the UV/VIS photodissociation experiments, we obtained the photodissociation channels of the hydrated $Fe^+$ clusters, water evaporation and elimination of atomic hydrogen[2]:

$$Fe^+(H_2O)_n \rightarrow Fe^+(H_2O)_{n-m} + m\,H_2O$$

$$Fe^+(H_2O)_n \rightarrow FeOH^+(H_2O)_{n-m} + (m\text{–}1)\,H_2O + H$$
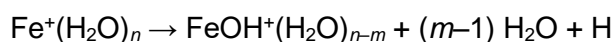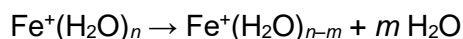
Complementary TD-DFT calculations of UV absorption bands will be presented.

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# Studying sink and source processes of Nitrous Oxide by the means of matrix-isolation infrared spectroscopy

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As a greenhouse gas with a heat-trapping ability that is 265 times stronger than that of $CO_2$, Nitrous oxide ($N_2O$) is an important component in the human-made climate change [1]. It is produced through bacterial degradation of nitrogen-containing molecules. To better understand the production and the source of the anthropogenic increase of $N_2O$ it is common practice to study the isotopic enrichment of $N_2O$ species. Traditional methods rely on isotopic ratio mass spectrometry (IRMS) and laser absorption spectroscopy (LAS) [2]. Whereas the latter has a difficulty in distinguishing different isotopocules of $N_2O$ due to their overlapping rotational-vibrational structure. We propose a novel approach based on matrix-isolation infrared spectroscopy (MIIR). To suppress the rotation of the molecule this spectroscopic approach isolates the $N_2O$ molecules in an IR inactive and chemically inert matrix (e.g. Neon) at low temperatures (~ 6 K). Therefore, only vibrational transitions are observed in the spectrum, which allows for a better distinction of different $N_2O$ isotopocules [3].

In this work, we confirm our experimental observations by anharmonic frequency calculations. We rely on vibrational self-consistent field (VSCF) and configuration interaction (VCI) approaches [4] that are based on a multi-mode expansion of the potential energy surface which was calculated at the CCSD(T)-F12/cc-pVQZ-F12 level of theory, including the full mode coupling of the system. The combination of MIIR and these high-level calculations allow for quantitative analysis [5] of the isotopic enrichment of $N_2O$. We show here our preliminary results for non-enriched $N_2O$ as a proof of concept.

Overall, our study provides a new application for matrix isolation infrared spectroscopy in atmospheric chemistry, aided by high-level calculations. This approach can potentially be used to study the sink and source processes $N_2O$ in order to gain a better understanding of the influence of anthropogenic $N_2O$ on climate change.

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# Gaining insights into dissociation patterns of hydrated magnesium sulfate clusters

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Scientific research is often driven by two questions: "What should be investigated to have the largest benefit for our society?" and "What is technically feasible with state-of-the-art approaches?". My goal is to focus on the first question and consider the second one afterwards. Clearly, one of the most pressing issues for our current society is climate change. Therefore, understanding, finding solutions, and fighting climate change should have paramount importance for a significant number of researchers all around the world.

According to the Intergovernmental Panel on Climate Change (IPCC), aerosols are one of the main sources of uncertainty in predicting future climate. My goal is to contribute to filling this gap by shedding some light on the dissociation of sea salt aerosols, which are aerosols originating from sea spray. To be specific, I am trying to improve the understanding of how hydrated magnesium sulfate clusters $[Mg_n(SO_4)_{n-1}(H_2O)_m]^{2+}$ dissociate. This could give important insights into aerosol decomposition and formation. At our institute, the dissociation of these clusters due to blackbody radiation has been measured in a Fourier Transform Ion Cyclotron Resonance mass spectrometer. For all cluster sizes, water loss has been observed. For clusters with four magnesium atoms and more, not only water loss, but also loss of $SO_3$ units has been observed. Both dissociation patterns are not trivial. Dissociation of a water molecule requires around 1.5 eV when going from minimum structure to minimum structure, whereas dissociation of sulfur trioxide lies in the range of around 3 eV. However, room temperature blackbody radiation is sufficient to trigger these dissociations.

I am using Master Equation Modelling combined with RRKM theory to understand these phenomena from a theoretical point of view. For a proper description, many isomers, their energies, their density of states and the reaction pathway must be considered. To find suitable structures, I complement manual search with genetic algorithms as a global search algorithm. For now, it seems like the observations can only be explained through long-living, high-lying isomers which store enough energy to make the observed dissociations possible.

