Frontiers in Size-Selected Cluster Research: Bridging the Gap

705. WE-Heraeus-Seminar

29 September - 04 October 2019
at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de.

Aims and scope of the 705. WE-Heraeus-Seminar:

This seminar brings together international researchers in the field of cluster science, in general, and those that work with gaseous or deposited size-selected clusters, in particular. The central goal is to highlight recent advances in the field, to discuss ways to bridge interdisciplinary gaps and to define new research frontiers. Topics will include the atomistic understanding of heterogeneous catalysis, the properties of water and ion solvation, probing and modelling chiral clusters and the design and production of functional cluster materials. The conference will also focus on the development of new experimental and theoretical methodologies, for example those related to using novel radiation sources like X-ray free electron lasers.

The conference is organized in a Gordon-conference style with three plenary lectures, sixteen invited talks and twelve hot-topic presentations with ample time for discussion in between presentations and free time during the early afternoons.

Scientific Organizers:

Prof. Knut Asmis	Universität Leipzig, Germany E-mail: knut.asmis@uni-leipzig.de
Prof. Bernd von Issendorff	Universität Freiburg, Germany E-mail: bernd.von.issendorff@uni-freiburg.de
Prof. Gereon Niedner-Schatteburg	Universität Kaiserslautern, Germany E-mail: gns@chemie.uni-kl.de

Program

Program

Sunday, 29 September 2019

16:00 – 20:00	Registration	
18:00	*BUFFET SUPPER and get-together*	
19:30 – 19:40	Scientific organizers	**Welcome words**
19:40 – 20:40	Manfred Kappes	**Resolving clusters**

Monday, 30 September 2019

08:00	*BREAKFAST*	
09:00 – 09:40	Andreas Wolf	**Molecular and cluster ions in a cryogenic storage ring – from internal cooling to merged-beam electron collisions**
09:40 – 10:20	Michael Martins	**Supported clusters in the view of X-rays**
10:20 – 10:40	*COFFEE BREAK*	
10:40 – 11:20	Gert von Helden	**Spectroscopy of clusters in clusters**
11:20 – 11:40	Rico Mayro Tanyag	**Nanostructures in superfluid helium droplets**
11:40 – 12:00	Michael Kelbg	**Temporal development of a laser-induced helium nanoplasma measured through auger emission and above-threshold ionization**
12:00 – 12:10	**Conference Photo** (in the front of the lecture hall)	
12:10	*LUNCH*	

Program

Monday, 30 September 2019

15:30 – 16:10	**Poster Pitch 1**	
16:10 – 16:30	*COFFEE BREAK*	
16:30 – 18:00	**Posters**	
18:00	*DINNER*	
19:30-20:10	Oliver Kühn	**Vibronic spectroscopy with classical trajectories**
20:10 – 20:30	David Müller	**Optical cryogenic ion spectroscopy of metalated flavin complexes**
20:30	**Posters**	

Tuesday, 01 October 2019

08:00	*BREAKFAST*	
09:00 – 09:40	Karl-Heinz Meiwes-Broer	**Charging, de-charging and detonation of metal clusters**
09:40 – 10:20	Lukas Bruder	**Coherent nonlinear spectroscopy in the gas phase**
10:20 – 10:40	*COFFEE BREAK*	
10:40 – 11:20	Ewald Janssens	**Altering geometry, stability, and chemical reactivity of gold cluster cations by palladium doping**
11:20 – 11:40	Vlasta Bonačić-Koutecký	**Tuning optical and catalytic properties of ligated noble metal clusters by synergistic role of metallic and organic subunits**
11:40 – 12:00	Lutz Schweikhard	**Tandem high-resolution multi-reflection time-of flight mass spectrometry for photodissociation studies of (doped) atomic clusters in an electrostatic ion beam trap**
12:00	*LUNCH*	

Program

Tuesday, 01 October 2019

15:30 – 16:10	**Poster Pitch 2**	
16:10 – 16:30	*COFFEE BREAK*	
16:30 – 18:00	**Posters**	
18:00	*DINNER*	
19:30-20:10	Michael Farnik	**Uptake and reactions of molecules on clusters and free nanoparticles in molecular beams**
20:10 – 20:30	Martina Lippe	**Direct observation of cluster size distributions during nucleation in pulsed Laval expansions**
20:30	**Posters**	

Program

Wednesday, 02 October 2019

08:00	*BREAKFAST*	
09:00 – 09:15	Stefan Jorda	**About the Wilhelm and Else Heraeus Foundation**
09:15 – 09:55	Martin Beyer	**The many faces of the hydrated electron**
09:55 – 10:15	Arghya Chakraborty	**Closer look at salt dissolution: Microhydration of LiX_2^- (X= Cl^-, I^-) studied by cryogenic ion trap vibrational spectroscopy**
10:15 – 10:35	Annika Steiner	**Strong temperature and size effects in iron-nitrogen interactions**
10:35 – 11:00	*COFFEE BREAK*	
11:00 – 11:40	Jonas Warneke	**Chemistry of electrophilic anions**
11:40 – 12:20	André Fielicke	**Size selective vibrational spectroscopy of neutral (boron) clusters**
12:20	*LUNCH*	
15:00	**Excursion** (Visit of a historic wine cellar and wine tasting)	
18:00	*DINNER*	
19:30-20:30	Daniel Neumark	**Studies of clusters using high resolution negative ion photoelectron spectroscopy**
20:30	**Posters**	

Program

Thursday, 03 October 2019

08:00	*BREAKFAST*	
09:00 – 09:40	Stefan Vajda	**Catalysis by mono- and bimetallic sub-nm clusters**
09:40 – 10:20	Barbara Lechner	**Can we control the charge state and structural dynamics of supported clusters?**
10:20 – 10:40	*COFFEE BREAK*	
10:40 – 11:20	Melanie Schnell	**Deciphering the structures and intermolecular interactions of weakly bound clusters using highresolution rotational spectroscopy**
11:20 – 11:40	Joost Bakker	**The adsorption of NO onto group IX transition metal cluster ions**
11:40 – 12:00	Andrey Lyalin	**Theoretical design of nanocatalysts for oxygen reduction and hydrogen evolution reactions**
12:00	*LUNCH*	

Program

Thursday, 03 October 2019

15:30 – 16:10	Bernd von Issendorff	**Structure and dynamics of metal clusters: old and new tales**
16:10 – 16:30	*COFFEE BREAK*	
16:30 – 17:10	Sandra Lang	**Water oxidation on free calcium-manganese-oxide clusters: gas phase model systems for the catalytically active center of photosystem ii**
17:10 – 17:30	Alexander Kononov	**Fullerene arrangement by vapor deposition on a well-ordered thin Al_2O_3 film grown on Ni_3Al (111) crystal**
17:30 – 17:50	Christian van der Linde	**Electron catalyzed reactions involving $CO_3^{\bullet -}(H_2O)_n$**
18:00	*HERAEUS DINNER* *(social event with cold & warm buffet with complimentary drinks)*	
20:00 – 21:00	Ludger Wöste	**45 years of research on metal clusters**
21:00	Scientific organizers	**Closing words**

Friday, 04 October 2019

08:00	*BREAKFAST*

Departure

Posters

Posters

Fabian Bär	**Photoelectron spectroscopy of size-selected metal clusters at FLASH 2**
Aristeidis Baloglou	**Gas-phase investigations of thiomolybdate nanoclusters as model catalysts for the hydrogen evolution reaction**
Martin Beck	**Probing electron correlation effects in sodium-ammonia clusters**
Thorsten Bernhardt	**Ultrafast photochemistry on oxide surfaces and supported metal clusters**
Kevin Bertrang	**Charge-transfer in the system Pt_n/SiO_2/metal and its effects on the activity of ethylene hydrogenation**
Friedrich Buttenberg	**IR spectroscopy of amantadine-water cluster cations: First step of microhydration**
Wolfgang Christen Paul Saftien	**Development of a piezoelectric detector for determining particle density and mean cluster size in a pulsed supersonic molecular beam**
Sreekanta Debnath	**Structural Properties of $[(Al_2O_3)_n(FeO)]^+$ Clusters studied by infared photodissociation spectroscopy**
Simon Dold	**Imaging the melting of silver nanoclusters in free flight**
Otto Dopfer	**Aromatic charge resonance interaction probed by infrared spectroscopy**
Moritz Eder	**Platinum and Nickel clusters on TiO_2 in heterogeneous photocatalysis**
Max Flach	**Probing electronic properties of cationic metal halides with x-ray absorption spectroscopy**

