ETTORE MAJORANA FOUNDATION
AND CENTRE FOR SCIENTIFIC CULTURE

INTERNATIONAL SCHOOL OF SOLID-STATE PHYSICS

90th Course:
Dynamics of electrons in atomic and molecular nanoclusters

21 – 27 May 2025

Directors

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Wednesday, May 21: arrival

Invited talks: 35 minutes + 5 minutes for discussion

“Hot topic” talks: 20 minutes + 5 minutes for discussion

Thursday May 22		**Friday May 23**		**Saturday May 24**		**Sunday May 25**		**Monday May 26**	
Session chair: V. Kresin		Session chair: M. Mudrich		Session chair: J. Tiggesbäumker		Session chair: J. Bakker		Session chair: A. Zehnacker	
9:00-9.10	Welcome – V. Kresin	*9:00-9.40*	L.-S. Wang	*9:00-9.40*	JH. Lee	*9:00-9.40*	E. Bieske	*9:00-9.40*	T. Gorkhover
9:10-9:25	G. Benedek								
9:25-10.05	W. Kong	*9:40-10.20*	G. Niedner-Schatteburg	*9:40-10.20*	B. Changala	*9:40-10.20*	M. Farnik	*9:40-10.20*	J. Bakker
10.05-10.45	J. Fedor	*10.20-10.50*	break	*10:20-10:50*	break	*10.20-10.50*	break	*10.20-10.50*	Break
10:45-11:15	break	*10:50-11:30*	R. Schäfer	*10:50-11:30*	B. v.Issendorff	*10:50-11:30*	P. Ferrari	*10:50-11:15*	O. Duda
11:15-11:55	J.Tiggesbäumker	*11:30-11:55*	A. Zehnacker	*11:30-11:55*	G. Benedek (Sicily and Erice history)	*11:30-12:10*	H. Zettergren	*11:15-11:40*	A. Scognamiglio
11:55-12:35	S. Sayres	*11:55-12:20*	I. Djavani-Tabrizi	*11:55-14:00*	Lunch	*12:10-12:35*	R. Hashemi	*11:40-12:05*	I. Vinklarek
								12:05-12:30	B. Credidio
12:35-16:00	lunch + free time	*12:20-16:00*	lunch + free time			*12:35-16:00*	Lunch, free time	*12:30-16:00*	Lunch, free time
Session chair: E. Gruber		*16.00-19:00* Posters		*departure 14:00* Excursion and excursion dinner		Session chair: G. Niedner-Schatteburg:		Session chair: E. Bieske	
16:00-16.40	M. Lemeshko					*16:00-16.40*	E. Gruber	*16:00-16:40*	S. Pedalino
16.40-17.05	A. Sheekhoon					*16:40-17:05*	J. Ďurana	*16:40-17:05*	N. Scheel
17:05-17:35	break					*17:05-17:35*	break	*17:05-17:15*	Concluding - K. Hansen
17:35-18:00	C. Rotteger					*17:35-18:15*	M. Mudrich		
18:00-18:25	M. Maslov					*18:15-18:40*	F. Foitzik		
	Dinner		Dinner				Dinner	*19:00*	Banquet (informal)

Tuesday May 27: departure

Unraveling the detailed expansion mechanism of nanoclusters in intense and moderately intense laser fields

Kim Tran, Steven Tran, Gage Rios, and Wei Kong
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Using the time-of-flight (TOF) technology, and by setting the flight axis coaxial with the cluster beam axis, we have explored the expansion mechanism of argon nanoclusters in ultrashort intense laser fields and in nanosecond moderately intense laser fields. The acceleration voltage of the spectrometer can be used to selectively discern the contributions of kinetic energy or the position of ionization of the detected electrons and ions in the TOF profiles. Retardation of the charged particles can also confirm or offer additional information on the detected energies. Covariant analysis from single shot spectra recorded under low laser intensities can provide the correlation of the different groups of charged particles. In nanosecond laser fields, we observe extensive above threshold ionization in Ar gas and clusters, with photoelectron kinetic energies above several hundred times of the ponderomotive energy, far exceeding the known cutoff energies in the literature. These high energy electrons correlate with the high energy multiply charged atomic ions, and the kinetic energy distribution of these ions fits the model of Coulomb explosion. We also observe low energy electrons and electrons ionized away from the initial excitation position after the laser pulse has terminated. The energy profiles of these electrons indicate features of shell expansion, with larger clusters showing more features of explosion-expansion events. These observations are to be compared with the results from ultrafast intense laser fields where the mechanisms of energy absorption and cluster expansion are considered well-understood. From these analyses, we piece together a detailed cluster expansion process, including the formation of a highly positively charged cluster in the laser field, surface field ionization of the exploding ions, reequilibration of the hot electrons and immobile ions in the remaining quasi-neutral clusters, and finally hydrodynamic expansion of the cluster core. The unprecedented details from our study should stimulate further molecular dynamics modeling of the cluster expansion process in ultrashort laser fields, and with the help of deep-learning, we hope to expand our understanding to the nanosecond regime, to clusters containing thousands to millions of atoms.

Autodetachment from electron-molecule resonances: statistical vs. non-statistical processes

Juraj Fedor[1]

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We address a decay dynamics of transient anions (resonances) formed in electron molecule collisions. Typically, a lifetime of such a resonance towards electron detachment, determined by the centrifugal barrier and by the light nature of an electron [1], lies in a femto- to pico-second time domain. In polyatomic molecules and in clusters, an efficient intramolecular vibrational redistribution (IVR) prior to the electron detachment can lead to the electronic stabilization of the resonance and create a vibrationally hot molecular anion. The total energy of such complex lies in the continuum and it can decay via competing statistical processes.

Our main experimental tool is 2D electron energy loss spectroscopy. There we control energy of the incident electrons, collide them with the target and monitor the outgoing energy of scattered electrons. By recording the spectra at many incident energies we construct 2D maps which provide a comprehensive picture of the nuclear dynamics on resonances.

I will first cover excitation of specific vibrational modes. Already in such a small polyatomic molecule such as CO_2 the dynamics is strongly non-Born-Oppenheimer and proceeds on a number of states strongly coupled via continuum [2]. I will then focus on processes involving IVR and slow-electron emission. This effect is observed in number of molecules and can be described by the Weisskopf model for particle emission which is based on the detailed balance principle.

In several molecules we have observed, in addition to the IVR signal, emission of electrons with preference for finite non-zero outgoing energies. This is a signature of a mode-specific electron autodetachment, most probably happening on the timescale longer than IVR. We suggest a mechanism for this process involving electron emission via non-valence anion states. [3]

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Nanoplasma dynamics of size-selected silver metal clusters

Josef Tiggesbäumker

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Analyzing particle emission from clusters exposed to intense laser pulses provides a bunch of information about the strongly non-linear response of nanoscaled systems. The focus in this talk on nanoplasmas is on the impact of plasmon excitations on the cluster Coulomb explosion. The first part concentrates on steering electron emission [1, 2]. Phase-sensitive spectrometry enables to resolve the attosecond dynamics and proves the impact of the collective mode on the electron energy gain. The second part shows our approach to solve long-standing problems with respect to target preparation, laser conditions and ion diagnostics [3, 4]. Namely, the dynamics of nanoplasmas generated from size-selected atomic clusters under restricted laser intensity conditions is investigated by photoemission and charge-state resolving ion recoil energy spectrometry, Fig. 1. The progress in the measurements is demonstrated by pump-probe experiments on size-selected Ag clusters. Pronounced peaks show up in the charge-state resolved ion energy spectra, which stem from the emission of ions from different geometrical shells, which proves that information on the initial geometry prevails in laser-triggered Coulomb explosions and is thus a stepping stone towards structural decoding of large many-atom systems

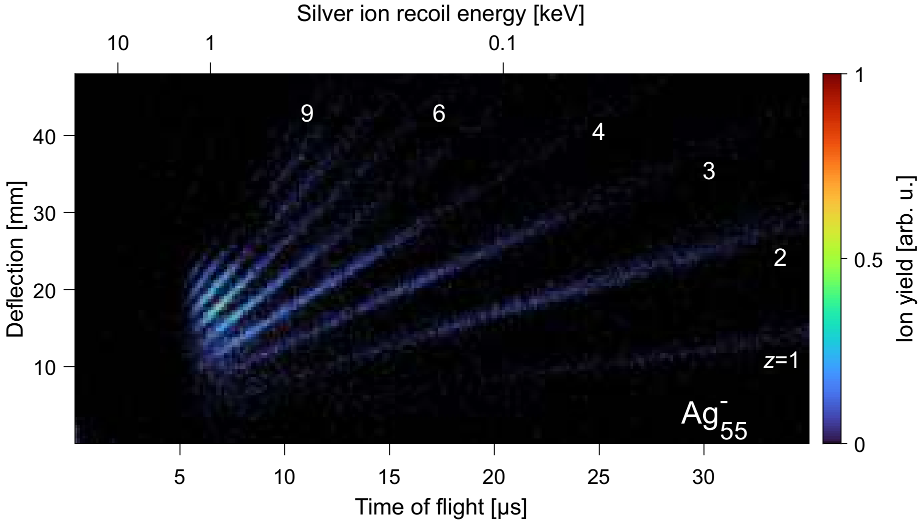

Figure 1: Time-deflection histogram of the strong-field induced Coulomb explosion of mass-selected Ag_{55}^-. To match the nanoplasma resonance, pump-probe excitation at an optical delay of Δt=300 fs was applied ($I_{\mathrm{pump}} = 4.5 \times 10^{14}\,\mathrm{W/cm^2}$, $I_{\mathrm{probe}} = 4.7 \times 10^{14}\,\mathrm{W/cm^2}$). Each stripe corresponds to a specific charge state Ag^{z+}, as indicated.

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Developing Predictive Capabilities for the Ultrafast Relaxation and Recombination Dynamics of Metal (Oxide) Clusters

C. H. Rotteger[1], M.Recio-Poo[2], F. Illas[2], S.T.Bromley[2], A. M. Garcia[2], A. Akimov[3],
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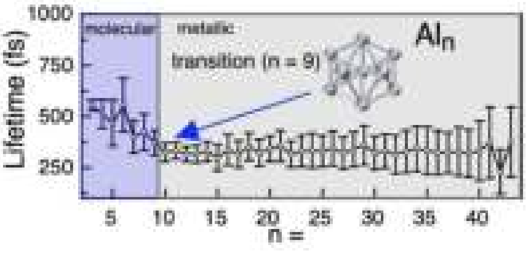
The exquisite tunability of gas-phase clusters, where physical properties change with atomic adjustment of their composition and size, enables new understandings of photodynamics and energy flow. I will present the systematic measurement of the excited state dynamics of sub-nanometer neutral titania clusters, $(TiO_2)_n$, with femtosecond time-resolved mass spectrometry. Previously, we employed time-dependent density functional theory to show the changes in sub-picosecond dynamics align with charge carrier localization/separation or polaron-like formation during relaxation to the S_1 excited state.[1] Upon revisiting these studies with higher energy photons, we now identify a slower (~100 ps) response that we attribute to carrier recombination using new non-adiabatic molecular dynamics (NAMD) calculations.[2] Our NAMD calculations predict subtle changes with size, in excellent agreement with the experimentally measured lifetimes for both relaxation and recombination. This combined experimental/theoretical approach has proven powerful for quantifying the metallicity of molecular sized materials and identifying the onset of metallic behavior in pure $(Al)_n$ clusters at $n = 9$.[3,4] The electronic relaxation properties are strongly dependent on both size and local structure, enabling sub-nanometer clusters to exhibit metallic or semiconducting properties, and even transition between the two at the molecular level in direct relation with calculated excited state topological parameters. The strong agreement between experimental measurements and theoretical calculations enables predictive capabilities for other clusters.



