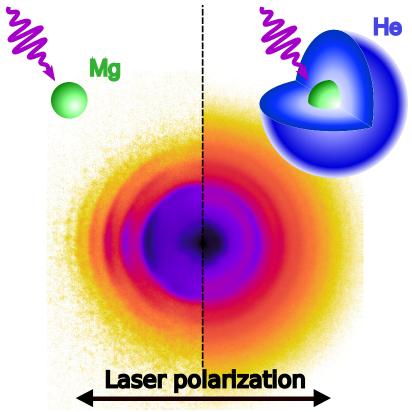
# Clustertreffen 2022

## Herzogenhorn

2.10.22-7.10.22

## Book of Abstracts

# Invited Talks



# Phase-of-the-Phase Electron Spectroscopy on Atoms and Clusters in Helium Nanodroplets

B. Krebs,[1] M. Zabel,[1] V. A. Tulsky,[1] L. Kazak,[1] D. Bauer,[1] K.-H. Meiwes-Broer,[1,2] and J. Tiggesbäumker[1,2]

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Strong field, two-color induced photoemission from atoms and clusters embedded in helium nanodroplets exemplarily allows to study coherent and cooperative phenomena in the interaction of electrons with nanoscaled media on the electrons natural timescale, hence conducting attoscience experiments on nanoobjects. Two scenarios will be discussed: (i) Impurity atoms as electron point sources serve to resolve electron motion within the neutral environment and its impact on the resulting ATI pattern, see Krebs *et al.* J. Phys. Chem. Lett. 13, 1526 (2022). (ii) Seeding ionization avalanches by impurity clusters allows to resolve different plasmon-enhanced electron acceleration mechanisms.

# Imaging ultrafast dynamics in isolated atomic clusters

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The excitation of gas-phase clusters with intense laser pulses provides a well-defined scenario to study the correlated dynamics of highly excited matter in a very controlled and near-background-free manner. Via coherent diffractive imaging of **single** clusters in free flight with the high-intensity pulses from XUV and X-ray free-electron lasers (FELs), we are able to explore the light-induced dynamics with high spatial and temporal resolution while avoiding any focal or size-distribution averaging. From the measured diffraction pattern of an isolated cluster, formed by the interference of elastically scattered photons, a snapshot of the cluster morphology can be retrieved. This technique allows the study of fragile, non-depositable specimen, such as superfluid helium nanodroplets, and of fast, laser-induced structural changes, e.g. ultrafast melting. Even faster electron dynamics in the clusters, such as excitation and ionization during the interaction with the intense X-ray pulses, also change the scattering response and can therefore in principle be mapped by diffractive imaging. In this context, the current development at XFELs and high-harmonic generation (HHG) sources towards intense attosecond pulses opens up unprecedented possibilities to directly visualize ultrafast electron dynamics in highly excited nanoscale matter on their natural time scale.

# Ultrafast multidimensional spectroscopy of cluster-isolated species

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Coherent multidimensional spectroscopy (CMDS) is an extension of femtosecond pump probe spectroscopy which unifies spectroscopic information otherwise only accessible in disjunct experiments [1]. However, applying CMDS in the gas phase, in particular to dilute molecular and cluster beams, is experimentally very challenging [2]. Recently, we have overcome these challenges and have performed the first CMDS studies of doped cluster beams [2]. Our findings include ultrafast dynamics induced by the interaction with the nano-cluster environment [3] and conformational information of molecules attached to solid clusters [4], as well as the extension of our experimental methods towards the XUV spectral domain [5,6]. I will give an overview over these recent results.

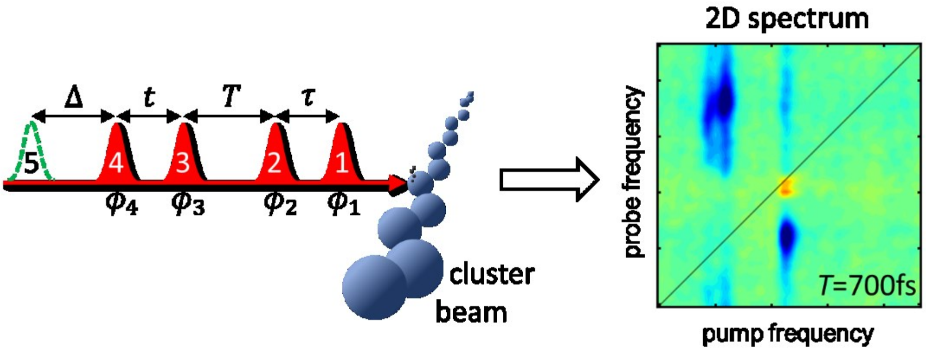

Figure: Experimental scheme. A sequence of femtosecond laser pulses excites and ionizes molecules isolated on rare gas clusters prepared in a molecular beam apparatus. Two-dimensional spectra are retrieved offering high spectro-temporal resolution and directly disclose inter-/intra-particle couplings.

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# How heteromolecular clusters promote the condensation of volatile components in multicomponent vapors

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Nucleation is the first step of a phase transition, in which a metastable parent phase spontaneously transforms into a thermodynamically stable daughter phase. This process lies at the heart of new particle formation and thus plays a key role in atmospheric science and many industrial processes. However, the underlying mechanisms and pathways of nucleation are in many cases not well understood. In our experiments we investigate gas-phase nucleation on the microsecond time scale, to gain insight into the processes accompanying this transition on the molecular level. We let molecular aggregates form in a pulsed Laval-expansion under constant temperature and pressure and probe them via soft ionization with vacuum ultraviolet light, coupled to time-of-flight mass spectrometry. From this, we retrieve time-resolved absolute cluster number concentrations, which enable us to calculate experimental nucleation rates and association rate coefficients for cluster growth. In a previous publication [1] we used this data together with a simple kinetic model to unravel how gas-phase nucleation can be significantly enhanced by the addition of a volatile substance. We found evidence that transient, mixed clusters play a crucial role in facilitating nucleation. Here [2] we investigate how clusters formed in this process can act as seeds for further particle growth. We demonstrate that the enhanced nucleation of low vapor pressure substances can promote the condensation of highly abundant, more volatile vapor components. Such processes involving $CO_2$ or other volatile components are relevant for natural gas separation and extraterrestrial cloud formation.

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# Non-local Electronic Processes: From Clusters to Solutions

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For molecules made of lighter atoms, the Auger-type decays represent the dominant relaxation pathway upon the interaction with ionizing radiation (X-ray photons, fast electrons, ions). Auger processes are typically thought of as local processes yet in the condensed phase, the relaxations involving neighboring molecular entities often contribute to the relaxation as well. In Intermolecular Coulombic Decay (ICD), the inner valence hole is refilled by a valence electron and a second electron from a neighboring molecule is ejected by the energy released. In Electron Transfer Mediated Decay (ETMD), the hole is refilled by an electron from a neighboring molecule, and the energy released is used to eject an electron from yet another neighboring molecule. Molecular clusters represent a unique environment to study such processes as it is possible to detect simultaneously the electrons and outgoing fragments.

In my presentation, I will focus on theoretical simulations of some recent experiments. I will contrast the reactive events in water and ammonia clusters. While these systems are isoelectronic, the character of hydrogen bonds and ground state structure is very different. The electronic decays are strongly coupled to the nuclear motion both in the ground and ionized states. For water, this coupled dynamics leads to closing the ICD decay upon inner valence ionization [1] while it enhances the non-local processes upon core level ionization [2]. The nuclear dynamics is much less prominent for ammonia systems in both cases [3, 4]. I will discuss experimental options to detect these processes in real time. Next, I will explore the ICD and ETMD [5] processes upon the ionization of aqueous ions.

In the final part of my talk, the ionization of large hydrogen-bonded clusters by fast electrons will be discussed [6]. The successive ionization and the role of ICD will be covered. I will also briefly cover the possible role of post-collision interaction in these processes.

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# Photochemical Hydrogen Evolution at Metal Centers

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Hydrated metal ions in the gas phase are useful model systems for precise (photo)chemical investigations of redox reactions. Using small, well-defined ions, we might understand their structure, hydration-dependent reactivity or spectral properties in detail. Comparing different hydrated metals, trends in the periodic table are elucidated. In the present contribution, we compare mechanisms of photochemical hydrogen evolution in $Mg^+$, $V^+$, $Al^+$ and $Zn^+$ [1–3].

On the experimental side, we used Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry to select the ions that were subsequently irradiated in a broad spectral range from IR to UV. Tunable optical parametric oscillators provide photons in the range 225 nm – 12 μm. Photodissociation events are observed by taking mass spectra as a function of laser wavelength. Reaction channels include loss of water molecules, as well as formation of atomic or molecular hydrogen.

A wide range of quantum chemical methods, including Equation of Motion Coupled Cluster (EOM-CC) technique and multi-reference calculations, was employed to rationalize the observations and propose photochemical mechanisms. For the investigated metals, we observe complicated photochemical behavior that includes switches of electronic states near conical intersections, intersystem crossings and electron transfer.

For the vanadium cation hydrated with one water molecule, the multitude of electronic states (194 states within 3 eV when including spin-orbit coupling) underlines the challenging nature of transition metals as photochemical agents. Finally, we show that the mechanism of photochemical hydrogen evolution is fundamentally different compared to the situation in the electronic ground state. The photon is not simply a source of energy, it re-defines the ion chemistry by lifting the system to an excited state potential energy surface.

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# Photochemical Properties of Astrochemically-Relevant Silicon Clusters: Bridging the Gap Between Diatomics and Grains

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Interstellar dust is part of the universal recycling process of matter. A major component of interstellar dust are silicon carbides, silicon oxides, and metal-containing silicates, as inferred from IR emission and the detection of grains in meteorites. On the other hand, small silicon-containing molecules (<10 atoms) have firmly been detected in circumstellar shells by radioastronomy. Linking these two size limits from small molecules to micron-sized grains is a longstanding and still open issue. Although some hypotheses assume nucleation of seed particles, details of the growth mechanism(s), potential intermediates, and the impact of physical parameters such as radiation field, temperature, and chemical composition, remain largely unexplored.

To shed further light on the nucleation process from the laboratory point of view, we investigate physical and chemical properties of small to medium-sized silicon carbide and silicon oxide clusters as a function of composition and charge state. To this end, the clusters are produced by laser vaporization techniques of various targets in molecular beams and probed by mass spectrometry, laser spectroscopy, and quantum chemistry. In a first step, geometric structures and chemical bonding of the clusters in the ground electronic state are obtained by IR spectroscopy using photodissociation and photoionization schemes, along with global optimization techniques in quantum chemical calculations [1-4]. In a second step, optical and photochemical properties are obtained by UV-VIS photodissociation spectroscopy, providing important information about electronic structure and fragmentation properties (appearance energies, competing fragmentation channels and branching ratios, particularly stable fragments) [5-6]. Results will be presented for selected $Si_nC_m^{(+)}$ and $Si_nO_m^{(+)}$ clusters as well as bare $Si_2^+$.

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# Cluster-decorated graphene as a platform for studying molecular adsorption and desorption kinetics

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In view of the appealing catalytic properties of small clusters, understanding the adsorption and desorption kinetics of molecules on clusters is of significant fundamental and applied interest. However, experimentally it is difficult to obtain information about thermodynamic quantities of molecular adsorption like binding energies and entropy changes.

The sensitivity of graphene's transport properties to adsorbed particles has attracted widespread attention because of its potential for sensing applications [1]. This inspired us to develop a graphene field-effect transistor on which preformed size-selected clusters are deposited with a high control over the deposition energy and the deposited density. In situ electronic transport measurements on cluster-graphene devices demonstrate that cluster adsorption causes charge transfer, and hence doping, which is detectable in field-effect measurements [2] and in enhanced spin relaxation in nonlocal graphene spin valves [3]. The binding of molecular oxygen on Au3-graphene and Au6-graphene was studied and a pronounced cluster size dependence in the corresponding doping was found, in agreement with first-principles calculations [4].

Upon oxygen adsorption the doping of gold cluster decorated graphene changes sign from n- to p-doping, directly evidencing electron transfer to the oxygen molecules and hence their activation. Subsequently, the oxygen desorption can be induced by controlled current heating. In combination with a kinetics model, in situ measurements of the shifts of graphene's charge neutrality point provide quantitative information about the oxygen adsorption barrier, the desorption energy, and the entropy change during the desorption process [5]. This novel method can be applied to other systems and is expected to lead to new insights in the size-specific sorption kinetics of molecules on few-atom clusters.

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# Ion-molecule reactive scattering: from classical to quantum dynamics

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Crossed-beam reactive scattering, in particular in combination with product ion velocity map imaging, has been established as a detailed probe of the atomistic dynamics of chemical reactions. We have been using this technique to study a range of ion-molecule reactions, in particular charge transfer, proton transfer, nucleophilic substitution and elimination [1,2,3]. Here I will report on recent results for the reaction of $F^-$ with $CH_3I$ that are indicative of a quantum mechanical effect in the underlying reaction dynamics [4]. Furthermore, we have studied the reaction dynamics of $O^-$ radical anions with $CH_3I$. Here, we found several competing product channels that provide evidence for fast and direct dynamics [5]. Currently, we are implementing a novel crossed-beam spectrometer with improved product velocity resolution, which will allow us to explore product vibrational state-resolved quantum dynamics in ion-molecule scattering.