Posters

Max Grellmann	**Joining microfluidics with infrared photodissociation spectroscopy: Structural characterization of transient intermediates**
Andrea Heilrath	**Proton buffered explosion of methane clusters**
Matthias Hillenkamp	**Structural, plasmonic and magnetic properties of physically prepared iron-silver nanoparticles**
Heinz Hövel	**Mass selected iron clusters on thin oxide films**
Norman Iwe	**Coulomb interaction in the photoemission of polyanionic silver clusters**
Alexander Jankowski	**Electron and photon interactions with size- and charge-state-selected anionic tin clusters**
Juraj Jasik	**Infrared spectroscopy of gas phase subnanometer particles**
Sebastian Kaiser	**How do Pd clusters move in the pore of a hexagonal boron nitride mesh?**
Matthias Klein	**Cryo kinetics and IR spectroscopy of N_2 adsorbed to size selected Tantalum clusters**
Katharina Kolatzki	**Setup and characterization of a Helium liquid jet for diffractive imaging experiments**
Bennet Krebs	**Comparison of electron and ion emission from xenon cluster induced ignition of Helium nanodroplets**
Uwe Kreibig	**Plasmonic information transport in monocrystalline pentagonal ag wires**
Stephen Leach	**A cationic oxide cluster with Fe-oxo. Insight from theory and experiment**

Posters

Chin Lee	**Gas-liquid interface studies by molecular beam scattering on water surfaces**
Nikita Levin	**Catalytic coupling of methane on $Ta_8O_2^+$**
Marius Lewerenz Roland Panzou	**Simulation of dissociation and caging inside Helium clusters**
Yake Li	**Experimental identification of the active site in the heteronuclear reaction (VPO_4^+/C_2H_4) by gas-phase IR spectroscopy**
Oksana Linnik	**Some aspects of nitrogen incorporation in metal ions' co-doped titania films used as catalysts in heterogeneous photocatalysis**
Olga Lushchikova	**IR action spectroscopy of Cu clusters with small-molecule adsorbed**
Rupert Michiels	**Probing plasma evolution and atomic recombination in XUV-induced nanoplasma in ammonia clusters**
Maximilian Münst	**Infrared spectroscopy of $CO_3^{\bullet-}(H_2O)_{1,2}$ and $CO_4^{\bullet-}(H_2O)_{1,2}$**
Felix Nuesslein	**Delayed electron detachment and fragmentation of laser-excited metal cluster anions**
Nitish Pal	**Acid solvation versus dissociation at ultracold temperatures: sequence matters**
Tobias Pascher	**Electronic and geometric structure of copper formate clusters probed by IRMPD and UV/Vis spectroscopy**
Sebastian Pedalino	**Long-baseline universal matter-wave interferometry**
Kai Mario Pollow	**Measurement of optical spectra of astrophysically relevant Si-bearing molecules**

Posters

Klara Raspe	**New setup for core-level and valence-band photoelectron spectroscopy of mass-selected metal clusters at FLASH**
Mahboobeh Ravankhah	**Temperature-induced processes for FexNi1-x nanoparticles on surfaces**
Oxana Sander	**Guided ion beam hydration energies of $FeOH^+(H_2O)_n$, n = 1 - 4, in comparison with theory**
Sascha Schaller	**Spectroscopy of neutral boron clusters using tunable VUV generated by 4-wave mixing**
Sonja Schmahl	**Isolation and characterization of the cyanoformate anion by infrared photodissociation spectroscopy**
Viviane Schmidt	**Studying the dynamics and decay channels of C_4O^- in the electrostatic cryogenic storage ring**
Sergii Snegir	**Assembling of gold nanoparticles: main gaps to be filled**
Carl Frederic Ußling	**Small silver clusters on porphyrin templates**
Lukas Weise	**Angle resolved photoelectron spectra of small copper clusters**
Frank Wensink	**Towards IR action spectroscopic characterization of CO_2 hydrogenation over metal clusters**
Henning Windeck	**Theoretical DFT study on the structure and reactivity of selected Cobalt Aluminate cluster ions**
Michael Zabel	**Temporal development of a fully ionized Helium nanoplasma**

Abstracts of Talks

(in chronological order)

Resolving Clusters

Manfred M. Kappes[1,2]

[1] *Institute of Physical Chemistry*
[2] *Institute of Nanotechnology, KIT, Karlsruhe, Germany*

Progress in the cluster field continues to rely on experimental method development which provides ever better resolution of size-dependent structure and dynamics. Often highly sensitive methods originally developed to probe ligand-free clusters in isolation have subsequently also significantly advanced other areas of chemistry. High resolution mass spectrometry, ion mobility spectrometry and ion trapping based structure determination methods are cases in point. I will illustrate this by showing how new and systematically improved experimental methods have led to advances in understanding of s^1-electron metal clusters (from bare alkali clusters to ligand stabilized coinage metal clusters) and carbon clusters (from chains to fullerenes and back).

References

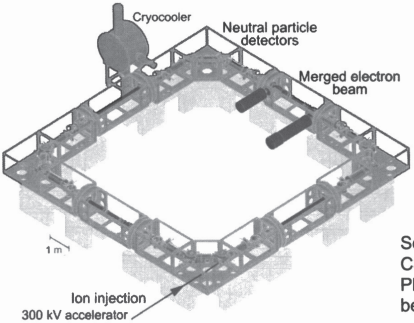
[1] M. M. Kappes, R. Kunz and E. Schumacher, Chem. Phys. Lett.,**91**, 413 (1982)
[2] P. Weis, F. Hennrich, R. Fischer, E. K. Schneider, M. Neumaier and M. M. Kappes, PCCP *Advance Article*, DOI: 10.1039/C9CP03326B (2019)

Molecular and cluster ions in a cryogenic storage ring – from internal cooling to merged-beam electron collisions

Andreas Wolf[1]
for the CSR team

[1]*Max-Planck-Institut für Kernphysik, Heidelberg, Germany*

The cryogenic electrostatic storage ring CSR has been set up to study atomic, molecular and cluster ions stored at kinetic energies between 20 and 300 keV and their interactions with photons, cold electrons and neutral particles. The vacuum chambers and the beam optics elements are cryogenic yielding a black-body radiation level with an equivalent temperature of the order of 10 K. The CSR has demonstrated ion beam lifetimes of 1000 s and more [1] over which the high-velocity ions move in vacuum in the absence of buffer gas. During storage, internal cooling can take place by radiation or – as recently observed – also by collisions in the merged, velocity-matched electron beam. We discuss the tools that are available for probing the internal cooling of molecular and cluster ions under these conditions and recently achieved experimental results. These include rotational-state selective rates for dissociative recombination in low-energy electron collisions [2] and photodetachment studies of anionic molecules and clusters [3,4].



Schematic view of the cryogenic storage ring CSR [1] at the Max Planck Institute for Nuclear Physics, Heidelberg, and the merged electron beam device. The ring circumference is 35 m.

References

[1] R. von Hahn et al., Rev. Sci. Instrum. **87**, 063115 (2016)
[2] O. Novotný et al., Science 10.1126/science.aax5921 (2019)
[3] C. Meyer et al., Phys. Rev. Lett. **119**, 023202 (2017)
[4] C. Breitenfeldt et al., Phys. Rev. Lett. **120**, 253001 (2018)

Supported clusters in the view of X-rays

M. Martins

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X-rays from modern 3. generation synchrotron radiation sources offer highly brilliant radiation from the soft to hard x-ray regime. They are ideal tools to study different properties of supported, mass selected clusters such as the magnetic or geometric structure using their element and site specificity. In this contribution examples on the noncollinear spin structure of alloy clusters and the geometric structure of small clusters in the few atom limit will be presented.

Storing information in magnetic structures is in general done by assigning the magnetic orientation of a small domain, e.g., up and down to the logical 0 and 1. Using this approach the lower size limit for magnetic nano structures are some 10 nm, as smaller particles are getting super-paramagnetic. In recent years skyrmions have attracted some interest, as they might enable a different way to store information in magnetic structures. Skyrmions are topologically protected, small noncollinear magnetic structures, which show a rather high stability.

