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TO PAY A PERMANENT TRIBUTE TO ARCHIMEDES AND GALILEO GALILEI, FOUNDERS OF MODERN SCIENCE
AND TO ENRICO FERMI, THE "ITALIAN NAVIGATOR", FATHER OF THE WEAK FORCES

INTERNATIONAL SCHOOL OF SOLID STATE PHYSICS

81st Course: *DYNAMICS OF ELECTRONS IN ATOMIC AND MOLECULAR NANOCLUSTERS*

ERICE-SICILY: 25 – 31 AUGUST 2022

Sponsored by the: · Italian Ministry of Education, University and Scientific Research · Sicilian Regional Government

Directors of the Workshop
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Thursday, August 25: arrival

Invited talks: 35 minutes + 5 minutes for discussion

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

Friday, August 26		**Saturday August 27**		**Sunday August 28**		**Monday August 29**		**Tuesday August 30**	
Session chair: V. Kresin		Session chair: D. Strasser		Session chair: P. Lievens		Session chair: J. Bakker		Session chair: M. Lemeshko	
9:00-9.10	Welcome	*9:00-9.40*	M. Arndt	*9:00-9.40*	J. Küpper	*9:00-9.40*	P. Scheier	*9:00-9.40*	I. Fabrikant
9:10-9:25	G. Benedek								
9:25-10.05	K. Hansen	*9:40-10.20*	B. v. Issendorff	*9:40-10.20*	E. Suraud	*9:40-10.20*	M. Mudrich	*9:40-10.20*	P. Ferrari
10.05-10.45	D. Rupp	*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*	E. Anderson	*10:50-11:15*	D. Strasser	*10:50-11:30*	M. Lemeshko	*10:50-11:30*	T. Shahbazyan
11:15-11:55	P. Slaviček	*11:30-12:10*	E. Narevicius	*11:15-11:40*	F. Suzuki	*11:30-12:10*	W. Ernst	*11:30-12:10*	T. Lau
11:55-12:35	V. Zhaunerchyk	*12:10-12:35*	S. Pedalino	*11:40-12:00*	G. Benedek (History of Erice)	*12:10-12:35*	V. Karle	*12:10-16:00*	Lunch, free time
12:35-16:00	Lunch, free time	*12:35-16:00*	Lunch, free time	*12:00*	Lunch	*12:35-16:00*	Lunch, free time		
Session chair: E. Miliordos		*16.00-19:00*	Posters	*departure 14:00*	Excursion and excursion dinner	Session chair: M. Nakamura		Session chair: M. Mudrich	
16:00-16.40	E. Hudson					*16:00-16.40*	K. Bowen	*16:00-16:40*	J. Bakker
16.40-17.05	L. Schweikhard					*16:40-17:05*	A. Cappellaro	*16:40-17:05*	D. V. Fries
17:05-17:35	break					*17:05-17:35*	break	*17:05-17:35*	Break
17:35-18:15	P. Gregory					*17:35-18:15*	V. Poterya	*17:35-18:15*	A. Lehr
18:15-18:40	N. Iwe					*18:15-18:40*	J. Asmussen	*18:15-18:40*	E. Miliordos
	Dinner		Dinner				Dinner	*19:30*	Banquet (informal)

Wednesday, August 31: departure

Nuclei, clusters and quantum gases: Ben. R. Mottelson in memoriam

Klavs Hansen

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Ben Roy Mottelson died May 13, 2022. Born July 9, 1926, in Chicago, he spent most of his life in Copenhagen, working at the Nordic Institute of Theoretical Physics, on the premises of the Niels Bohr Institute. Together with his lifelong collaborator Aage Bohr he was awarded the Nobel Prize in 1975 for the work of rotating nuclei and the effect on their shape. The similarities of nuclei with metal clusters made him a natural and enthusiastic member of the cluster group that was established in Copenhagen in the late 1980's under the leadership of Sven Bjørnholm. His and Aa. Bohr's two volume Nuclear Structure [1] remains a classic and a resource for understanding finite fermion systems. This span across disciplines was put to good use even later in his contribution to both quantum dots and to quantum gases, demonstrating his remarkable scientific reach
After a short biography, the presentation will focus on the theory of supershells [2] and their discovery [3], in which I took part as a PhD student at the Bohr Institute.

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Probing ultrafast electron dynamics in isolated nanoparticles with coherent diffraction imaging

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The excitation of atomic clusters and nanodroplets in strong laser fields has been used as an ideal model scenario over all wavelength regimes for exploring the ultrafast physical processes underlying the formation and evolution of highly excited matter. Via single-pulse single-particle coherent diffractive imaging (CDI) using the intense femtosecond pulses from short-wavelength free electron lasers (X-FELs), it became possible to study single specimen in free flight instead of averaging over ensembles of clusters.

In CDI, the elastically scattered light from a single nanoparticle forms an interference pattern that encodes the particle's structure. This allows to investigate the morphology of such fragile and short-lived specimen as rare-gas clusters and nanodroplets. Also light-induced dynamics after pulsed laser excitation can be visualized by time-resolved CDI. Even changes in the electronic properties were found to be imprinted in the coherent diffraction patterns [1,2], but their temporal evolution could not be investigated with the typical pulse durations of tens or hundreds of femtoseconds.

In this regard, the current advent of intense few-femtosecond and sub-femtosecond pulses from X-FELs and high-intensity laser-based High Harmonic Generation (HHG) is opening up new pathway towards resolving electron dynamics in nanoscale matter in time and space. We recently showed that, under favorable conditions, single helium nanodroplets can be imaged with an intense HHG source [3]. In a series of time-resolved experiments, we found that a moderately intense near-infrared (NIR) laser pulse, too weak to ionize helium nanodroplets, dramatically changes their scattering response in the extreme ultraviolet (XUV) regime. A new beamline for few-femtosecond NIR pulses and intense XUV pulse trains was developed [4] and utilized for attosecond-resolved CDI experiments, revealing an ultrafast oscillation of the XUV diffraction signal twice each NIR laser cycle.

The ability to switch the optical properties of nanoscale matter within less than a femtosecond, and the availability of a spatially and temporally resolved method to study these dynamics, promise to impact a broad field of science from non-linear XUV optics to ultrafast material science, working towards ultimate-speed nano-opto-electronics.

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Radiation Chemistry in Attosecond Era: Molecular Cluster Perspective

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Radiation chemistry explores the effects of ionizing radiation (X-ray and gamma photons, electrons, ions) on matter. While the subject is rather old, our knowledge of the primary processes in radiation chemistry is surprisingly humble. This has recently changed with the new technologies both on the side of experiment and theory. On the experimental side, the change was brought about by the wider availability of tunable X-ray sources such as synchrotrons. The time resolution was enabled with the X-ray free electron lasers or table-top sources (HHG). The theory has then transplanted the technology of computational photodynamics into the high-energy region, directly simulating the coupled electron-nuclear dynamics. Radiation chemistry is mostly connected with water as the ubiquitous environment for life and technologies. While the elementary processes in radiation chemistry can be studied in liquid water, molecular clusters offer a unique advantage as it is possible to detect directly the molecular fragments and the detection of electrons is not complicated by inelastic scattering events.

In my talk, I will focus on molecular modeling of the first few femtoseconds in radiation chemistry. The theoretical modeling is always connected to recent experiments. I will start with a brief discussion of the structure of hydrogen-bonded clusters, focusing primarily on the role of nuclear quantum effects. Next, I will discuss various radiation phenomena and their relevance. Even at low energies, the hydrated electron is formed during the radiolysis.[1] Its formation and thermalization are related to the formation of hydronium radical, H_3O.[2] At higher energies, valence ionization and proton transfer take place. The dynamics of this process was directly traced with time-resolved coincident ion momentum spectroscopy, using the X-ray free-electron laser source for the pump-probe experiment.[3] Next, I will discuss the inner valence ionization and non-local Auger processes.[4] I will also cover double ionizations initiated by electrons. The role of inelastic scattering will be discussed in this context.[5] Finally, I will comment on the novel phenomena observed in the core ionization of water clusters.[6]

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Hot-electron emission upon single-photon ionization

Vitali Zhaunerchyk

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In my presentation I will discuss a new mechanism to ionize matter upon absorption of single photon which was observed in our EUV photoionization experiments of C_{60} carried out at the synchrotron Elettra facility, Trieste [1]. Electrons were detected in coincidence with ions employing a VMI electron energy analyzer in tandem with a TOF mass spectrometer. The spectrum of the emitted electrons is characterized by a Boltzmann distribution with temperature exceeding 10^4 K. This is a signature that electron emission occurs before the excess energy is statistically distributed among all possible degrees-of-freedom (i.e., well-known thermionic emission) since otherwise the temperature would be an order of magnitude lower. Instead, in the process the energy deposited to the system by a photon is distributed among valence electrons such that that one or several electrons are boiled off on sub-ps timescale. In our subsequent experiments performed on the similar system of C_{70} we have also observed hot-electron emission, which suggests that this mechanism is a general phenomenon for systems with a large number of valence electrons.

References

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Quantum tools for chemistry and chemistry for quantum tools

Eric R. Hudson
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The boundary between quantum information science and chemistry is rapidly blurring. Already, tools developed for quantum science, mostly from the atomic and molecular physics community, are being used to further fundamental chemistry. Meanwhile, it has become clear in the last few years that the use of chemistry (such as chemical design principles and new chemical systems) is a powerful new avenue for realizing quantum information science goals. I'll present work on both fronts, showing how atomic physics tools provide a nearly perfect system for studying charged-neutral chemistry at low temperature, as well as work demonstrating the use of chemical design principles to take the first steps towards creating a universal quantum functional group.

Molecule-molecule and atom-molecule collisions with ultracold RbCs molecules

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Jeremy M. Hutson[2], and Simon L. Cornish[1].

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[2]Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Understanding and controlling collisions is crucial to the field of ultracold molecules, where fast two-body losses typically limit the lifetime for molecules confined to optical traps. In our experiments at Durham, we study collisions in an optically-trapped ultracold gas of ground-state RbCs molecules produced by association from a pre-cooled atomic mixture [1,2].

We observe two-body loss of molecules that is fast, but with a rate below the thermally averaged universal limit [3]. Recent theories [4,5] suggest that these fast losses can be caused by pairs of molecules forming collision complexes, that then scatter photons from the optical trap before they are able to dissociate. We verify this hypothesis by demonstrating partial suppression of the loss by applying square-wave modulation to the intensity of the trap, such that the molecules spend 75% of each modulation cycle in the dark [6]. By varying the frequency of the modulation, we show that the lifetime of the complex formed when both molecules are in the absolute ground state is 0.53(6) ms in the dark. We repeat our experiment for molecules in excited hyperfine states and measure a lower suppression of the loss, indicating some dependence of the loss mechanism on the nuclear spin [7].