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Molecules rotating in solids: polaron models for lead-halide perovskites

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Lead-halide perovskites have recently attracted a lot of attention due to their unique properties for photovoltaics and other applications [1]. In these materials, organic molecules rotate in an inorganic crystal framework, which makes the system similar to molecules trapped in superfluid helium nanodroplets or parahydrogen.

I am going to present our attempts to develop simple models to describe soft semiconductors containing rotating molecules, as a counterpart to the DFT and other numerical techniques usually employed [2,3]. In particular, we demonstrate that already in a very simple model one can see the formation of ferroelectric polarons that have been previously discussed in the community from the DFT and experimental perspective.

If time allows, I am going to present our recent progress on interaction of molecules and clusters with light carrying orbital angular momentum [4]

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Probing the Structures and Chemical Bonding of Boron Clusters

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The study of carbon clusters led to the discoveries of fullerenes and carbon nanotubes [1,2]. Are there other elements that can form similar nanostructures? We have been investigating boron clusters as a function of size using photoelectron spectroscopy in combination with computational chemistry and have found that bare boron clusters possess planar structures [3], in contrast to that of bulk boron, which is dominated by three-dimensional polyhedral building blocks. The propensity for planarity has been found to be a result of both σ and π electron delocalization over the molecular plane [4]. The B_{36} cluster was found to have a highly stable planar structure with a central hexagonal vacancy (Fig. 1), providing the first experimental evidence that single-atom boron-sheets with hexagonal vacancies (borophenes) are viable [5]. Borophenes have since been synthesized and characterized on inert substrates, forming a new class of synthetic 2D materials [6]. The B_{40} cluster was found to be an all-boron fullerene [7], whereas the largest cluster (B_{48}^-) characterized to date possesses a bilayer structure [8], suggesting the feasibility of bilayer borophenes [9,10]. Boron forms important bulk boride materials with most metals in the periodic table. Many transition-metal borides are superhard materials, while lanthanide borides are essential magnetic materials. Metal boride clusters are ideal systems to probe the metal-boron bonding in boride materials. We have observed that transition-metal atoms can be doped into the plane of boron clusters, indicating the possibility of metallo-borophenes [11]. We will also discuss recent advances in our investigation of large boron clusters.

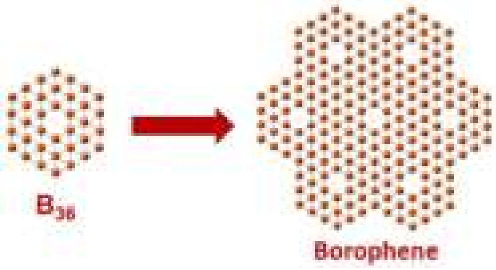

Fig. 1. From planar boron clusters to borophenes.

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Morphology and Activity of Size Selected Transition Metal Clusters

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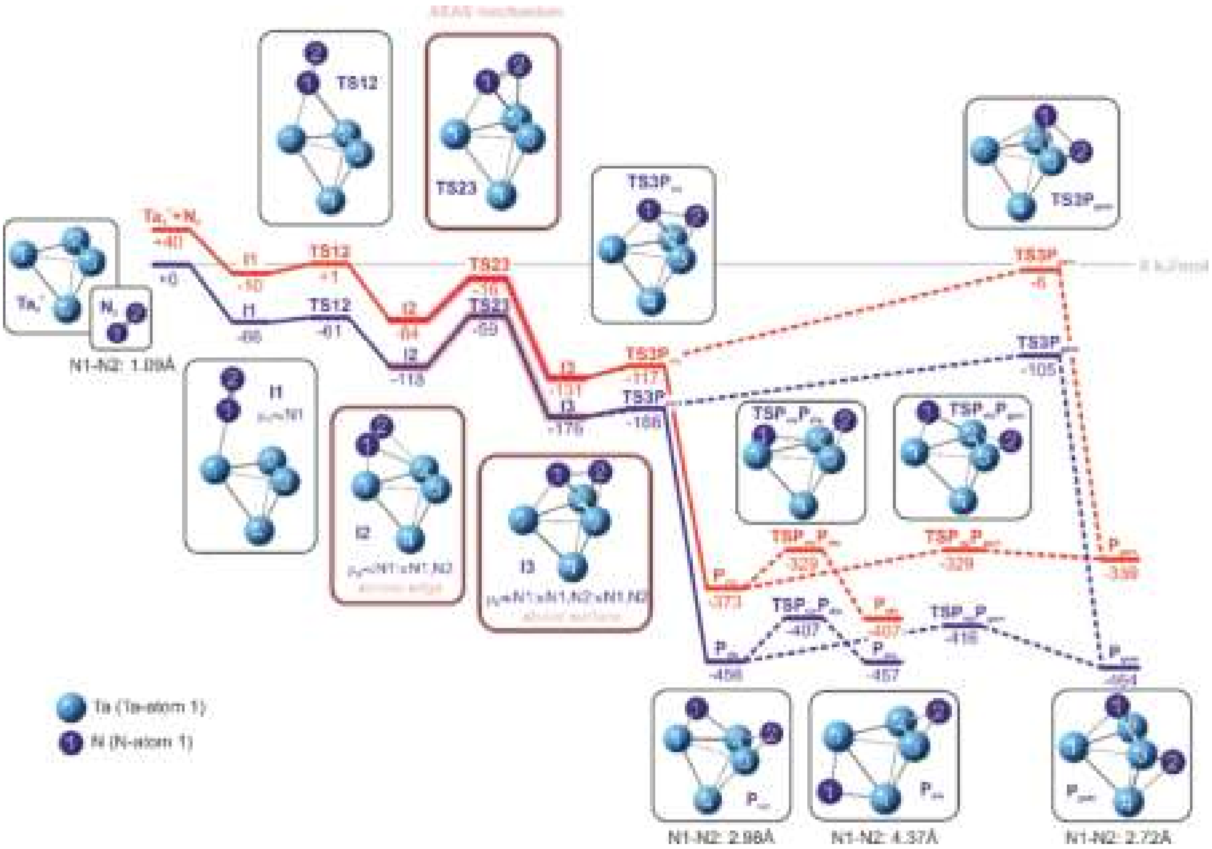
Cations and anions of size selected transition metal (TM) clusters attach N_2 molecules under single collision cryo conditions, and they may or may not subsequently activate the adsorbates. Cryo kinetics, infrared photon dissociation (IR-PD) spectra and DFT modelling reveal insights on the cluster morphologies and on likely or unlikely activation pathways. The analysis of spin states and molecular orbitals unveils the fluxional electronics of adsorbate cluster complexes. Our studies have so far covered clusters of Cobalt [1], Nickel [2,3,4], Rhodium [5,6], Iron [7,8], bimetallic Rhodium-Iron mixtures [9,10], Tantalum [11,12,13], and Ruthenium [14]. This presentation shall cover selected examples and outline routes to future work.



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The effect of symmetry, vibrational excitation, spin-orbit coupling and hyperfine interaction on electron spin dynamics probed by magnetic deflection experiments

Rolf Schäfer

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Technische Universität Darmstadt

Isolated tetrel clusters containing a single paramagnetic dopant are suitable for systematically investigating the influence of symmetry, vibrational excitation, spin-orbit coupling and hyperfine interaction on electron spin dynamics. Stern-Gerlach as well as refocusing experiments are used for this purpose. The discussion of the observed spin dynamics is carried out with a model that takes avoided state crossings in dependence of the various parameters into account.

Towards full quantum state control of chiral molecules

JuHyeon Lee[1], Elahe Abdiha[1], Shilpa Yadav[1], Boris G. Sartakov[1], Gerard Meijer[1],
Sandra Eibenberger-Arias[1]
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Controlling the internal quantum states of chiral molecules for a selected enantiomer has a wide range of fundamental applications from collision and reaction studies, quantum information to precision spectroscopy. Using tailored microwave fields, Enantiomer-Specific State Transfer (ESST) enables the control and manipulation of chiral molecules at the quantum level. This enables rapid switching between samples of different enantiomers in a given state, holding great promise, for instance, for measuring parity violation in chiral molecules [1]. For such applications, achieving full enantiomer-specific state transfer is crucial. While ESST can theoretically reach 100% transfer efficiency, early studies reported only modest state-specific enantiomeric enrichment, limited to a few percent [2,3]. This is primarily due to the thermal population of rotational states [2,3] and the spatial degeneracy of these states [4].

To mitigate the effect of thermal population, we developed a new experimental scheme utilizing both ultraviolet and microwave radiation to deplete one of the rotational states before the ESST process, thereby significantly enhancing the transfer efficiency. In this way it has been possible to perform quantitative studies of ESST [5, 6], albeit under conditions that were not yet ideal. Recently, we realized near-ideal conditions, overcoming both the limitations of thermal population and spatial degeneracy in rotational states [7]. Our results show that 96% state-specific enantiomeric purity can be obtained from a racemic mixture, in an approach that is universally applicable to all chiral molecules of C1 symmetry.

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Single-quantum-state control, structure, and dynamics of large molecular systems with precision light-matter probes

Bryan Changala

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Recent advances in precision light sources and spectrometers at optical and radio wavelengths have greatly expanded the size and complexity of molecular systems that we can probe and control at the level of individual quantum states of the constituent electrons and nuclei. In this talk, I will highlight the applications of such cavity-enhanced frequency comb and microwave techniques to the high-resolution spectroscopy of molecules containing dozens of atoms, including fullerenes and polycyclic aromatic hydrocarbons, which have resulted in new discoveries in fields ranging from fundamental quantum dynamics to interstellar organic chemistry. I will discuss the prospects for improving our wavelength coverage, molecular cooling techniques, and detection sensitivity to target nanoscale molecular systems like diamonoids and molecular magnets that may allow us to use precision spectroscopy of isolated gas-phase systems to gain new insights into localized electron dynamics in condensed-phase environments.

High resolution photoelectron spectroscopy on simple and not so simple metal clusters

Bernd v. Issendorff

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Judged from the closeness of its electronic system to an ideal electron gas, sodium is the simplest metal in the periodic system. Its clusters exhibit the well-known electron shell structure, a highly discretized density of states consisting of approximate angular momentum eigenstates. Deviations from true angular momentum eigenstates is caused by the non-spherical ionic structure of the clusters, which significantly perturbs the states [1,2]. Nevertheless, the icosahedral symmetry adopted by most clusters in the size range up to a few hundred atoms leads to an electronic structure very close to that for a simple spherical potential. Therefore, the observation of a strong change of the electronic density of states just few sizes below the perfect icosahedron with 309 atoms was puzzling. We could now show that this is due to a new cluster symmetry, a chiral (twisted) form of a truncated tetrahedron. This cluster shape interestingly leads to a much stronger mixing of angular momentum eigenstates, something reflected also in the angular distribution of the photoelectrons.

The metal gold is monovalent like sodium, yet exhibits rather peculiar properties due to strong relativistic effects, which lead to rather stiff bonds and a preference for unusual cluster properties. New improved DFT calculations combined with extensive global minimum searches performed by Andres Aguado (Valladolid) could now shed more light one the adopted structures – a broad range of high symmetry geometries have been discovered, demonstrating that gold clusters with a few ten atoms do not prefer amorphous structures, as was stated sometimes.

Niobium finally is a complex metal because of its only partially filled d-band, which leads to a rather complicated density of states at the Fermi energy. Nevertheless, this metal is highly interesting due to the superconducting properties of its bulk form already at the rather high temperature of 9.2 K. New high resolution photoelectron spectra on ultracold clusters reveal a wealth of details of their electronic structure and vibrational properties - but no clear sign yet of an onset of cooper pair formation.