To understand the properties of these nano structures and a possible design of new types of storage devices, the knowledge of the underlying noncollinear magnetic coupling is essential. Clusters are now systems, where this effect can be studied atom by atom. Using x-ray magnetic circular dichroism (XMCD) we have investigated the magnetic properties of different alloy clusters in the few atom limit. We see strong variations of the magnetic moments depending on alloying and the size of the clusters [1]. Using in particular angular resolved XMCD we can measure in very small clusters the orientation of the magnetic moment of the individual atoms, which gives a direct picture of the noncollinear coupling.

An important question in all these experiments on supported, mass selected clusters is the exact shape of the clusters. To solve this questions we have performed a feasibility study using grazing incidence small angle x-ray scattering (GISAXS) using highly brilliant x-rays from the storage ring PETRA III [2]. Here, the general shape of the clusters can be estimated. The limitations of the method will be discussed and an outlook on the possibilities of ultimate storage rings will be given.

References

[1] T. Beeck et al., New J.Phys **18**, 113007 (2016)
[2] D. Chekrygina et al., Scientific reports **8**, 12371 (2018)

Spectroscopy of Clusters in Clusters

Daniel Thomas, Eike Mucha, Gerard Meijer and Gert von Helden

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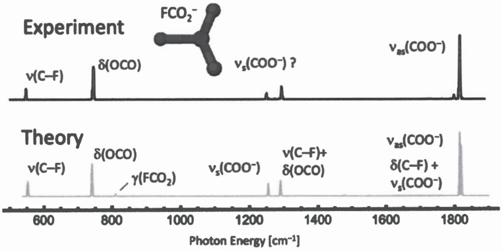
Helium droplets can pick up mass/charge selected cluster ions from an ion trap and the doped droplets can be investigated using optical spectroscopy. We use that technique to investigate cations and anions ranging in size from ions containing only a few ions up to mass/charge selected protein ions containing several thousand atoms.

Here, we will present recent results on small mass/charge selected anions, specifically products from reactions between fluoride (F^-) ions with CO_2 and H_2O. It is observed that in the ion source region of our mass spectrometer, FCO_2^- as well as an ion that is heavier by the mass of one H_2O molecule are readily formed. Those ions can be mass/charge selected, stored in an ion trap and be picked up by helium droplets.

The doped droplets are irradiated by tunable IR light from the FHI free electron laser. Upon the resonant absorption of IR photons, the helium atoms are evaporated and/or the ion is ejected from the droplet. Monitoring the ion yield as a function of IR wavenumber gives the IR spectrum of the ion. The experimental spectra can be compared to theoretically predicted spectra. In the case of the FO_2^- ion, narrow lines with a width close to the linewidth of the FEL can be observed (see Figure). With the help of high-level theory, those lines can be assigned to stem from various modes, including some Fermi resonances. The spectrum and the structure of the ion 18 amu higher in mass are surprising and will be discussed.



Further, results from ion mobility as well as spectroscopic investigations of polyoxometalate clusters will be presented. There, a transition from one- to two- to three-dimensional can be observed.

References

[1] D. A. Thomas, E. Mucha, S. Gewinner, W. Schöllkopf, G. Meijer, G. von Helden, J. Chem. Phys. Lett. **9**, 2305-2310 (2018)

[2] D. A. Thomas, E. Mucha, M. Lettow, G. Meijer, M. Rossi, G. von Helden, J. Am. Chem. Soc. **141**, 5815-5823 (2019)

Nanostructures in superfluid helium droplets

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A. Hoffmann[1], M. Ilchen[5], M. Izquierdo[5], C. Jones[3], K. Kolatzki[1],
B. Krebs[9], B. Kruse[9], M. Kuster[5], B. Langbehn[2], J. Mahl[4], T. Mazza[5],
K.-H. Meiwes-Broer[9], J. Montaño[5], V. Music[5], G. Noffz[2],
S. O'Connell[3], W. Pang[3], D. Rivas[5], C. Saladrigas[4], D. Schlosser[10],
P. Schmidt[5], F. Seel[2], L. Seiffert[9], B. Senfftleben[1], H. Stapelfeldt[7],
L. Strüder[10], J. Tiggesbäumker[9], B. Toulson[4], D. Verma[3], H. Yousef[5],
M. Zabel[9], P. Walter[6], M. Meyer[5], Y. Ovcharenko[5], C. Bostedt[6],
O. Gessner[4], D. Rupp[1,2], A. Vilesov[3], and T. Möller[2]

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Helium droplets are unique media for particle growth and allow the formation of far-from-equilibrium nanostructures, which are otherwise difficult or impossible to grow in other isolation matrices. In this contribution, we report on x-ray coherent diffractive imaging of dopant particles grown in free, single, rotating, superfluid helium-4 droplets with diameters ranging from 150 to 2000 nm. The data presented here were collected from experiments conducted at the Linac Coherent Light Source and at the European X-ray Free Electron Laser. The different dopants employed for the experiments have different interatomic or intermolecular forces of attraction: for van der Waals interaction, xenon was used as the dopant; for metallic bonding, silver; for hydrogen bonding, water; and finally for dipole-dipole interaction between polar molecules, acetonitrile and iodomethane. In addition to the nature of the dopant's chemical bonding, the instantaneous positions of the dopants are influenced by the interplay between the two-fluid components of liquid helium (the normal viscous and the superfluid components), and by the presence of quantized vortices in the superfluid component. Ultimately, it is the intention of these measurements to develop a model for dopant aggregation in helium droplets and the possibility of controlling their growth.

Temporal Development of a Laser-Induced Helium Nanoplasma Measured through Auger Emission and Above-Threshold Ionization

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Femtosecond pump-probe electron and ion spectroscopy is applied to study the long-term development of strong-field induced helium nanoplasmas up to the nanosecond timescale. Quasi-free electrons, bound by the deep confining mean field potential, are elevated towards the vacuum level in the nanoplasma expansion. Subsequent electron recombination gives rise to transitions between He^+ states, resulting in autoionization [1] (see Figure 1). The time-resolved analysis of the energy transfer to quasi-free electrons reveals a transient depletion of the Auger emission and allows for a temporal mapping of the distribution of delocalized electrons in the developing mean field. Furthermore, we introduce transient above-threshold ionization (ATI) as a diagnostic tool to trace the recombination of delocalized electrons near the vacuum-level into highly excited Rydberg states. This process is reflected in the temporal evolution of the yields of He^+ and He^{2+}. Thus, the development of the electron distribution in the nanoplasma mean field potential can be traced by monitoring the multiple features observed in the emission spectra.

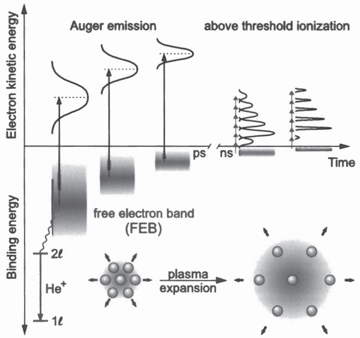

Figure 1: Schematic representation of the temporal development of the free electron band in the expanding nanoplasma. With time, the electron energy distribution follows the shift of the nanoplasma potential towards the vacuum level and simultaneously narrows in energy. Bound-bound transitions like $(1\ell \leftarrow 2\ell)$ in He^+ trigger the emission of Auger electrons from the free electrons band.

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[1] M. Kelbg, M. Zabel, B. Krebs, L. Kazak, K.-H. Meiwes-Broer, and J. Tiggesbäumker. Auger emission from the coulomb explosion of helium nanoplasmas. *J. Chem. Phys.*, 150(20):204302, 2019.