Finally, we study collisions between RbCs molecules and either Rb or Cs atoms [7], where collisions with the latter are nonreactive. In both cases, we observe fast two-body losses in the atom-molecule collisions with rates similar to the molecule-molecule collisions. For the nonreactive collisions, we may expect again a loss mechanism comprising the optical excitation of a RbCs+Cs complex, though the lifetime of this complex is expected to be x10^4 shorter than for $(\mathrm{RbCs})_2$. However, we find that we are unable to suppress the loss in these collisions by modulating the intensity of the optical trap. I will discuss possible interpretations of this result including the possibility that the lifetime of the RbCs+Cs complex is significantly longer than predicted.

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Quantum Tools for ‘Flying Elephants’

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In 2023 we will be celebrating the centenary of Louis de Broglie’s idea[1] that all moving matter has to be treated as ‘in phase with a wave’. His idea was soon confirmed in diffraction experiments with electrons, atoms and even diatomic molecules, but it took more than 75 years until the quantum nature of the center of mass motion was observed for complex hot molecules[2]. Since then we have been able to demonstrate the matter-wave nature of atoms, vitamins, molecular clusters[3], polypeptides[4], and organic molecules even beyond a mass of 25 kDa [5] – in good agreement with the predictions by non-relativistic quantum mechanics. With increasing mass and complexity, the challenges are however continuously also increasing: it requires novel beam sources, coherent wave-front dividers for bound many-body systems in free flight as well as efficient interferometer and detection schemes. I will discuss the development of novel ideas and tools, based on single photon ionization and photocleavage to control and probe the quantum wave nature of entire biomolecules and metal clusters.[6]

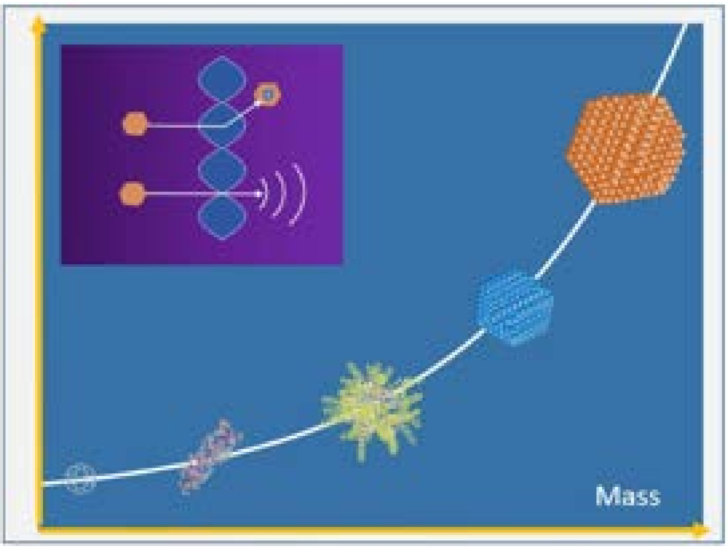

Fig.1 Mesoscopic objects in advanced matter-wave experiments. Accomplished: fullerenes, polypeptides, large organic molecules. In preparation: proteins and metal clusters.

Acknowledgements:

This work by QNP University of Vienna includes contributions the SuperMaMa consortium (www.supermama-project.eu). Our research is funded by the Austrian Science Funds (FWF #P32543-N), the EU Commission (Horizon 2020, #860713) and by the Gordon & Betty Moore foundation (#10771).

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Dissipation induced semiclassical photoemission from simple metal clusters

Bernd v. Issendorff

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Simple metal clusters exhibit the well-known electron shell structure, a highly discretized density of states consisting of approximate angular momentum eigenstates. The deviation from true angular momentum eigenstates is caused by the non-spherical ionic structure of the clusters, which significantly perturbs the states [1,2]. Nevertheless, we have shown some time ago that the angular distributions of photoelectrons exhibit characteristic patterns which depend only on the approximate angular momentum of the initial states of the emitted electrons and not on the size or geometric structure of the clusters, demonstrating that despite the perturbation the electron wavefunctions mainly keep their overall character [3].

Collecting angular distributions for a broad range of cluster sizes and materials, we could now show that when scaled properly by the cluster radius and the initial approximate angular momentum, all measured angular distributions converge to a single universal function.

The origin of this universal function is semiclassical, as it reflects distributions of particle-like electrons rotating within the clusters before emission. The reason why this behavior can be observed so clearly is that the clusters are practically opaque for the photoelectrons, suppressing interference effects between certain trajectories which otherwise would dominate the angular distributions.

Usually semiclassical or classical behavior emerges when systems become large compared to the length scale of typical wavelengths. Here, instead, it emerges due to strong dissipation, which can be seen as an interesting new route across the quantum/classical border.

This example illustrates again that clusters are close to ideal model systems for the study of many-particle phenomena.

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Phys. Rev. Lett. 126, 233201 (2021)

Fragmentation and detachment of hot Ag_2^- and Cu_2^-

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Measurements of the spontaneous decay of highly excited stored beams of dimer anions of silver and copper will be presented. The decays were measured using one of the storage rings of the Double ElectroStatic Ion Ring ExpEriment (DESIREE) [1]. A coincidence measurement was performed to directly measure the products from fragmentation events, Fig 1. In addition, the total rate of neutral particles was measured (from both electron detachment and fragmentation) such that the relative contributions of fragmentation and electron emission can be deduced. The decay curves for these two systems have striking similarities with fragmentation processes found to dominate at early times, however, electron emission from dimers undergoing vibrational autodetachment processes (VAD) becomes significant at longer times, dominating for storage times exceeding 100 ms. The VAD process is driven by breakdown of the Born-Oppenheimer approximation and was only revealed due to the very low residual gas density of the DESIREE environment [2].

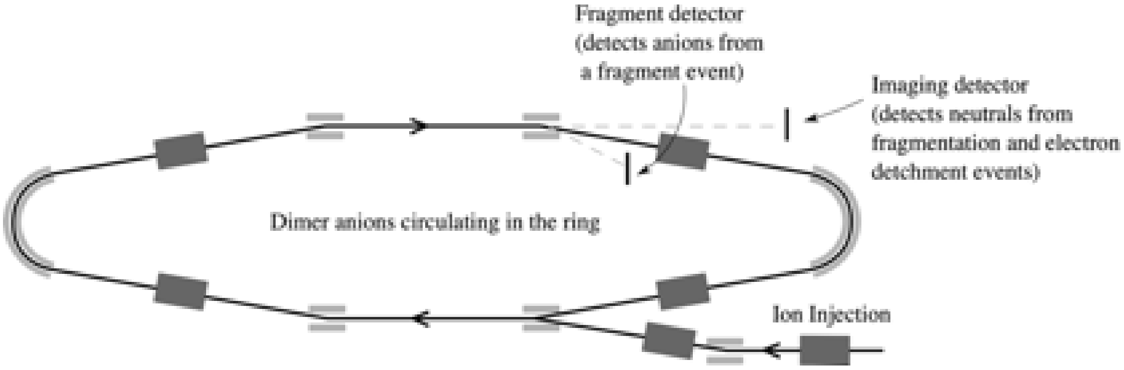

Fig. 1 Schematic of the electrostatic storage ring of DESIREE with the locations of the detectors used.

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

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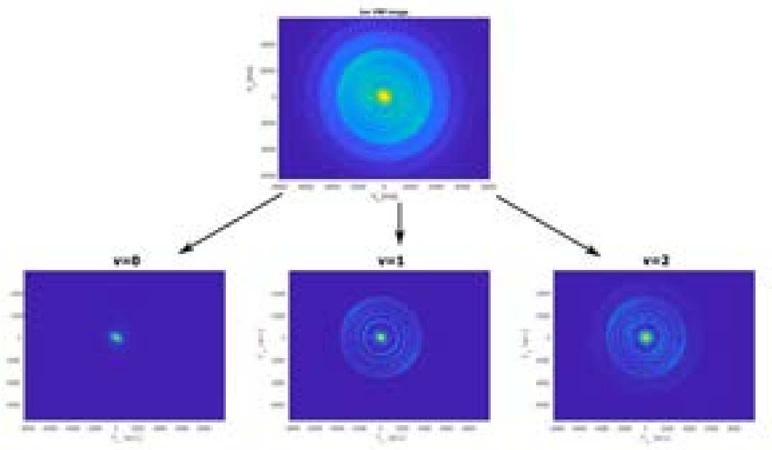
During collisions coupling between relative and internal atomic and molecular degrees of freedom leads to the formation of Feshbach resonances. The large phase space volume that particles explore in this metastable scattering state supports interference between many different quantum pathways that include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

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

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



$$\begin{tikzcd}
Ne + H_2^+(v = 0) & Ne + H_2^+(v = 1) \arrow[d] & Ne + H_2^+(v = 2) \arrow[d] \arrow[dd, bend right] \\
 & Ne + H_2^+(v = 0, j) & Ne + H_2^+(v = 1, j') \\
 & & Ne + H_2^+(v = 0, j'')
\end{tikzcd}$$

Ultrafast dynamics in microsolvated biomolecules

Jochen Küpper

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

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

Unexpected behaviors of small molecules after ultrafast XUV irradiation

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We investigate the depletion of single-electron states in small molecules under the influence of very short XUV pulses. For some XUV energies we observe a marked occupation inversion, where depletion of the deep bound state becomes much larger than other ones. This drives a dipole instability, i.e. a spontaneous reappearance of the dipole signal long after the laser pulse is over and the dipole signal has died out. The dipole signal that emerges from this instability can be identified as a particular low-energy structure in photo-electron spectra. This instability can be explored simplifying the excitation mechanism by instantaneous generation of a hole in one of the occupied states of the system. We investigate how the dipole instability depends on the system, the state in which the hole is cut, and the amount of depletion which is given to the hole state. The mechanism might appear in other systems described by mean field approaches although the role of dynamical correlations might not be the definitive key here.