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Spectroscopy and Dynamics of Charged Carbon Rings and Fullerenes

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Carbon clusters (C_n) are formed in flames and furnaces with some species, including C_{60} and C_{60}^+, being identified constituents of interstellar space.[1] Depending on the environment and how they are generated carbon clusters adopt structures as linear chains ($2<n\leq9$), rings ($n\geq7$), bi-rings ($n \geq22$) and fullerenes ($n \geq20$), with the latter family including the celebrated C_{60} molecule (buckminsterfullerene).[2] In principle, one can gather valuable information on the structures and properties of carbon clusters through their infrared and electronic spectra measured in the laboratory. Laboratory spectra are also essential for the identification of carbon clusters in remote and hostile regions, including in interstellar space. Unfortunately, spectroscopic investigations of carbon clusters are often confounded by the coexistence of several different isomers in the probed sample. For example, ion mobility investigations demonstrate that C_{36}^+ exists as a ring, bi-ring and fullerene isomers (Fig. 1).[2, 3] To avoid potential isomeric confusions, we have developed strategies to isolate and spectroscopically probe charged carbon clusters with a particular size and structure. The approach involves separating carbon cluster isomers using ion mobility and mass spectrometer stages prior to spectroscopic interrogation in a cryogenically cooled ion trap.[4] Here we focus on positively charged cyclocarbons and fullerenes, contrasting their infrared and electronic spectra and their photodissociation behaviour. Astonishingly, we find that C_{4n}^+ cyclocarbons containing between 20 and 44 carbon atoms possess narrow IR absorption bands with intensities that increase rapidly with ring size, and which far exceed the band intensities of the corresponding C_{4n}^+ fullerene and bi-ring isomers. We will discuss the nature of the cyclocarbon infrared resonances and their possible roles in the detection of cyclocarbons in interstellar space and in the cooling of heated cyclocarbons in fast ion beams.[5] As well, newly acquired spectra of smaller fullerenes, including C_{32}^+, C_{34}^+ and C_{36}^+, provide clues to their structures and necessary data for their detection in remote environments.

Fig.1 Isomers of C_{36}^+.

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Electron attachment to pure and doped PAH clusters

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The motivation to investigate polyaromatic hydrocarbon (PAH) molecules and clusters and their interaction with electrons stems from astrochemistry and atmospheric chemistry, where these species play a significant role. We investigate various PAH clusters using cluster beam apparatus CLUB in Prague [1], where the PAH clusters can be generated and doped with other molecules and low-energy electron attachment to these species can be investigated by a TOF mass spectrometry.

Benzene (Bz) is known to have a negative electron affinity of about −1.12 eV resulting in benzene radical anion which is unstable in the gas phase. We have identified a free stable $C_6H_6^-$ anion in the mass spectra after an electron attachment to benzene clusters at about 8 eV [2]. However, this $C_6H_6^-$ has a linear structure formed by the opening of the benzene ring. The benzene radical anion can be stabilized in a bulk solvent such as ammonia. We have observed stabilization of the benzene radical anion in ammonia clusters yielding $(NH_3)_n{\cdot}C_6H_6^-$ cluster anions ($n \geq 37$) at an electron energy of about 1.3 eV [3].

Naphthalene (Np) anion is still unstable with an electron affinity of about −0.19 eV. Solvation with an additional Np molecule already stabilizes the anion $Np{\cdot}Np^-$. However, we have shown that the dimer anion cannot be produced directly by an electron attachment to the neutral dimer $(Np)_2$ nor to the trimer $(Np)_3$: in our case, $(Np)_2^-$ was produced by the electron attachment to $Ar{\cdot}(Np)_2$, where Ar evaporation stabilized the anion [4].

For the larger PAH molecules the gas phase monomer anions are stable. Particularly interesting examples are the phenanthrene (Ph) and anthracene (An), which are both composed of three aromatic rings. While the electron affinity of Ph is presumably positive but close to zero (< 0.025 eV) [5], the electron affinity of An is large, 0.54 eV. We discuss the dynamics of the electron attachment to different PAH molecules and their clusters from Bz, over Np, to Ph and An. We also investigate, how this process changes, when the PAH cluster is doped by other molecules. We dope the clusters with O_2 as a molecule with a high electron affinity (0.45 eV), and CO_2 that does not support a stable anion in its neutral ground state geometry. Our present results are relevant to astrochemistry and atmospheric chemistry where similar processes can occur.

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Far-infrared spectroscopy of gas-phase neutral molecules for astrochemistry research

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The interstellar medium (ISM), where new stars and planets are formed, hosts a very rich and complex chemical network, often among species not present under atmospheric conditions [1]. It is critical for astrochemistry to determine the composition of the ISM, which requires astronomical observations in conjunction with detailed laboratory spectroscopic data measured under the relevant conditions of low density and cold temperatures. Often, such experiments are conducted on charged particles, but although ions have been detected in space, the large majority of molecules composing the ISM are neutrals [2]. In this contribution, I will discuss the use of far-infrared spectroscopy of neutral molecules in molecular beams to elucidate the composition of the ISM. This is performed by merging the molecular beams of neutrals with the light of the free electron laser FELIX, in Nijmegen (The Netherlands). FELIX uniquely covers the wavelength range in which the James Webb Space Telescope (JWST) is most sensitive, making far-infrared spectroscopy crucial for astrochemistry research. A series of examples will be presented, including the spectroscopy of neutral polycyclic aromatic hydrocarbons (PAHs) [3], the study of weakly-bound complexes [4], the spectroscopy of sulfur allotropes (Fig. 1) [5], and the investigation of carbon-bearing molecules in high-spin excited states.

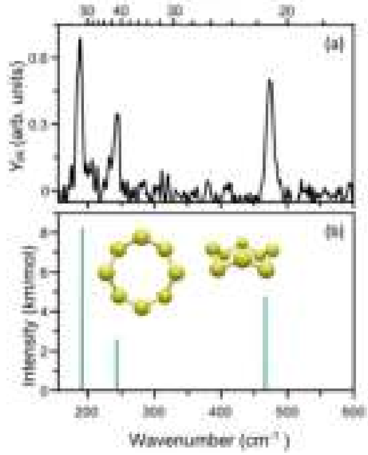

Fig.1 Measured (a) and computed (b) far-infrared spectrum of gas-phase octasulfur [5].

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Mutual neutralization in low-energy ion-pair collisions

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Mutual neutralization (MN) in collisions between oppositely charged ions is expected to be a key reaction for the ionization balance in any dilute environment where atomic or molecular anions are the dominate negative charge carriers. This includes e.g. dark interstellar clouds where polycyclic aromatic hydrocarbon (PAH) anions are believed to be the most prominent electron donors in MN reactions with atomic cations [1]. The cryogenically cooled ion beam storage facility DESIREE (Double ElectroStatic Ion Ring ExpEriment) is uniquely designed for studying MN reactions with atomic and molecular ions prepared in well-defined or narrow ranges of quantum states and with fine-control of the collision energy down to the sub-electronvolt regime [3,4]. In recent years, this has allowed a range of studies in which the final-state excitation energy distributions in atomic MN have been measured (see e.g. Ref. [5] and references therein) and for the first ever MN studies with cooled molecular ions [6-8].

This presentation will highlight recent DESIREE results from studies of MN reactions involving complex molecular ions such as fullerenes [8] (Fig. 1), PAHs, and biomolecules. These are important to benchmark theory and models that may be used for reliable predictions of electron transfer rates that are expected to strongly influence the charge balance and hence the chemistry in e.g. interstellar environments [2]. In addition, these studies reveal the importance of energy transfer, bond-breaking and bond-forming reactions in head-on collisions, which are driven by the Coulomb force between the oppositely charged ions. Here, support from quantum chemistry calculations is key to advance the understanding of such reactive charge transfer processes and to obtain accurate values of their rates.

The present results are based upon work from COST Action CA21126 - Carbon molecular nanostructures in space (NanoSpace) supported by COST (European Cooperation in Science and Technology).

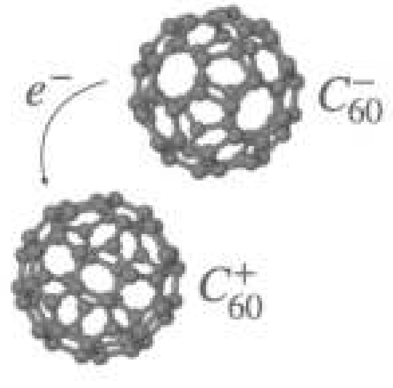

Fig.1 $C_{60}^+ + C_{60}^- \rightarrow C_{60} + C_{60}$ MN reaction

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New frontiers in cold ion spectroscopy and ion storage using multiply charged helium nanodroplets

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Helium nanodroplets (HNDs) are ultra-cold, nanometer-sized clusters of helium atoms that provide an ideal environment for forming tailored molecular and cluster ions, enabling precise studies of the ions' chemical reactivity and photophysical properties. While most research has focused on neutral species, our group explores highly charged HNDs [1], which open new experimental avenues, such as the formation of helium-tagged molecular ions for messenger spectroscopy [2], the formation of transient multiply charged dopants [3], the controlled growth of narrow-sized (metallic) clusters [4], and the storage of multiply charged HNDs within (electrostatic) ion beam devices.

This contribution presents our latest experimental advancements, focusing on using multiply charged HNDs for the efficient formation of helium-tagged molecular ion species for high-resolution electronic spectroscopy. We have successfully applied this approach to perform electronic spectroscopy of astrochemical relevant carbonaceous molecular ion species [2, 5], as well as to examine the shift in electronic transitions for various metal phthalocyanines in dependence on the central metal atom. Furthermore, we report on the integration of a multiply charged HND source with a multiple-reflection time-of-flight (MR-TOF) mass spectrometer [6]. The setup enables the trapping of charged HNDs, containing more than 10^8 helium atoms and approximately 3×10^5 helium atoms per charge, for several seconds. A systematic study of the storage time as a function of MR-TOF vacuum conditions has been conducted, and future experimental directions using this setup will be discussed.

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Indirect interatomic decay of XUV-ionized He nanodroplets

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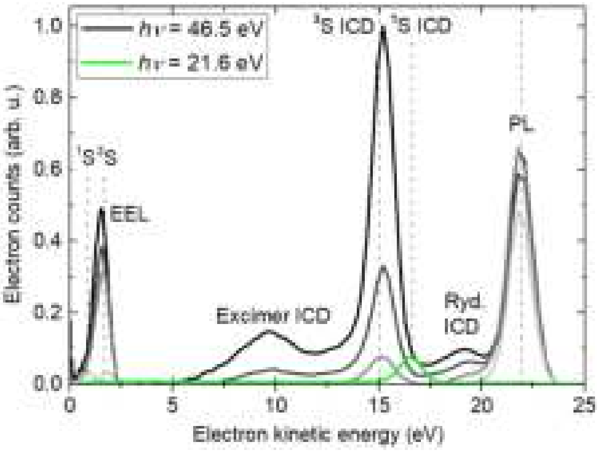
Ionization of matter by energetic radiation generally causes complex secondary reactions that are hard to decipher. Helium nanodroplets are ideally suited to unravel these secondary processes thanks to their unique properties -- the simple electronic structure of the He constituent atoms, the extremely weak binding of He atoms to one another and the quantum-fluid properties of He nanodroplets [1]. Using large He droplets irradiated by extreme ultraviolet (XUV) photons with energy $h\nu \gtrsim 44.5$ eV, we show that the full chain of processes ensuing primary photoionization can be tracked in detail by means of high-resolution electron spectroscopy [2]. We find that elastic and inelastic scattering of photoelectrons efficiently induces *inter*atomic Coulombic decay (ICD) in the droplets, similarly to ICD in resonantly excited He nanodroplets at $h\nu \approx 21.6$ eV [2]. Indirect ICD induced by electron-He scattering even becomes the dominant process of electron emission in nearly the entire XUV range in large He droplets with radius $\gtrsim 40$ nm, see Fig. 1 [3].