Vibronic Spectroscopy with Classical Trajectories

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Vibronic spectra provide a fingerprint of the coupling between electronic and nuclear degrees of freedom and thus between electronic structure and molecular geometry. Well resolved vibronic spectra of small to medium-sized molecules can be obtained, e.g., for gas phase or liquid helium droplet conditions. The standard analysis assumes shifted harmonic potentials leading to a superposition of Franck-Condon progressions with the electron-vibrational coupling being quantified by the Huang-Rhys factors of the different vibrational modes. Perfoming accurate quantum dynamical simulations including effects, e.g., due to Dushinsky rotation, anharmonicity, and nonadiabatic transitions, is a demanding task, if not impossible for larger molecules. Therefore, it is tempting to resort to classical trajectory-based approaches having a more favorable scaling with system size. Surprisingly, it turns out that reproducing a well-resolved vibronic progression provides a serious challenge for trajectory-based methods even at the level of a single vibrational coordinate. The link between molecular dynamics trajectories and vibronic spectra is provided by time correlation functions of the energy gap between the considered electronic states [1,2]. To incorporate quantum effects in the sampling of the nuclear distribution the imaginary-time path integral approach can be used [3]. At this point one normally has to decide on which state the distribution of nuclear coordinates is sampled. Unfortunately, common choices such as ground or excited state or the averaged classical limit yield rather different results, none of them being very accurate. Therefore, a modified correlation function has been proposed, which is capable of incorporating information on the potential energy surfaces of both involved states simultaneously [3]. This leads to a considerable improvement, but not yet perfect agreement. Alternatively, a modification of the so-called Matsubara ansatz has been suggested and shown to yield an almost quantitative agreement with exact quantum dynamics results at least for the one-dimensional test cases considered [4].

References

[1] S. Karsten, S. D. Ivanov, S. G. Aziz, S. I. Bokarev, O. Kühn, J. Phys. Chem. Lett. **8**, 992 (2017)

[2] S. Karsten, S. D. Ivanov, S. G. Aziz, S. I. Bokarev, O. Kühn, J. Chem. Phys. **146**, 224203 (2017)

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Optical cryogenic ion spectroscopy of metalated flavin complexes

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Flavins are a large family of yellow dye biomolecules. The tricyclic heteroaromatic isoalloxazine chromophore can absorb light in a broad spectral range (UV-VIS). Therefore, flavins are utilized by nature for light-dependent processes. Most studies on flavins were performed in the condensed phase. The optical properties of flavins depend strongly on their surrounding environment, such as metalation, (de-)protonation, and solvation. Consequently, gas-phase spectroscopy under controlled microsolvation conditions is required to reveal the intrinsic photochemical properties. However, most gas-phase studies were performed at room temperature, yielding only broad and unresolved spectra with only limited information [1].

We systematically investigate flavins with increasing complexity ranging from lumichrome (LC, R=H) and lumiflavin (LF, R=CH_3) to riboflavin (RF, vitamin B_2, R=ribityl). To this end, we record photodissociation spectra in the visible range (VISPD) of large biomolecules trapped in a cryogenic 22-pole (4-300 K) [2]. After optical excitation, the parent ion and its fragments are detected simultaneously in a time-of-flight mass spectrometer. The combined approach of high resolution gas phase spectroscopy with TD-DFT coupled to Franck-Condon simulations provides precise information about structural, vibrational and electronic properties. Here, we present high resolution vibronic VISPD spectra (S1 - S0) of M^+LF (M=Li-Cs) of the O2 isomer, which is predicted by DFT calculations and IRMPD measurements [3]. This work shows the strong dependency on the site and type of metalation on the optical properties [4]. Future research will concentrate on even larger and biologically more relevant flavins, such as FMN and FAD.

References

[1] M. Stockett, Phys. Chem. Chem. Phys.**19**, 25829 (2017)
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Charging, de-charging and detonation of metal clusters

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Photoelectron spectroscopy (PES) is a mature method to explore also faint details oft the cluster's electronic structure. Thousands of spectra have been taken in the past decades round the world, many of them led – mostly in conjunction with theoretical work – to a detailed picture of cluster properties, e.g. [1]. On the other hand, however, the majority of the spectra is not understood yet. Notwithstanding, even today PES pops up in highly topical cluster studies such as strong laser excitations, emission from clusters embedded in Helium droplets, or experiments at free electron lasers.

E.g., femtosecond laser impact on clusters may lead to emission of electrons in the 1000 eV range, which is driven and can be controlled by the light-induced polarization field of the collective electron motion. [2] Upon the resulting detonation (Coulomb explosion) highly charged ions escape with energies up to MeV. In the later stage electrons recombine into Rydberg states of the highly charged ions. [3] Scattering ultrashort free electron laser light pulses in the 100 eV range laser from clusters establishes a unique way to image their geometrical structure. [4] Most recently we prepared size selected silver clusters with a defined and adjustable number of excess electrons. Here a technique is used in which a digital trap allows to successively attach electrons to already negatively charged clusters [5]. From PES with different excitation wavelengths on such *poly anions* details of the Coulomb barrier are extracted, which is a unique signature of those systems.

The talk will start with few fundamentals of PES, add some historical remarks and eventually tackle experiments with single- and multi-photon laser excitation.

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Coherent nonlinear spectroscopy in the gas phase

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Coherent nonlinear spectroscopy techniques are powerful tools to selectively probe specific features of the system's ultrafast nonlinear response, e.g. molecular couplings, inhomogeneities and energy transport [1]. These experiments have been mostly limited to the condensed phase due to insufficient sensitivity to probe dilute gas phase samples. Based on precise timing and phase control of the optical excitation pulses, we have recently managed to established several coherent nonlinear spectroscopy methods in the gas phase. Our examples comprise of two-dimensional electronic spectroscopy of doped helium nanodroplet samples (Fig. 1) [2], the detection of weak couplings in extremely dilute samples [3] and quantum interference experiments with phase shaped XUV pulses [4].

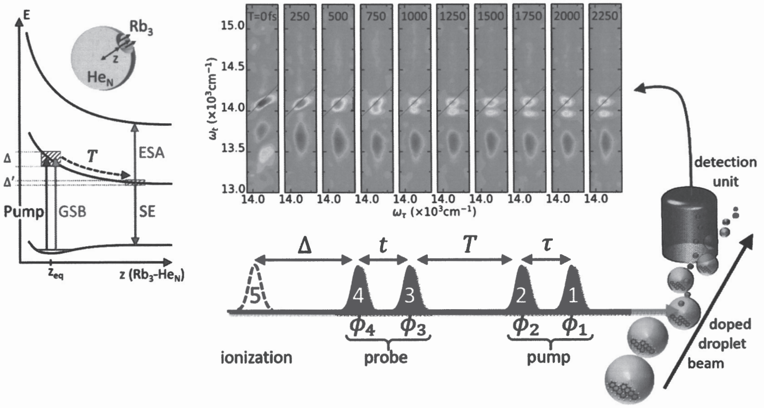

Figure 1: In 2D spectroscopy the interaction with multiple femotsecond laser pulses reveals the time evolution upon electronic excitation. The plotted sections of the 2D maps reveal the dynamic Stokes shift induced by the droplet-molecule interaction.

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Altering geometry, stability, and chemical reactivity of gold cluster cations by palladium doping

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Small gold clusters are unique objects with fascinating features, such as surprisingly large sizes up to which they are two-dimensional [1]. Their properties are strongly size-dependent, as reflected in electronic-structure related features including optical response, relative stability, and chemical reactivity [2]. The introduction of a dopant atom is an effective way to modify the properties of the gold clusters [3,4,5]. From a fundamental point of view, palladium is an interesting dopant atom, since its ground-state electronic configuration has a closed 4d shell and no valence s electrons, in contrast to gold with a closed 5d shell and one 6s valence electron. In this work, we analyse how doping Au_n^+ ($n \leq 11$) with Pd modifies the geometry and electronic structure, and how this determines the stability of the clusters. Structural information is obtained by far infrared multiple photon dissociation (IRMPD) spectroscopy and density functional theory calculations (DFT), whereas photofragmentation experiments are used to investigate the size dependent stabilities [6]. The influence of Pd doping on the bonding between cationic gold clusters and CO is studied by low-pressure collision cell reactivity measurements in combination with IRMPD and DFT calculations [7].

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TUNING OPTICAL AND CATALYTIC PROPERTIES OF LIGATED NOBLE METAL CLUSTERS BY SYNERGISTIC ROLE OF METALLIC AND ORGANIC SUBUNITS

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Theoretical investigation of the linear and nonlinear optical properties of thiolate-protected low nuclearity noble metal clusters will be first presented. In this context theoretical approaches for reliable description of two-photon absorption spectra will be addressed. Goal is to design species exhibiting strong one-photon and/or two-photon absorption and emission in the UV-VIS spectral range. We will show that the optical properties can be tuned by creating the appropriate interplay between electronic excitations within the cluster core and selected prototype of ligands. Comparison with available experimental results will be discussed. We conclude that such low nuclearity protected noble metal clusters are promising for bio-labelling and imaging as alternatives to the standard fluorescent probes such as quantum dots or organic dyes.