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[5] A. Khan *et al.*, in preparation

# Different experiments with clusters of (poly)aromatic hydrocarbons

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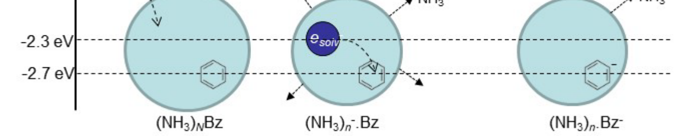
A versatile cluster beam apparatus CLUB in Prague allows for different experiments with clusters in molecular beams, where molecules are deposited in a pickup process on large clusters (nanoparticles), and interactions with photons and/or electrons of different energies trigger various processes such as UV-photodissociation, IR and UV excitation, ionization, electron attachment and ion-molecule reactions [1]. Our present research is inspired mainly by atmospheric chemistry (aerosols) and astrochemistry (ice/dust grains) [2]. Polyaromatic hydrocarbon (PAH) molecules play an important role in these areas. We will report our recent experiments with PAH molecules (including benzene) in clusters.

We quantified the uptake of hydrogen bonding molecules by nanometer-size neutral benzene $(Bz)_N$ clusters (average size $N \approx 300$, $R \approx 2.2$ Å) [3]. Subsequently, we have investigated the uptake of different molecules (water, methanol, ethanol, methane, ammonia, oxygen, carbon dioxide, benzene, toluene, α-pinene) on nanoparticles of different PAHs (naphthalene, anthracene, phenanthrene, pyrene, indene, fluoranthene, adamantane). This will be briefly reviewed.

Further, we focus on benzene radical anion $C_6H_6^-$. It is an intriguing species, representing a stable anion in solutions, but it has the character of metastable shape resonance in gas phase with a negative electron affinity. We show an evidence for a stable $C_6H_6^-$ ion in the gas phase generated upon a slow electron (<10 eV) attachment to large benzene clusters. The formation and structure of this anion will be discussed.

Benzene radical anion represents an important intermediate in organic chemistry in Birch reduction, which includes ammonia, benzene and solvated electron [4]. To understand the process at a molecular level, we generate large ammonia clusters and dope them with benzene and subsequently attach slow electrons. Formation of solvated electron in ammonia and its subsequent localization on benzene, generating solvent-stabilized $C_6H_6^-$ anion in ammonia, are revealed and discussed.



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# Classical molecular dynamics of systems far from equilibrium – from nanoparticles to nanotribology

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Molecular dynamics has proven a versatile tool to understand equilibrium processes in bulk and nanoscale material systems (such as equilibrium phase transitions, elastic behavior, wetting, dissipation, diffusive transport, heat transport) and to calculate corresponding materials constants (such as melting points, boiling points, elastic moduli, surface tensions, viscosities, diffusivities). Often however, material systems are driven by strong external fields to microscopic states far from equilibrium. In such cases, non-equilibrium molecular dynamics is sometimes the only means to explore fundamental mechanism.

In this contribution, I will advocate the use of non-equilibrium molecular dynamics as a numerical microscope to provide atomic scale resolution of strongly driven systems. We will have a closer look at a couple of examples where non-equilibrium molecular dynamics helped experimentalists to interpret their results properly. First, an example from cluster physics will be presented. We will have a close look into the melting, inflation and explosion of superheated plasmonic nanoparticles [1]. Then, we will switch to nanotribology and address the atomic scale mechanisms of friction reduction and wear protection by graphene [2]. The presentation will end with current research into the field of superlubricity [3] that shows that the in-situ formation of nanoscale surface patterns is a crucial cornerstone for friction reduction.

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# Trends in the stability and synthesizability of clusters: A theoretical study of their energy landscapes

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I will first discuss the question of whether the experimentally found structure of a cluster is necessarily the theoretical ground state. I will present a counterexample, namely the $Si_{20}H_{20}$ cluster. Its decahedral hydrogen saturated fullerene is the theoretically established ground. However it has never been observed experimentally. Based on an extensive exploration of the potential energy surface and by constructing theoretical reaction pathways from possible initial structures to the ground state of $Si_{20}H_{20}$, I show that there is no driving force towards the global minimum. There exists a huge number of intermediate structures that consist mainly of collapsed cages. Visiting all these intermediate states to find the ground state is not possible on experimentally relevant time scales. In this way the ground state becomes kinetically inaccessible [1]. I compare the features of the potential energy landscape of $Si_{20}H_{20}$ with that of another covalent cluster, $C_{60}$, which spontaneously forms by condensation.

The behavior of $Si_{20}H_{20}$ is in strong contrast to the behavior of metallic clusters. An analysis of the potential energy landscape of several thousand metallic clusters shows that there is a a coherent driving force towards the ground state. So metallic clusters are expected to find their ground state in experiment.

Based on a huge data set of DFT structures, I will finally unveil other trends in the stability of isomers of various clusters with respect to shapes and bond lengths.

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# Monitoring the dynamics of cluster/oxide support systems

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Oxide-supported clusters are pivotal in heterogeneous catalysis. The cluster-support interaction intricately affects structural, diffusion and reaction dynamics of these metastable particles. In this talk we present our recent studies on size-selected Pt clusters supported on magnetite $Fe_3O_4(001)$, a reducible oxide that can contribute lattice oxygen to catalytic reactions while maintaining its surface stoichiometry upon reduction, thanks to the high cation mobility. But where does oxidation catalysis take place – at the interface or on the clusters? And what is its impact on support morphology and cluster mobility?

By a combination of high resolution, fast scanning tunneling microscopy (STM), with time resolution down to the 10ms timescale [**?**], and a highly sensitive pulsed valve sniffer setup [**?**], we investigate fundamental aspects of this catalytic system, namely: (i) reverse lattice oxygen spillover, (ii) size-dependent cluster diffusion and ripening, (iii) support restructuring, as well as (iv) cluster encapsulation.

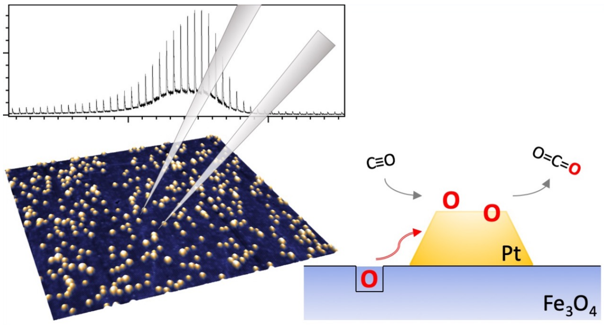

Figure 1: Schematic summary: STM image of $Pt_5$ clusters on $Fe_3O_4(001)$, temperature-dependent $CO_2$ production upon CO pulses and reaction sketch (taken from [**?**]).

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# Unexpected sharp absorption peaks in silica-embedded gold clusters

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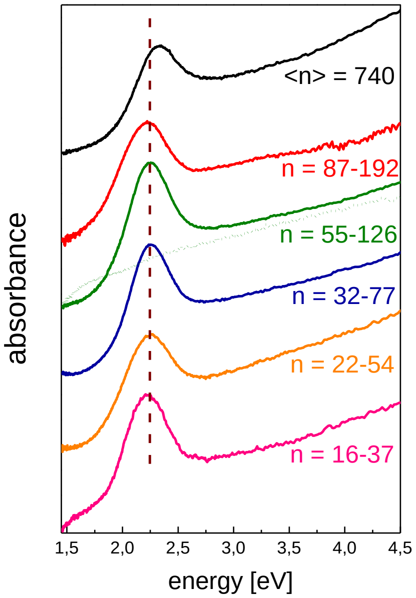
Gold nanoparticles are known to have a strong localized surface plasmon resonance in the visible. Upon reduction of the particle size, this resonance is damped and broadened and eventually disappears in the flank of the interband transitions below ~2nm diameter (~250 atoms) [1]. Very small Au clusters (or some specific functionalized chemical particles with a small core) show distinct molecular-like absorption lines [2]. In the intermediate range, between ~20 and ~200 atoms, no clear absorption lines are expected.

Here we show unusually sharp absorption bands for embedded Au clusters in the whole range down to <40 atoms. The metallic clusters are fabricated in a magnetron cluster source and mass-selected before embedding in a silica matrix [3]. No such strong peaks are observed for alumina as matrix (cf. figure). The peaks are red-shifted with respect to those of larger nanoparticle, as well as to theoretical predictions and only appear after several hours of exposure to ambient air. These observations hint at an entirely different physico-chemical mechanism than the conventional surface plasmon resonance. The details of this process, probably linked to interface chemistry, are currently under investigation.



Optical absorption spectra of size-selected silica-embedded Au clusters. The dotted line for n = 55-126 atoms shows the spectrum for alumina-embedded Au clusters.

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# Probing the Vibrational Wave Packet Dynamics of Mass-selected Neutral Metal Clusters

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Small silver clusters possess remarkable luminescence and photoelectric properties, making them subject of current research. Studies on isolated gas phase clusters do not only provide detailed information on their intrinsic properties, like their electronic structure, vibrational frequencies, bonding energies and time scales for internal energy redistribution in the absence of a perturbing environment, but such clusters also represent ideal model systems for benchmarking modern quantum chemistry methods. However, obtaining vibrational information on small, neutral silver clusters remains challenging, due to difficulties in mass-selecting neutral clusters, in general, and a lack of easily accessible and widely wavelength-tunable far infrared light sources.

Here, we report on recent results on the mass-selected neutral silver clusters $Ag_2$ and $Ag_4$ that allow us to access detailed vibrational information in the far-IR spectral region. To this end, we combine femtosecond pump-probe spectroscopy with the negative-neutral-positive (NeNePo) excitation scheme and using a cryogenic ion-trap tandem mass spectrometer.[1,2] An ultrafast pump pulse is used to produce a vibrational wave packet on the neutral ground state potential energy surface by photodetachment from the corresponding mass-selected, vibrationally cold anion. The wave packet dynamics are probed using a second ultrafast pulse (30 – 40 fs), which ionizes the neutral cluster. The mass-selected cation yield as a function of the delay time ($\Delta t$) between the two femtosecond laser pulses then yields the fs-NeNePo spectrum. The frequency analysis with a resolution down to about 0.5 $cm^{-1}$ ($\Delta t > 60$ ps) by way of fast Fourier transformation of the transient traces yields insights into the vibrational frequencies. The time scale for rephrasing of the wave packet gives access to the determination of vibrational anharmonicities. Finally, the dependence of the NeNePo signal on the polarization of the fs laser pulses reveals information on the nature of the partial waves involved in the photodetachment process.

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# Ion trapping for cluster studies at Greifswald

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Atomic clusters have been studied (a) for several decades in a Penning-trap setup and (b) lately in an electrostatic ion beam trap. These are two recent developments and results:
(a) The "ClusterTrap" setup combines a Smalley-type source with a Penning trap where metal clusters are stored in magnetic and electric fields, and monoanionic clusters are charged up by attachment of further electrons [1]. Earlier, photofission of dianionic lead clusters was deduced from their decay pattern – observed as time-of-flight spectra after ejection of the ions from the trap [2]. These studies have recently been extended to tin clusters: Their decay patterns are more complicated (Fig. 1, left), but the abundances of precursor and charged product clusters can be monitored as a function of time after the laser pulse [3], as earlier demonstrated for singly-charged clusters [4]. Preliminary results confirm the assumption of photofission [3].

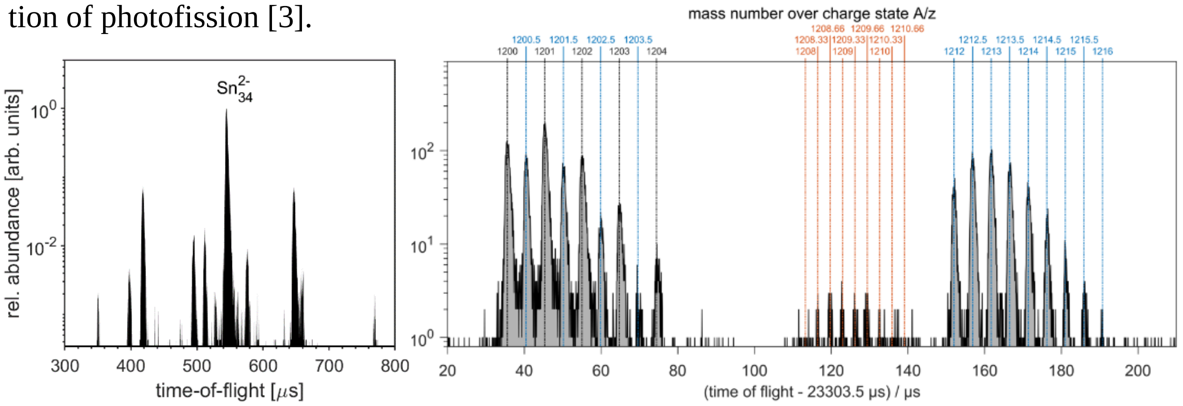

Fig. 1: Mass spectra from ClusterTrap (left) and the MR-ToF setup (right). See text for details.