Likewise, in He nanodroplets doped with lithium (Li) atoms, indirect ionization of the Li dopants is observed in addition to direct photoionization of the He droplets [4]. Specifically, Li ions are produced by ICD involving metastable He* atoms and He_2^* excimers which are populated by inelastic scattering of photoelectrons in the droplets and by electron-ion recombination. This indirect ICD process turns out to be even more efficient than Li dopant ionization by ICD following direct resonant photoexcitation at $h\nu = 21.6$ eV [5] and by charge-transfer ionization ($h\nu > 24.6$ eV). Indirect ICD processes induced by scattering of photoelectrons likely play an important role in other condensed phase systems exposed to ionizing radiation as well, including biological matter.



Electron spectra of He nanodroplets inferred from velocity-map images recorded at a photon energy of $h\nu$=46.5 eV. The line color from light grey to black indicates radii of the droplets R=5, 20, 35, and 75 nm. The green reference spectrum was measured at $h\nu$=21.6 eV and R=50 nm. The vertical dashed lines indicate expected electron energies based on He atomic levels. Adapted from [3].

In the specific photon energy range around $h\nu$=60.5 eV, we recently discovered another type of ICD in He nanodroplets [6]. Here, a doubly excited He** atom, despite its extremely short *intra*atomic autoionization lifetime, transfers its internal energy to a neighboring He atoms which in turn is ionized. This type of ICD proceeds by relaxation of the He**He atom pair into excited He*He$^+$ pair states. ICD occurring by resonant excitation far above the single-ionization threshold opens opportunities for controlling radiation damage to a high degree of element specificity and spectral selectivity.

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X-RAY IMAGING AT THE NANOSCALE WITH ATTOSECOND TIME RESOLUTION

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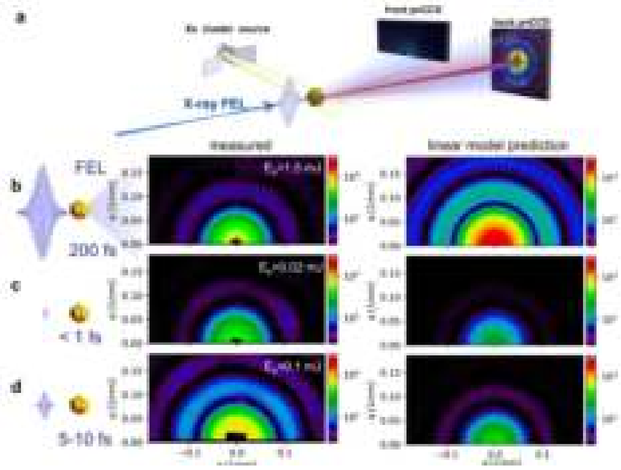
Most far field imaging methods have to compromise between temporal or spatial resolutions. Electron microscopy is limited in time resolution, optical light scattering within the femtosecond domain lacks spatial resolution. X-ray Free Electron Lasers (FELs) are capable of producing very bright bursts of coherent X-rays with femtosecond pulse durations. X-ray FELs offer unique opportunities to visualize transient processes as “frozen” in time with high temporal and spatial resolutions before the sample is destroyed. I will present examples of state- of-art nanoparticle imaging experiments with new developments such as intense and isolated sub-fs X-ray pulses, and discuss current challenges and opportunities for the study of chemical reactions and light-matter interactions.



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The influence of doping on the reactivity of metal clusters

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Gas phase metal clusters can act as a model system to investigate the active sites of more complex catalyst materials whose reaction mechanisms are poorly understood. However, real-world catalysts often comprise multiple elements with a mixing ratio optimised for better selectivity and reactivity based on screening. We present experiments using a controlled laser generation of bimetallic clusters, of which we study the interaction with small molecules. We do these investigations using a combination of mass-spectrometry and free-electron laser-based IR spectroscopy. The experimental work is complemented by DFT calculations, allowing for structure determination and rationalisation of the formed products. In a systematic study of the effect of element substitution, we elucidate the influence of local geometric and electronic structure on the interaction and, thus, of potential catalytic activity. In this contribution, we present our investigations on how doping of cationic cobalt clusters with foreign elements affects the adsorption modes of CO_2 and H2/D2. The experimental results pertain to adsorption reactions on pristine cobalt clusters doped with first-row transition elements (V, Cr, Mn, and Fe). These findings may aid in the design of future catalysts for CO_2 hydrogenation to methanol or other C2 products.

Advancements in Matter-wave Interferometry: From Molecules to Nanoparticles

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Exploring the transition between quantum mechanics and classical physics is a fundamental challenge in physics, with the superposition principle being a key feature distinguishing the two realms. Matter-wave interference experiments serve as a powerful tool to explore these boundaries and deepen our understanding of quantum mechanics at the interface to macroscopic systems [1].

The Long-Baseline Universal Matter-wave Interferometer (LUMI) in Vienna has achieved significant milestones, including the interference of molecules with masses up to 28,000 amu [2]. Building on this foundation, we are now extending our research to include metal nanoparticles and clusters [3]. The upgraded LUMI setup, which integrates 133 nm depletion gratings in a Talbot-Lau configuration with a metal cluster aggregation source, enables us to observe interference of nanoparticles with masses up to 10^6 amu, pushing the limits of quantum physics further towards the macroscopic scale.

Our current experiments focus on metal clusters, as they can be aggregated in a wide mass range and their optical properties are accessible by our optical gratings [4]. By observing matter-wave interference of these nanoparticles, we can investigate quantum coherence and decoherence mechanisms in systems with increasing complexity and mass.

The high sensitivity of the interference fringes to small phase shifts also allows for the precise measurement of molecular and atomic properties, such as magnetic [5], electric [6], and optical properties [7]. These measurements can be applied to mass-dependent metal clusters and provide insights into their potential applications in nanotechnology and materials science.

In this talk, I will present the evolution of matter-wave interferometry from molecules to metal nanoparticles and share our most recent preliminary results using sodium clusters.

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Unveiling Electronic-Structural Interplay in Metal Nanoclusters via Accurate Measurements of Temperature-Dependent Ionization Energies

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The work function (WF) of a solid surface or the ionization energy (IE) of a nanocluster is the minimum energy required to remove an electron and is a fundamental material property. Despite its significance, the temperature dependence of WF and IE remains underexplored due to the small magnitude of the effect. However, studying this dependence provides valuable insights into the interplay between a material's electronic properties and its structural dynamics. In particular, nanoclusters exhibit melting behavior that deviates significantly from that of bulk materials, offering a unique platform to explore size-dependent thermodynamic and electronic effects. Our high-precision, size-resolved photoionization measurements on isolated alkali metal nanoclusters reveal several intriguing features in the temperature dependence of IE. We observed a distinct transition in the slope of the IE(T) curve, marking the melting point of the nanoclusters. Furthermore, a sharp drop in IE was observed during the melting transition, highlighting significant changes in the electronic structure as the phase change occurs. The observed suppression of the melting temperature aligns with predictions from the Gibbs–Thomson equation, which describes finite-size phase transitions. Furthermore, isotope-resolved measurements of Li-6 and Li-7 nanoparticles revealed an isotope-dependent variation in the temperature dependence of IE, reflecting differences in their quantum lattice dynamics. These findings provide new insights into the fundamental relationship between electronic and structural properties.

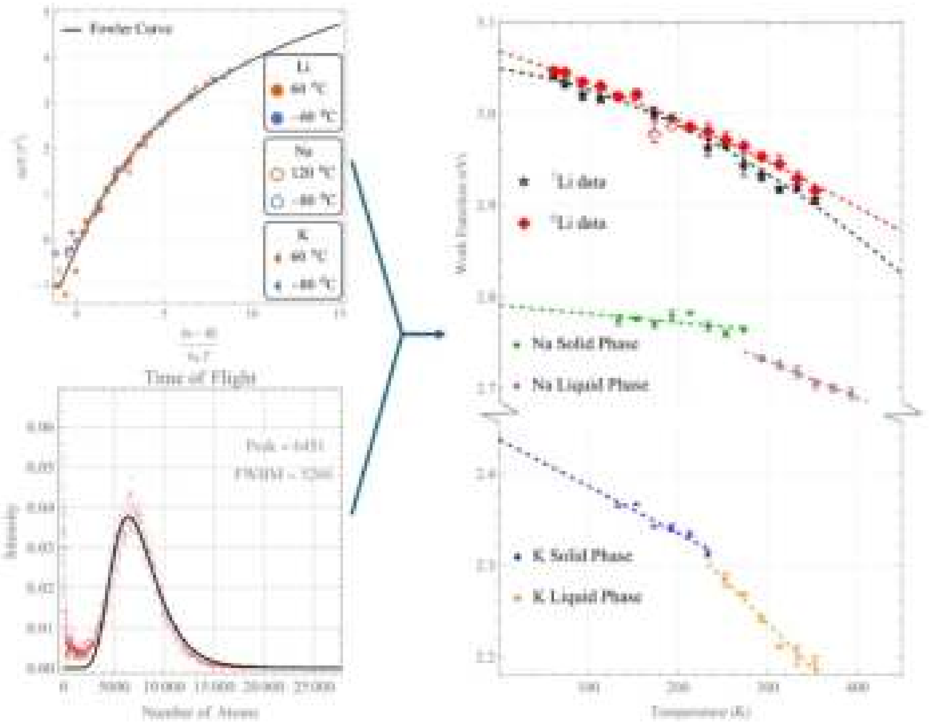

Fig.1 Temperature vs. Work functions of Li, Na, and K extracted from time-of-flight measurements and Fowler fits.

Oxidation and Spin Effects on the Sub-Picosecond Ultraviolet Relaxation Dynamics of Neutral Copper Oxide Clusters

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Copper oxides are particularly special to the physical chemistry community as the prototypical semiconductor where both excitons, and more recently their Rydberg analogues, were discovered. Their unique electronic structures enable application to catalysis, spintronics, water splitting, and high temperature superconductivity, thereby making detailed knowledge of the fundamental Cu-O interaction critically important. I will present the ultrafast dynamics of more than 35 sub-nanometer neutral copper oxide clusters measured with pump-probe spectroscopy coupled with time-of-flight mass spectrometry. The addition/subtraction of each atom produces strong changes to both the cluster stability and excited state behavior, revealing trends associated with oxidation and stoichiometry. The addition of each Cu atom increases the measured lifetimes by ~ 40 fs, whereas the addition of each O atom is the opposite [1,2]. Density functional theory calculations reveal that strong ferromagnetic coupling produces structures containing high spin states [3]. Topological descriptors for the excited states are calculated (time-dependent density functional theory) and show that the measured excited state dynamics align with changes in the charge carrier delocalization. In particular, structural terminal Cu atoms are found to be important for the production of Rydberg excitons in $(Cu_2O)_n$ clusters, where upon photoexcitation, the electron resides on the dangling metal atoms [4]. The onset of terminal atoms with increasing Cu also marks a distinct change in lifetime behavior trends. Copper oxide clusters have potential to shape a new era of quantum materials, providing a consistent picture of electronic dynamics in a size regime where such properties are typically non-scalable.

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Theory of angular momentum transfer from light to molecules

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Motivated by recent advancements in studies and applications of the orbital angular momentum (OAM) of light [1], we suggest a theoretical framework for the analysis of the angular momentum transfer from a structured light field to a material particle [2]. In particular, we express the general light-matter interaction Hamiltonian through couplings between spherical gradients of an electric field and (transition) multipole moments of a particle of any non-trivial rotation point group. Our model can accommodate an arbitrary complexity of the electric field and particle's structure. To demonstrate its predictive power, we apply our framework to the following scenarios:

◊ *Ro-vibrational spectroscopy of molecules using vortex beams:* we uncover the mechanism of angular momentum exchange between the spin and orbital angular momenta of light, molecular rotation, and its center-of-mass motion. We demonstrate that the nonzero vorticity of light beams can strongly enhance certain ro-vibrational transitions that are considered forbidden in the case of nonhelical light.

◊ *Optimal OAM transfer*: we draw a comparison between solenoidal components of an electric field and its spherical gradients, which quantify the angular momentum transfer from light to matter. We provide recipes for the optimization of the electric field structure to enable efficient OAM transfer to molecules.