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Multiply-charged helium droplets: efficient breeders of size selected clusters

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Helium droplets have been demonstrated to pick up dopants from the gas phase and subsequent evaporative cooling enables experiments at temperatures below 1 K [1]. In mass spectra obtained upon electron ionization of neutral helium droplets low-mass cluster ions have been reported that often exhibit a log-normal size distribution superimposed with some magic numbers and shell closures [2]. Massive doping of neutral droplets leads to the formation of nanoparticles and quantum wires which was studied after deposition with high resolution microscopy [3] and in situ via coherent X-ray diffraction [4]. Recently, we discovered that large helium droplets can become highly-charged [5]. The charge centers self-organize as two-dimensional Wigner crystals at the surface of the droplets and act as seeds for the growth of dopant clusters [6,7]. Cluster ions and charged nanoparticles of a specific size and composition can be formed by this technique with unprecedented efficiency [8]. Dopant cluster ions can be extracted by collision induced evaporation of the host droplet or by splashing of the droplet upon surface impact. Both methods are suitable to form high yields of He tagged ions of both polarities which enables messenger type spectroscopy of all kinds of cold ions. Several existing and future applications of highly charged helium droplets for AMO physics [7], ion spectroscopy and nanotechnology will be presented.

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XUV spectroscopy and imaging of helium nanodroplets

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Pure and doped superfluid helium nanodroplets are particularly attractive targets for both tunable XUV radiation generated by synchrotrons, and for ultrafast XUV and X-ray pulses generated by free-electron lasers (FELs). The extremely weak binding and the simple electronic structure of helium atoms render electron spectra simple and easy to interpret. The quantum fluid properties of helium droplets, and their ability to pick up virtually any foreign atom or molecule without chemically interacting with it, makes them ideal test beds for probing XUV-induced correlated electronic decay processes in heterogeneous condensed phase systems.

In recent synchrotron experiments, we have investigated interatomic Coulombic decay (ICD) and related electronic decay processes by resonantly exciting the droplets [1,2], by directly photoionizing them [3,4], and by simultaneously ionizing and exciting them [5]. In this way, we have evidenced new intermolecular decay mechanisms such as electron-transfer mediated decay (ETMD), ICD induced by electron-helium scattering, and double-ionization ICD [2]. In recent X-FEL experiments we have traced the ultrafast relaxation of resonantly excited helium nanodroplets [6,7,8] and the time-evolution of ICD in multiply excited helium nanodroplets [9]. We found that ICD is mainly determined by the peculiar nano-fluid dynamics initiated by resonant excitation of the droplet, see Fig. 1. Furthermore, we observed a massive enhancement of above-threshold ionization (ATI) of XUV-excited helium nanodroplets due to collective coupling of excitations [10].

Using intense soft x-ray pulses, even the internal structure of helium droplets and of the embedded aggregates can be visualized by single-particle diffraction imaging; owing to the peculiar aggregation mechanisms inside the droplets, an extraordinary variety of aggregate structures is observed. In my contribution, I will briefly review these recent advances and I will point out intriguing prospects for the research on free clusters and nanodroplets using advanced photon sources.

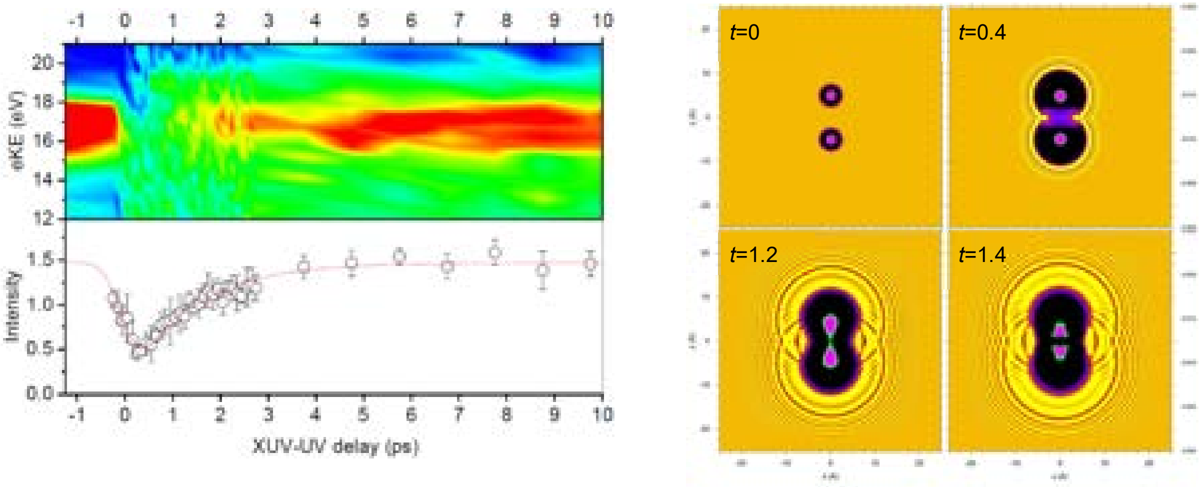

Fig. 1, left: XUV-UV pump-probe measurement of ICD electrons (red band around 17 eV in the top panel, integrated signal in the bottom panel). The minimum at 0.3 ps indicates that ICD is quenched by UV photoionization of the XUV-excited He droplets. The subsequent signal increase informs about the ICD dynamics. Right: Simulated He density distributions around two excited He atoms spaced by 10 Å.

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Abstract template for the August 2022 Erice workshop
Rotationally excited states of simple molecules: interactions and topology

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I am going to highlight two topics currently studied in my group, related to highly excited rotational states of molecules: molecular excitations in superfluid helium nanodroplets [1,2] and topological states of periodically kicked molecules [3].

Recently it became possible to study highly excited rotational states of molecules in superfluid helium through nonadiabatic alignment experiments [1]. This calls for theoretical approaches that go beyond explaining renormalized values of molecular spectroscopic constants, which suffices when only the lowest few rotational states are involved. As the first step in this direction, here we present a basic quantum mechanical model describing highly excited rotational states of molecules in superfluid helium nanodroplets [2]. We show that a linear molecule immersed in a superfluid can be seen as an effective symmetric top, similar to the rotational structure of radicals, such as OH or NO, but with the angular momentum of the superfluid playing the role of the electronic angular momentum in free molecules. The simple theory sheds light onto what happens when the rotational angular momentum of the molecule increases beyond the lowest excited states accessible by infrared spectroscopy. In addition, the model allows to estimate the effective rotational and centrifugal distortion constants for a broad range of species and to explain the crossover between light and heavy molecules in superfluid ^{4}He in terms of the many-body wavefunction structure. Some of the above mentioned insights can be acquired by analyzing a simple 2x2 matrix.

In the second part of my talk I am going to show that even the simplest diatomic molecules feature non-trivial topological structures if kicked by periodic laser pulses [3]. A periodically kicked molecular rotor can be mapped onto a "crystalline" lattice in angular momentum space. This allows to define quasimomenta and the band structure in the Floquet representation, by analogy with the Bloch waves of solid-state physics. By appropriately choosing the period of laser kicks one can create a band structure featuring Dirac cones similar to that seen in graphene. This potentially allows to study topological physics in gas phase experiments with molecules.

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Relaxation and charge transfer dynamics after electronic excitation of atoms and molecules in cluster environments

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Electronic excitation of atoms and molecules solvated in otherwise chemically inert cluster environments may lead to relaxation pathways not observed in the corresponding free gas phase species. In the case of direct contact of molecules with a metallic cluster surface, electronic interactions can cause charge transfer processes that alter the overall optical response of the combined system. In this lecture, examples will be shown for each of the two phenomena at the scale of individual nanometer sized clusters.

Superfluid helium nanodroplets (He_N) serve as a weakly interacting solvent for atoms or molecules. The 0.4 Kelvin environment allows for the stable formation of isomeric species with different bonding than observed in the gas phase. Electronic excitation in combination with the helium environment can lead to a conversion into different configurations rather than a decay into the original state. For example, the combination of two or three alkali atoms on a helium nanodroplet predominantly creates dimers or trimers in van der Waals bound triplet or quartet states, respectively. Laser excitation into corresponding excited triplet or quartet states [1] results in spin state conversion on the time scale of the electronic lifetime. Excitation of the $y\ ^7P_{2,3,4} \leftarrow a\ ^7S_3$ transition of the Cr atom inside He_N yields relaxation into the quintet manifold of Cr as fast as the radiative decay into septet states [2]. Cr_2 molecules formed in He_N were excited to the $A^1\Sigma_u^+$ state which leads to predissociation into two Cr atoms one of which remains as septet ground state atom in the droplet center and one takes a surface in a quintet electronic state [3]. The observed spin state conversions and unusual relaxation pathways can all be attributed to repulsive interactions with the helium environment. The repulsion of the helium environment by an electronic orbital of a dopant excited by a femtosecond laser pulse leads to an expansion of the helium solvation shell initiating a collective shell oscillation [4]. Separated ground state atoms on a single helium droplet that were forming a diatomic molecule only after electronic excitation, were observed for the case of an Sr atom in the interior and Rb on the droplet surface [5], a process which may involve the conservation of energy and momentum through the interactions of the atoms with He and the laser photons.

In core-shell clusters consisting of a metal core and a semiconductor or a fluorophore shell, the optical excitation of a plasmonic resonance of the core significantly alters the photoelectric or fluorescent light emission of the shell material as we have shown for Ag@ZnO [6] or Au@RhB [7] clusters.

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Electron Induced Proton Transfer

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This talk will report on the developing saga of electron induced proton transfer (EIPT), beginning with previous work on thymine-glycine heterogeneous dimer anions and ammonia-hydrogen halide anions. After presenting new work on the latter systems, which further supports and refines the model for EIPT, we will present results which show that small ammonia cluster anions are, in all likelihood, EIPT systems.

Radicals and electrons reactions with deposited species on large argon clusters.

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The ion-molecular reactions and reactions initiated by radicals characterized by high rates. The processes involving electrons or species with odd number of electrons are very important in a wide range of the chemistry fields. However, it is very difficult to identify the intermediate steps of many reactions which happen in a sequence especially in a macroscopic environment. In our laboratory we use the pickup method to generate nanoparticles which are composed of clusters of certain size complexed by the controlled number of guest species. The properties of both the clusters and deposited particles determine the degree of reactivity of the complex. Recently we investigated the processes induced by electron attachment to hydrogen peroxide molecules, H_2O_2, deposited on large argon and water clusters, Ar_M and $(H_2O)_M$, respectively.[1] The recorded mass spectra showed the prevalence of $(H_2O_2)_nO_2^-$, $(H_2O_2)_n^-$ ions, which are not characteristic for electron attachment reaction in a gas phase hydrogen peroxide. Mass spectrometry results and theoretical investigation[2] showed that argon surface is suitable environment for free movement of deposited H_2O_2 molecules in contrast to the restricted mobility due to preferential formation of the water-hydrogen peroxide bonds on $(H_2O)_M$ surface. The electron attachment experiments to $(H_2O_2)_n$ clusters resulted in the initiation of intra-cluster reactions between negative ions and newly formed neutral products.