(b) An electrostatic ion beam trap, a.k.a. Multi-Reflection Time-of-Flight Mass Spectrometer (MR-ToF MS), has been equipped with a laser-ablation ion source. By (MR-ToF MS)$^2$ for mass separation as well as determination, bismuth clusters doped with a lead atom were selectively photodissociated and checked with respect to the fragment doping [5]. Another study showed the MR-ToF method's applicability for time-resolved decay studies [6]. More recently, carbon clusters were laser-ablated from glassy carbon, resulting in a well-known [7] log-normal cationic fullerene spectrum. This spectrum is now found to include several charge states $z$ (Fig. 2, right) with similar $m/z$ distributions [8], i.e. larger clusters attain higher charge states. Cluster-growth modeling by coalescence reproduces this behavior [8].

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# Formation and spectroscopy of He-tagged dopant ions by using highly charged helium nanodroplets

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Helium nanodroplets (HNDs) provide an inert matrix with outstanding properties to isolate diverse molecular ions and to grow complexes and clusters at sub-Kelvin temperature. The conditions inside HNDs are ideal to study chemical reactions and to perform spectroscopic studies of the dopant ions.

In this contribution, we will present a newly developed setup which combines several experimental techniques and methods, developed and tested in the last years.

One of these techniques is the formation of highly charged HNDs by electron impact [1]. In dependence of the electron energy, positively or negatively charged HNDs are formed. The charges are distributed across the droplet, attract the dopants, which are then ionized by charge transfer processes [2]. The formation of several nucleation sites in a single HND enables the production of intense beams of cold ions.

The release of the dopant ions from the HND environment, decorated with a few He-atoms, is achieved by ‘splashing’ the doped HNDs onto a surface [3] or by gentle evaporation of the helium matrix due to collisions with helium gas at room temperature [4]. The latter technique is used in the new setup to produce He-tagged dopant ions, which are further mass-per-charge selected in a quadrupole, and studied by laser spectroscopy in combination with a time-of-flight mass-spectrometer. Recent results obtained with this setup will be presented.

This work is supported by the Austrian Science Fund, FWF (project number T1181 and W1259-N27)

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# Isolated Calcium Manganese Oxide Clusters: Bioinspired Model Systems for Sustainable Catalytic Water Splitting

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Artificial photosynthesis, i.e., the conversion of solar energy into storable fuels via oxidation of water, represents one of the hot topics of today's catalysis research. In nature this reaction takes place at an inorganic $Mn_4CaO_5$ cluster embedded in the organic environment of photosystem II. Inspired by this natural catalyst, we have embarked on a novel hierarchical modeling strategy, starting with small clusters and increasing the model system's complexity in a staged, controlled manner to aid the future design of artificial water oxidation catalysts.

We started by studying the reactivity of isolated manganese oxide cluster ions, $Mn_xO_y^+$, of different size and composition with $D_2{}^{16}O$ and $H_2{}^{18}O$. Gas-phase ion trap experiments and infrared multiple-photon dissociation spectroscopy, in conjunction with first-principles calculations, revealed the facile water deprotonation by various clusters. In a further step we investigated binary calcium manganese oxide clusters and found that the number of Ca atoms is crucial to the water oxidation capabilities of the small $Ca_{4-x}Mn_xO_4^+$ and $Ca_{5-x}Mn_xO_5^+$ clusters. Finally, we started modeling the ligand environment of manganese oxide clusters by small carbonic acids. Propionic acid was identified as a promising candidate in this respect since the smaller acids easily decomposed in the presence of $Mn_xO_y^+$.

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# Spin switching and vibrations of molecular clusters on surfaces

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Aspects of interactions in molecular clusters on surfaces will be discussed. First, spin-crossover (SCO) molecules will be addressed. These molecules can be switched between low spin and high spin states by applying external stimuli. Although the adsorption to surfaces may significantly change the SCO behaviour, electron-induced spin-switching of single adsorbed molecules has already been reported. By now there is little information about cooperative behaviour of SCO molecules in two-dimensional arrays. I will present a low temperature STM investigation of metal-based SCO complexes condensed to tetramers on Ag(111). Second, we used superconducting Pb surfaces to detect spin effects in molecular layers and oligomers and showed that diamagnetic molecules can turn paramagnetic once embedded in a suitable array of neighbors. The experimental data are analysed using model calculations that reveal the relevant interactions. Finally, we demonstrated a resonance-enhanced form of inelastic tunneling spectroscopy that has much higher sensitivity and spectral resolution than previous approaches. Sub-meV energy changes caused by molecular interactions can now be detected on individual molecules.

# XUV spectroscopy and imaging of helium nanodroplets

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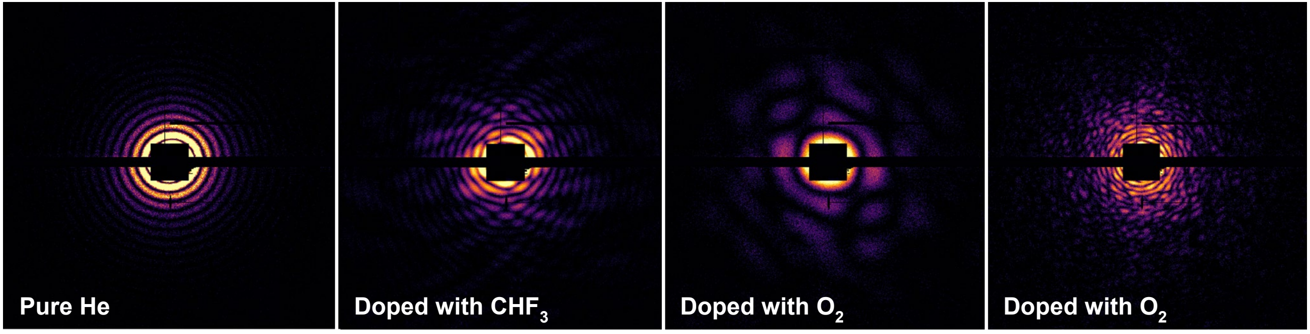
Superfluid helium nanodroplets are fascinating objects from the point of view of atomic and molecular physics, physical chemistry and condensed matter physics. Their quantum fluid properties, and their ability to pick up virtually any foreign atom or molecule, makes them ideal substrates for high-resolution spectroscopy and cold chemistry studies.

I will present experiments where pure and doped helium nanodroplets are directly excited or ionized by irradiation with tunable XUV synchrotron radiation or soft x-ray free-electron laser pulses. Resonant excited helium nanodroplets undergo ultrafast internal relaxation [1,2] and inter-molecular interactions with picked-up species [3]. We observe various types of energy-transfer and charge-transfer processes which may also play a role in radiation damage of biological matter, such as interatomic Coulombic decay (ICD) [4-7] and electron-transfer mediated decay (ETMD) [8,9]. For multiply excited helium droplets, we observe a massive enhancement of above-threshold ionization (ATI) 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, see below.

**X-ray single-droplet diffraction imaging (1 keV photons)**



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# The dark side of Coherent Diffraction Imaging: an honest journey from rare-gas clusters to silver nanocrystals

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Single-shot Coherent Diffraction Imaging (CDI) is a lensless technique for the study of isolated samples [1]. The spatial density distribution of the sample is reconstructed from the diffraction pattern of coherent light that impinged on it. The recent developments of X-ray Free Electron Lasers, capable of providing extremely short and bright X-ray pulses, rendered CDI the method of election for studying ultrafast dynamics in isolated nanostructures, thanks to its unmatched spatial and temporal resolution. We present our recent imaging results on isolated, individual clusters in free-flight. Two-dimensional reconstructions from small-angle scattering data reveal unexpected protruding surface structures in homogeneous rare-gas clusters, giving unique insights in their formation process. Via resonant imaging of heterogeneous clusters, we characterize the spatial distributions of the different components, which are not in line with theoretical predictions. Using wide-angle diffraction from individual silver clusters allows us to even retrieve three-dimensional information from a single scattering pattern [2]. The 3D reconstructed shapes range from regular polyhedra to distorted faceted shapes, combinations of structural motifs, and agglomerates, which, in many cases, would not be identifiable from only two-dimensional CDI. The presentation of the results will also be an opportunity to unveil less-known and sometimes ignored aspects of CDI, which derive from theoretical limitations as well as from intrinsic features of real diffraction patterns, to better understand the achieved results and the challenges involved.

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# Gas Phase Cations in the Condensed Phase. What are the Limits...?

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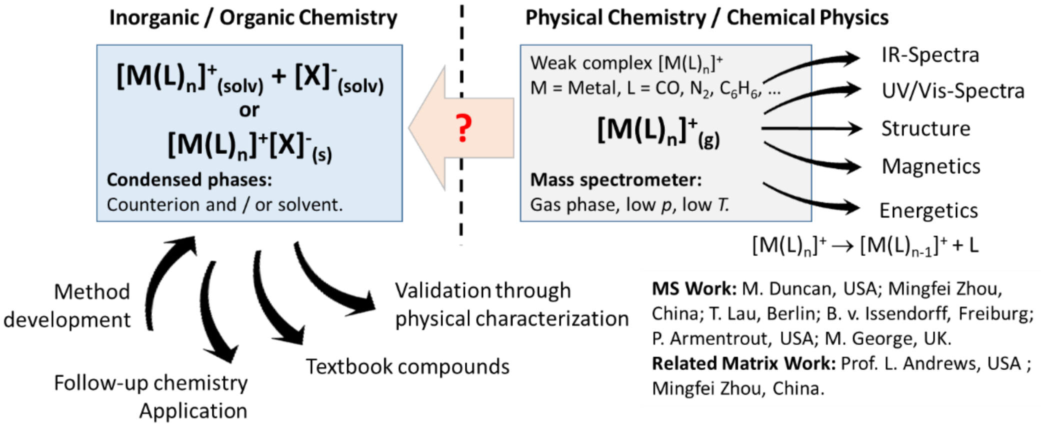
A chemist's view on gas phase cations! Inspired by the magnitude of work to identify and characterize (cluster) cations in the gas phase by one of the advanced mass spectrometric methods [1], as well as those stabilized and characterized at helium temperatures by matrix isolation spectroscopy, our group embarked on the endeavour to prepare stable salts of such gas phase cations in the condensed phase.



The lecture will report [2] on the thermodynamic framework provided by large and very weakly coordinating anions (WCAs) that allow for the stabilization of such delicate substance classes like transition metal carbonyl cations ($[M(CO)_n]^+$, n = 4, 5, 6, 7 [3]), give ideas on the need for innocent solvents and innocent deelectronators that are required to prepare such salts and end with a section on the clustering of group 13 cations, that yield tri-, tetra- or even pentavalent [4] aggregate cluster cations, all of which are unstable towards a Coulomb explosion in the gas phase, but stabilized by lattice energies in the solid state. Exemplary examples for those will be presented.

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# Observation of surface healing dynamics in laser driven clusters

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In recent years coherent diffractive imaging at X-ray free-electron lasers (FELs) has been established as a well suited method for the structural investigation of unsupported nanoparticles. Applications range from the visualization of quantum vorticies in Helium nanodroplets [1] to the observation of highly symmetric metastable morphologies in free metal clusters [2]. The method can be readily adopted to time-dependent investigations by adding a second pulse in a pump-probe scheme.

Recently, such dynamic measurements have been utilized to characterize the expansion of a plasma into vacuum with nanometer spatial and femtosecond temporal resolution [3]. There, intense near-infrared (NIR) laser pulses have been used to ionize and heat monodisperse $SiO_2$ nanospheres of roughly 120nm diameter. The resulting plasma expansion quickly softens the initial surface density step, resulting in a very fast increase of the radial slope of the resulting ring pattern on the scattering detector, as predicted by theory [4].

In a very recent experiment at the European XFEL we returned to $SiO_2$ as a target, but operated in a completely different excitation regime. In the early stages of the expansion process we find a similar behaviour. However, instead of the known fast and irreversible surface softening we observe decreasing signal slopes for larger delays indicating the recovery of a sharp density profile on the picosecond timescale. In this talk, we present the current state of our analysis including preliminary molecular dynamic simulations taking the local near-field enhancement into account.

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# Size selected sub-nm clusters in heterogenous catalysis: Exploring size, composition and support effects

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## Abstract

This presentation will provide a glimpse of recent studies devoted to the performance of supported subnanometer size clusters in select reactions.