◊ *Helical dichroism for chiral enantiomer resolution*: we connect leading terms of a multipole expansion of the light-matter interaction with various point symmetry groups of a molecule. This allows us to analyze the requirements for detecting chirality via an OAM-sensitive dichroism measurement.

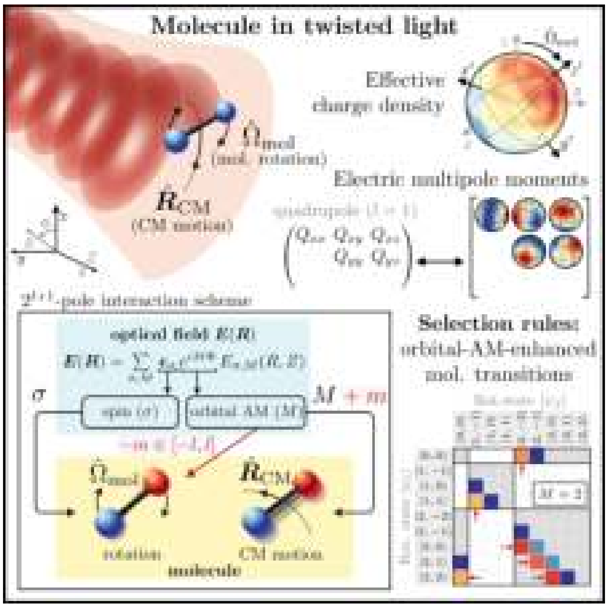

Fig.1 Pictorial summary of the theory.

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Conformer-selective photoelectron circular dichroism

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Photoelectron circular dichroism (PECD) is defined as a forward-backward asymmetry in the photoelectron angular distribution for randomly oriented chiral molecules photo-ionized by circularly polarized light (CPL). Most of the previously developed PECD experiments rest on 1-photon or non-resonant multiphoton ionization where all the conformers of a flexible molecule are ionized simultaneously.

We recently developed a conformer-selective PECD scheme based on resonance-enhanced multiphoton ionization (REMPI).[1] This experiment was applied to flexible molecules, such as 1-indanol. The two conformers of the same enantiomer of 1-indanol show PECDs that differ in magnitude and are opposite in sign. (see Fig. 1).

We extended these experiments to the study of induced chirality on an achiral molecule interacting with a chiral environment.[2] Ionizing the non-chiral phenol chromophore within a hydrogen-bonded complex with a chiral molecule, methyloxirane, results in the appearance of a PECD signal for the ionization of the phenol highest occupied orbital (HOMO). This induced PECD is related to a chiral deformation of the HOMO. In this system too, different conformers exhibit different PECD, in relation to their structure determined by IR spectroscopy, and symmetry. These results evidence the non-local nature of chirality.

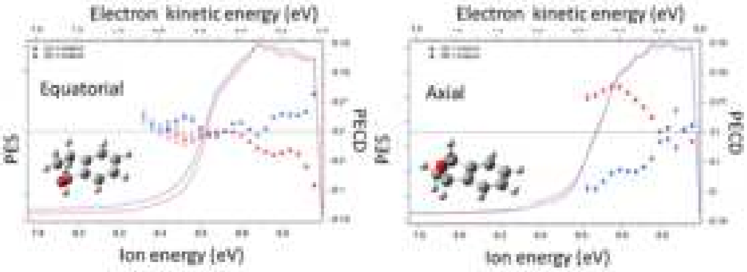

Fig.1 Photoelectron (lines) and PECD spectra (squares) of the two conformers of 1-indanol ionized with a REMPI process via their respective S_0-S_1 transition origin. The (R) and (S) enantiomers are shown in blue and red, respectively.

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Freezing Out Structural Effects: Gas-Phase Fluorescence from Rhodamine Homodimers and Trimers at Cryogenic Temperatures

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Studying electronic communication between light-absorbers is vital to understand energy transport processes, among them photosynthesis, UV-induced DNA damage and FRET. In FRET, for instance, the rate of energy transfer between a donor and acceptor dye varies with the inter-dye separation, leading to the application of FRET to study biomolecular structure. The microenvironment such as nearby charges, however, affects the dye photophysics, which calls for fundamental studies on isolated systems and at low temperatures where spectral signatures stand out most clearly.[1-3] Here, we study the intrinsic photophysics of homodimers and homotrimers of rhodamine dyes linked together by rigid alkyne spacers at cryogenic temperatures (100 K). Fluorescence from gaseous ions is collected at the LUNA2 setup in Aarhus where mass-selected ions are stored in a cylindrical ion trap. We measure multiple absorption bands from homodimers and trimers of chemically identical cold rhodamine-575 dyes, clearly indicating that multiple conformers are being interrogated. Surprisingly, we measure large redshifts in the emission upon cooling, in contrast with an expected blueshift upon lowering the temperature. This measured Stark shift indicates geometries where two dyes are close together, which is supported by DFT calculations. These findings push our understanding of interactions between dyes at cold temperatures further and help complete our understanding of the fundamental photophysics that underlie such systems, of relevance to the use of cryo-FRET for biomolecules.

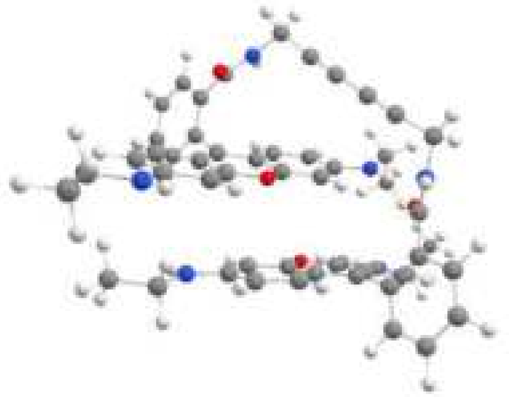

Fig. 1: Computed structure of rhodamine-575 dimer, showing stacked configuration

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Dust grain collisions in Interstellar Medium

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Interstellar dust, encompassing its elemental nature, chemical composition, formation, and destruction, has long been a topic of debate among astronomers, astrophysicists, and astrochemists. While the elemental building blocks are now well understood, the precise chemical composition remains uncertain, though it is generally agreed to be primarily silicate and/or (hydro)carbonaceous in nature. The processes of formation and destruction continue to be active areas of research.

This study aims to investigate the collisions between interstellar dust grains of varying sizes and compositions, focusing on uncovering key parameters—such as shattering velocity thresholds, coagulation processes, and the effects of grain size and composition—that are essential for accurate astronomical modeling. To this end, we design spherical, non-porous, and amorphous dust structures with varying chemical compositions, including silicates, hydrocarbons, and astrodust (Mg, Fe/Ni, SiO) [1,2]. We then simulate the collision process between grain pairs of different sizes and compositions, using molecular dynamics simulations with potentials derived from DFTB or ReaxFF. Our results reveal significant differences from previously used parameters in existing models. Notably, the shattering velocity is found to be considerably higher than earlier estimates.

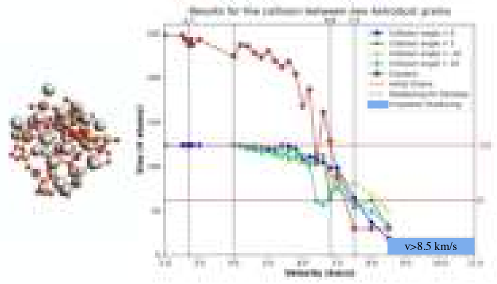

Fig.1 Collision between two grains of $Mg_{26}Fe_6Si_{20}O_{72}$.

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“Magic numbers” in naphthalene and cyanonaphthalene-water clusters

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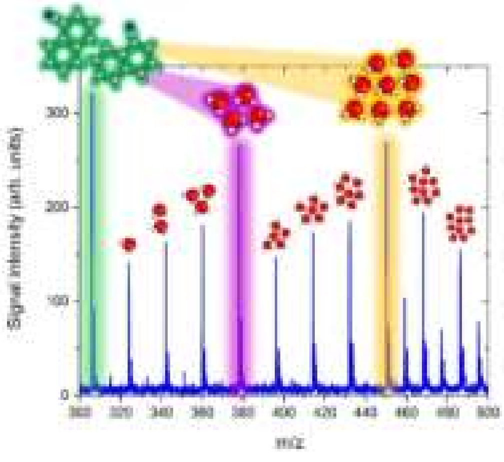
Ever since the first unambiguous detection of a specific PAH – cyanonaphthalene (here denoted CNN) in the Taurus molecular cloud (TMC-1) [1], both CNN and its precursor naphthalene (here denoted Np) have been the focus of several astrochemical studies. Our interest concerning these two chemical species lies in the interaction with water, and how the differences between CNN and Np could affect their behavior in similar astrochemically relevant environments, such as the ice mantles of dust grains.

The experiments were performed on a cluster beam apparatus CLUB in Prague [2]. In the experiment, we examined the interaction of low energy electrons (<10 eV) with the mixed $(PAH)_N(H_2O)_M$ clusters (PAH = CNN / Np). Obtained negative ion mass spectra slightly differ with each specific PAH, but one feature remains common – pronounced intensity of $(PAH)(H_2O)_4^-$ and $(PAH)(H_2O)_8^-$ fragments compared to the other fragments of the series. We further discuss this observation and the subtle variations associated with each PAH.



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Dicationic atomic and molecular clusters: How to form and stabilize them in helium nanodroplets

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For the majority of doubly charged atomic and molecular clusters, there is a limit in size at which the cluster becomes unstable against Coulomb-driven fission. Determining this so-called Rayleigh limit (n_{Ray}) experimentally however is difficult, as environmental factors such as temperature etc. can lead to the spontaneous fission also of clusters that are significantly larger than the Rayleigh limit. The size of the smallest doubly charged cluster that can be detected experimentally is called appearance size (n_{a}) and provides an upper bound for n_{Ray} [1]. By tweaking experimental parameters, the size of detectable dicationic clusters can be decreased more and more to approach the Rayleigh limit.

In this contribution, we show how the appearance size of dicationic clusters could be significantly lowered compared to previous experiments by using helium nanodroplets as a matrix for the formation of the clusters, in combination with a newly developed method for the ionization, where the charge state of initially singly charged clusters is increased via Penning ionization [2]. With this technique, for noble gas clusters of argon, krypton and xenon the appearance sizes could be lowered from 91, 69, and 47 to 73, 43, and 25, respectively [3]. Following this study on atomic van der Waals clusters, we also studied molecular clusters. Here, for $(CO_2)_n^{2+}$ the appearance size was lowered from 43 to 30, which is quite close to the Rayleigh-limit, estimated to be 26 for this type of cluster [4].

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Probing the fate of vibrational excitation in small molecules

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The ability of molecules to absorb individual quanta of vibrational energy is the cornerstone of infrared spectroscopy. However, once deposited in a molecule, the absorbed energy can either stay in the excited degree of freedom (the bright state) or it will be dissipated by the system until it is released through such processes as fragmentation or photon emission.

Using a combination of resonance-enhanced multi-photon ionisation (REMPI) spectroscopy and the broadly tuneable infrared free electron laser FELIX, we probe the fate of energy deposited in molecules through resonant infrared excitation. We show how IR excitation evolves from no dissipation in the four-atomic ammonia to complex vibrational populations in phenol and its halogenated derivatives, depending on the excited coordinate. We finally discuss how a competing process of isomerization in conformational isomers could experimentally be probed.