# Impact of the Cu(II) ion probe on the anti/pro-oxidant and DNA-intercalating properties of flavonoids

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Owing to their potential beneficial health effects, polyphenolic compounds have attracted significant attention during the past two decades. Chelation of the metal ion, e.g., Cu(II), may significantly affect their activity in biological systems. The antioxidant/prooxidant properties of phenolic compounds, mainly flavonoids (FL), are related mainly to the number and positions of hydroxyl groups and to their redox metal (Cu, Fe) chelating capacity. In presented work, antioxidant/pro-oxidant activity of selected flavonoids and their Cu(II)-flavonoid complexes and their impact on DNA-damage are investigated using spectroscopic techniques supported with computational approaches and molecular docking [1]. Copper as an essential bioactive metal was selected as a probe for investigating switch in the antioxidant properties and concomitant production of Cu(I) species active in Fenton type reaction.
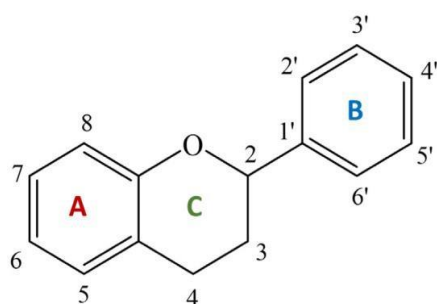


*Figure 1. The basic structure of flavonoid*

UV-Vis and EPR spectroscopy confirmed the interaction between selected flavonoids and Cu(II) ion indicating changes of the π- electronic properties of the parent FL molecule. The most promising binding site appears to be chelation *via* the 5-OH and 4-CO groups in case of the most flavonoids under study (luteolin, kaempferol, myricetin, morin, apigenin, fisetin). Binding mode was further investigated and supported by DFT and QTAIM calculations. In case of 1:2 complexes, Cu(II) ion is coordinated by four oxygens from two FL moieties oriented in *trans* conformation.

Cu(II) ion adopts the square planar coordination environment. Radical scavenging activity of flavonoids in the presence/absence of Cu(II) ion was monitored using ABTS assay. Additionally, EPR spin trapping experiments using DMPO spin trap confirmed that the coordination of luteolin/kaempferol to Cu(II) significantly suppressed formation of hydroxyl and superoxide radicals ( up to 80%) in a Cu-Fenton system. Results shown significant effect of copper on modulation of radical scavenging capacity.

Absorption titrations with CT-DNA, amplified with viscometry studies, also indicate that copper ions can modulate the DNA binding affinity of flavonoids *via* the formation of their Cu-chelates [2]. In addition, molecular docking studies confirmed the ability of Cu(II)-FL complexes to interact with DNA molecule *via* intercalation. It has been revealed that the charge distribution has a drastic impact on the outcome of the docking protocol, i.e., the free energy of binding and the predicted pose.

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# Fock space multireference coupled cluster study of the potential energy curves and spectroscopic constants of LiMg$^+$

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Recently, dimers of alkali and alkaline earth metals have been of particular interest to researchers due to their wide range of applications in studies of ultracold molecules. These molecules are highly useful in studying fundamental physical and chemical phenomena, quantum computing, or superaccurate determination of the physical constants [1,2]. Moreover, these studies also involve cations of the molecules mentioned above, but in this case, the number of works is significantly smaller [3]. In this kind of research, extremely accurate knowledge of the potential energy curves (PECs) is crucial. Sadly, the theoretical description of the dissociation process in excited states remains challenging in computational chemistry. This is due to the fact that a molecule with a closed-shell structure near the equilibrium bond length assumes an open-shell character at the dissociation limit. Therefore, using computational methods based on the Restricted Hartree-Fock (RHF) becomes improper when applied to bond lengths far from the equilibrium distance.