Second, we present our study of small coinage metal hydride ligated nanoclusters showing their capability to release the hydrogen. We propose the concept of synergistic role of ligand and substrate in catalysis on example of formic acid. This new catalyst neatly fits into a zeolite which does not perturb reactivity, thus providing a unique example on how "heterogenization" of a homogenous catalyst for the selective catalyzed extrusion of carbon dioxide from formic acid can be achieved, with important application in hydrogen storage and in situ generation of H_2. The above results motivated us to investigate the selective decomposition of formic acid driven by highly porous aluminum based metal-organic framework in order to design new materials for the heterogenous catalysis.

Thus, we illustrated that unique optical and reactivity properties of ligated noble metal clusters which can be tuned by appropriate interplay between metallic and organic subunits have significant potential for different applications.

Tandem high-resolution multi-reflection time-of flight mass spectrometry for photodissociation studies of (doped) atomic clusters in an electrostatic ion beam trap

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Metal clusters are produced by laser ablation and stored in a multi-reflection time-of-flight (MR-ToF) mass spectrometer, also known as electrostatic ion beam trap (EIBT). The storage time exceeds several hundred milliseconds and, due to long flight paths folded into a drift section between two electrostatic ion mirrors, these traps – recently introduced for the study of masses of exotic nuclides [1] – attain high mass resolving powers ($R>10^5$) for mass analysis [2] as well as separation [3].

For the present experiments, precursor clusters are selected on a scale of single atomic mass units and irradiated with laser pulses at their turn-around point, leading to all fragment ions remaining stored in the trap and exhibiting identical kinetic energies. Photodissociation spectra were recorded for both the cations and anions of pure bismuth clusters Bi_n (n = 2 through 19) [1], from which their decay pathways have been deduced. In the meantime, for compound-cluster precursors Bi_nPb_m, the photofragment branching ratios has been studied. To this end, tandem MR-ToF mass measurements, $(\text{MR-ToF MS})^2$, have been introduced which employ the full capacity of the MR-ToF method for both precursor selection and product analysis. Additionally, delayed dissociation of clusters has been found with time-resolved investigations by evaluating the fragment-ion signals with respect to decays during the revolution periods after the photoexcitation pulse.

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Uptake and reactions of molecules on clusters and free nanoparticles in molecular beams

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A versatile, universal, cluster beam apparatus (CLUB) in Prague allows for a large variety of different experiments with clusters:[1] pickup experiments,[2] mass spectrometry after photoionization, electron ionization[3] and electron attachment,[4,5] photodissociation and velocity map imaging including IR-UV pump-probe experiments,[6] etc. The talk will concentrate on different heterogeneous clusters and nanoparticles generated in coexpansion of different gases and/or by pickup of different molecules on clusters, and we observe reactions in the clusters triggered by photons and/or electrons of different energies, figure 1, in relevance to atmospheric chemistry, astrochemistry and surface assisted technologically relevant processes such as FEBID (focussed electron beam deposition) or nanocatalysis.

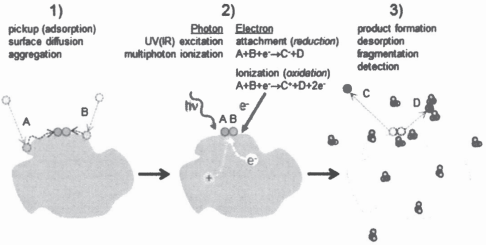

Figure 1 Photon and/or electron triggered chemistry on free nanoparticles.

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Direct observation of cluster size distributions during nucleation in pulsed Laval expansions

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We have recently reported gas phase nucleation studies of water [1]. The clusters were formed in the uniform postnozzle flow of pulsed Laval expansions and detected with time-of-flight mass spectrometry after soft, single photon ionization using vacuum ultraviolet light (VUV). The uniform postnozzle flow allows cluster formation at constant temperature and supersaturation. Soft VUV ionization ensures that the original, neutral cluster size distribution is largely preserved upon ionization, which is a prerequisite to perform controlled nucleation experiments and determine accurate nucleation rates. Experimentally, we tune the conditions from *pre*-nucleation to *post*-nucleation conditions by either varying the flow temperature or by varying the observation time. This enables direct observation of the onset of nucleation.

Here, we present data on homogeneous gas phase nucleation of water. From the molecular-level information contained in the mass spectra, we extract number concentrations of clusters of different size, from which we determine nucleation rates. These rates are compared with predictions from established nucleation theories and with a prediction based on an *ab initio* transition state theory [2]. In addition, we determine the association rate coefficients between monomer and clusters of different size by fitting cluster number concentrations predicted by a kinetic model to the experimentally obtained data [3]. These results indicate that dimerization is the limiting step for water nucleation at our experimental conditions.

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The many faces of the hydrated electron

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The hydrated electron is an extremely short-lived species in the condensed phase. In contrast, water clusters with an excess electron $(H_2O)_n^-$, $n > 50$, are stable in the collision-free environment of an Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer for several minutes if black-body infrared radiative dissociation is suppressed by cooling the ICR cell. Under these conditions, spectroscopic and chemical properties of the hydrated electron can be studied in great detail.

Using nanocalorimetry, we have shown that the thermochemical properties of $(H_2O)_n^-$, $n \geq 100$, resemble the ones of a bulk hydrated electron. In the reaction with SF_6, $F^-(H_2O)$ is formed. With a thermochemical cycle using condensed-phase literature values and the nanocalorimetry result from the gas phase, the F_5S-F bond dissociation energy was determined as $\Delta H(T = 298\text{K}) = 455 \pm 24$ kJ mol^{-1}, in excellent agreement with all high-level quantum chemical calculations in the literature [1]. Also spectroscopically, $(H_2O)_n^-$, $n \geq 100$, closely resembles the bulk hydrated electron, as evidenced by photodissociation spectra in the range of $n = 20$–200. Smaller clusters $n \leq 40$ exhibit two isomers with clearly separated absorption maxima, and the position of the maxima shifts with increasing cluster size to the blue.

A particularly intriguing variant of the hydrated electron is encountered in $Mg(H_2O)_n^+$, $n \geq 20$. Due to the high binding energy of H_2O to Mg^{2+}, spontaneous charge separation occurs, and the former 3*s* electron of Mg^+ is displaced from the metal center. The electronic absorption spectrum resembles the spectrum of the bulk hydrated electron [2], but not as closely as in the case of $(H_2O)_n^-$.

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Closer look at salt dissolution: Microhydration of LiX_2^- ($X= Cl^-, I^-$) studied by cryogenic ion trap vibrational spectroscopy

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A general rule for the minimum number of solvent molecules required for transforming a contact ion pair (CIP) into a solvent-shared (SIP) and subsequently into a solvent-separated ion pair (2SIP) remains unclear more than 130 years since the introduction of solvent-induced charge separation by Arrhenius at the end of the 19th century.[1] Kosmotropic (order-maker) ions exhibit higher water affinities than chaotropic (disorder-maker) ions do and hence, according to *Collins' empirical rule*,[2] the corresponding salt pairs represent viable systems for the formation of SIP/2SIP with the smallest number of water molecules possible. Here, we study microhydration of ion pairs consisting of a kosmotrope and a chaotrope in the gas phase to obtain a molecular-level view of the interplay between hydrogen-bond network-formation and solvent-induced charge separation.

The microhydrated salt complexes $[LiX_2(H_2O)_n]^-$ ($X = Cl^-, I^-$, $n = 1\text{-}15$) are probed by cryogenic ion vibrational spectroscopy in the spectral region 2600 – 4000 cm^{-1} covering IR-active modes of the solvent molecules, i.e. the free (> 3600 cm^{-1}) and H-bonded OH stretching (< 3600 cm^{-1}), IRPD spectra of the D_2-tagged species were obtained for $n \leq 6$ and IRMPD spectra of the untagged species are recorded for the larger clusters. The assignment of the IRPD spectra are aided by DFT calculations; predicted anharmoinic spectra agree well with experimental measurements. In accordance to *Collin's* rule, SIPs are identified early in $LiX_2(H_2O)_n^-$ at $n \geq 2$.