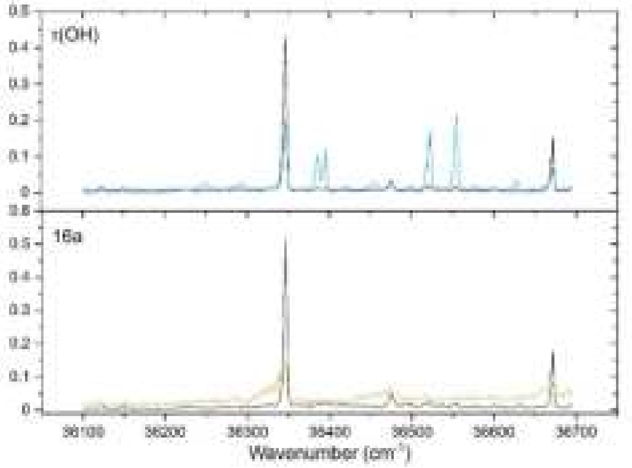

Fig.1: REMPI spectrum of phenol following the excitation of the OH torsional mode (top) and the out-of-plane vibration 16a (bottom). The top spectrum illustrates the modulation of Franck-Condon factors by vibrational excitation while the hot band progression in the bottom spectrum suggests intramolecular vibrational energy redistribution (IVR).

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High-Resolution Structure And Energetics Of The DABCO Molecule Attached To Clusters For Modelling Energy Transport In Matter

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The diffusion of electrons in matter generates secondary species, such as secondary electrons and radicals, that can interact with nearby species. In cells, these interactions may cause DNA damage and increase cancer risk [1]. Recently, studies have shown that data on both elastic and inelastic scattering in small water clusters can support the development of theoretical models to predict energy transport at the macroscopic scale [2]. Clusters, in particular, provide effective models for describing organized condensed matter [3]. Our approach uses a highly symmetrical molecule, DABCO, known for its atomic-like orbitals [4], deposited on argon and water clusters and ionized via a 1-photon transition with synchrotron light (DESIRS beamline). Coincident ion and electron detection allows precise identification of the products formed and their photoelectron distributions. We have gathered detailed information on the electronic and vibrational structure of the isolated molecule and small clusters – examined here with unprecedented precision. We have as well retrieved information on the photoelectron angular distribution in both cases, from which we aim to gain insights on electron scattering processes.

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Comprehensive Insights into the Initial Dynamics of Ionized Water Dimers

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Radiation chemistry in biochemical systems is primarily driven by the ultrafast dynamics of water molecules following the absorption of ionizing radiation. The initial response of the aqueous environment to valence ionization involves the formation of hydrated electrons and ultrafast proton transfer, which was recently probed in ionized water dimers $(H_2O)_2^+$ [1]. However, the subsequent fragmentation pathways leading to highly reactive intermediates have thus far been explored primarily through molecular dynamics simulations.

Our experimental investigation, utilizing purified molecular beams of $(H_2O)_2$ [2] and strong-field ionization at 800 nm, revealed that $(H_2O)_2^+$ can either stabilize or fragment along more than ten distinct reaction pathways. To address dynamics of these pathways, we employed a disruptive-probing scheme [3] that enable us to simultaneously track formation of all the ionic species, thereby directly yielding effective reaction-rate constants. These findings provide crucial insights into post-ionizing processes in both the Earth's atmosphere and living organisms.

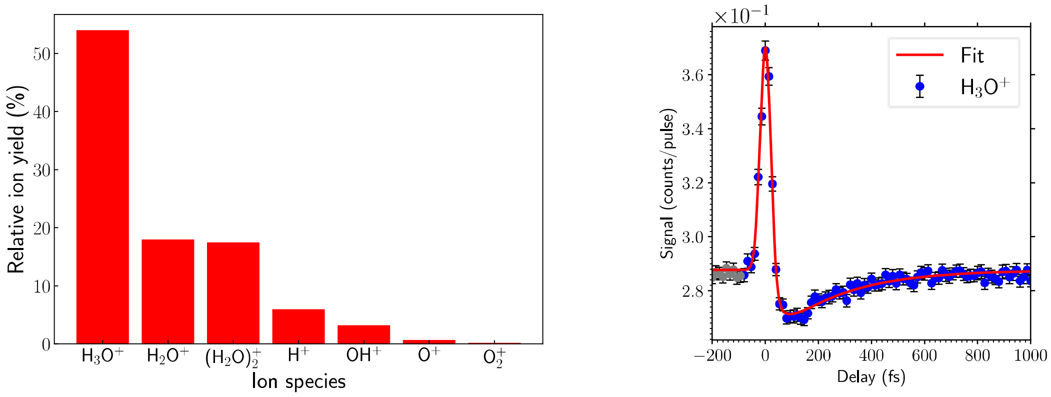

Fig.1 (Left) Comparison of the relative populations of selected ion species from singly charged water dimers $(H_2O)_2^+$ produced by strong-field ionization. (Right) Observed dynamics of hydronium H_3O^+, related to proton transfer and $(H_2O)_2^+$ fragmentation, obtained using the disruptive probing technique.

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Photoelectron spectroscopy and molecular beam scattering from liquid water flatjets

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Cylindrical liquid jets of micrometer-sized diameters, or microjets, enabled the study of liquid water under high-vacuum conditions. This opened a breadth of new techniques such as LJ-PES (Liquid Jet Photoelectron Spectroscopy). Despite its enormous success in various fields, the microjet is not without important drawbacks for specific applications, e.g., its curved surface and relatively large thickness with a small cross-section. These pushed the development of so-called flatjets almost a decade ago, having recently reached a technically mature stage with different methods and applications.

We have been utilizing flatjets to approach questions that were elusive until their development. We used the luminol chemiluminescence reaction to show that, when generated from the impingement of two microjets, flatjets create a well-defined liquid–liquid interface, acting as a steady-state chemical reactor accessible to optical spectroscopies [1], see figure. We have also shown that its small thickness allows for liquid temperature assessment using straightforward infrared imaging techniques, facilitating the analysis of the entire flat region from a single image [2]. Recently, we have demonstrated the possibility of aligning molecules at the liquid surface by applying electric potentials to each parent microjet, creating a potential difference through the bulk of the flat part, directed through the surface normal [3]. We can also exploit surface-active solutes as a means to achieve molecular alignment in the liquid phase – a capability significantly reduced in cylindrical jets due to their curved geometry.

One important aspect of PES is the photoelectron angular distribution (PAD), that embeds deeper information on the studied system. This property emerges from fundamental physics of photoemission. The degree of anisotropy in PADs carries knowledge on the system such as probing depth, and elastic and inelastic mean-free-path [4]. Typical PAD analysis relies on randomly oriented target molecules, although by probing aligned molecules at the surface of a flatjet, we expect a symmetry breaking process and the PADs would reveal themselves in a totally different fashion. This is one of our ongoing projects using flatjets.

In another recently started project, we aim to reveal the water vapor density around liquid microjets and flatjets by means of crossing them with a neutral molecular beam of metastable CO molecules. Metastable CO has a lifetime of 3 ms and decays by emitting a 206 nm photon [5], making it the perfect tool for imaging the vapor distribution around liquid jets. We will explore the evaporation dynamics of water at the molecular scale, to a level of detail never achieved before.

I will present our recent developments with flatjets emphasizing their potential relative to microjets, comparing the different methods we use to generate them and how they enabled our latest findings.

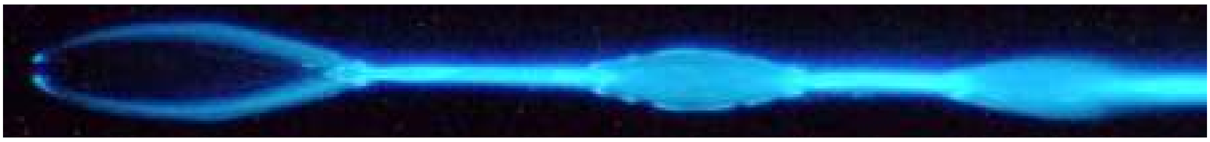

Fig.1 A flatjet generated by the impingement of two microjets, one containing a luminol + copper sulfate solution and the other composed of highly concentrated hydrogen peroxide solution. The flow direction was downwards, but the figure was tilted such that the flow here is shown from left to right, and the original microjets are at the plane perpendicular to the paper. The characteristic blue chemiluminescence of luminol is seen where the two liquids mix efficiently. The most important aspect here is that the first flat part of the jet (the first *leaf*) is mostly dark, with a faint glow appearing at its end, highlighting that a well-defined liquid–liquid interface is created there. We have demonstrated that the liquids only mix in this region due to diffusion through the interface [1].

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XUV Photoionization of Microhydrated Biomolecules

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Water plays a fundamental role in sustaining life, particularly by stabilizing essential biomolecular building blocks such as DNA bases. Understanding how ionizing radiation interacts with biomolecules in aqueous environments is key to elucidating mechanisms of radiation-induced damage in biological tissue. We investigate the XUV photoionization of microhydrated biomolecular clusters—small systems where key aspects of hydration are preserved and which are small enough such that photoelectron spectroscopy can be used.

Photoelectron-photoion coincidence (PEPICO) spectroscopy is a powerful technique to obtain ion mass-selective photoelectron spectra. Our PEPICO spectrometer has recently been upgraded to enable double-sided electron-ion imaging [1]. By comparing photoelectron spectra from hydrated and non-hydrated samples of biomolecules, including pyridine, thymine, and uracil, we can determine whether ionization occurs on the biomolecule or the water side of the complex.

Following photoionization, the resulting microhydrated cation relaxes via fragmentation or protonation. As previously observed for microhydrated biomolecules embedded in helium nanodroplets, the parent biomolecule is stablized against fragmentation, when it is in the microhydrated state [2]. Strikingly, we observe spectral features indicative of water ionization in coincidence with bare thymine and uracil cations. On figure 1, photoelectron and ion mass spectra from the photoionization of thymine-D_2O clusters at hν = 21 eV are shown. This reveals a previously unreported charge transfer process: ionization initially occurs on the water moiety, followed by a charge transfer from the biomolecule to the water, resulting in the ejection of a bare biomolecular cation. This mechanism underscores the intricate interplay of hydration and charge migration in radiation chemistry of biological matter.

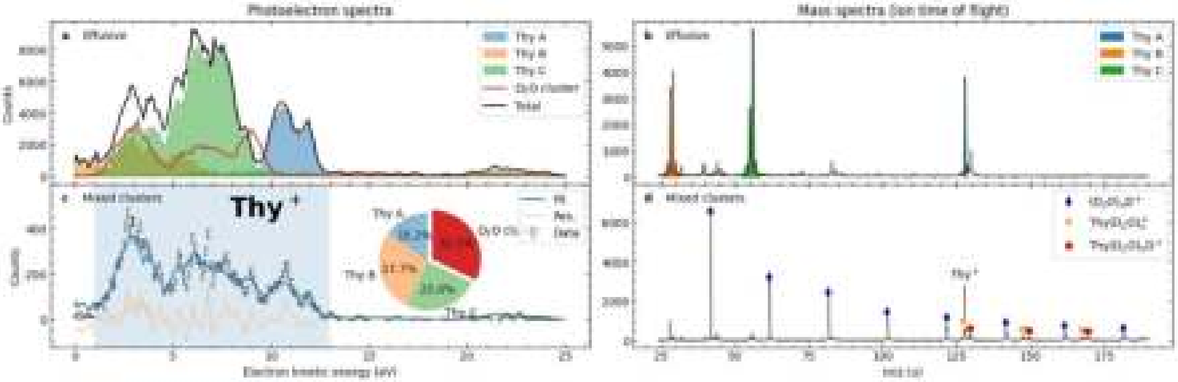

Fig. 1 Photoelectron (left panels) and ion time-of-flight mass spectra (right panels) for the photoionization (hν = 21 eV) of bare thymine (upper panels) and microdeuterated thymine (lower panels). **a**, Photoelectron spectra in coincidence with the parent thymine cation (Thy A) and fragments (Thy B and C), as shown in the mass spectrum, panel **b**. **c**, Photelectron spectrum in coincidence with the parent thymine cation (black symbols) from a mixed cluster measurement, yieling the mass spectrum in panel **d**. A linear combination of the photoelectron spectra from panel **a** is fittet (solid blue line and the pie chart).