Our research focused on calculating PECs and spectroscopic constants of the LiMg$^+$ cation. It can be used, e.g., for the precise measurements of the electron dipole moment [4]. For this purpose, we used the Fock space multireference coupled cluster method (FS-MRCC) in the (2,0) sector within the Intermediate Hamiltonian (IH) formalism [5]. We determined the energies of excited states using the double electron affinity (DEA) scheme to calculate the desired states by adding two electrons to the system. The presented approach overcomes the previously mentioned problem by adopting the LiMg$^{3+}$ cation as a reference system. This allows us to use the RHF function for the entire spectrum of interatomic distances and obtain closed-shell fragments upon dissociation. Notably, the FS-MRCC formalism used in our study is an *ab initio* method used with the correlation of all-electrons, in contrast to often used models based on pseudopotentials. Our research provided very accurate PECs obtained for a large number of singlet and triplet states of the LiMg$^+$ cation for the entire spectrum of interatomic distances. The calculations were carried out using the uncontracted ANO-RCC basis set with added diffuse functions (unANO-RCC+, as we call it). Moreover, relativistic effects were taken into account using the third-order Douglas-Kroll scalar relativistic correction (DK3).

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# Controlling the fluorescence emission of carbon dots by surface modification

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The use of fluorescent materials containing toxic metals such as Cd, Se, and Te, etc., is prohibited in biological applications such as medical diagnostics and bioimaging [1,2]. Due to their environmental sustainability and biocompatibility, carbon-based fluorescent quantum dots (CDOTs) have been identified as a possible solution to this problem. [8]. However, even after the prevalent drive to know the properties of carbon quantum dots (CDOTs), fewer methodical studies appear to explore the fluorescent mechanisms of CDOTs. The main goal of this study is to make CDOTs with desirable optical properties and understand fluorescence mechanisms in these systems so that the emission characteristics can be controlled. The functional groups (-OH, -CHO, -COOH, -CO, and - COO) formed on the surface of CDOTs substantially impact their optical properties. Primarily, the nature and number of functional groups are determined by the preparation method, post-synthesis treatment, and precursor materials. This study used ascorbic acid as the starting material to synthesize CDOTs using microwave-assisted synthesis techniques. The impact that the microwave power level and the post-synthesis annealing temperature had on the oxygen-based functional groups found on the surface of the dots was analyzed methodically. It was discovered that as the microwave power level increases, the density of functional groups on the surface of CDOTs increases, which positively affects the fluorescence. Nonetheless, annealing at elevated temperatures reduces the concentration of functional groups and the fluorescence intensity. After deconvoluting the fluorescence emission peaks, the emission wavelengths that correspond to each functional group were determined. This study highlights the role that oxygen-based functional groups play in fluorescence emission and how physical methods can be used to regulate those groups.

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# Towards rotationally resolved spectroscopy of protonated Glycine

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The combination of an electro-spray ionization source with an ion trap is a common and successful technique to study the interaction of radiation with biomolecules. Electronic and vibrational transitions have been investigated and this has led to an overall better understanding of the geometrical structures of the studied species [1,2].

Our goal is to perform rotationally resolved predissociation spectroscopy of charged biomolecules. Our setup uses a custom-built nano-electro-spray ionization source which produces biomolecular ions in the gas phase. The ion source is followed by two skimmers, which gently guide the ions into high vacuum, without the use of high voltages or strong RF fields. This keeps clusters of ions with water or methanol intact, as seen in (Fig. 1).
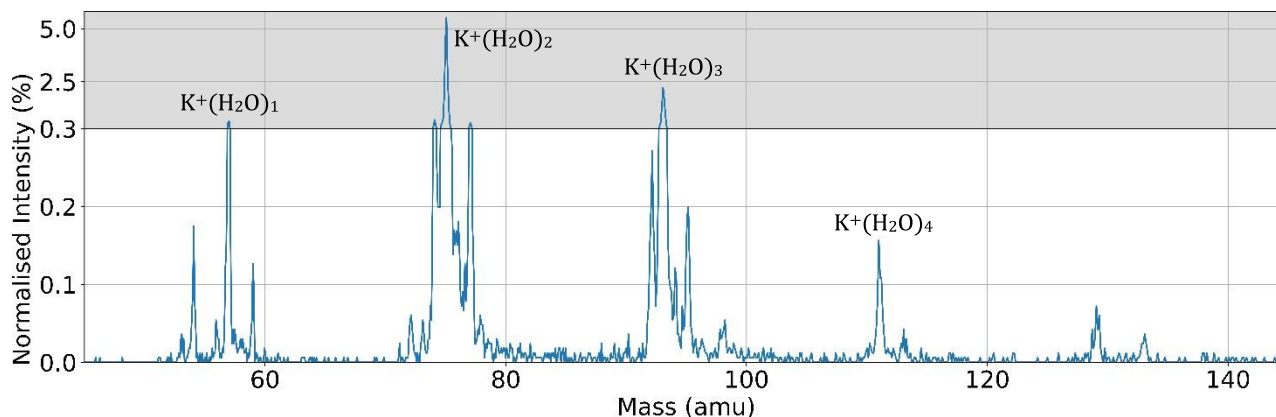