Reactivity of neutral deposited species was investigated between pyrolytically generated chlorine containing radicals and methane molecules. We observed the new products formed in the reactions initiated by Cl atoms and propagated in a sequence involving several chlorine containing species. The experimental results supported the previous conclusions that reactivity on the argon surface is facilitated by much higher ability of the molecules to meet and thus, to react.

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Theory of electron attachment to molecules and clusters

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Dissociative electron attachment (DEA) to polyatomic molecules is a complicated process involving couplings between electron and nuclear motion. Completely *ab initio* calculations are presently possible only for diatomics, and model approaches should be developed for more complex targets, particularly if nonlocal effects, leading to vibrational Feshbach resonances and threshold cusps, are important [1-4].

In this talk we will start with a review of an extension of the nonlocal theory to two and more degrees of freedom.. The general theory will be applied to the CF_3Cl compound. In some cases a simpler formulation is possible in terms of the effective range theory which was applied recently to description of cusp structure in DEA to $Fe(CO)_5$ [5], and to a series of 5-membered heterocyclic rings [6].

We will continue with a discussion of condensed-matter and cluster effects in DEA. Surface environment can catalyze, but also suppress, electron-initiated reactions. As an example, chlorofluorocarbon molecules adsorbed on surface of ice particles in polar stratospheric clouds influence the process of ozone depletion. Another important example is the process of electron-induced bond breaking in DNA bases which can be strongly influenced by surrounding water molecules. We have found two effects in the N-H bond breaking in thymine due to electron impact, one leading to the enhancement of the DEA cross section due to the increased lifetime of the intermediate negative-ion state [7], and the other leading to the decrease of the yield of the anionic fragments due to the hydrogen bonding between the nucleobase and the solvent [8]. The hydrogen bond rapidly channels the kinetic energy away from the N−H, into the surrounding water molecules, and back into the nucleobase. As a result, hydrogen bonding between the nucleobase and the solvent can suppress the dissociation channel [9].

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Electronic radiative cooling in metal clusters

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The radiation from thermally populated excited electronic states has recently been recognized as an important cooling mechanism in carbon-based molecules and small metal clusters [1]. Experiments have demonstrated that many of these systems radiate at surprisingly high rates, often with a distinct dependence on the precise size of the particles. There are several consequences of an active radiative cooling channel, as for example in the production of size-selected particles in an evaporative ensemble, where abundances of highly radiating sizes will be enriched. In an astrophysical context, radiative cooling provides a mechanism to dissipate internal energy in star-forming processes, which stabilizes molecules selectively in the circumstellar medium. Despite its relevance, there are several open questions about the fundamental mechanism responsible for the radiative cooling process of clusters. For instance, even though experiments provide strong evidence for photon emission via low-lying electronic excited states, conventional theoretical calculations fail to predict the existence of such states. In this contribution, the radiative cooling of different laser-excited small metal clusters will be discussed [2-6]. Moreover, different computational methods will be employed, in order to elucidate the fundamental mechanism behind the photon emission of these systems, involving low-lying electronic excitations and the effect of cluster temperature in the process.

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Landau damping of surface plasmons in metal nanostructures

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Plasmon-assisted hot carrier excitation and transfer across the interfaces has recently attracted intense interest due to wide-ranging applications in photovoltaics and photochemistry [1]. In metal nanostructures with characteristic size below the diffraction limit, excitation of hot carriers is enhanced due to resonant plasmon absorption followed by plasmon decay into electron-hole (*e-h*) pairs. In small nanostructures, the dominant decay mechanism is Landau damping (LD) due to carrier scattering from the metal surface (see Fig. 1).

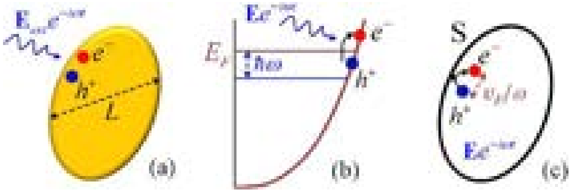

Fig. 1. Schematics for surface-assisted an *e-h* pair excitation. (a) An external optical field incident on a metal nanostructure, (b) excites a surface plasmon that decays into an *e-h* pair, (c) accompanied by momentum relaxation via carrier surface scattering.

We developed a quantum-mechanical model for surface-assisted carrier excitation by alternating electric field **E** in metal nanostructures of arbitrary geometry. For small nanostructures with characteristic size smaller that the radiation wavelength, we obtained a closed-form expression for the surface scattering rate, which is highly sensitive to the field polarization relative to the metal-dielectric interface and can be tuned in a wide range with an appropriate choice of system geometry [2].

In Fig. 2, we show the calculated LD rates for nanorods and nanodisks, modeled by prolate and oblate spheroids, together with the standard classical scattering (CS) model calculations. The rates for longitudinal (PL and OL) and transverse (PR and OR) modes exhibit dramatic differences in behavior with changing the system geometry, in contrast to CS rate.

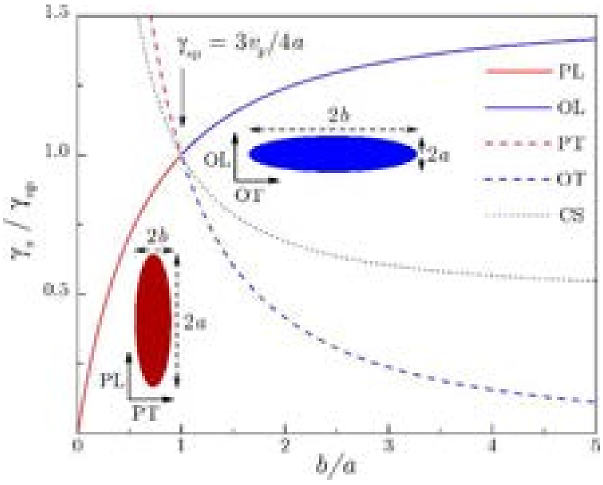

Fig. 2. Calculated surface scattering rates, normalized with respect to a sphere of radius a, are plotted against aspect ratio for nanorods (red lines) and nanodisks (blue lines). The CS rate is shown by black dotted line.

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Highest and unusual oxidation states in oxido transition metal clusters

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Metal centers and oxido ligands in oxido transition metal clusters display a large variety of oxidation states, spin states, and oxygen species that are traditionally characterized in reactivity studies, valence photoelectron spectroscopy, or infrared photodissociation mass spectrometry. Here, we use element-specific x-ray absorption spectroscopy of cluster ions, held in a cryogenically cooled ion trap, to independently characterize oxidation states and oxygen ligands in oxido clusters of 3d, 4d, and 5d transition metals. We present the characterization of reactive oxygen species in a series of oxygen-centered radicals, the discovery of rhodium(VII) as the highest oxidation state of rhodium, [1] and a rare high-spin dioxido manganese(V) species. [2]

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Adsorption of H_2 and CO_2 on copper clusters: model for the CO_2 reduction catalyst?

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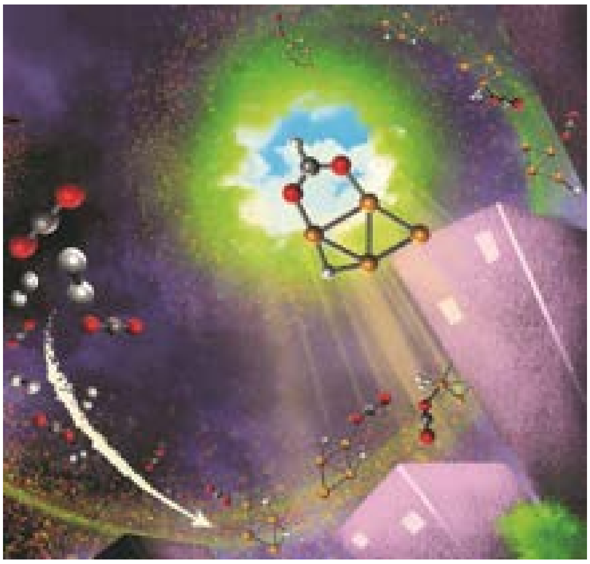
Atomic clusters are small particles consisting of a countable number of atoms that can exhibit physical and chemical properties that are often different from bulk materials. Clusters of transition metals can also be considered as model systems for the active site in heterogeneous catalysis, due to the large number of undercoordinated atoms. The study of gas-phase clusters utilizing mass-spectrometric and spectroscopic techniques offers the possibility to elucidate fundamental interactions of molecules with a surface that is known with atomic precision, offering a well-defined local geometric and electronic structure.

In this contribution, I will present experimental studies characterizing how clusters interact with small molecules of relevance for catalytic processes. In particular, I will focus on a study of copper clusters as a model system for the CO_2 hydrogenation catalyst.



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Abstract for the August 2022 Erice workshop

Magnetic Properties of MSn_{12} (M = Al, Ga, In) Nanoclusters: The Origin of Their Surprisingly Large g-Factors

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The study of magnetic properties of isolated neutral clusters requires their preparation in molecular beams. Only a few experimental techniques exist of which the Stern-Gerlach experiment is able to reveal the electronic *g*-factor of superatomic clusters being an interesting probe for the underlying electronic structure, the spin-orbit coupling in particular. Driven by the recent observation of surprisingly large *g*-factors of 2.7 in endohedral MSn_{12} (M = Al, Ga, In) nanoclusters [1-3], effort was made to gain a more profound understanding of its origin by applying sophisticated quantum chemical methods.

For each cluster species a nonpolar isomer with pyritohedral symmetry could be identified which behaves superatomic in the magnetic beam deflection experiment. The characteristic beam splitting in the magnetic deflection profiles observed at nozzle temperatures of 16 K is a consequence of the small number of avoided crossings being present in the rotational Zeeman diagram of such spherical rotors, even though the clusters are found to perform spin flips on practically every crossing they pass. [3] The increased probability for spin flips indicates a strong spin-orbit interaction contributing to the spin-rotation coupling constant, which also manifests in the extraordinarily large *g*-factors. A simple picture drawn based on density functional calculations suggests that a large part of the *g*-shift stems from a single low-energy electronic transition between (degenerate) molecular orbitals with resembling spin density on the tin cage, itself contributing with a large spin-orbit coupling constant. This picture is then refined by elaborate multireference calculations providing a superior treatment of the spin-orbit coupling. The importance of further low-lying electronic excitations and their accurate description is highlighted. Here, it is promising to glimpse towards the magnetic deflection experiments on MPb_{12} (M = Al, Ga, In) nanoclusters which are characterized by near-orbital degeneracy in their ground states as well as highly pronounced spin-orbit effects leading to even larger *g*-factors while being at the very edge of today's computational feasibility.