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Strong temperature and size effects in iron-nitrogen interactions

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It is a pending challenge to characterize the interaction of N_2 with transition metal surfaces and clusters in detail. For our experiments, we utilized a modified Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS). Our setup combines a hexapole ion trap for kinetic studies with an FT-ICR cell for IRPD studies and mass analysis. Both ion traps are cryogenically cooled to temperatures below 11 K. With this tandem cryo trap instrument we investigate N_2 adsorption on Co, Ni, Rh [1-3] and N_2 and H_2 co-adsorption on Ru_8^+[4].

Currently, we investigate Fe_n^+ clusters for reductive nitrogen activation. We conduct kinetic and temperature dependent studies of N_2 adsorption and found size and pressure dependent effects, such as extremely slow N_2 adsorption on Fe_{17}^+. Also, we identified two isomers for the Fe_{18}^+ cluster one of which is unreactive. With DFT studies we try to understand the different adsorption behaviour.

Futhermore, we present gas phase IR spectra of N_2 adsorption on isolated cationic Fe_n^+ clusters at cryo temperatures. We find cluster size dependent and adsorbate number dependent effects in the IR spectra. All complexes show single or multiple IR active bands. These bands are significantly red shifted with respect to the IR inactive stretching mode of free N_2 (2330 cm^{-1}).

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Chemistry of electrophilic anions

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Molecular dianions with formula $[B_{12}X_{12}]^{2-}$ (X = H,halogen), are known for their exceptional electronic stability and chemical inertness. For example, due to their high resistance against electrophilic attack, these ions are able to stabilize highly reactive cations in condensed phase. Furthermore, $[B_{12}X_{12}]^{2-}$ compounds are of high interest to a the precisely localized cancer treatment known as Boron Neutron Capture Therapy (BNCT).

In this presentation we explore the gas phase ion chemistry of these compounds to understand their properties on a fundamental molecular level using photoelectron spectroscopy, computational methods and collision induced dissociation. We introduce new models to understand the electronic stability of $[B_{12}X_{12}]^{2-}$ dianions.[1] Bond breaking of a B-X bond results in the formation of highly electrophilic sites which even bind noble gases spontaneously at room temperature[2] and are able to insert into C-H bonds of saturated alkanes. Finally, it is shown that reaction products of these special gas phase anions can be obtained in the condensed phase using ion softlanding.[3]

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Size selective vibrational spectroscopy of neutral (boron) clusters

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Properties of small clusters are often not only strongly dependent on their size but also on their charge state. A prominent example for this is the transition from 2D to 3D structures for gold clusters which is observed to occur at n=8 for the cations and at n=12 for the anions.[1] While such ionic clusters are susceptible to common mass spectrometric techniques for size selection and storage similar manipulations are more difficult for neutral species and, hence, different experimental techniques for their structural characterization need to be applied.

Recently, a range of methods has been developed that apply resonant vibrational excitation of strongly bound neutral clusters in molecular beams with infrared Free Electron Lasers. These IR sources provide intense and tunable radiation even in the far-IR region where the vibrational fundamentals of metal or semi-metal clusters are located. Size selectivity is obtained by coupling the IR excitation with a subsequent soft ionization step, i.e. avoiding fragmentation, and mass spectrometric analysis of the ionic distribution [2, 3].

Here I will focus on the discussion of more recent developments in the investigation of boron clusters. Pure boron clusters are predicted to exhibit a wide range of structural motives from planar structures, double layered rings to cages. So far, most detailed insights for their structures comes from anion photoelectron spectroscopy in combination with quantum chemical calculations [4]. IR spectra of neutral boron clusters have been obtained in the past via an IR-UV two color ionization scheme. However, this technique is limited by the availability of UV laser sources that need to closely match the ionization energy of the clusters to be studied. Using an F_2 laser (hv=7.9 eV) IR spectra only of B_{11}, B_{16}, and B_{17} have been measured [5]. We are now combining 4-wave mixing VUV generation in the 6-9 eV range with the cluster mass spectrometer to cover a wider mass range and in particular to study clusters around n=40 where the presence of stable boron cages has been suggested [6].

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Studies of clusters using high resolution negative ion photoelectron spectroscopy

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Negative ion photoelectron spectroscopy (PES) has proved over the years to be a versatile probe of cluster structure and dynamics. However, the application of this method has been limited by its relatively low spectral resolution. In this talk, seminal PES experiments on clusters will be presented and methods to enhance the resolution of the technique are described.

Catalysis by mono- and bimetallic sub-nm clusters

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This paper discusses the catalytic performance of mono- and bimetallic clusters as the function of cluster size, atomically varied composition and support. The samples of supported size- and composition-selected clusters are fabricated by soft-landing of cluster cations of desired size and stoichiometry on oxide- and carbon-based supports, followed by interrogation under realistic conditions of pressure and temperature. The catalysts are characterized using *in situ* X-ray techniques to determine their stability and the oxidation state of their components under working conditions. Fundamental understanding of the function of the catalysts and the role of their individual components emerges from accompanying theoretical calculations. Comparisons with the performance of monometallic clusters will be made, and the effect of the support discussed. The applicability and promises of this approach will be illustrated on three examples: i) low-temperature oxidation of CO on Ag-Pt and Pt clusters in bridging the materials and pressure gap [1-2], ii) oxidative dehydrogenation of cyclohexane on Co, Cu-Pd, Cu and Pd clusters with control of selectivity and activity [3-4], and iii) conversion of propane on Cu-Pd, Cu and Pd clusters into selected products [4].

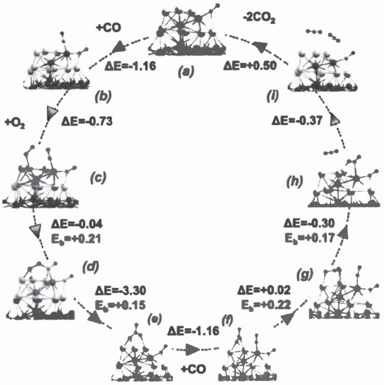

Fig. *1: Ag-Pt clusters in CO oxidation – understanding the catalytic cycle from theory [2].*

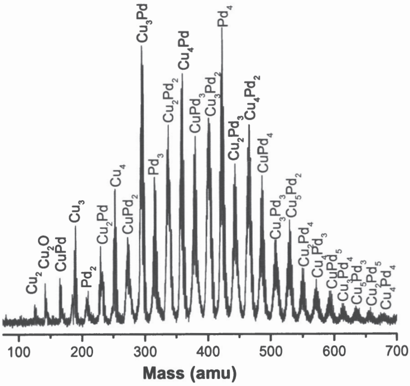

Fig. 2: *Tuning of cluster size and composition with atomic precision*

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Can we control the charge state and structural dynamics of supported clusters?

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It has been shown in several examples that the charge state of supported clusters can influence its catalytic activity. Negatively charged Au_8 clusters on MgO, for instance, are highly active CO oxidation catalysts whereas neutral Au_8 is inactive [1]. Similarly, the internal structural fluxionality of clusters can also be responsible for a high catalytic activity [2], while sintering typically leads to catalyst deactivation. The question thus arises whether we can control the charge state and structural dynamics of supported clusters in order to optimize their properties as a catalyst.

We have accelerated our scanning tunneling microscopy (STM) to video frame rates [3] to investigate the dynamics of clusters on single crystalline supports. In the case of Pd_n ($1 \leq n \leq 19$) on an h-BN mesh, we successfully monitored reversible cluster isomerization *in situ* and found that while an atom diffuses rapidly along the rim of pores, a small cluster jumps between six sites around the pore center [4]. In contrast, Pt_n clusters on $Fe_3O_4(001)$ do not exhibit dynamics and instead appear to sink into the surface with increasing temperature, indicating a change in cluster–support interface. $Pt_n/SiO_x/Si(001)$ is another strongly interacting and thus sinter-resistant system. We change the doping in Si to control the charge state of clusters without altering the cluster–support interface. In ambient pressure X-ray photoelectron spectroscopy (AP-XPS), we observe a systematic difference in the interaction with oxygen and catalytic activity of Pt_n clusters on p- and n-doped Si wafers.