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High-Resolution Electron Spectroscopy of Helium Nanodroplets with a Hemispherical Electron Analyzer

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Helium nanodroplets (HNDs) are intriguing quantum fluid clusters, notable for their exceptionally low temperatures and superfluidity. Moreover, their simple electronic structure and the superfluid properties make them the ideal candidate for studying ultrafast electronic relaxation processes in weakly bound systems. Among these, a key process is interatomic Coulombic decay (ICD), in which an atom or molecule in an excited state transfers its excess energy to a neighboring species, leading to electron emission [1-4].

In these systems, excitation by extreme ultraviolet (EUV) photons leads to complex pathways of energy and charge transfer between helium atoms within the droplet or between a helium atom and a foreign “dopant” particle.

A key technique to access these processes is photoelectron spectroscopy, which allows one to resolve the energy distribution of emitted electrons with high precision. In particular, the use of a hemispherical electron analyzer (HEA) is instrumental in isolating ICD electrons and analyzing their dynamics. This spectrometer enables high-resolution measurements (<0.1 eV) by selecting narrow energy windows and suppressing background contributions.

High-resolution electron spectra revealed that indirect ICD induced by photoelectron impact excitation becomes the dominant relaxation mechanism in large droplets exposed to XUV light, especially for droplet radii above ~40 nm [5]. In addition, the high resolution provided by the HEA allows the identification of subtle secondary features in the ICD electron spectra, such as contributions from metastable He*(1s2s ^{3}S) atoms and from He_2^* excimers forming by electron-ion recombination with the droplet (as can be seen in Fig. 1) [6].

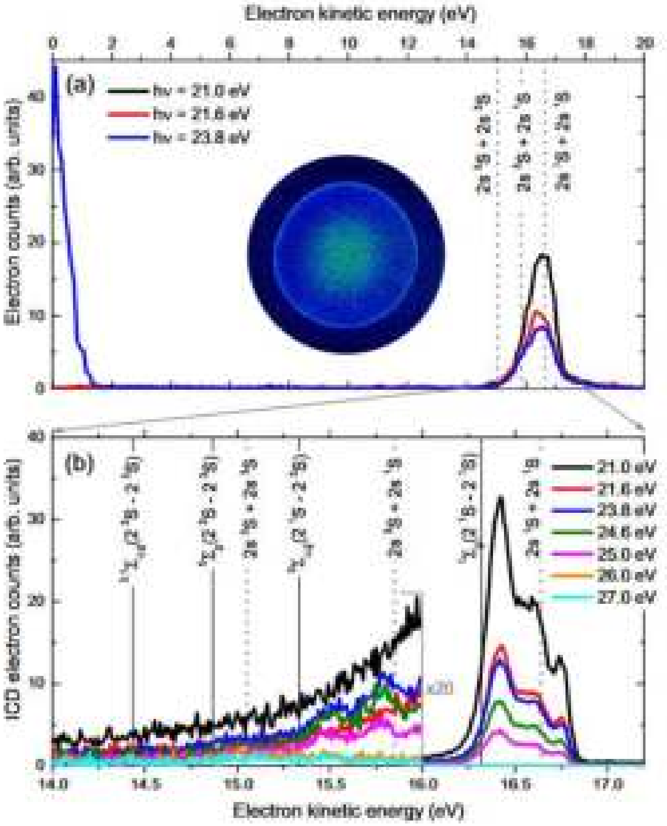

Fig.1 Background-corrected total electron spectra acquired for pure helium nanodroplets with a radius of 75 nm, at photon energies close to the ionization threshold of helium, using (a) the VMI spectrometer and (b) the HEA [5].

Motivated by these findings, we aim to implement an HEA-equipped electron spectrometer in our laboratory at the University of Kassel. The setup will be complemented by a source of helium nanodroplets and by various sources of UV up to X-ray radiation. In the long term, we plan to extend these investigations to a broader class of liquid clusters and doped systems.

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Penning electron detachment of SF_5^- and H^- caused by electronically excited potassium, helium, and hydrogen atoms

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Penning detachment is a process where an electronically excited neutral interacts with an anion to cause electron detachment by transferring its excitation energy ($N^* + A^- \rightarrow N + A + e^-$). This phenomenon plays roles in environments where anions and excited neutrals coexist, such as stellar atmospheres including the sun. Especially, Penning detachment of H^- is of higher interest. In the photosphere of the sun, photons of higher energy ($hv > 0.75$ eV) are absorbed by H^- via photodetachment ($H^- + hv \rightarrow H + e^-$). Penning detachment of H^- by excited hydrogen or helium atoms could be a competing process in the energetic environment of the sun. While Penning detachment has been studied theoretically [1–3] and observed experimentally in several kinetic studies [4–6], systematic understanding based on experiments has not been developed yet.

In this study, the dependence of Penning detachment cross section on the excited state of the neutral was studied by the combination of SF_5^- and K^{**}. An ion beam of SF_5^- was crossed with potassium atoms excited to high Rydberg states using two tunable-wavelength dye lasers. Scanning the excited states of the potassium in the range of 8d ~ 32d and 10s ~ 33s showed that Penning detachment cross section highly depends on the excited states of the neutral. The experimentally observed behavior was explained by the energetic relationships between the anion and the excited neutral, and the dipolar transitions of the excited neutral. In addition, the occurrence of Penning detachment of H^- by excited helium and hydrogen atoms produced by electric discharge was experimentally observed for the first time.

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Platinum and Nickel Monoxide Anions Convert Methane to Methanol

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The ability to take a catalyst and directly convert methane to methanol is extremely desired, as while methane is plentiful, it is expensive and requires a large amount of energy to transform into a useable fuel. The advantages of methanol as a fuel is that it has a high energy density per gram, a flame speed that propagates rapidly, low temperature combustion, and at atmospheric standard temperature and pressure it is a liquid. Amongst many other advantages it is also known as a clean burning fuel [1]. Unfortunately, the problem with most catalysts is that they will over oxidize due to the strong C-H bond in methane; whereas, the C-H bond in methanol is much weaker. Certain metal monoxide anions have been calculated to partially oxidize the methane, where the metal then interacts weakly with the methanol product in order to prevent over oxidation to formaldehyde, $MO^- + CH_4 \rightarrow M^- + CH_3OH$ [2,3]. In two separate experimental studies, NiO^- and PtO^- anion beams were made and interacted with methane gas. A cryo-trap, cooled down with liquid nitrogen was used to collect the reaction products. Analysis of the cryo-trapped reaction products were monitored with a quadrupole mass spectrometer while incrementally increasing the heat to desorb the evolved species. Both experiments showed confirmation of methanol formation, and calculations for NiO^- and PtO^- showed in agreement that these reactions would selectively form methanol [4,5].

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The not even just odd even-odd effect in the cooling of gold clusters

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The spontaneous and photo-induced decays of anionic gold clusters, $\mathrm{Au}_N{}^-$, of sizes $N = 2 - 13$ and 15 have been measured in the cryogenic ring DESIREE [1]. The size-selected clusters, produced in a cesium sputter source, were stored between 0.1 and 100 s. Radiative cooling is observed for all cluster sizes apart for the dimer. For $N = 6 - 13$ the cooling times have a strong odd-even oscillation with an amplitude that decrease with cluster size. Strikingly, the even N clusters have the faster cooling, in a complete reversal of the pattern seen for the cationic gold cluster cooling previously [2]. Another striking difference is the absolute cooling rate which is orders of magnitude slower for anions than for cations. The non-radiating dimer was observed to decay by electron emission in parallel to neutral atom emission at long times, implying a breakdown of the Born-Oppenheimer approximation. The behavior for the gold dimer anion is almost identical to the behavior seen for the copper and silver dimers [3], and contrasts strongly with decays of dimers of silicon and carbon [4,5,6].

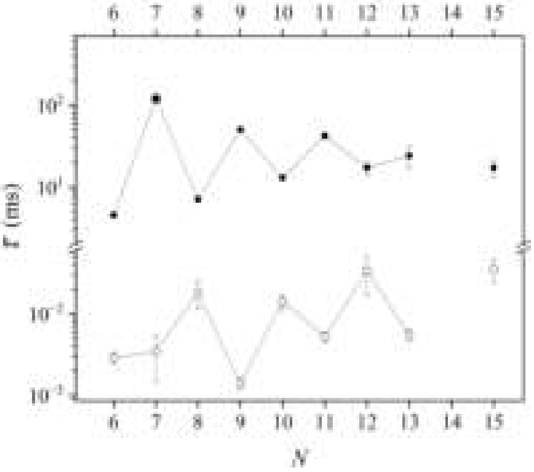

Fig.1 Cooling time constants for gold anionic and cationic clusters (filled and unfilled circles, respectively).

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Mechanistic Aspects of Dehydrogenation Reactions on Metal-fullerene Complexes

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The pursuit for sustainable and environmentally friendly alternatives to fossil fuels has become a noteworthy global challenge, prompting extensive endeavors to cultivate efficient energy conversion technologies. Hydrogen, as a convenient, safe, and versatile fuel source, can be converted to a desired form of energy without the emission of greenhouse gases and pollutants [1]. The hydrogen evolution reaction serves as a crucial source of hydrogen that can be widely utilized, with water splitting representing a vital step in this process [2]. One approach is the dehydrogenation of water on a Buckminsterfullerene (i.e. C_{60}) supported vanadium cation, which has shown a strong involvement of the fullerene support as hydrogen shuttle and as electron sponge [3-5]. In this method, the complexes will be produced in vacuum by a dual-target dual-laser vaporization source. Water and ammonia dehydrogenation on neutral and cationic metal-fullerene clusters will be studied using gas phase reactivity experiments in a collision cell and in an ion trap. The reactants, intermediates, and reaction products will be characterized by visible light and infrared spectroscopy, and the reaction mechanisms will be modelled with quantum chemical calculations. Since the studied metal-fullerene clusters can be viewed as gas phase model systems for single atom or single cluster catalysts consisting of dispersed metals on fullerene supports, the generated knowledge about the structure-reactivity relationship, structural fluxionality, and metal-support interaction will provide guidance for the design of better dehydrogenation catalysts that can efficiently make use of scarce raw materials and generate green hydrogen, a major challenge in the current energy transition.

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An effective rotor lattice model in two dimensions shows how ferroelectric domain-wall polarons might form in soft semiconductors

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Ferroelectric domain-wall polarons are postulated to be responsible for the remarkable optoelectronic properties of soft semiconductors such as hybrid organic-inorganic perovskites [1]. In the direction of the domain walls, (molecular) rotors are polarized in opposite directions, which causes the electron to localize along one axis of the lattice [2]. However, besides the existing computational studies, a theoretical description of the ferroelectric domain-wall polaron is missing. In this work, we attempt to bridge this gap by showing that these polarons form in a minimal two-dimensional model of electrons interacting with freely rotating (molecular) dipoles embedded in the inorganic lattice [3]. Based on a variational phase diagram analysis, we identify the rotor-electron coupling as the origin of a structural instability, which leads to the formation of the domain walls via a pseudo-Jahn-Teller symmetry-breaking process. These results agree with and generalize computational results on soft semiconductors [4].

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Electron triggered processes in halogenated carboxylates and their clusters

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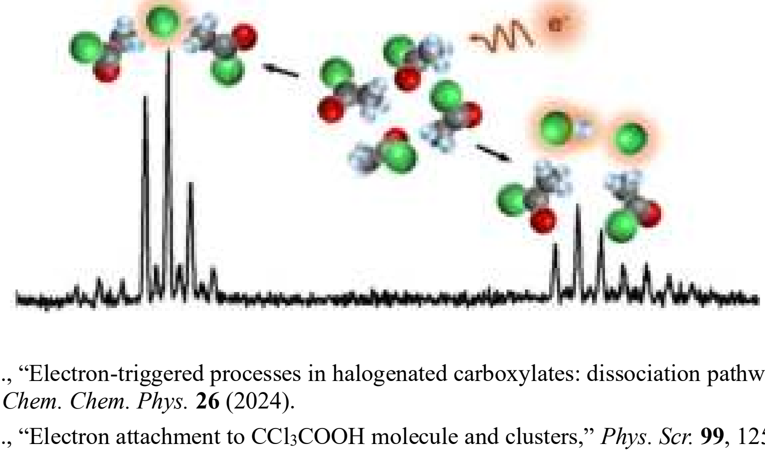
The interactions between molecule and electron can be strongly influenced by the environment. Such effects can be shown by comparing the results of such interactions for isolated molecules with the same experiments of molecules in clusters. This work presents results of our long-term study on the interaction of electrons with halogenated carboxylic acids and their halo-derivates, specifically CF_3COCl [1], CCl_3COOH [2] and CH_3COCl [3].