Such endohedral, singly *p*-doped tin (and lead) clusters of spherical symmetry state magnetically-relevant systems which fall not into the same category as transition metal complexes and organic radicals hindering a straightforward explanation of their magnetic properties by ligand field theory and spin density arguments. Hence, this study can be seen as an attempt to uncover the magnetic features for this class of compounds.

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Ion Trapping for Cluster Research

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Atomic clusters have been studied at the University of Greifswald for several decades in a Penning-trap setup and, more recently, an electrostatic ion beam trap. The report will focus on the latest developments and results.

The "ClusterTrap" setup combines a Smalley-type cluster ion source with a Penning trap where metal clusters are stored in a strong magnetic field and an electric potential well along the magnetic field lines. Monoanionic clusters can be charged up by attachment of further electrons in an "electron bath" [1]. Earlier, photofission of dianionic lead clusters had been deduced from the decay pattern – observed as time-of-flight spectra after ejection of the ions from the trap – in comparison with that of monoanionic precursors [2]. These investigations have been extended to tin clusters and the observation of the precursor and various product-cluster intensities as a function of time after the pulsed photoexcitation (as earlier demonstrated for monoanionic lead clusters [3]). Preliminary results further confirm the assumption of photofission (Fig.1) [4].

Electrostatic ion beam traps are also known as Multi-Reflection Time-of-Flight Mass Spectrometers (MR-ToF MS). Such an instrument has been coupled with a laser-ablation ion source. The MR-ToF MS can serve for mass determination as well as for separation. Thus, bismuth clusters doped with a single lead atom could be selected and in an (MR-ToF MS)^2 experiment their photodissociation was investigated with respect to what fragment carries the lead atom [5]. In another measurement it was shown that the MR-ToF method can also be applied for time-resolved decay studies [6]. Furthermore, the high mass resolving power (Fig. 2) was applied in a recent investigation of carbon-cluster ablation from glassy carbon, and it was observed that the product spectrum is composed of several charge states, although the m/z spectra of cluster abundance versus mass-to-charge state is very similar for the different charge states [7].

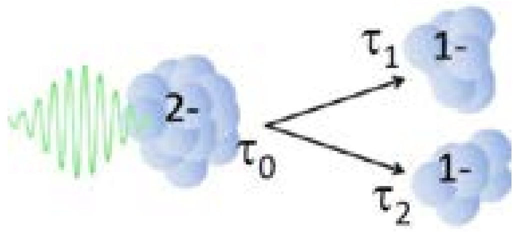

Fig. 1: Schematic of time-resolved photofission study. Decay and appearance constants ($\tau_{0,1,2}$) are observed to match.

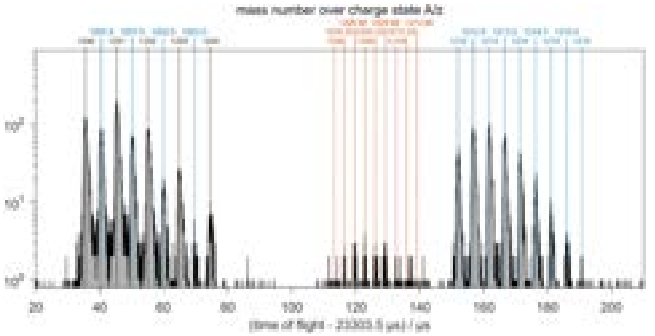

Fig. 2: ToF spectra of isotopoloque distribution of fullerenes C_{100}^{+}/C_{200}^{2+} (left) C_{302}^{3+} (center) and C_{202}^{2+} (right).

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Coulomb barriers and negative electron affinities in polyanionic metal clusters

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In order to tune the properties of free, nanoscopic particles for investigation and application purposes, the size as well as the charge state are important parameters. Previous studies focused mainly on neutral and singly positively or negatively charged species [1]. For multiply negatively charged clusters, the Coulomb interaction between the excess electrons strongly influences the cluster properties. On the one hand, the charging energy limits the number of electrons that can be attached to a specific cluster size, whereas on the other hand, the emerging Coulomb barrier allows for bound electronic states even above the vacuum level.

This contribution presents studies on size-selected (N up to 800 atoms) polyanionic silver clusters with up to $z = 7$ excess electrons. Thus, an essential step of the target preparation process is the electron attachment to monoanions within a 3-state Paul trap [2]. By conducting photoelectron spectroscopy, the size and charge-state dependent electronic structures are analyzed, revealing metastable species with negative electron affinities (Fig.1). From the spectra, detachment energies are extracted and compared to the liquid drop model [3]. Moreover, a low kinetic energy cutoff in the data for $z > 1$ is observed, providing details about the Coulomb barrier. By taking into account electron tunneling, first information about the barrier heights and shapes in metal cluster polyanions are obtained [4].

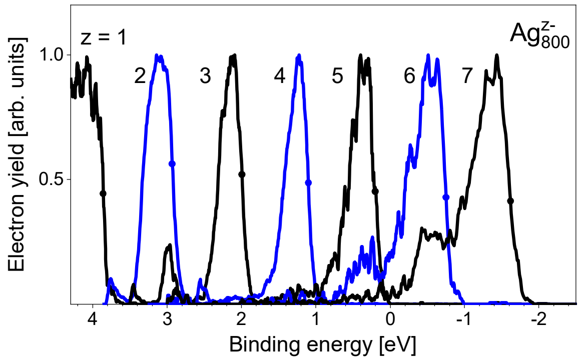

Fig.1 Series of photoelectron spectra of silver cluster (poly-)anions with $N = 800$ atoms taken at photon energies of 5.6 eV (z=1), 3.9 eV (z=2), 3.5 eV (z=3) and 3.3 eV (z=4-7). With increasing number of excess electrons z, the detachment energy (dots) shifts towards negative binding energies [3].

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Experimental evaluation of Y and Hf clusters for matter-wave interferometry

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Matter-wave interferometry with massive objects [1] is **consistently maintaining interest of researchers** since the last years as it is a **paradigmatic example of quantum physics at the interface to classical phenomena**. In order to push the limits of matter-wave interference towards higher masses it is important to find **suitable molecular sources and efficient detection mechanisms**. We here present a material class that fulfills all requirements for future matter-wave experiments.

We have experimentally explored the **feasibility of a magnetron sputtering aggregation source as a possible molecular beam source for an all-optical Talbot-Lau interferometer** with a grating period of 133 nm [2]. We have analyzed **yttrium and hafnium nanoparticles** with respect to their clustering properties, beam brilliance, velocity distribution and photo-ionization efficiency at 266 nm [3].
Using the high ionization yield of the metal clusters we were also able to show **up to 40-fold increased detection rates with UV photo-ionization** compared to electron impact ionization.

The results of this study show that the **metal cluster source together with the improved detection scheme will allow realizing a next generation Talbot-Lau interferometer** with three 266 nm depleting lasers as beam splitters. Furthermore, the analyzed metal nanoparticles will **push to quantum interference of massive objects with masses up to half a million mass units** in the near-future.

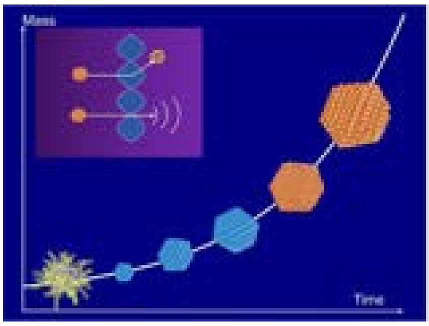

Fig. 1: Pushing the limits of matter-wave interferometry towards higher masses with metal cluster.

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Long-Range Electron Transfer Probed by Coulomb Explosion Imaging

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In the well-known harpoon reaction, long-range electron-transfer results in Coulombic attraction between initially neutral reactants that leads to dramatic increase in the reaction rate. Here a different "inverse harpoon" mechanism is presented, in which electron-transfer from a neutral reactant to a multiply charged cation results in strong repulsion that encodes the electron-transfer distance in the kinetic energy release. While the nascent products of such a reaction may themselves be unstable, recent 3D coincidence imaging experiments allowed identifying and characterizing the electron-transfer events that are predicted by non-adiabatic molecular dynamics simulations to occur following double-ionization of isolated methanol molecules between a roaming neutral H_2 and $HCOH^{2+}$. Figure 1 shows a typical time evolution of the relative velocity of the two moieties, exhibiting a sudden acceleration after the electron transfer, which occurred at a ~7a.u. distance and resulted in a 3.4 eV kinetic energy release. Detailed comparison of the experimental and theoretical kinetic energy distributions provides intimate information about the electron-transfer distance. Furthermore, ultrafast EUV pump – near IR probe experiments time-resolve the roaming H_2 dynamics by monitoring the competing proton-transfer mechanism that forms H_3^+ + COH^+.[1]

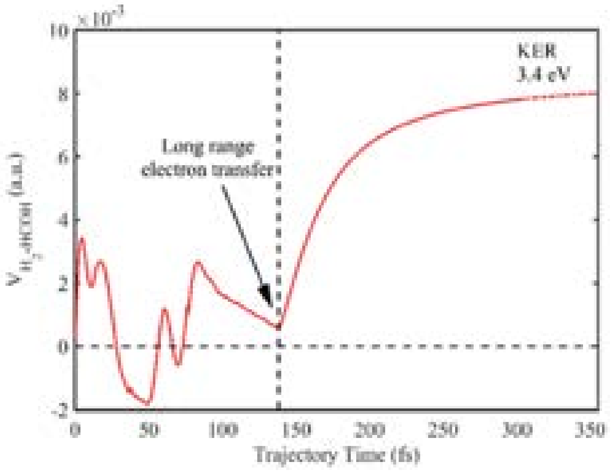

Fig.1 Time-resolved relative velocity between the centers of mass of the H_2 and HCOH fragments in a representative AIMD ground state trajectory, showing long-range electron transfer.