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Deciphering the structures and intermolecular interactions of weakly bound clusters using high-resolution rotational spectroscopy

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The precise knowledge of the structures of molecular clusters is of fundamental use for understanding the non-covalent intermolecular interactions that keep them together. Molecular-jet high-resolution rotational spectroscopy provides an outstanding tool to determine accurate molecular structures in the gas phase and thus free of solvent and crystal effects. These conditions allow for a direct comparison and benchmarking with quantum-chemical experiments.

Of particular interest for us are the roles of conformational flexibility, non-covalent interactions, and chirality in molecular cluster formation. We use broadband rotational spectroscopy (complemented by quantum-chemical calculations and other spectroscopy techniques) to evaluate how molecules bind to each other and to establish a hierarchy of intermolecular interactions. These studies are also relevant with respect to the first steps of aggregation, such as in soot and grain formation, and can thus provide important insight into the transition from the isolated molecule to the bulk. Molecular clusters with water reveal important insight into how the structure of the solute changes at the molecular level. In return, structural changes to the surrounding water clusters can be observed.

In the lecture, the technique of broadband rotational spectroscopy employing molecular jets will be introduced. Its application to the study of molecular clusters will be discussed based on selected examples such as glycolaldeyde-water and PAH-water systems as well as aggregation of large ether molecules with various polar and apolar binding partners.

The adsorption of NO onto group IX transition metal cluster ions

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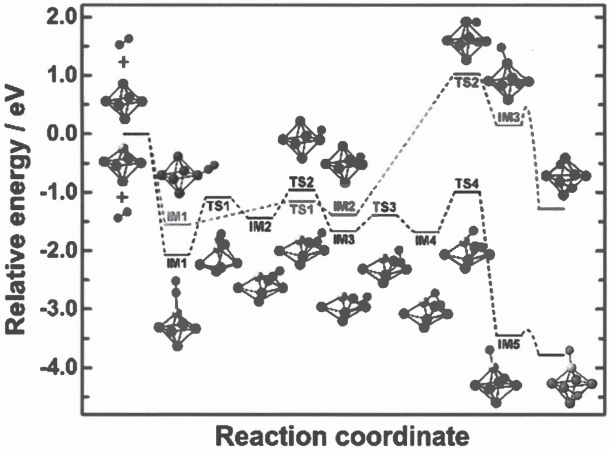
Rhodium and Iridium are group 9 elements that can both catalytically reduce NO to N_2 and O_2, and are therefore widely used in three-way catalytic converters. Since the rate-limiting step for NO reduction is the dissociative adsorption of NO, it is of great interest to understand this adsorption mechanism on a detailed level. For this, we study the adsorption of NO molecules onto clusters of these materials, using mass-selective FEL-based IR action spectroscopy.



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Theoretical design of nanocatalysts for oxygen reduction and hydrogen evolution reactions

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Development of the effective electrocatalysts for oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) is an emerging challenge for the sustainable energy conversion technology [1]. Currently, the most efficient electrocatalysts for the ORR and HER are based on platinum which prevents the wide use of such catalysts in practical applications due to the high cost and limited resources of platinum. In this presentation we will show that effective electrocatalysts for ORR and HER can be rationally designed using inert and insulating materials, such as hexagonal boron nitride (h-BN) and gold. It is predicted theoretically and proved experimentally that small two-dimensional clusters of h-BN deposited on Au surface, as well as small Au clusters deposited on h-BN/Au substrate demonstrate superior catalytic activity for ORR and HER with the operating characteristics similar to platinum [2,3]. It is shown that the perimeter interface areas between h-BN clusters with the Au support as well as Au clusters with the h-BN/Au support provide catalytically active sites for effective ORR and HER. Thus, for example, stabilization of oxygen at the perimeter interface between Au clusters and h-BN/Au(111) support promotes OOH* dissociation opening effective 4-electron pathway of ORR with formation of H_2O. Increase in the perimeter interface area results in increase of the ORR and HER activities. Our calculations demonstrate the principal ability to functionalize inert materials for the ORR and HER and open new way to design effective Pt-free catalysts for fuel cell technology.

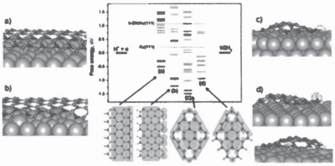

Fig. 1 Theoretical design of the active sites for HER at the h-BN/Au(111) interfaces [3].

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Structure and dynamics of metal clusters: old and new tales

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One of the clearest examples of a quantum size effect is the electron shell structure of simple (and not so simple) metal clusters, which has been studied in detail since the beginning of cluster physics. Photoelectron spectroscopy on size-selected clusters turned out to be a powerful tool to monitor the discretized electron density of states. Angle resolved photoelectron spectroscopy is even able to yield information about the wavefunctions of the electron, as well as on the dynamics of the photoemission process [1]. The recent years have seen a constant improvement of the experimental techniques as well as of the theoretical methods used to simulate the results, which yields a new quality of insight. This will be demonstrated for systems like zinc clusters [2].

Additionally the rapid development of new light sources like high intensity synchrotrons, free electron lasers and high harmonic sources offer a huge potential for experiments on clusters. I will discuss a number of experiments which have been done recently or are under development.

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Water Oxidation on Free Calcium-Manganese-Oxide Clusters: Gas Phase Model Systems for the Catalytically Active Center of Photosystem II

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The catalytic oxidation of water in plants takes place at an inorganic Mn_4CaO_5 cluster located in photosystem II. To aid the design of new artificial water oxidation catalysts we embark on a novel hierarchical modeling strategy, starting with small clusters and increasing the model system's complexity in a staged, controlled manner.

In the first steps we studied 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 (IR-MPD) spectroscopy in conjunction with first-principles calculations, revealed the facile water deprotonation and the exchange of the oxygen atoms of the cluster with water oxygen atoms [1-4]
In a further step we investigated binary calcium manganese oxide clusters and found that the number of Ca atom is crucial to the water oxidation capabilities of the small $Ca_{4-x}Mn_xO_4^+$ and $Ca_{5-x}Mn_xO_5^+$ clusters [5].

Finally, we started modeling the ligand environment of the manganese-clusters cluster by small acids. First experiments identified propionic acid as the most promising candidate since the smaller acids, formic and acetic acid, easily decompose in the presence of $Mn_xO_y^+$ [6].

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Fullerene arrangement by vapor deposition on a well-ordered thin Al_2O_3 film grown on Ni_3Al (111) crystal

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A very thin (~0.5nm) aluminium oxide film (Al_2O_3) on a Ni_3Al(111) surface that shows an well-ordered network structure in scanning tunneling microscopy (STM) at a tunneling voltage of 3.2 V presents a corresponding dot structure formation at 2.0 V. The dot structure acts as nucleation pattern when metal islands are grown by atom deposition [1]. For mass-selected Cu clusters it provides thermal stabilization and a specific arrangement of the clusters with respect to the dot structure [2]. This initial situation offers a huge potential for film oxide functionalization with different mass-selected clusters. Due to its easy fabrication, fullerenes (C_{60}) with their properties represent a model system for the metal clusters (e.g. Pb-Clusters), which are planned to be used for future experiments in our surface science facility. We present experimental ultraviolet photoelectron spectroscopy (UPS) and STM results for vapor-deposited submonolayers of C_{60} on the surface of well-ordered Al_2O_3 / Ni_3Al(111), which show different behavior (e.g. shift in UPS spectrum, island growth in STM images) for different surface temperatures during vapor deposition. We will compare the results of the UPS experiments with data for C_{60} on rare gas layers [3]. These showed similar shifts in the spectra for C_{60} on Argon films as a change within one hour after deposition. However, it was not possible to produce STM images on these Argon films.

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Electron catalyzed reactions involving $CO_3^{\bullet-}(H_2O)_n$

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The hydrated $CO_3^{\bullet-}$ carbonate radical anion is an important tropospheric ion. The formation of $CO_3^{\bullet-}$ in the atmosphere has been unraveled by Fehsenfeld et al. [1]. However, its reactivity towards most atmospheric trace compounds is mostly unknown. Recently we studied reactions of $CO_3^{\bullet-}(H_2O)_{0,1,2}$ with different organic acids like formic acid [2] and acrylic acid in our laboratory by FT-ICR mass spectrometry. Information on the reaction path and neutral products are obtained via a combination of kinetics and quantum chemical calculations of the potential energy surface of the reactions.