Chosen group of compounds is relevant mainly for atmospheric chemistry, since these molecules are found among the degradation products of hydrochlorofluorocarbons (HCFCs). Residues of those compounds are present in the environment due to their chemical resilience, even though the use of HCFCs is being abandoned.

All data were measured on the CLUB [4] apparatus. The molecular beam was created by continuous supersonic expansion of the sample with a buffer gas (Ar or He) through a conical nozzle. Helium was used to generate a beam of individual molecules, while the clusters were formed in argon. After the low energy electron attachment, the anions were probed with a reflectron time-of-flight mass spectrometer.

The results suggest not only the influence of the electron density distribution over the molecule on the dissociation pathways, but also strong effect of the environment, as the fragmentation patterns differ for all three compounds when comparing molecular and cluster mass spectra.

This work is supported by the Czech Science Foundation project Nr. 24-11390S.



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Isolated Green Fluorescent Protein Chromophore Anions: Indeed They Shine

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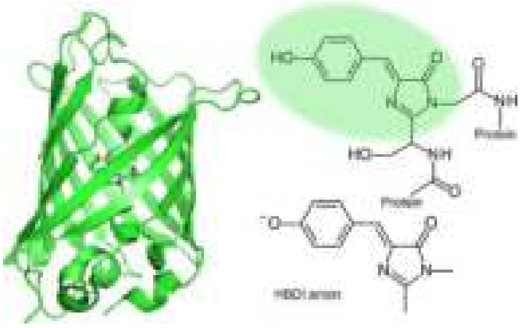

Fig. 1. GFP and its chromophore.

The green fluorescent protein (GFP) derived from the jellyfish *Aequorea victoria* consists of a barrel-like β-sheet structure wherein its photoactive chromophore molecule is buried (Fig. 1). Upon exposure to blue-light irradiation the chromophore undergoes excited-state proton transfer, resulting in an anionic form that fluoresces with a yield of 80%. Our group performed the first gas-phase action absorption measurements of the HBDI$^-$ model chromophore (Fig. 1) in 2001, which revealed an absorption band maximum in line with that of the protein [1]. The protein microenvironment is, however, essential for fluorescence as photo-excited bare HBDI anions quickly undergo internal conversion through a conical intersection in a twisted geometry. Thus, earlier attempts to measure gas-phase fluorescence at room temperature all failed. Here, we unequivocally show that the chromophore exhibits fluorescence in the gas phase when cooled to low temperatures (<150 K) [2] in accordance with previous predictions [3]. LUNA2 experiments at 100 K reveal an absorption-band maximum at 481.6±0.2 nm (in agreement with photoinduced action spectroscopy [3]) and maximum emission at 483.6±0.5 nm [2]. Remarkably, both values closely resemble those for proteins cooled to 77 K. After excitation at the 0-0 transition, we estimate radiation is the dominant pathway back to the ground state. Franck-Condon simulations at the ωB97XD/aug-cc-pVDZ level of theory nicely reproduce the experimental spectra and identify the fluorescent form to be planar, and that an in-plane scissoring mode (80 cm^{-1}) is active for both absorption and emission.

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Secondary ionization of pyrimidine nucleobases and their microhydrated derivatives in helium nanodroplets

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Radiation damage in biological systems caused by ionizing radiation primarily results from secondary processes such as charge and energy transfer, which lead to the breaking of DNA bonds. In this study, we investigate the fragmentation behavior of cytosine (Cyt) and thymine (Thy) molecules, their clusters, and their microhydrated forms under extreme-ultraviolet (XUV) irradiation in helium droplets.

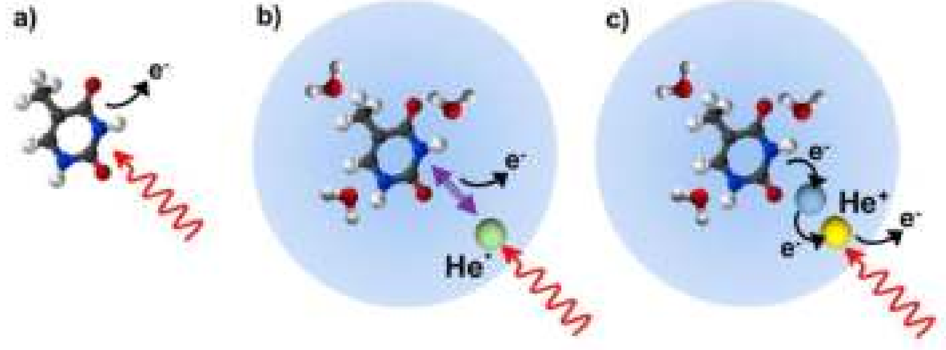

Fig. 1 **Illustration of the three ionization mechanisms for thymine and microhydrated thymine:** a) Direct photoionization of the isolated molecule, b) Penning ionization occurring within a helium nanodroplet following resonant excitation of the droplet (hν = 21.6 eV), and c) Charge-transfer ionization within a helium nanodroplet initiated by direct ionization of the droplet (hν = 26 eV). Taken from [1].

Using photofragmentation mass spectrometry and photoelectron spectroscopy, we compare the responses of isolated Cyt and Thy molecules to those of their clusters and hydrated derivatives formed within superfluid helium (He) nanodroplets. We compare direct photoioniyzation of the complexes with indirect ionization via energy transfer (Penning ionization) or charge transfer, see Fig 1. Our findings reveal that Penning ionization, occurring after resonant excitation of the He droplets, generally results in less fragmentation than either direct photoionization or charge-transfer ionization initiated by He droplet photoionization.

Moreover, when Cyt and Thy molecules are complexed with water, fragmentation is significantly reduced, see Fig. 2, similar to previous findings [2]

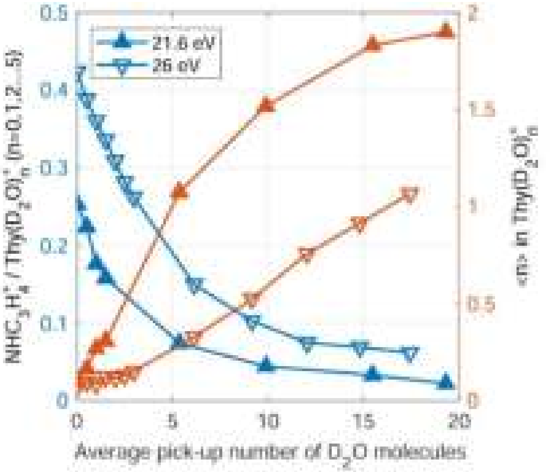

Fig. 2 **Relative hydration levels and yields and of Cyt and Thy fragments under different ionization conditions:** Fragment-to-parent ratios for both Penning ionization (hν = 21.6 eV) and charge-transfer ionization (hν = 26 eV) drastically drop with the number of attached water molecules. Taken from [1].

Inspired by these findings, we plan to extend these studies into the X-ray regime, both using tunable synchrotron radiation and laboratory-based sources at the University of Kassel. A particular focus will be on exploring various types of intermolecular decay processes [3], which play an important role in radiation chemistry of biological systems.

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Investigating Photodissociation Mechanisms and Photoproducts of Polycyclic Aromatic Hydrocarbons

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Characteristic mid-infrared (mid-IR) emission bands in the 3-19 μm range are observed towards a variety of interstellar objects. These mid-IR emission bands are believed to be the result of polycyclic aromatic hydrocarbons (PAHs) decaying to the ground state after being electronically excited by the interstellar radiation field.[1,2] Due to their ubiquitous nature, it has been hypothesized that PAHs are important reservoirs of interstellar carbon, with estimations that up to 20% of all cosmic carbon is locked in these species.[1,2] In photon-dominated regions (PDRs) in space, PAHs are exposed to a very high flux of radiation which may induce isomerizations and ultimately photodissociation.[1-3] It has been suggested that only PAHs with more than 30 carbon atoms can survive in the ISM and that small molecules get photodissociated.[2]

The mechanism of PAH dissociation depends strongly on the PAH's size and structure. Previous laboratory studies have shown that dissociation of PAH cations does lead to dehydrogenation and fragmentation to form a common series of carbon-only fragments ($C_{11}^{\cdot+}$ - $C_{15}^{\cdot+}$).[4] These carbon-only fragments have only been observed for larger PAHs (i.e. coronene ($C_{24}H_{12}^{\cdot+}$))[4], while smaller PAHs (i.e. anthracene ($C_{14}H_{10}^{\cdot+}$))[5] do not exhibit their formation. I will present our latest results on the photodissociation of a series of acene cations of increasing size; anthracene ($C_{14}H_{10}^{\cdot+}$), tetracene ($C_{18}H_{12}^{\cdot+}$), and pentacene ($C_{22}H_{14}^{\cdot+}$) that we recorded on our ion trap time-of-flight mass spectrometer by photodissociation the parent ions using a Nd:YAG laser operating at 532 nm. Based on our experiments we show that there is a critical PAH size that determines the onset of formation of these carbon-only fragments.

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Stern-Gerlach Deflection of Atoms as a Probe of Spin Thermalization in Superfluid Helium Nanodroplets

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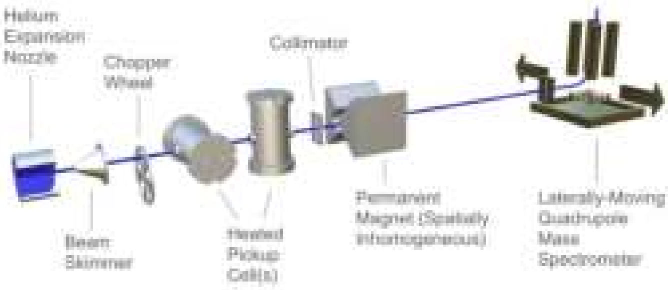
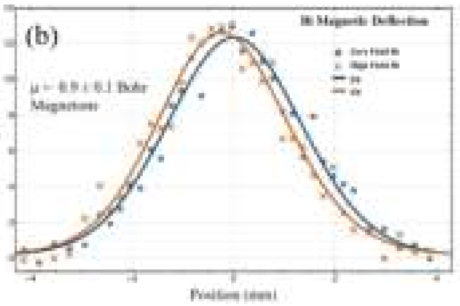
Beams of superfluid helium droplets have found many uses as a cold, inert, non-interacting environment in which to study species of interest, but the way in which dopant spin states thermalize within the droplets remains a mystery. By measuring the deflection of such a beam through an inhomogeneous magnetic field, it is possible to deduce information about the spin states of magnetic atoms and molecules within the helium matrix.

In previous work in our lab, one-sided, fully thermalized deflections have been observed for chloride salts within the droplet center [1] as well as sodium dimers on the droplet surface [2], which indicate that these species thermalize well within the magnet flight time of our apparatus.

More recently, the same experiments were performed on atomic bismuth and europium. In both cases, the deflection is one sided, but weaker than expected. Simulations fitting the data to a thermal distribution indicate that the spin temperatures of the atoms during deflection are several kelvins higher than the droplet temperature. We attribute the difference from the molecular case to the lack of rotational degrees of freedom to couple to electron spin, but a deeper theoretical interpretation is as yet still desired.





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