The focus of the presentation will be on catalysts by supported monodisperse subnanometer clusters made of a handful of atoms, such as

- Cu, Pd and CuPd clusters in the oxidative dehydrogenation of cyclohexene: example of opportunities provided by atomic precision design of mono- and bimetallic clusters in fine-tuning their activity and selectivity by varying the composition of the cluster in an atom-by-atom fashion and alternating the support between oxide- and carbon-based ones.
- Cu clusters in $CO_2$ conversion to methane vs methanol: addressing the effect of support and cluster size on activity and selectivity

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# Hot Topic Talks

# Title: Size-selected nanoparticles from superfluid helium droplets

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With a special focus on the production of thin films, numerous studies have concentrated on the characteristics of nanoparticles and their application in medicine, life sciences, optics, and energy and environmental engineering. Metallic nanoparticles are of high importance in these fields due to their unique electrical, optical and plasmonic properties. Since the characteristics of nanoparticles do not only depend on their composition, as is the case for bulk materials but are also strongly governed by their size, controlling the size of nanoparticles delivers a powerful tool to further optimise their application in surface modification and nanotechnology. One goal of the presented project is the comparison of different deposition methods and the resulting influence on the nanoparticles' properties. The main focus lies on the production of size-selected nanoparticles utilising superfluid helium nanodroplets (HNDs). HNDs have in recent years proven to be an optimal cryo-matrix for the production, investigation and deposition of nanoparticles due to their ability to pick up any metallic species that can be brought into the gas phase [1, 2].

Studies of our group have recently shown that in pre-charged helium droplets, the number of charge carriers controls the growth of the nanoparticles within the droplets, as they act as individual condensation seeds [3-5]. Hence, the mean size of the nanoparticles can be controlled accurately by selecting the size and charge of the helium nanodroplets. Consecutive deposition on specific substrates then allows for surface modifications depending on the nanoparticles' elemental composition and sizes, and the thickness of the resulting nanoparticle film.

This poster presentation gives an overview of the implemented physical and experimental methods leading to the production of size-selected metallic nanoparticles in superfluid helium droplets. Additionally, an outlook on the proposed surface characterisation methods, the aspired surface modifications and on differences to conventional deposition methods is given.

This work is supported by the Austrian Science Fund, FWF (project number W1259-N27), and the state of Tirol (K-Regio project SUPREMEbyNANO).

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# A low cost, tuneable vacuum ultraviolet light source for determination of ionization potentials of clusters in molecular beam experiments

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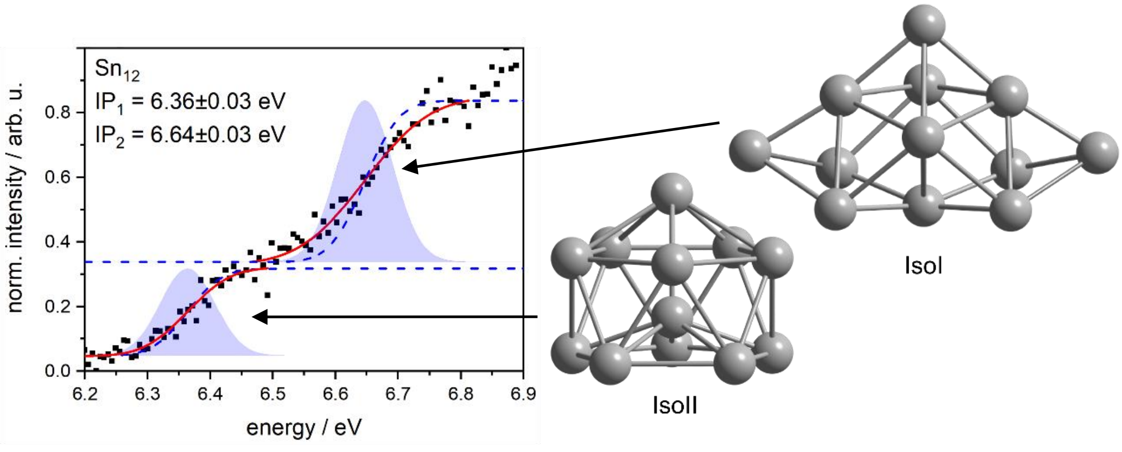
We present a low-cost alternative to complex laser setups or synchrotron light sources to determine the ionization potential of clusters in molecular beam experiments. A xenon flash lamp with a vacuum monochromator is used to reach continues energies from 2.5 eV to 8 eV. The uncertainty of this setup is mainly caused by the grating of the used monochromator, which is ±0.5 nm (±0.02 eV) to ±1 nm (±0.04 eV), depending on the cluster intensity. Additionally, the calibration of the setup is verified by measuring the ionization potential of five different atoms with great accuracy.

The ionization potentials are extracted from the measuered ion yields by fitting an error function to the experimental data. Furthermore, the ion yields are compared to theoretical calculations. The shape of the theoretically predicted[1] ion yield curves matches the experimental data very well. In addition, the onset of the theoretical values with respect to experimental ionization potentials is discussed. In this work tin clusters are investigated and their ion yield curves are measured for the first time. Ionization potentials of the $Sn_n$ clusters in eV are determined to be: 6.53, 6.69, 6.93, 6.35 and 6.36 for the clusters with n = 8 - 12. Finally, the possibility of multiple isomers present in the experiment is analysed and compared with other experiments performed in our group. [2]



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# Determination of the Adenine-Thymine binding energy

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Among the many intermolecular interactions known between biomolecules, the hydrogen bonding between the nucleobases Adenine (A) and Thymine (T) as well as between Guanine and Cytosine take a special place since they shape the DNA double strand structure. The strength of these hydrogen-bond interactions, at the center of the genetic code, is thus of significant interest for radiobiology.

We will present a study of the single photon ionization of gas phase A and T molecules and their dimers AA, AT and TT using double imaging photoelectron photoion coincidence (i2PEPICO) spectroscopy performed at the VUV beamline DESIRS of the French SOLEIL synchrotron. By evaluating the threshold photoelectron spectra (TPES) and photon energy-dependent ion kinetic energy release data we determined the threshold for photoionization and dissociative photoionization of the different clusters. By comparison with high-level ab initio calculations dealing with neutral and ionic species, we can relate the determined quantities to the binding energy of the neutral AT pair. The favourable comparison between theory and experimental results gives further credibility in theoretical predictions for similar systems.

# Influence of multilevel transitions for Quantum Coherent Diffractive Imaging

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Coherent diffractive imaging (CDI) of isolated helium nanodroplets has been successfully demonstrated with a lab-based HHG source [1] operating in the vicinity of the 1s - 2p transition of helium. To reconstruct the shape and orientation of nanoparticles, CDI experiments have so far been analyzed in terms of a classical linear response description, neglecting nonlinear quantum effects that may play an important role for resonant excitation and high intensities. We developed a density matrix-based scattering model in order to include such quantum effects in the local medium response and explore the transition from linear to non-linear CDI for the resonant scattering from Helium nanodroplets [2]. We found substantial departures from the linear response case for already experimentally reachable pulse parameters. An important next step in this approach is the implementation of additional levels next to the 1s - 2p transition. This way, we can describe multiple non-resonant transitions and study transient shifts of energy levels as well as light-induced coupling in pump-probe scenarios. Particularly, their influence on CDI experiments is currently unknown as these effects are usually measured in the gas phase in attosecond transient absorption experiments [3].

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# Reactivity of Sea Salt Clusters with Atmospherically Relevant Acids in the Gas Phase

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As we are increasingly facing the effects of global warming, identifying and studying the main climate drivers gains enormous significance. Aerosols represent one of these main climate drivers. Since more than 70% of the Earth`s surface is covered by the ocean, sea salt aerosols belong to the most important aerosols in the atmosphere, significantly affecting the climate on Earth. They contain mainly sodium chloride and water, but also a huge variety of other ions (e.g. $K^+$ or $I^-$) and organic compounds (e.g. acids). Sea salt aerosols are involved in numerous atmospheric processes such as scattering and absorption of solar radiation. They also provide condensation nuclei for cloud droplets and they exhibit complex photochemical reactions as well as a rich chemistry with atmospheric trace gases.[1]

In our experiment, gas-phase sodium chloride cluster ions are used to model chemical reactions in sea salt aerosols. Singly and doubly charged anions as well as cations are generated by electrospray ionization (ESI) and reaction kinetics are recorded via a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). The atmospherically relevant acids - formic acid and pyruvic acid - are used as reaction gas.

A sequential uptake of formic and pyruvic acid by anions as well as cations with release of HCl is observed (see Figure 1), similar to previously observed reactions of sea salt particles with sulfuric or nitric acid in the atmosphere[2] and in laboratories[3]. Furthermore, the sodium chloride cluster ions show a higher reactivity towards pyruvic than towards formic acid, which might result from the lower proton affinity of pyruvate compared to formate.

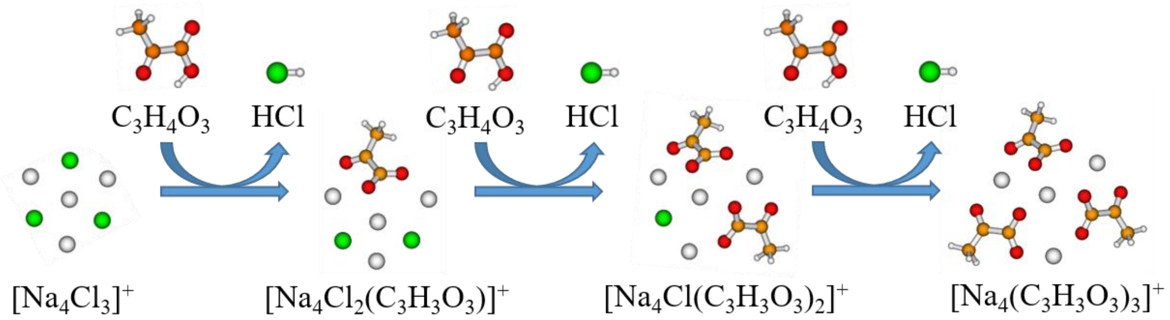

**Figure 1:** Observed reaction of $[Na_4Cl_3]^+$ with pyruvic acid.

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# Coulomb barriers 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 cluster of a specific 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].

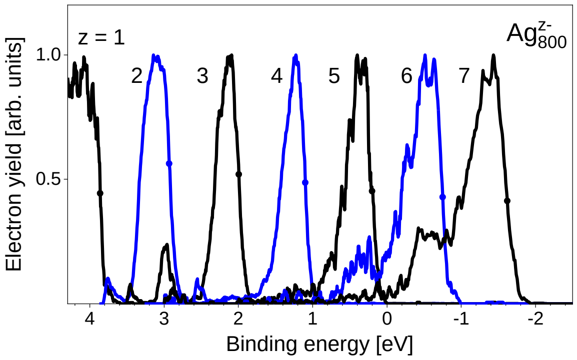

**Fig.1** Series of photoelectron spectra of silver cluster (poly-)anions with $N = 800$ atoms taken at photon energies of 5.6 eV ($z$=1), 3.9 eV ($z$=2), 3.5 eV ($z$=3) and 3.3 eV ($z$=4-7). With increasing number of excess electrons $z$, the detachment energy (dots) shifts towards negative binding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

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# Modelling of ultra-cold helium nanodroplet dynamics

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For the past 30 years, helium nano-droplets have been of particular interest to experimentalists. Indeed, this is a cold dense finite liquid environment which is an excellent matrix for spectroscopy applications, in atomic and molecular collision physics as well as in ultra cold chemistry with ability of isolating interesting reactions intermediates like HOCO in OH + CO → $CO_2$ + H or to synthesize new materials as metallic nano-wires. These phenomena are consequences of the quantum collective behaviour of helium atoms at temperature $T < 1$ K which classify helium nano-droplets as quantum liquids. In this thesis work we propose to model photo-dissociation [1] of immersed diatomic as molecular iodine, doping and rotational excitation of these droplets by using an home-made molecular dynamics developed by Pr. Marius Lewerenz, the CLUSTER code. To take the quantum nature of helium atoms into account the methodology exploits the quantum effective potential technique [2] at experimental work temperature 0.37 K.

With the photo-dissociation, an excitation above a molecular fragmentation limit leads to two possible scenarios depending one the amortised energy by the helium droplets. The first one is the fast recombination so-called ’cage effect’ [3] and the second is where photo-fragments reside in the helium bath. But with nano-meter scale of droplets a third scenario is possible with fragments leaving the cluster surrounded by a helium solvating shell. Results are shown for helium nano-droplets containing thousands atoms (2500 to 9000 He) and statistics on size and velocity of $I@He_n$ photo-fragments have been computed and are similar to experimental outcomes for analogous system $CH_3I$ [4].

According experiments using 1 fs X-ray flashes [5], the helium nano-droplets are geoids which is a clue indicating a rotation on itself as the Earth. Our code can set precise angular momentum in order to study the pattern of distortion from fission to multiple splitting. To evaluate the numbers of sub-cluster a Complete Clustering algorithm based on graph theory has been programmed exhibiting a linear complexity.

To conclude a study of xenon doping is presented where the recombination dynamics unveils a metastable state called Atkins’ snowball [6] and different patterns of aggregation as nano-crystals and nano-wires well known by experimentalists.