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Chiral Casimir-Polder Forces

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Casimir-Polder forces are effective quantum electrodynamical forces between molecules and macroscopic bodies which arise from the interaction of the objects' charge and current densities with the vacuum electromagnetic field. Originally predicted by Casimir and Polder, they are typically attractive and purely monotonic for ground-state molecules and bodies with a purely electric response. However, it was found that, the force can depend on chirality of molecules. The forces can be attractive for molecules of the same handedness and repulsive for opposite handedness.
Here we propose the setups aiming at the observation of chiral Casimir-Polder forces using a Stern–Gerlach type separator or matter wave interferometers.

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Abstract for the August 2022 Erice workshop
Multiband topological phases of periodically kicked molecules [1]

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We show that the simplest of existing molecules - closed-shell diatomics not interacting with one another - host topologically nontrivial phases when driven by periodic far-off-resonant laser pulses. A periodically kicked molecular rotor can be mapped onto a "crystalline" lattice in angular momentum space. This allows to define quasimomenta and the band structure in the Floquet representation, by analogy with the Bloch waves of solid-state physics. Applying laser pulses spaced by 1/3 of the molecular rotational period creates a lattice with three atoms per unit cell with staggered hopping, whose band structure features Dirac cones. These Dirac cones, topologically protected by reflection and time-reversal symmetry, are reminiscent of (although not equivalent to) the ones seen in graphene. They - and the corresponding edge states - are broadly tunable by adjusting the laser intensities and can be observed in present-day experiments by measuring molecular alignment and populations of rotational levels. This paves the way to study controllable topological physics in gas-phase experiments with small molecules as well as to classify dynamical molecular states by their topological invariants.

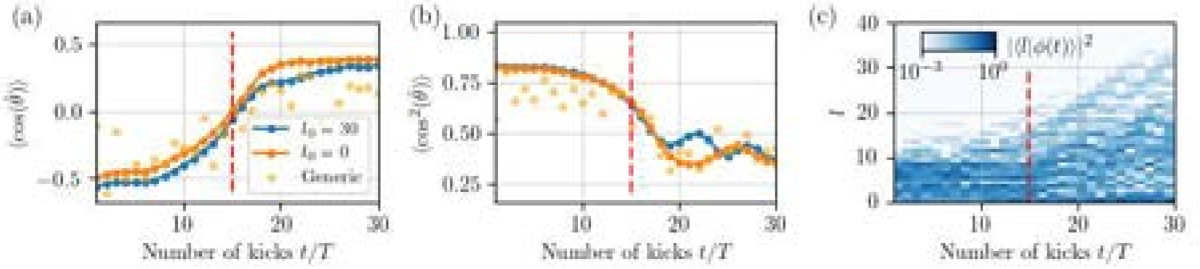

Fig.1 Time evolution of three different molecular states, which are evolved through the Dirac cone. To demonstrate that the phenomenon is generic we show a Gaussian state peaked at l=30 (orange), l=0 (blue) and a generic state prepared with one laser pulse from l=0 (dotted). As a function of the number of laser kicks are shown: (a) the orientation cosine, cos(θ), (b) the alignment cosine, $\cos^2(\theta)$ and (c) the absolute values squared of the wavefunction components of the generic state. The dynamics changes drastically in the vicinity of the Dirac cone, marked by vertical dashed lines (red).

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Friction and torque on rotating impurities

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Over the last decades, impurity problems have been an invaluable framework to gain significant insight on the physics of many-body quantum systems [1]. The usual setup involves a small quantum system (oftentimes just a single degree of freedom) coupled to a many-body environment. In order to control (or probe) the impurity dynamics, external driving fields can be turned on, eventually resulting in a time-dependent Hamiltonian. However, despite a deep theoretical effort, resulting in a plethora of refined theoretical approaches both in and out of equilibrium, a relevant shortcoming has been pointed out in the last years: most of these models deal with point-like entities with no internal structure or a very simple one as in the case of two-level systems.

Molecules are an obvious example: they are extended objects and their ability to perform rotations in real spaces forces us to deal with the non-trivial algebra of quantized angular momentum [2]. Therefore, a reliable understanding has to be constructed within a framework where a coupling between rotational degrees of freedom and a many-body bath is established [3,4]. By focusing on the bosonic case, where the environment is made of the low-energy excitations over the broken-symmetry state (i.e. superfluid ^{4}He or, in principle, a BEC), we will show how familiar concepts such such as friction and torque are significantly modified for a rotating impurities.

Concerning friction, by using a path integral formulation [5], we will rederive a modified version of the Caldeira-Leggett action functional, where the impurity-environment coupling is mediated by the spherical harmonics. Therefore, crucially, being a highly non-linear process, there is no guarantee to end up with a standard diffusive dynamics. On the other hand, for impurities immersed in quantum liquids, the concept of force is intimately connected to the survival of superfluidity (where no drag is expected) [6]. Indeed, a careful calculation for point-like entities shows that a residual drag force, due to quantum fluctuations, is present even for small impurity velocities, while, at higher values, a plateau is reached, providing a generalization of the renowned Landau criterion (which exclusively relies upon the mechanism of thermal activation).

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Ultrafast relaxation and autoionization dynamics of photoexcited helium nanodroplets

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Ultrafast energy relaxation of photoexcited nanosystems are a fundamental process across many research fields. Helium nanodroplets serve as an ideal model system to unravel elementary steps in the relaxation path due to their extremely weak interatomic binding and the simple electronic structure of the helium atom which simplifies electron spectra. I will at the conference show our recent results from experiments at the free-electron laser (FEL) FERMI in Trieste, Italy. Here, we have investigated the relaxation dynamics of helium nanodroplets photoexcited at different XUV wavelengths. Tuning the FEL to higher-lying absorption bands of the droplet and thereby forming superexcited states leads to relaxation into both the *1s2s* ^{1}S and ^{3}S metastable atomic states [1]. Relaxation into the metastable singlet state happens through intra- and interband relaxation, whereas the relaxation path into the metastable triplet state consists of autoionization of the initial superexcited state followed by recombination of the electron with the cation.

The high photon flux available at FELs makes it possible to multiply excite the helium nanodroplets. Two excited helium atoms formed in close proximity to each other can undergo interatomic coulombic decay (ICD) in which one of the excited atoms is ionized as the other relaxes to the ground state. By depletion of ICD with a probe laser, we have measured the decay time of ICD between two excited helium atoms in the nanodroplet and the decay time of ICD between an excited helium atom and dopant sodium atoms (traditionally termed Penning ionization) [2].

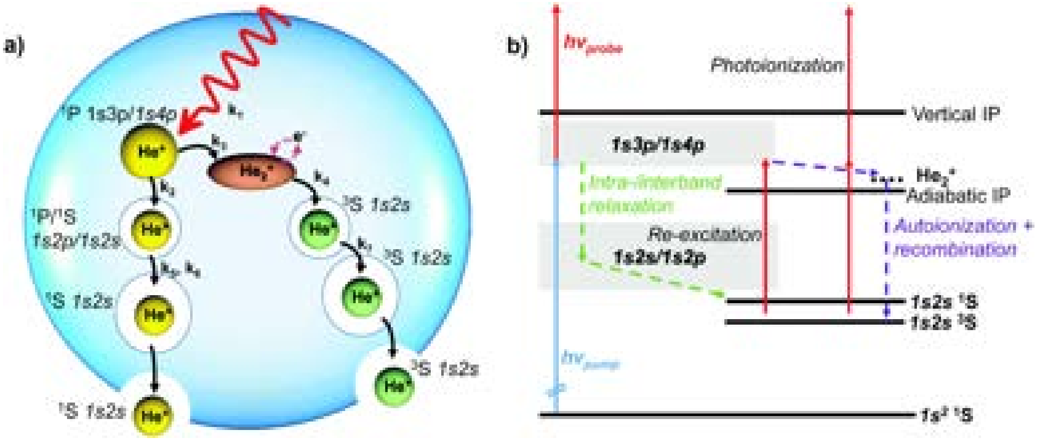

Fig.1 Illustration of the relaxation dynamics of superexcited helium nanodroplets. Two relaxation paths are possible leading to either the *1s2s* ^{1}S or ^{3}S metastable atomic states. The ^{1}S singlet path follows interband and intraband relaxations through electronic droplet states whereas the ^{3}S triplet state is formed by recombination after autoionization.

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Cryo IR Spectroscopy and Kinetics of Nitrogen on Tantalum Cluster Ta_{2-8}^+

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We investigate tantalum clusters Ta_n^+, n = 2 – 8, for their capability to cleave N_2 adsorption without further activation. We utilize adsorption kinetics and infrared spectroscopy of isolated and size selected clusters under cryogenic conditions within a buffer gas filled ion trap, and we augment our experiments by quantum chemical simulations (at DFT level) along the lines of our prior studies [1-4].

We observe a strong size dependence of N_2 cryo adsorption kinetics and cryo IR spectra. Small Ta_n^+ clusters, n = 2 – 4, seem to cleave N_2 efficiently. We confirm and extend a previous study on Ta_2^+ cluster under ambient conditions [5], and we identify an overlooked entrance channel barrier. Our cryo studies and the concomitant DFT simulations of the tantalum trimer Ta_3^+ suggest consecutive cleavages of up to three N_2 molecules across submerged barriers and along a much-involved multidimensional reaction path. This is much in line with our previously investigated and published case, the Ta_4^+ cluster [6]: The N_2 cleavage takes place by an "across edge-above surface (AEAS)" mechanism that involves (a) initial end on N_2 coordination to a single Ta center, (b) bending towards an adjacent Ta atom, across edge, (c) rearrangement into threefold coordination, above surface, (d) followed by ultimate N-N bond cleavage unfolding into the final dinitrido motif (Ta_2N). In direct comparison, the n = 2 – 4 clusters experience evolving steric constraints on the N_2 cleavage mechanism with increasing cluster size.

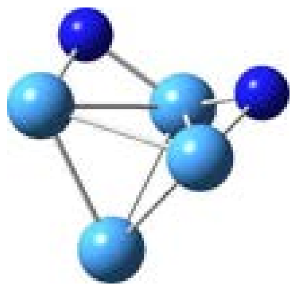

Fig. 1 $[Ta_4(NN)]^+$ dinitro motive as found spontaneously from $Ta_4^+ + N_2$ (PBE0/def2-TZVP).

Upon the advent of the fifth tantalum atom, and beyond, the larger tantalum clusters loose the capability to cleave N_2 molecules on their cluster surface. Instead, the cryo kinetics of these larger Ta_n^+ clusters, n = 5 – 8, reveal particular features which indicate isomerization of some clusters and their cluster-adsorbate complexes in the course of stepwise N_2 adsorption.