*Fig. 1: Progression of $K^+(H_2O)_n$ clusters as created by our ion source.*

The ions are then confined in a cryogenic 16-pole wire trap [3]. Our trap achieves sub 4 K opeoration temperature. The ions are sympathetically cooled by a buffer gas. The content of the trap is mass separated using a Wiley-McLaren type reflectron time of flight spectrometer. Previous studies have shown up to four He tags on a single Glycine ion [4], provng low temperature inside our trap. The laser system used is a Nd:YAG pumped OPO/OPA in the mid IR range. The Nd:YAG pump laser is seeded by a fiber laser, resulting in a width of the mid IR radiation of 0.05 $cm^{-1}$.

The sub-wavenumber width of our laser system, the low temperatures of the trapped ions and the flexibility of our ion source are a promising combination for future experiments. The current status will be presented.

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# Ultraprecise calculations – how to create an accurate wave function

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Theoretical studies of hydrogen molecule are the cornerstone of ultraprecise quantum chemistry.

Due to its simplicity, the achieved precision is the highest among all molecules and still has a potential for significant enhancement.

Moreover, there are many narrow transitions between rotational and vibrational levels in hydrogen molecule which can, in principle, be measured very accurately which opens new perspectives for the determination of fundamental physical constants from its spectra.

Such precision which reaches the sub-MHz level requires special computational methods. To control numerical uncertainty calculations, several wave functions with regularly increased expansion must be performed, i.e. N=128, 256, 385, 512. We will present methods that enable obtaining wave functions of such quality.

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# In silico study of flavonoid-Cu complexes towards biological systems

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In silico investigation of the intercalation ability, as well as suitability for transfer in blood stream by means of human serum albumin (HSA), of selected flavonoids and their copper (II) complexes have been carried out at the molecular mechanics and molecular dynamics level of theory. FL-Cu complexes were investigated in ratios 1:1 and 2:1. Autodock 4.2.6 [1] have been used for molecular docking calculations to predict the binding poses and inhibitory potential of investigated compounds towards double-stranded DNA (PDB ID: 1bna) [2] and HSA (PDB ID: 1bm0) [3]. The two Sudlow's sites and third site positioned in sub-domain IB have been considered as the putative binding sites of HSA [4].

It is revealed that introduction of copper atom improves flavonoids affinity towards DNA strand, possibly due to presence of positive charge. Although the introduction of second flavonoid moiety to complex with copper leads to weaking of electrostatic interactions as the total positive charge is distributed over more atoms, the overall binding energy between ligand and DNA increases, which stems from higher number of possible pair-wise interactions. The introductions of copper atom and second flavonoid led to conformational changes in complexes with DNA. The selected approach is unable to distinguish the binding site of simple flavonoids with HSA with desired certainty. The presence of copper atoms in both 1:1 and 2:1 FL-Cu complexes causes them to bind with HSA at site 3. These observations are in agreement with reported affinities of various compounds towards investigated binding sites [4] and were partially verified by experiment.

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# Apparatus for creating and studying a Bose-Einstein condensate of CaF molecules

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Dipolar molecular gases can be used to study many-body quantum systems with long-range interactions. We aim to create a quantum degenerate gas of CaF and explore the behaviour of this strongly dipolar quantum gas, both in bulk and in a lattice. In our apparatus, a beam of calcium monofluoride (CaF) molecules is created using a cryogenic buffer gas source, collimated using a combination of a magnetic lens and transverse laser cooling, and then slowed to low speed by the radiation pressure of a counter-propagating laser beam. The slow molecules are then captured and cooled in a magneto-optical trap. From here, the molecules will be loaded into an optical dipole trap in the presence of a molasses which is capable of cooling the molecules to 5 µK. Evaporative cooling will then be used to increase the phase-space density towards BEC. To suppress reactive and inelastic collisions, a static electric field at 22 kV/cm will be applied to create a potential barrier that prevents the molecules from getting too close and also enhances elastic collision rates. We predict that it is possible to reach BEC in 0.7 s, with $10^5$ molecules at 250 nK and a density of $1.4 \times 10^{13}$ cm-3. The molecular condensate will be an inspiring platform for a variety of research, especially the quantum simulation of strongly-interacting manybody quantum systems.

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