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# $FeAl_7O_{12}^+$: Spin state of the Fe(IV)=$O_t$ unit

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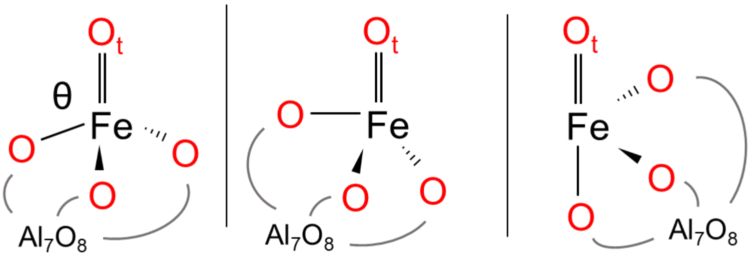
This transition metal containing cluster features a terminal oxo group that is inert with respect to $CH_4$ activation. Theoretical work suggests that the Fe spin state can influence both structure and reactivity of the cluster. However, the spin state is not directly measured in the structurally sensitive messenger-tagged-IR-PD method. The IR-PD spectrum is convincingly assigned by DFT but a completely coherent picture with respect to spin state from DFT, wavefunction methods and experiment is missing. Whereas best agreement with the measured spectrum is obtained for the triplet and singlet states, these are not the lowest energy states according to DFT, regardless of the functional used.



| | | | |
|---|---|---|---|
| 2S+1: | 1 | 3 | 5 |
| $r(FeO_t)$ | | increases with spin | |
| $\tilde{\nu}(FeO_t)$ | | decreases with spin | |
| θ/deg. | ~130 | ~100 | ~170 |

Figure 1. $FeAl_7O_{12}^+$ structural diagrams highlighting the structural variation of the terminal oxo unit with the spin state (2S+1). Also described are the trends relating to the calculated structural parameters (bond distance, r, stretching vibration, $\tilde{\nu}$, and O-Fe-$O_t$ angle, $\theta$).

# Paramagnetic Properties of Neutral Sodium Doped Solvent Clusters: Clustertreffen 2022

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The discovery of concentration-dependent colours of alkali metal-ammonia solutions [1], sparked vast interest in studying excess electrons in alkali metal solutions. They are ubiquitous in liquid-phase chemistry [2] and play an essential role in several chemical reactions [3], and biology [4]. Extensive experimental and theoretical work has been done on solvated electrons in alkali metal solutions [2] (and references therein). However, the underlying correlation effects of solvated electrons are still not well understood. While magnetic measurements have probed such effects on alkali metal solutions [5, 6], diamagnetic and paramagnetic species have not yet been identified in the bulk phase [2].

We present an experimental study of the paramagnetic properties of sodium-doped solvent clusters ($Na(Solv)_n$, n = 1-4). We choose ammonia [7], water, dimethyl ether, and methanol as solvent molecules. Via a pulsed Stern-Gerlach deflector, we measure the magnetic deflection of a neutral cluster beam. The experimental deflection is compared to molecular dynamics simulations based on the Zeeman interaction of an atom-like free spin ½ system.

The comparison of experiment and simulation reveals unperturbed magnetic properties of a spin ½ system for the smallest clusters $NaNH_3$ and $NaH_2O$. Larger clusters $Na(NH_3)_n$ (n = 2-4), $Na(H_2O)_n$ (n = 2-4), $Na(DME)_n$ (n = 1-3) and $Na(MeOH)_n$ (n =1-4), in contrast show reduced deflection compared to simulations of a spin ½ system. The deviations from a spin ½ deflection behavior are attributed to intracluster spin-relaxation processes, occurring on time scales similar to or faster than the experiment. Determining characteristic spin relaxation times for these clusters allows us to identify trends in their paramagnetic properties. The observed trends are discussed in terms of spin and rotational angular momentum interactions of thermally accessible rovibrational states.

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# Direct spectroscopic identification of reactive metal-oxygen species

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In transition metal-oxygen species, the way the oxygen atoms are bonded to the metal center is found to play a significant role in their reactivity, in view of different types of oxygen ligands and unusual oxidation states. [1,2] In particular, finding of compounds that present transition metals with unusual oxidation states or reactive oxygen species (superoxido, peroxido and oxygen centered radical) is of great scientific and technological interests, as they have key applications as oxidizing agents, catalysts, or reaction intermediates. [1,2]

Here, we use X-ray absorption spectroscopy (XAS) at the oxygen K and metal $L_3$, $M_3$ or $N_3$ edges of $[MO_n]^+$ systems (M = transition metal, n = integer) to identify the spectroscopic signatures of oxygen ligands and assign the oxidation state of the metal.[3,4] The $[MO_n]^+$ species in the gas phase are produced by argon sputtering of a metal target in the presence of oxygen. The cationic species are mass selected and accumulated in an ion trap. X-ray absorption spectra are then recorded in partial ion yield mode. [5] Our ion trap instrument is installed at the undulator beamline UE52-PGM at the Berlin synchrotron radiation facility BESSY II.

Reactive species, such as the schematically showed in Fig. 1, are analysed in stable conditions in the ground state inside the cryogenic ion trap. This method is here demonstrated to be an important tool to identify oxygen ligands, offering direct access to element specific electronic structures.

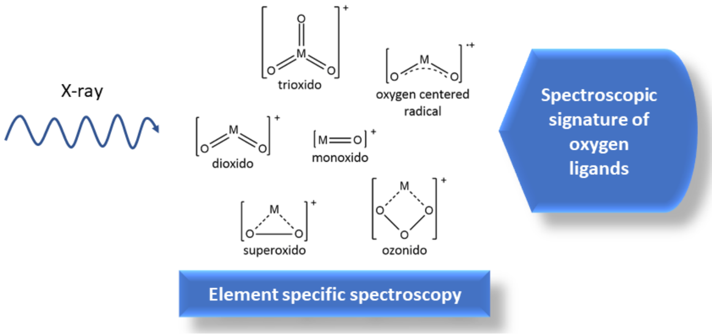

Fig. 1. Schematics of the identification of different cationic metal-oxygen species via X-ray absorption spectroscopy. M = transition metal.

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# Posters

# High-resolution photoelectron spectroscopy on deeply cold tantalum and gold clusters

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The properties of deeply cold tantalum clusters $\mathrm{Ta}_4^-$ to $\mathrm{Ta}_{23}^-$ and gold clusters $\mathrm{Au}_3^-$ to $\mathrm{Au}_{40}^-$ at 3.9 K have been investigated by high-resolution photoelectron spectroscopy.

In combination with a time-dependent potential applied to the flight tube, our magnetic bottle time-of-flight photoelectron spectrometer has a current resolution of $\Delta E/E = 0.22\%$ (5.5 meV at 2.0 eV kinetic energy for Pt ions). This is at least a factor five better than a standard magnetic bottle spectrometer and still competitive with a hemispherical energy analyzer whose drawback is a significantly worse collection efficiency. Combining the improved spectrometer with a low-jitter, short-pulse picosecond laser operating at 211 nm, we gain access to states bound up to 5.9 eV at a so far unreached precision in such a setup [1].

By this means, we are able to observe better resolved features in our spectra than ever before. Especially vibrational patterns as seen for small gold clusters shown in figure 1 on the right are of high interest. Here we identify a 17 meV spacing of states at 4.3 eV binding energy. This would not be possible if the Doppler broadening of the peaks was not compensated as seen for the previous setup.

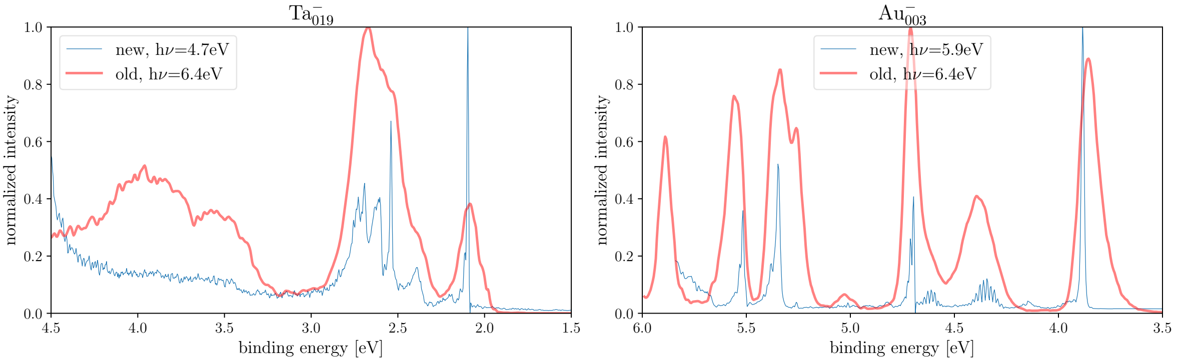

Figure 1: Expemlary photoelectron spectra of $\mathrm{Ta}_{19}^-$ and $\mathrm{Au}_3^-$: After multiple improvements in the photoelectron spectrometer system the initial peakwidth (red) has been reduced significantly which results in the emerging of vibrational structures around 4.5 eV in the blue spectrum on the right.

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# Ultrafast multidimensional spectroscopy of cluster-isolated species

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Coherent multidimensional spectroscopy (CMDS) is an extension of femtosecond pump probe spectroscopy which unifies spectroscopic information otherwise only accessible in disjunct experiments [1]. However, applying CMDS in the gas phase, in particular to dilute molecular and cluster beams, is experimentally very challenging [2]. Recently, we have overcome these challenges and have performed the first CMDS studies of doped cluster beams [2]. Our findings include ultrafast dynamics induced by the interaction with the nano-cluster environment [3] and conformational information of molecules attached to solid clusters [4], as well as the extension of our experimental methods towards the XUV spectral domain [5,6]. I will give an overview over these recent results.

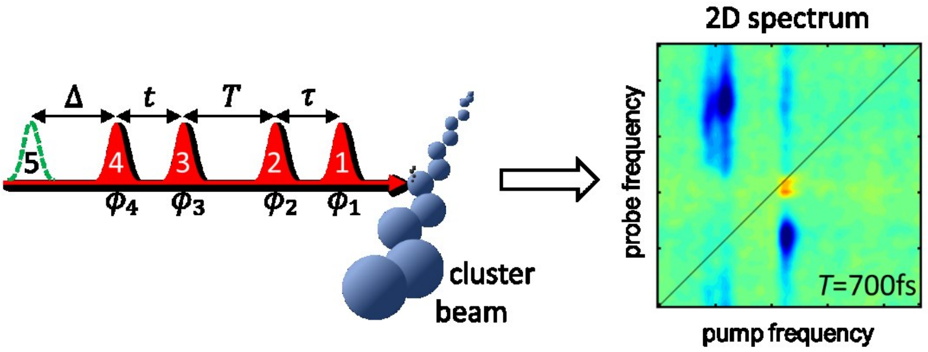

Figure: Experimental scheme. A sequence of femtosecond laser pulses excites and ionizes molecules isolated on rare gas clusters prepared in a molecular beam apparatus. Two-dimensional spectra are retrieved offering high spectro-temporal resolution and directly disclose inter-/intra-particle couplings.

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# Photo-activated processes and charge transfer in aggregates of organic molecules attached to rare gas clusters

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Collective effects like singlet fission, super-radiance, and triplet-triplet annihilation are known to strongly affect the excited state lifetimes of organic semiconductor molecules and are of utmost importance for organic optoelectronic and photovoltaic applications. Previous studies in our group addressed radiative and non-radiative decay mechanisms of the processes connected to the collective effects in aggregates of polyacenes attached to the surface of solid ultra-cold neon and argon clusters. It was observed that the fluorescence quantum yield as well as the excited singlet state's lifetime decrease substantially upon increasing the surface density of sample molecules on the rare gas clusters [1,2]. The limited temporal resolution of a few nanoseconds, due to the ns-laser excitation and photomultiplier tube detection, made disambiguation of different contributions to the lifetime reduction challenging.

These previous problems motivate the present project aimed at the enhancement of the temporal resolution of fluorescence measurements by implementing time correlated single photon counting (TCSPC). This technique allows us to cover the sub-nanosecond lifetime region currently not achievable in our cluster doping apparatus. I will present the current status of the ongoing upgrade of our setup and discuss advantages and implementational challenges of TCSPC.

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# Poster: Time-resolved imaging of laser-induced phase transitions of free silver nanoclusters

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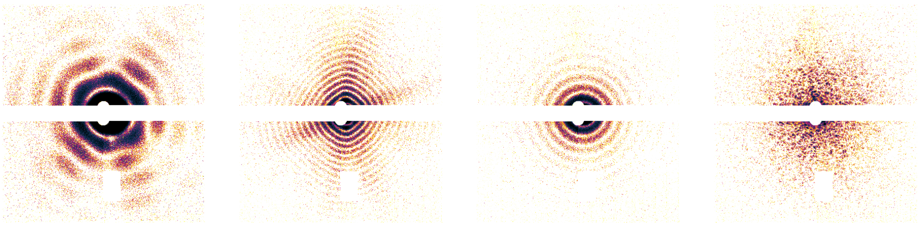
Wide angle x-ray diffraction (WAXD) has been proven a viable tool to determine the 3D structure of single metal clusters[1] in one single shot. The temporal resolution of this technique is only limited by the duration of the FEL x-ray puls (<100fs) and so far the potential to image ultrafast processes has not been combined with the shape revealing capabilities of WAXD. Such diffraction experiments on metal clusters in gas-phase are highly demanding as they require high intensities of both, clusters and X-ray beam to vanquish low cross-sections for scattering processes and low fraction of probed particles in a continuous beam. To overcome this difficulties a carefully taylored source for large clusters was set up. I will present the results of a unique experiment that used WAXD to investigate the fast structural dynamics of silver clusters induced by an optical pump laser. A combination of atomistic simulation of heated cluster dynamics, phase retrieval of small angle data and forward simulations of scattering patterns with MSFT([1]) lead to a comprehensive model for the rich dynamical behaviour optical ps pulses induce in silver nanoclusters.