Future N_2-H_2 co-adsorption studies aim to verify conceivable amine formation, and to elucidate further mechanistic details.

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Mimicking atoms and predicting novel materials by placing diffuse electrons around metal ammonia complexes

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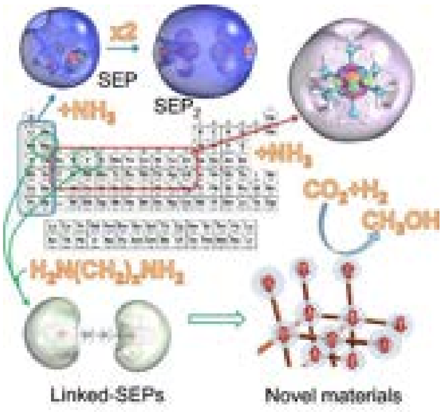

Fig.1 Pictorial summary of our findings.

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 (see top left and right corner of Fig. 1). 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 (see middle top of Fig. 1 for a σ orbital) [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 (linked-SEPs; see bottom left of Fig. 1). 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 (see bottom right corner of Fig. 1), which can serve both as quantum computing materials and redox catalysts. Calculations of the electronic band structure for such materials are under way.

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Photoluminescence Enhancement in Transition Metal Dichalcogenides using Plasmonic Nanoantennas

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Since the exfoliation of graphene in 2004 [1], there has been a still growing pool of two-dimensional materials, which for example includes semiconducting transition metal dichalcogenides (TMDCs). One of their most prominent features is the nature of their optical bandgap: Bulk TMDCs are indirect bandgap semiconductors, whereas TMDC monolayers possess direct bandgaps which makes them promising candidates for optoelectronic devices. However, due to various channels that facilitate nonradiative recombination, the quantum yield of TMDC monolayers is naturally low [2]. We aim at enhancing the photoluminescence (PL) signal of the transition metal dichalcogenide MoS_2 using plasmonic nanoantennas [3,4]. To this end, we adopt two different approaches: (i) Arrays of gold bowtie nanoantennas fabricated by thermal-scanning probe lithography and (ii) Ag clusters with a diameter of 3 nm acting as plasmonic nanoparticles [5] deposited on a Si/SiO_2 substrate. For both antenna systems, MoS_2 monolayers that have been exfoliated from a bulk crystal are placed on top of the respective nanoantennas via viscoelastic stamping [6]. PL spectra of the various systems are recorded and the PL enhancement factors obtained are discussed.

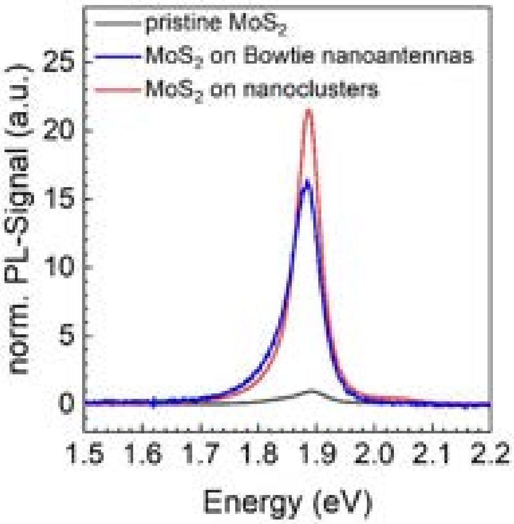

Fig.1 Photoluminescence spectra of monolayer MoS_2: Compared to pristine MoS_2, PL emission is enhanced on Au Bowtie nanoantennas and Ag nanoclusters.

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Activation of Small Molecules by Single Metal Atomic Anions Studied via Negative Ion Photoelectron Spectroscopy

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Activation is required to convert small molecules such as methane into high-value chemicals. Single metal atoms are sometimes seen as models for mimicking active sites in heterogeneous catalysts. Gas phase studies of small molecules' activation by single metal atoms have provided insight into the mechanisms of bond activation, dissociation, and new bond formation at the molecular level. The interactions of small molecules, i.e., methane and hydroxylamine, with platinum, gold, and iridium single metal atomic anions have been studied via negative ion photoelectron spectroscopy. In combination with theoretical calculations, the photoelectron spectra presented evidence of chemisorption and chemical reaction, i.e., activation of the small molecule by the single anionic metal atom. Calculations also revealed the reaction mechanisms [1,2,3].

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Two Color Diffractive Imaging of Helium Nanodroplet Dynamics

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Diffraction imaging offers an insight into the structure of non-depositable nanoscale objects like helium nanodroplets [1]. With intense ultra-short light pulses from free electron lasers (FEL) in the extreme ultraviolet (FERMI, Trieste) or x-ray regime (XFEL, Hamburg), it is possible to capture a nanoobject in a single shot before it gets destroyed [2]. One can facilitate this technique to learn about the structure of biological samples, like viruses [3], or the spatiotemporal evolution of transient atomic states driven by processes like ionization, plasma formation, or locally excited electrons [4]. With pump-probe schemes, one can study the dynamics. Usually, these schemes use an intense infrared pulse as a pump pulse. However, this limits the knowledge of the initial state as the nanodroplets vary in shape and size from shot to shot, thus binding one to average statements.

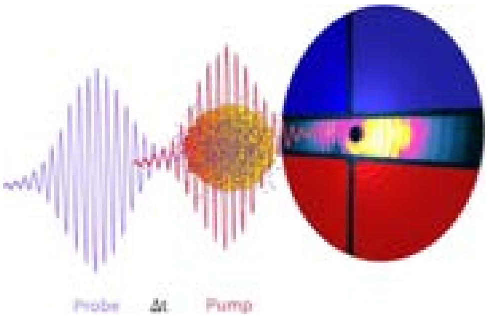

Fig.1 Two color pump-probe scheme with color filters in front of the detector.

With the advent of sophisticated machine tuning settings at the FEL facilities, it is now possible to create two pulses with different wavelengths, separated by some femto- to picoseconds. With these two colors, we can capture an image of the initial and final state of the same object in one shot. The challenge lies in separating the two produced images. To do so, we use two filters in front of the detector at FERMI. As most of the images are spherically symmetric little information is lost. At XFEL, we exploit the linear detector response to separate the images pixelwise, as a single photon of a lower wavelength produces more charge. On this poster, we will present the proof of principle results. Techniques to enhance the data, such as near resonance measurements or doping of the droplets, as well as challenges due to detector effects, will be discussed.

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Beam Deflection Studies of the Dipole Moments of Cold Atomic and Molecular Assemblies Within Superfluid Helium Nanodroplets

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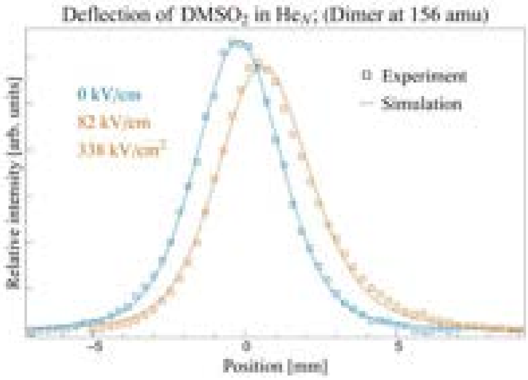
The electric and magnetic moments of atoms, molecules, or groups thereof, describes their electrons' state and behavior within that system. By embedding them within a beam of superfluid helium nanodroplets these systems are cooled to their lowest vibrational and low rotational states and can be almost fully oriented by externally applied fields. As a result, direct beam deflection measurements can be carried out [1].

By using electrostatic beam deflection we have investigated the geometry of molecular dimers, trimers, and atom-fullerene complexes [2-4]. The appearance of highly polar metastable molecular configurations has been confirmed, and the formation of an ionic bond has been identified.



Current work aims to extend this technique to the measurement of magnetic moments, using a recently constructed permanent-magnet Stern-Gerlach deflector [5]. Preliminary experiments with atomic dopants such as Bi and Eu are in progress.

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Nonlinear optical absorption of gold-alloy nanoparticles

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The interaction between matter and high intensity electric fields (e.g. high power or focused lasers) may trigger previously inaccessible electronic transitions in the linear regime. This nonlinear response can be attributed to and tuned with the composition, size, and structure of the material in question. One such method to investigate these nonlinear optical properties is the z-scan technique [1]. In this technique, the transmitted light from a sample is measured as it is moved from a position before to a position after the focal point of a focused laser beam. At the focal point, an increase or decrease in transmission may qualitatively indicate the underlying mechanism for the nonlinear optical behavior. The measurement can be further quantified through numerical fitting of such data, allowing the extraction of relevant nonlinear optical coefficients, e.g. two-photon absorption coefficient, nonlinear refractive index, and intensity saturations [2]. Among the interesting materials to study are gold nanoparticles. They are known to exhibit plasmonic behavior [3] and are promising materials in photonics, chemistry, energy, and life sciences [4, 5, 6]. While pure gold nanoparticles have been studied extensively, research on the effects of alloying and their associated nonlinear properties are scarce. Initial experiments show that in the linear regime, the plasmonic peaks and absorbance of gold nanoparticles were found to diminish upon alloying. However, in the nonlinear regime, pure gold was found to become more transparent at the focal point indicating nonlinear saturation, but nonlinear absorption was observed upon allowing. This study reports on early investigations on the nonlinear absorption of gold nanoparticles alloyed with iron or cobalt, which were prepared by laser ablation synthesis in solution [7].

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Collisional Excitation and Dissociation of CO molecule by Proton Impact: Application to Astrophysics

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The CO molecule is one of the most abundant molecules in interstellar space [1] and a major component of the stellar (solar) winds is proton. Thus, the collisional excitation and collision-induced dissociation (CID) by proton impacts are expected play important roles in the chemical evolution of interstellar molecules. A considerable amount of study has been performed to study this process in both experimentally and theoretically. [2-3] Here we present a theoretical work on the energy transfer and fragmentation of CO molecule by proton impact at hyperthermal energies. The classical trajectory (CT) calculation and the sudden-limit model [4,5] are applied to estimate the energy transfer from translational to internal degrees of freedom.