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# Photodissociation of atomic clusters in a multi-reflection time-of-flight mass spectrometer

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Multi-reflection time-of-flight mass spectrometry (MR-ToF MS) is known as a powerful tool for precision mass measurements [1] and high-resolution isobar separation [2] in nuclear physics. In atomic and molecular physics, MR-ToF devices are appreciated as electrostatic ion (beam) traps [3]. At Greifswald, MR-ToF MS is employed for high-resolution investigations of atomic clusters. Specifically, in-trap photodissociation is applied for fragmentation studies.

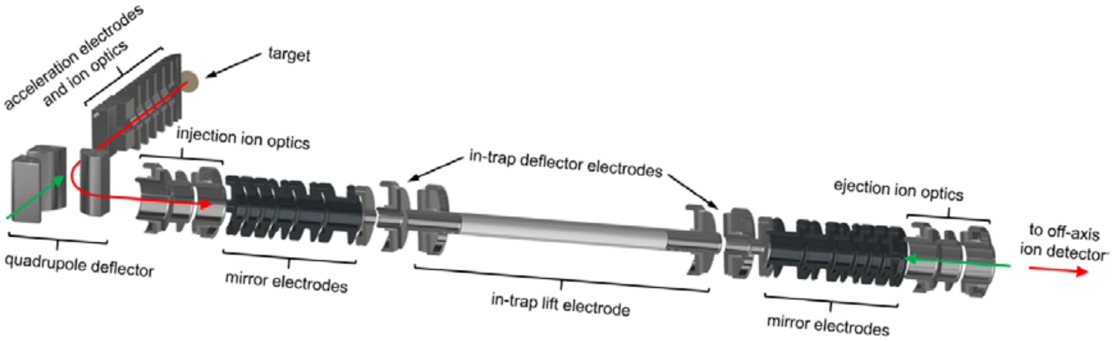

Fig. 1: Experimental setup including multi-reflection time-of-flight mass spectrometer and laser-ablation source.

Bunches of atomic clusters produced by laser ablation are captured in an MR-ToF mass spectrometer (Fig. 1). While the ions revolve between the device’s opposing electrostatic mirrors, in-trap deflector electrodes are used to clean precursor species from contaminants with high separation resolving powers. The mass-selected species of interest are excited by a laser pulse synchronized to their revolution period. Cluster dissociation leads to new (fragment) species lapping between the mirrors with distinct periods, which can be analyzed with high resolution by increasing the post-excitation storage time.

Cases of interest include the dissociation channels of various cluster species composed of a single element and the changes thereof upon doping with a single atom from a different element. If the elements are close together in mass, high resolving powers are needed to reliably select precursor species and analyze products, which are provided by the MR-ToF mass spectrometer [4].

The MR-ToF principle also allows time-resolved studies due to the periodic nature of the ions’ flight path. Fragments that are continuously produced, while a bunch of excited precursors is revolving between the mirrors, are monitored to determine the dissociation rate as a function of delay time after the excitation [5]. Comparing these time-dependent rates with a statistical model yields information on the cluster ensemble’s temperature or the species’ threshold energy.

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# First steps to solvation of iron contact ion pairs studied by x-ray absorption spectroscopy

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The interaction between a metal center and its ligands is of great interest in a variety of fields, as this interaction influences stability and reactivity of complexes. In bulk solution of dissolved metal salts, the surrounding solvation shell can influence charge transfer and bond properties of formed contact ion pairs. To understand the influence of polar solvents on the metal-ligand interaction we study the changes in the element-specific electronic structure of $[FeOH]^+(H_2O)_n$ and $[FeCl]^+(H_2O)_n$ (n=0-3) with x-ray absorption spectroscopy in the gas phase. As expected, x-ray spectra of the iron L-edge of both species show only little change when successively attaching $H_2O$ molecules. However, the oxygen K-edge suggests an increasing influence of $H_2O$ molecules on the OH ligand, as signatures assigned to the metal ligand bond dominating the spectrum are superseded by features assigned to bonds in $H_2O$ molecules. For the $[FeCl]^+(H_2O)_n$ species changes of the oxygen K-edge are less prominent in comparison to the hydroxide species, as expected. However, the changes in the spectra of the chloride species series still suggest valence interactions not exclusively between the $H_2O$ molecules. These preliminary findings are part of an ongoing study.

# Infrared Photodissociation Spectroscopy of $[Cu(H_2O)(H_2)_2]^+$ and its Isotopologues

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Dihydrogen complexation by metal cations has been extensively studied in the context of the $H_2$ activation.[1] More recently, it has been suggested that dihydrogen adsorption at metal sites, in particular Cu(I), in metal-organic framework materials can be exploited for $H_2/D_2$ separation.[2] In the present study, our focus lies on the spectroscopic characterization of mass-selected $[Cu(H_2O)(H_2)_2]^+$ complexes and its isotopologues to investigate the influence of microhydration on the isotope effects in metal centre dihydrogen binding under isolated conditions in gas phase.

The vibrational spectra of these complexes are measured in the spectral range from 2400 to 4400 $cm^{-1}$ by way of infrared photodissociation (IRPD) spectroscopy in a cryogenic ion trap maintained at 8 K and 13 K for $H_2$ and $D_2$, respectively. Structures and band assignments are determined by comparison of the IRPD spectra to anharmonic vibrational spectra (VPT2/MP2/def2-TZVPP). The symmetric and antisymmetric OH stretching fundamentals ($\nu$(OH)) of $[Cu(H_2O)(H_2)_2]^+$ and $[Cu(H_2O)(D_2)_2]^+$ are observed at 3627 $cm^{-1}$ and 3700 $cm^{-1}$, respectively, only slightly higher in energy (+4 $cm^{-1}$) than in the IRPD spectra of $[Cu(H_2O)(Ar)_2]^+$.[3] Three bands observed at 2567, 2783 and 3125 $cm^{-1}$ are assigned to the D-D stretching fundamental as well as two D-D stretching combination bands involving $Cu^+$-($D_2$) waging and symmetric stretching excitation. The latter bands are interpreted as an indication for larger amplitude motion of the dihydrogen ligands. The corresponding, strongly red-shifted $H_2$ bands are not observed, because of the spectral overlap with the OH stretching bands of $H_2O$. Excitation of similar vibrational modes is observed in the IRPD spectra of $[Cu(D_2O)(H_2)_2]^+$ and $[Cu(D_2O)(D_2)_2]^+$, including the $H_2$ stretching fundamental at 3566 $cm^{-1}$ as well as two combination bands at 3734 $cm^{-1}$ and 4322 $cm^{-1}$. The observed frequency ratio $\nu_{(H_2)}/\nu_{(D_2)}$ of these three bands is slightly smaller than the one estimated from the reduced masses of the isolated isotopes (1.41). Moreover, the measured $H_2/D_2$ frequencies are about 160/80 $cm^{-1}$ lower than those observed for $[Cu(H_2)_4]^+$ and $[Cu(D_2)_4]^+$, indicating a stronger bonding to the microhydrated Cu(I) centre.

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# Title: C–N coupling in the gas phase reaction of $V_3C+$ with $N_2$ investigated by cryogenic ion vibrational action spectroscopy

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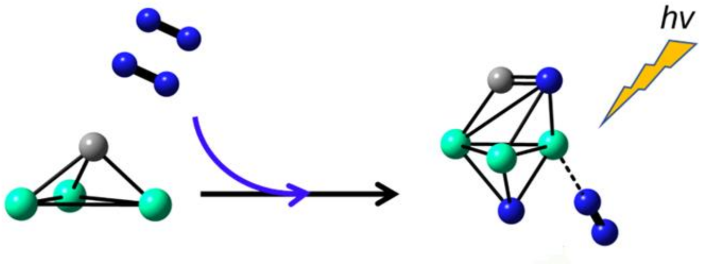
N-containing organic compounds are considered as important building blocks for natural products, pharmaceuticals, and multifunctional materials. The common route to form C−N bonds is based on ammonia ($NH_3$) which is mainly produced by the Haber-Bosch process associated with harsh reaction conditions, high energy consumption and greenhouse gas emission. Therefore, $N_2$ activation and the development of alternative routes for C-N bond formation under mild conditions is a fundamental challenge in organic chemistry.

Here, we study the gas-phase reaction between $V_3C+$ and $N_2$ using a combination of ion trap mass spectrometry, vibrational action spectroscopy and density functional theory calculations. A cryogenic ion trap triple mass spectrometer with access to the free electron laser (FEL) of the Fritz Haber Institute (FHI) in Berlin is used to characterize the structures of the reactant and the product ions. The adsorption of $N_2$ to the pyramidal $V_3C+$ leads to the spontaneous cleavage of the N≡N triple bond and subsequent covalent C−N coupling. Adduct complexes with C-N units in singlet spin state are formed exclusively, which is unambiguously confirmed by the infrared signatures of the C=N stretching modes as well as V–N (interstitial nitrides form) stretching modes. To the best of our knowledge, this work represents the first example of a spectroscopic study on the activation and dissociation of $N_2$ followed by C-N coupling by gas phase metal clusters.



# Growth of clusters on $Al_2O_3||Ni_3Al(111)$ thin film by annealing a sub monolayer amount of bismuth.- STM and UPS studies of clusters size and shift of the $5d_{5/2}$ bismuth core level state.

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For bismuth quantum mechanical effects appear earlier than in common metals with decreasing dimension (from bulk over thin films to clusters), such as semimetallic-to-semiconductor transition in thin films with the thickness of a few tens nm [1] or superconductivity at a few Kelvin in bismuth clusters [2] (in contrast 0.5 mK for bulk bismuth [3]). Nevertheless, all these effects are highly controversial and not yet fully understood. For example, the substrate or embedding matrix seems to play an important role and must not be left out of the discussion [4]. Therefore, further experiments with different combinations of substrates and adsorbates are necessary.

A thin layer of $Al_2O_3$ film grown under controlled conditions in ultra-high vacuum by controlled oxidation on $Ni_3Al(111)$ shows large well-structured terraces in scanning tunneling microscopy (STM) images. Two structures become visible: the so-called network structure at tunneling voltage of 3.2V and the dot structure at 2.0V. The dot structure acts as a nucleation pattern in the growth of metallic clusters by atomic vapor deposition [5]. We present here the results of our experiments for bismuth clusters with ultraviolet photoelectron spectroscopy (UPS) and STM in ultra-high vacuum at low temperatures. The clusters are formed in sub monolayer regime by the gradual increase of coverage and/or temperature. We study the growth of the bismuth clusters (STM) and the resulting decrease of binding energy of the $5d_{5/2}$ core level state of bismuth (UPS HeII) in sub monolayer regime.

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# Targeting high symmetry structures in structure predictions

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Ground state structures found in nature are in many cases of high symmetry. But structure prediction methods typically render only a small fraction of high symmetry structures. Especially for large crystalline unit cells there are many low energy defect structures. For this reason methods have been developed where either preferentially high symmetry structures are used as input or where the whole structural search is done within a certain symmetry group. In both cases it is necessary to specify the correct symmetry group beforehand. However it can in general not be predicted which symmetry group is the correct one leading to the ground state. For this reason we introduce a potential energy biasing scheme that favors symmetry and where it is not necessary to specify any symmetry group beforehand. On this biased potential energy surface, high symmetry structures will be found much faster than on an unbiased surface and independently of the symmetry group to which they belong. For our two test cases, a $C_{60}$ fullerene and bulk silicon carbide, we get a speedups of 25 and 63. In our data we also find a clear correlation between the similarity of the atomic environments and the energy. In low energy structures all the atoms of a species tend to have similar environments.

# Water clusters bridge the attosecond electronic dynamics from isolated molecules to the liquid phase

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Attosecond (1 as = $10^{-18}$ s) is the time scale of electronic processes, e.g. photoionization. Our group has previously measured the time delays between gaseous [2] and liquid [3] water using the reconstruction of attosecond beating by interference of two-photon transitions (RABBIT) [1], where a relative time delay of 69 ± 20 as between the liquid and gas phase was found. Recently, our group reported the experimental and theoretical study of photoionization delays in size-resolved water clusters using ion-electron coincidence measurements [4]. As shown in Fig. 1, the time delay increases as a function of the cluster size from $(H_2O)_1$ to $(H_2O)_4$, after which it remains approximately constant up to $(H_2O)_{6\sim7}$ and approaches the measured value in the liquid phase. We attribute this trend to that the molecular orbitals delocalize from $(H_2O)_1$ to $(H_2O)_4$, but partially localize as the cluster continues to grow. Our study of water clusters reveals the transition of the electronic structures from isolated molecules to the liquid water.

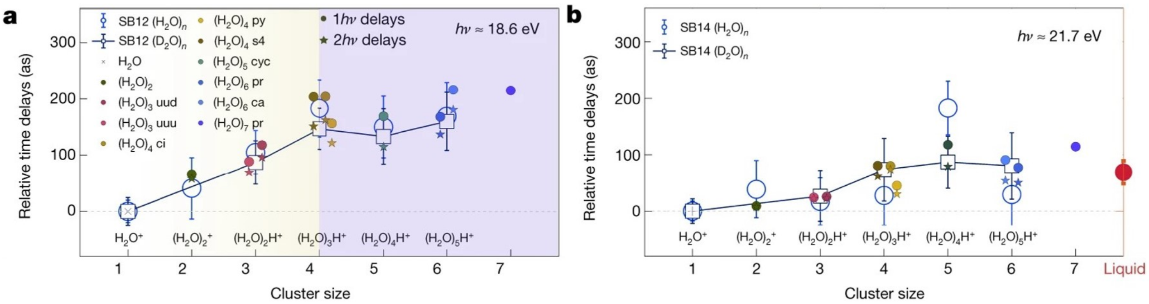

Figure 1: Relative photoionization time delays of the $1b_1$ band of $H_2O$ or $D_2O$ clusters referenced to the monomer at SB12 (a) and SB14 (b) in comparison to the calculation at kinetic energies of 6.0 eV and 9.1 eV, respectively. The filled circles and stars stand for the one-photon and two-photon delay calculations, respectively. The liquid-water time delay shown in (b) was reported in ref. [3]. The figure is adapted from ref. [4].

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# Probing the Vibrational Wave Packet Dynamics of Mass-selected Neutral Silver Clusters

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Obtaining molecular vibrations for neutral metal clusters in far-IR terahertz spectral range remains challenging, due to difficulties in mass-selecting neutral molecules and a lack of easily accessible and widely wavelength-tunable far infrared light sources. We report our recent setup of a new instrument focusing on studying vibrational wave packet dynamics of selected neutral metal clusters and their 'vibrational spectra' in far-IR range. Here we show first results on neutral silver dimer $Ag_2$ and tetramer $Ag_4$, benchmark systems for small neutral metal clusters, and unambiguously acquire their wave packet dynamics within 100 ps delay time ($\Delta t$) and 'vibrational spectra' in $20 - 300$ cm$^{-1}$ frequency range. We combine femtosecond pump-probe spectroscopy employing the NeNePo (negative-neutral-positive) excitation scheme with a cryogenic ion-trap tandem mass spectrometer. A linear polarized ultrafast pump pulse ($30 - 40$ fs) is used to produce a vibrational wave packet of the neutral cluster by photodetachment from the corresponding anion. The vibrational coherence is then probed using a second ultrafast pulse ($30 - 40$ fs), which ionizes the neutral cluster. The mass-selected cation yield as a function of the delay time ($\Delta t$) between the two femtosecond laser pulses yields the fs-NeNePo spectrum. The frequency analysis with a resolution down to about 0.5 cm$^{-1}$ ($\Delta t > 60$ ps) by using Fourier transform of transient traces shows vibrational frequencies of the silver clusters. The reviving period of the wave packet allows determining vibrational anharmonicities in frequency domain. The fragmentation channels and temperature effect of the wave packet dynamics are discussed.

# Electronic Spectroscopy of Helium Tagged Ionic Polycyclic Aromatic Hydrocarbons

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Messenger spectroscopy is a powerful tool in the search for carriers of diffuse interstellar bands (DIBs). Attaching only weakly interacting messengers to the molecule of interest ensures that the induced spectral shift is small. In our experimental setup we dope multiply charged helium nanodroplets (HNDs) with polycyclic aromatic hydrocarbons (PAHs) and collide them with a stainless-steel surface to obtain helium decorated ions that we detect with a time-of-flight mass spectrometer (TOF-MS). The helium tagged ions interact with a tunable pulsed laser. Absorption spectra of the ions are obtained by tracing the change in the ion yield between mass spectra that were recorded after laser illumination and mass spectra without laser illumination for different wavelengths. We determine the spectral shift for different numbers of attached helium atoms and compare our laboratory absorption spectra to astronomical observations. [1]

This work was supported by the Austrian Science Fund, FWF, via project I4130.

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# Elementary Processes of cryo cooled Transition Metal Clusters: Cations versus Anions

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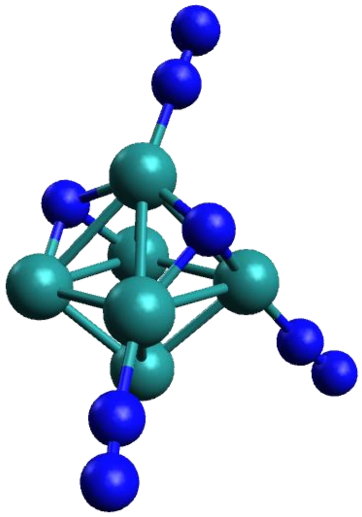
Isolated Transition Metal Clusters (TMCs) serve as model systems for the study of elementary processes in heterogeneous catalysis, and they may help to unravel the mutual interdependencies of their surface morphologies and charge states with molecular activation pathways and product yields and structures.

Our experiment utilizes atomically precise cationic and anionic TMCs in conjunction with two consecutive ion traps each of which is held at cryo conditions, below 30 K, and which allow for independent admission of prospective adsorbate molecules at will [1]. The recording of isothermal uptake kinetics is augmented by IR-photodissociation (IRPD) spectroscopy of selected TMC adsorbate complexes. We augment our experiments by high level quantum chemical modelling, and we gain an enhanced level of insights through the combination of these methods, in some favourable cases with magnetic characterization on top.



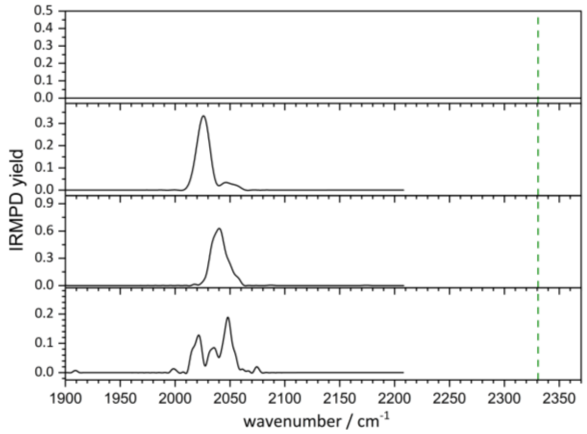


**Figure 1:** Calculated structure of $[Ru_6(N_2)_4]^-$ (left side); IRPD spectra of $[Ru_6(N_2)m]^-$ (m=1-4) from 1900 $cm^{-1}$ to 2210 $cm^{-1}$ at 26 K (right side).

Our current presentation will focus on the adsorption, spontaneous activation and co-adsorption of molecular Nitrogen ($N_2$) and molecular Hydrogen ($H_2$). We extend and augment previous investigations of Nickel, Iron, Cobalt, Rhodium, Ruthenium and Tantalum TMC cations and their adsorbate complexes, where we have found remarkable dependencies of adsorbate yields and structures on the cluster morphologies. [2,3] Recently, we were able to show the precise reaction process of the $N_2$ adsorption to Tantalum clusters and the subsequent activation and the formation of Tantalum nitrides. [4] Our latest work focusses on according processes with anionic TMCs, and we will highlight outstanding examples that reveal strong influences of charge states.

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# Characterization results of coherent femtosecond spectroscopy on molecular and cluster beam samples

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Two-dimensional electronic spectroscopy (2DES) is a powerful method to investigate many ultrafast processes in matter, for example singlet fission or charge and energy transfer. The simultaneous high resolution in the time and energy domain of 2DES spectra suggests particularly interesting studies on singlet fission [1]. Singlet fission has been conventionally investigated in condensed or liquid phase samples [2]. In our setup we have recently extended 2DES to cold samples isolated in the gas phase [3,4]. Molecular samples are isolated in superfluid and solid rare-gas clusters, which provide cryogenic temperatures as well as weak perturbation by the environment [5]. Results on the characterization of the current experimental conditions based on mass spectroscopy by electron impact ionization and wave-packet interferometry will be presented along first results on fluorescence yields of possible candidate systems for singlet fission studies.

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# Inter-molecular $H_2$-roaming processes in (2-amino)ethanol

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The trihydrogen cation ($H_3^+$) is among the most abundant and simplest triatomic cations in the universe. It plays a crucial role in interstellar gas-phase chemistry as it facilitates molecule-forming chemical reactions. We experimentally investigated the competition between pathways leading to $H_3^+$ formation in ethanol and 2-aminoethanol molecules and clusters using time-resolved XUV-UV pump-probe spectroscopy. While ionization of ammonia clusters, which we have studied before at FERMI [1], leads to $H_3^+$ production by intermolecular proton transfer, $H_3^+$ formation in doubly-ionized alcohol molecules is due to intramolecular $H_2$ roaming [2]. The XUV-induced dynamics in aminoethanol molecules and clusters is expected to feature competing $H_3^+$ formation pathways involving both $H_2$-roaming and proton transfer. As aminoethanol is similar to important head groups of phospholipids found in biological membranes, these studies add to the understanding of radiation damage of biological tissue.

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# Light controlled electronic properties of graphene decorated with surface modified clusters

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The classic approach towards the design of information processing systems involves miniaturisation, increase in power efficiency and parallelisation of processes. Since all these paths have certain limitations, numerous groups' research efforts aim to utilise new phenomena, paradigms and unconventional approaches. It also translates into the intensification of studies on new materials – including nanostructures and nanocomposites [1, 2]. One of the considered candidates here is graphene, which electronic properties can be easily tuned through the application of the potential bias, but also through the introduction of different modifiers [3]. If light-absorbing entities are used, the properties of such a hybrid may be further affected (dynamically) with the use of irradiation. This feature makes graphene-based systems a suitable platform for designing optoelectronic information processing devices [4].

The main idea I would like to present is the modification of graphene monolayers with metallic and semiconducting nanoparticles of precisely selected size/composition and binary systems – nanoparticles with adsorbed molecules – as well as the influence of such modification on the electronic and transport properties of the hybrid. I will also present how these may be dynamically tuned with light allowing the design of optoelectronic elements, including switches, logic gates, sensors and neuromimetic devices.

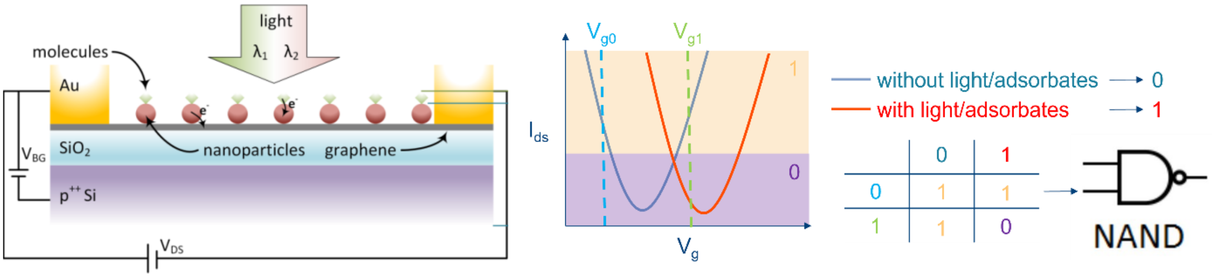

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**Fig. 1.** Schematic of a graphene field effect transistor modified with nanoparticles (red spheres) and adsorbed molecules (green diamonds). The system's interaction with the light is depicted. A possible implementation of the binary logic gate (NAND) is shown on the right side.

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# The $Au_2^+$ System And Its Interaction With Ligands

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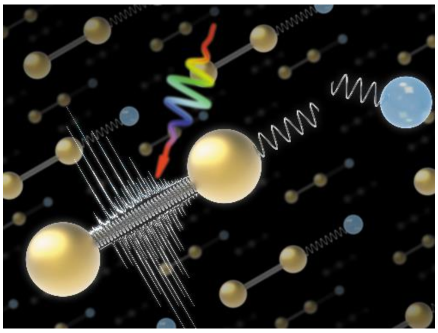
An understanding of the interaction of gold with ligands at the molecular level is of fundamental interest in inorganic and organometallic chemistry. In particular, the interaction of excited states of metal clusters with ligands is important because these states may interact differently with the ligands than the ground state, opening up new possibilities for molecular activation and/or reactivity changes that could be selectively switched on or off by light.



We will present the optical spectrum of $Au_2^+$[1] as well as the optical spectra of $Au_2^+L$ (L = Ar[2], $N_2$[3], $N_2O$[3]) compared to quantum-chemical calculations. The observed vibronic transitions allow for determination of relevant excitation, binding and vibrational energies as well as anharmonicity constants.

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# Coulomb explosion of 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].