Figure 1 represents the calculated excitation spectrum of CO molecule by proton impacts at the collision energy E=27 eV. The spectrum is obtained with the CT calculation (solid curve) as well as with the model (dashed curve). The sudden-limit model estimates the energy-transfer from the translational to the internal degrees of freedom with less efficiency. As shown in the figure, the calculated spectral profile presents a triply-peaked structure in both calculations. One peak is the nearly elastic scattering and the other two peaks correspond to the binary collision between projectile and atoms in the target molecule. It is found that the probability of CID depends strongly on the orientation angle at the moment of the contact. It is found that the CID takes place predominantly when a proton hits the molecule either perpendicular or parallel to the molecular axis.

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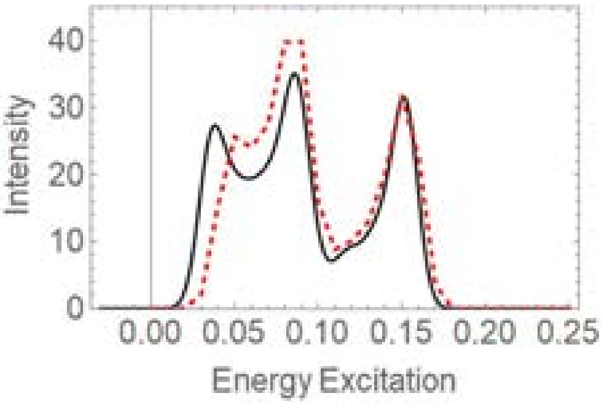

Fig.1 Excitation spectrum of CO by proton impact.

Strong field experiments on size-selected metal clusters

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Ions emitted from a laser-induced Coulomb explosion of clusters in a molecular beam feature broad charge-state and energy distributions. When conducting studies in order to resolve finer details of the nanoplasma dynamics, interesting aspects are the maximum recoil energy of the atomic ions and the highest charge state of the ionization process. Another issue to examine is the role of the cluster size and laser intensity distribution concerning the ion [1] and electron energy spectra.

In this contribution, we demonstrate an experimental setup that enables plasma studies to be carried out on mass-selected metal clusters of high target density using laser pulses with a kHz repetition rate. Silver clusters of a defined size are accumulated in a digital 3-state Paul trap [2] in which they are exposed to strong optical laser fields during the field-free trapping periods. The emission of energetic and highly charged ions from the formed nanoplasma is analyzed by recording charge-state selective recoil energy spectra (Fig. 1) using the CRIEA [3].

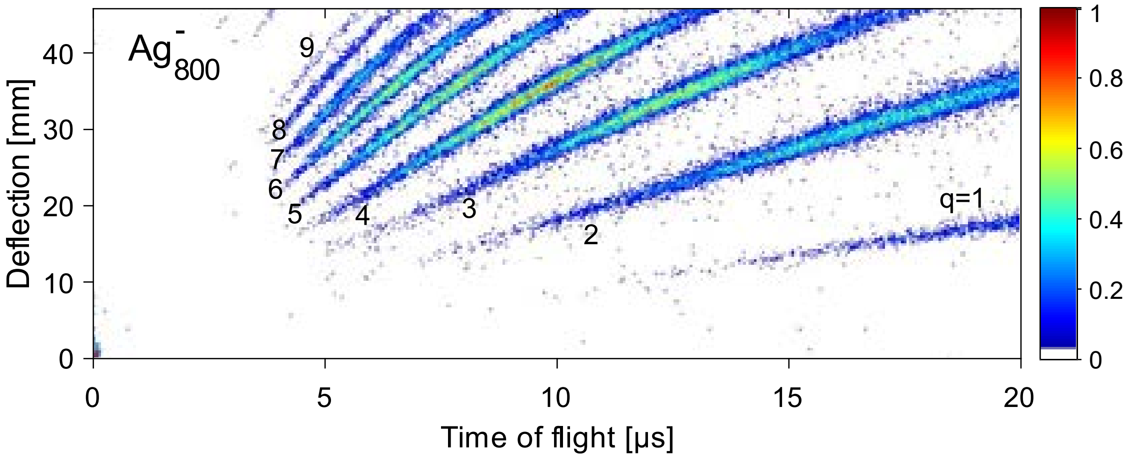

Fig.1 Time-deflection histograms of the Coulomb explosion of size-selected silver clusters (Ag^-_{800}) after exposure to strong femtosecond laser fields ($I_L = 4 \cdot 10^{14}\ W/cm^2$). A charged-state resolving ion energy analyzer (CRIEA) records the recoil energy spectra of the highly charged atomic ions. The diagonal lines in the time-deflection histogram indicate the different atomic charge states.

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IR spectroscopic characterization of N_2 adsorbates on size selected anionic nickel clusters under cryo conditions

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Transition metal cluster are established as model systems for the study of elementary processes in heterogeneous catalysis [1], and they offer the unique opportunity to check for the influence of charge states. Having studied numerous cases of cationic transition metal clusters before [2-4], we have most recently started to investigate anionic clusters. Here, we probe nitrogen molecules (N_2) adsorbate complexes of size selected anionic nickel cluster, Ni_n^-, with a current focus on $n = 11$, $[Ni_{11}(N_2)_m]^-$, and a wide range of m value up to $m_{max} = 11$, which is the observable saturation limit. We utilize cryo ion trapping of such complexes to conduct InfraRed PhotoDissociation (IRPD) experiments.

We obtained IRPD spectra for all of these adsorbate cluster complexes, $m = 1 - 11$. These spectra reveal sharp absorption bands that signify vibrational absorptions of the surface bound N_2 chromophores, which are significantly red shifted and spread out across a range of 2000 - 2200 cm^{-1}, and beyond. The spectra show some stepwise variations by the amount of N_2 load m, and a superimposed general trend, which is a decrease of red shift with increasing m. This contrasts with the observed behaviour of cationic nickel clusters [2].

The IRPD spectrum of the saturated cluster adsorbate complex $[Ni_{11}(N_2)_{11}]^-$ reveal at particularly low band at 1895 cm^{-1} that deserves special attention. It seems to signify a special adsorption site and/or adsorption geometry. Our own DFT modelling – in line with previous attempts [5] – suggests a largely convex geometry of the naked cluster Ni_{11}^-, with an icosahedron-like structure but two surface atoms (C_{2v}) missing. This leads to a concave pocket structure (Fig. 1) which might act as a least preferred adsorption site that might host the weakest bound "last" N_2 adsorbate molecule. It seems that this last adsorbate N_2 might induce a general symmetry reduction and thus induce a rapid increase of band complexity, as observed in the IRPD spectrum of $[Ni_{11}(N_2)_{11}]^-$, as compared to the simpler IRPD spectra of m=10 and smaller.

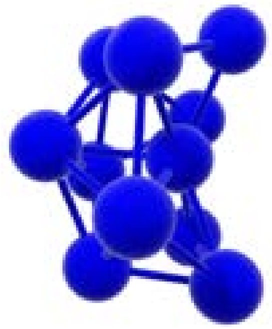

Fig. 1 Optimized icosahedral pocket structure using DFT (PBE0/ecp-10-mdf (Ni))

The weakly bound N_2 adsorbate at the concave pocket site likely orients into a tilted, almost side-on adsorption geometry, which would lead enhanced electron back donation and a large red shift of the N_2 stretching mode – much in line with the observed band at 1895 cm^{-1}. Other conceivable cluster geometries fail to provide for such explanations.

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Abstract for the August 2022 Erice workshop
Studying the Correlation of the Stark- and Zeeman Effect with Combined Electric and Magnetic Beam Deflection Experiments on MSn_{12} Clusters (M = Al, Ga, In)

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$M^{(120)}Sn_{12}$ Clusters (M = Al, Ga, In) were studied in electric and magnetic beam deflection experiments at nozzle temperatures of 16 K and 30 K. The results of the electric beam deflection show a nonpolar and polar fraction simultaneously present in the molecular beam with the amount of the polar fraction decreasing from Al to In. The results of the magnetic beam deflection also indicate two fractions one of which shows atom-like deflection (superatomic) with a surprisingly high g-factor of about 2.7, indicating a significant orbital contribution.

Based on these observations, it is investigated by several setups combining the electric and magnetic experiments how the superatomic and polar fractions are correlated. By filtering out the polar fraction with the help of an inhomogeneous electric field, the observed nonsuperatomic fraction in the magnetic deflection is decreasing. The amount of this reduction is strongest for the Al doped cluster and correlates with the amount of the polar fraction. These observations prove a direct link between the polar and the nonsuperatomic fraction. To further study this correlation, the electric beam deflection of the superatomic and nonsuperatomic fractions in the molecular beam is investigated separately by splitting the molecular beam with the aid of the magnetic field. By studying only the nonsuperatomic fraction in the electric field, a decrease in the nonpolar fraction can be observed. For the electric deflection of the superatomic fraction it can be observed that the polar tailing in the electric beam profile disappears completely.

These various observations can be interpreted only by assuming that two structural isomers with different symmetry are present: A highly symmetrical one that shows only a vanishing electric dipole moment allowing a superatomic magnetic response to be observed and an isomer with lower symmetry that is considerably polar showing Brillouin-type magnetic behavior.

The magnetic beam profiles can be quantitatively simulated based on avoided crossings in the rotational Zeeman diagram comprising computed rotational constants, vibrational modes, g-factors and spin-rotation coupling constants [1,2]. These simulations allow a discrimination of possible structural candidates for the observed superatomic behavior.

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Atomic and Molecular Anions of Uranium Studied by Anion Photoelectron Spectroscopy

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Elucidation of the electronic structure of ground and excited states of neutral uranium clusters is an essential first step in understanding their behavior in molecular activation, catalysis, and nuclear fuel technology. Because of near-degeneracies among open atomic sub-shells, as well as very strong spin-orbit interactions, complex anion photoelectron spectra are expected. Using laser vaporization and anion photoelectron spectroscopy, the ground and electronically-excited states of neutral uranium containing atom/molecules and their atomic/molecular anions have been mapped. When combined with theoretical methods, both electron affinities and copious electronic structure information about the anions' neutral counterparts are determined. Here, we report the electron affinity of the U atom as well as the anion photoelectron spectrum of U_2^- dimer, giving crucial insight into complex bonding nature expected when 5f orbitals are involved[1,2]. Moreover, due to the promise of uranium nitrides being fuel for Gen IV power reactors, the electronic structure of UN_2 has been observed as well as its implications for activation been deduced[3]. Finally, subtle insight on the electron structure of UF_6, a chemical ubiquitous in the nuclear industry, has been rationalized by using Au as a surrogate for F, with the anion photoelectron spectrum of UAu_6^- substantiating such an analogy[4].

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