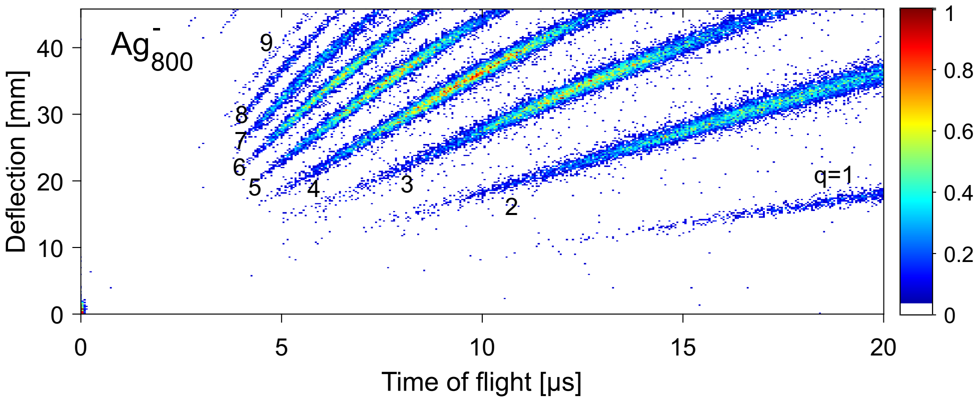

Figure 1: Time-deflection histograms of the Coulomb explosion of size-selected silver clusters ($Ag^-_{800}$) after exposure to strong femtosecond laser fields ($I_L = 4 \cdot 10^{14}\,\mathrm{W/cm^2}$). The different atomic charge states and their corresponding recoil energy distribution are indicated by diagonal lines in the time-deflection histogram.

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# Dynamics of photoexcited cesium atoms attached to helium nanodroplets: Clustertreffen 2022

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The low-perturbative character of superfluid He exploited in He isolation spectroscopy is challenged for electronically excited or ionized dopants. The electronic excitation and ionization of a dopant attached to a He droplet can trigger numerous dynamics. For example, ejection of electronically excited atoms due to the repulsive electron-He interaction can take place along with electronic relaxation induced by the He environment [1]. Additionally, He-dopant exciplexes can form due to pairwise He-dopant interaction [2, 3]. We present an experimental study of the dynamics of photoexcited Cs atoms attached to He droplets [4]. The timescales for desorption and solvation as well as CsHe exciplex formation are determined for the 6p states of Cs using velocity-map-imaging spectroscopy and ion-time-of-flight spectrometry in a femtosecond pump probe setup. Our findings are compared to results of density-functional theory simulations published earlier [5] and to previous studies on Cs and Rb atoms attached to He nanodroplets [6-8].

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# Blackbody Infrared Radiative Dissociation (BIRD) Masurements and Master Equation Modelling of Hydrated Carbonate and Peroxicarbonate Radical Anions

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If molecular clusters are stored for several seconds in ultra-high vacuum conditions, and not irradiated with any laser, they are still exposed to ambient blackbody radiation. Absorption of blackbody infrared photons leads to vibrational excitation and eventually to dissociation of the cluster. It is a well-established technique to use blackbody infrared radiative dissociation (BIRD) kinetics measured at different temperatures, along with master equation modelling, for the determination of binding energies. However, master equation modelling is particularly difficult for hydrated clusters, as water molecules can move easily around the central ion, and several low-lying isomers are populated.

In our work, we investigate the hydrated clusters $CO_3^{\bullet-}(H_2O)_{1,2}$ and $CO_4^{\bullet-}(H_2O)_{1,2}$. These molecular clusters are found in the lower region of the ionosphere and in the troposphere and play a role in reactions relevant to atmospheric chemistry. In the experimental part of our work, we measure BIRD kinetics at different temperatures. Therefore, a laser vaporization source is used to generate the molecular clusters. Afterwards, the ion clusters are guided to a Fourier Transformation Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer. The temperature of the ICR cell is regulated with a variable supply of liquid nitrogen or warm water, allowing measurements of BIRD kinetics at different temperatures. In the theoretical part of this work, we model the BIRD process with Master Equation Modelling. To describe the population occurring in the experiment better, we take into account several low-lying isomers that are populated at the experimental temperatures. Comparison with high-level *ab initio* calculations shows for $CO_3^{\bullet-}(H_2O)_{1,2}$ that including all isomers in the model leads to a higher accuracy in the determined water binding energies. First evaluations suggest that this is also the case for $CO_4^{\bullet-}(H_2O)_{1,2}$. For $CO_4^{\bullet-}(H_2O)_2$, we observe loss of $CO_2$ competing with the water loss channel. Along with the growing number of local minima, this increases the complexity of the master equation model.

# Imaging the Morphology of Xenon in Argon Clusters

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Rare gas clusters are an ideal testbed in theory and experiments to investigate the interaction of intense light with matter. They are in gas phase with no possibility of energy dissipation and simply bound via Van-der-Waals forces. When they are photoionized by an intense laser pulse first electrons will leave the cluster, while later created electrons potentially will be trapped as quasi-free electrons by the building positive Coulomb potential of the cluster. The energy deposited into the cluster will force it to disintegrate accompanied by complex relaxation processes, e.g., electron-ion recombination. These dynamics, however, strongly differ radially. To discriminate bulk and surface dynamics heterogeneous core-shell clusters are often applied [1]. In the typical picture the lighter element forms a shell around the core of the heavier element. Since in imaging experiments on pristine rare gas clusters many non-spherical clusters were observed [2], it is questionable if heterogeneous rare gas clusters indeed form a perfect core-shell structure with a sharp core-shell transition.

The intense and short laser pulses from X-ray free-electron lasers (FEL) allow to resolve the structure of a single nanoparticle within a single shot with the method of coherent diffractive imaging (CDI). We performed a CDI experiment at the new Maloja endstation at SwissFEL to clarify the structure of xenon in argon clusters. The clusters were

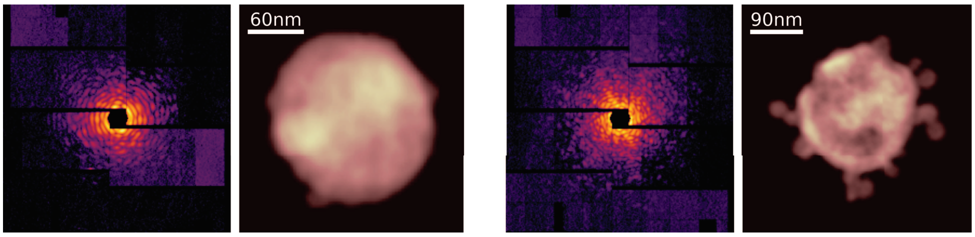

Figure 1: Diffraction patterns and their reconstructions of xenon in argon clusters at a photon energy of around 700 eV. Left: 2 % Xe in Ar gas at 70 bar and 160 K, right: 5 % Xe in Ar gas at 20 bar and 140 K.

produced by expansion of xenon in argon gas mixtures ranging from 0.1 % to 10% Xe at different gas pressures and temperatures. We used complementing photon energies to resolve both, the outer structure of the clusters and the inner spatial distribution of the two materials. The high-resolution reconstructions show many different cluster shapes from spherical clusters to very complex architectures (see Fig. 1), including shapes we have never seen before, even not for the pure Ar clusters, which were also studied as a reference. So far it remains challenging to clearly assign the Xe and Ar parts in the reconstructions, but the analysis is still ongoing. We will give an insight and discuss the morphology.

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# Construction of an Electron Optic for Synchrotron-Photoelectron-Spectroscopy on Stored Ions

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We present the development and construction of a new apparatus for cluster research at the BESSY II synchrotron at the Helmholtz Centre in Berlin (HZB). In this work, special attention is paid to the simulation and development of an electron optics which pursues the goal of focusing photoelectrons into an Hemispherical Energy Analyser (HSA). A magnetron sputter source provides the clusters for the apparatus. The setup allows mass selection with a Quadrupole Mass Spectrometer (QMS) before the clusters are stored. The trap is a linear Radio Frequency (RF) trap. Photoelectrons are emitted through interaction with the synchrotron beam. These are forced out of the trap with a magnetic field using the principle of the magnetic bottle on parallel trajectories in one direction. In this way, sufficient intensities can be achieved. The photoelectrons then pass through an magnetic guiding field and experience a deflection from the synchrotron axis. Subsequently, the photoelectrons are directed and focused by electric ion optics so that the photoelectrons can be guided into the HSA as magnetic field-free as possible. The schematics of the setup, including simulated photoelectron trajectories is shown in Figure 1. In this poster, simulations are presented that compare different concepts for guiding fields, deflection, and electron optics. Electro-magnetic deflection turns out to be the most effective method. Simulations also showed the behaviour of photoelectrons from being emitted in the trap to the HSA so that the functionality of the setup could be confirmed by the simulations. We also present the detailed design of the setup of the whole experiment. Currently it is under construction. In the course of this year, the first tests will be carried out on the structure.

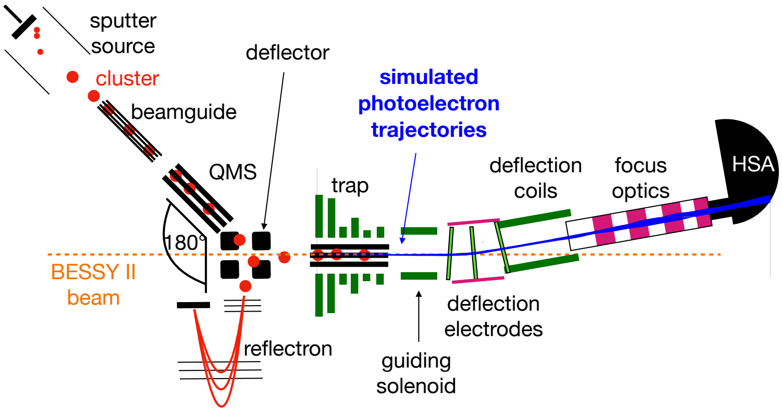

Figure 1: Schematics of the full setup with both the cluster and the photoelectron path. The simulated photoelectron trajectories were added to the sketch in blue.

# Adsorption of Helium on Ionic PAHs: Influence of Hydrocarbon Structure on the Microsolvation Pattern

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The adsorption of helium atoms on ionic polycyclic aromatic hydrocarbons (PAHs) was studied by combining helium nanodroplet mass spectrometry with classic and quantum computational methods. The obtained time-of-flight mass spectra revealed unique structural features in the ion abundance as a function of the number of attached helium atoms for ionic PAHs. Magic numbers, anomalies seen in the ion abundance, indicate more stable structures of the ionized PAH-He complexes. Path integral molecular dynamic simulations were used with a polarizable potential to determine underlying adsorption patterns of helium around the studied PAH ions and are in good general agreement with experimental data. The calculated structures of helium-PAH complexes indicates that the solvated ionic PAH structure greatly influences the microsolvation pattern of adsorbed helium atoms. Solvation shell closures are indicated by stepwise drops in the ion yield, correlating with specific numbers of attached helium atoms depending on the PAH ion. Helium atoms were shown to preferentially adsorb onto small and planar polyaromatic solutes like anthracene and phenanthrene following the $\sqrt{3} \times \sqrt{3}$ commensurate pattern common for graphitic surfaces [1], compared with a $1 \times 1$ commensurate phase exhibited by larger carbonaceous molecules like corannulene, coronene and fullerenes [2,3].

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# Optical Absorption and Photodissociation Properties of $Si_2O_2^+$

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Interstellar dust is mainly µm-sized silicate particles. Their origin and formation processes remain poorly understood. To date, only one possible precursor, molecular SiO, has been identified in a circumstellar disk [1].
Based on experimental data (spectroscopy and mass spectrometry) and quantum chemical calculations, we present absorption and dissociation properties of $Si_2O_2^+$ clusters which are potential intermediates between the circumstellar diatomic SiO molecule and the silicate grains observed in the interstellar medium. The spectra are the first optical absorption spectra of $Si_2O_2^+$ cations (and any other $Si_nO_m^+$) and generated by photodissociation of mass-selected ions produced in a laser vaporization source [2]. The experimental results are compared with TD-DFT calculations and discussed in an astrophysical context.

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# Angle resolved photoelectron spectra of $\mathrm{Cu}_n^-$, $n = 91 - 95$ and $\mathrm{Ag}_m^-$, $m = 91 - 92$: premature shell closing

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Angle resolved spectroscopy provides an important test of the theoretical description of clusters since these spectra carry more information than the bare energy levels. The anisotropy of photoelectron spectra for example depends on the angular momentum state. The cluster anions are produced in a magnetron sputter source, cooled to 7 K and enter a time-of-flight spectrometer for mass measurement and selection. Afterwards electrons are detached by linear polarised laser light and projected onto a MCP detector in a velocity map imaging setup.

The presented analysis utilises the additional information from angle resolved spectroscopy to gain a better understanding of photoelectron spectra, that have not been predicted by theory so far. For $\mathrm{Cu}_{91}^-$ an electronic shell closing is expected. Previous experiments [1, 2], however, have shown an additional peak associated to the occupation of the next orbital, that would be predicted for $\mathrm{Cu}_{92}^-$. Based on the angle resolved measurements an f-type character can be assigned to the additional state.

Furthermore, for lower lying levels a curve of the anisotropy parameter $\beta$ with two minima is found, while most $\beta$ curves have shown only a single minimum so far.

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