In the reaction of formic acid with $CO_3^{\bullet-}$ signal loss as the dominant first reaction step is observed. This indicates the formation of neutral reaction products accompanied by electron detachment [2], not directly detectable in FT-ICR mass spectrometry. For acrylic acid, the first reaction step is a transfer of $O^{\bullet-}$, and electron detachment occurs later in the reaction sequence. Quantitative scavenging of electrons produced in the reactions via SF_6 works well and corroborates that the signal loss is due to electron detachment. In atmospheric conditions, the electrons can lead again to formation of $CO_3^{\bullet-}$, closing a catalytic cycle via O_2^- and ozonide [1]. Gas-phase electrons seem to play an important role as catalysts in atmospheric negative ion chemistry.

Latest results on the reactivity with acrylic acid, propionic acid and their methyl esters will be presented.

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45 Years of Research on Metal Clusters

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When I met my thesis adviser Ernst Schumacher in 1973 in Berne, he presented me the latent image problem of silver photography: Neither the elementary process that occurs, when light hits a photographic plate, was known so far, nor was the material, which stores the engraved optical information, allowing it later to be retrieved and stabilized in the development process. Luminosity- measurements and silver deposition experiments provided, however, an evidence, that neither the silver atom, nor the solid silver halide material were the mysterious “latent image germ”. It had to be something different; E. Schumacher spoke of “Clusters”!

We wanted to learn more about these new particles, which neither were atoms, nor solids. Unique optical and chemical properties could, however, be attributed to them. So, after consulting the literature we contacted various colleagues in Germany and France, who already were working with “Clusters”: Among them are O. Hagena, J. Gspann, U. Buck, R. Farges, J. Friedel, E. Recknagel. They showed us different approaches, how to make metal clusters, to detect and to characterize them. So, we learned about supersonic molecular-beam machines, laser-vaporization sources, as well as sputter- and electrospray- aggregates, which we copied and characterized. For this, we employed different types of mass spectrometers like magnetic instruments, quadrupoles, Time of Flight machines, etc. The instruments were also assembled as tandems, ion guides and traps, so also reactions on size-selected particles could be performed: in a beam, in an ion trap and softly deposited on surfaces. From such “soft-landing experiments” we learnt later, that the “latent image germ” in silver photography is the cluster “Ag_4”.

For the characterization of our clusters a wide palette of light sources was employed: arc- lamps, (home-made) dye lasers, synchrotron radiation sources, free electron lasers, ultrafast Ti:Sapphire- lasers and the necessary equipment for pump-probe as well as coherent control experiments. So, we were able to record not only the electronic, vibrational and rotational spectra of individual cluster sizes, but also dynamic responses coming from fragmentation cascades, ionization processes or reaction pathways, which could be optimized by using optimally shaped femto-second laser pulses. During these times, I could always rely upon a magnificent team, which was well integrated into efficient national and international networks. In addition our work was always accompanied by very competent theoretic partners. Since there is not enough space here: Their names appear all in my publication list.

Abstracts of Posters

(in alphabetical order)

Photoelectron spectroscopy of size-selected metal clusters at FLASH 2

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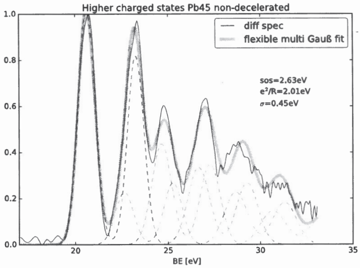
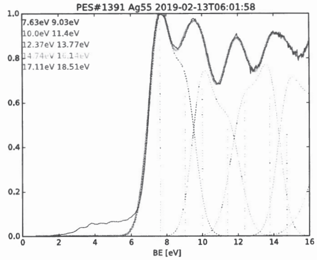
A newly designed XUV magnetic bottle photoelectron spectrometer (MBPES) has been tested at the free electron laser FLASH2 in Hamburg in combination with a cluster source and two time-of-flight spectrometers in order to address the core levels of metal clusters. The high photon energy of 47 eV with decent bandwidth allowed us to investigate the 5d levels of lead and the 4d band of silver clusters with a unique resolution and short measurement time. In this high intensity regime, multiphoton absorption and therefore up to five different charge states have been observed. The results provide a rather comprehensive characterization of the size dependence of the valence and shallow core states density of lead cluster anions in the size range from $n = 3$ to $n = 50$ and silver cluster anions in the size range from $n = 8$ to $n = 70$.



(a) Photoelectron spectra of the cluster Pb45 with the 5d5/2 & 5d3/2 peaks including higher charged states



(b) Photoelectron spectra of the cluster Ag55 with the 4d and valence band including higher charged states

Gas-Phase Investigations of Thiomolybdate Nanoclusters as Model Catalysts for the Hydrogen Evolution Reaction

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Power-to-Hydrogen is an attractive approach towards achieving the goals of the 2030 climate & energy framework of the EU. Molybdenum sulfide nanoclusters, such as $[Mo_3S_{13}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ are highly active hydrogen evolution reaction (HER) catalysts, which can be supported on various electrode surfaces [1]. However, the detailed mechanism of H_2 formation is still under debate and mechanistic investigations on amorphous MoS_x are particularly difficult [2]. Herein we use the bottom-up approach and study precisely defined gas-phase clusters, like $[^{92}Mo_3S_{13}]^{2-}$ and $[^{92}Mo_2S_{12}]^{2-}$, as key building blocks of said materials. For this task a Fourier transform ion cyclotron mass spectrometer (FT-ICR MS) is used, as it is an excellent tool for the examination of ion-molecule reactions in gas-phase. Coupling FT-ICR MS with laser spectroscopy techniques, allows us to further characterize the HER reaction intermediates. Collision Induced Dissociation (CID) experiments provide insight into the structural flexibility of the clusters, indicating that roaming H/SH moieties may be a key feature of HER catalysis [3]. With photodissociation spectroscopy in the UV-Vis region (0.5 – 5.5 eV) we can probe the electronic structure of the examined clusters. Here, $[HMo_3S_{13}]^-$ for example, shows a broad absorption band starting at 1.7 eV, with distinct features in the UV at 3.7 eV and 4.5 eV. Furthermore, infrared multiphoton dissociation (IRMPD) spectra of protonated $[HMo_3S_{13}]^-$ and $[HMo_2S_{12}]^-$, show distinct H-S stretching vibrations at 2450 cm^{-1} and 2530 cm^{-1} respectively. Combining these results with theoretical calculations allows us to identify terminal disulfide units as H adsorption site, hence implying a sulfur-centered HER mechanism.

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Probing electron correlation effects in sodium-ammonia clusters

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Already in the year 1808, concentration-dependent color changes were observed when dissolving potassium in ammonia (see ref. 1 and refs. therein). However, the underlying correlation effects of the solvated electrons are still not well understood. While such effects have been probed by magnetic measurements on alkali metal ammonia solutions,[2-4] the involved species have not yet been identified in such bulk phase experiments.[1]

To study magnetic correlation effects in the better-defined environment provided by size-selected clusters, we are developing a new setup that combines a Stern-Gerlach type magnetic deflector with a velocity map imaging setup for photoions and -electrons. The deflector spatially separates neutral, alkali metal-doped ammonia clusters in a molecular beam due to their different magnetic properties. As subsequent photoionization of the clusters allows time-of-flight based selection of individual cluster sizes, the position sensitive detection will reveal the critical cluster sizes needed to facilitate spin pairing in multiple metal-doped clusters. The deflector will also allow us to simplify photoelectron images by sorting the clusters by their spin state. In this contribution, we present the current state of the setup along with its initial characterization. While for effusive alkali metal beams quantitative agreement with theory is achieved, deviations are observed for small, sodium-doped ammonia clusters. Issues with the current experimental setup and possible solutions are discussed.

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Ultrafast photochemistry on oxide surfaces and supported metal clusters

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The photo-induced reaction dynamics of adsorbate molecules on well-defined ultra-thin oxide films and on supported metal particles is investigated using femtosecond laser pump-probe mass spectrometry with resonance enhanced multi-photon ionization detection. It is demonstrated that this technique is able to reveal the real-time dynamics of the transition state and the product formation in a surface-aligned photoreaction as a function of oxide film thickness and cluster size.

In this experiment, methyl halide molecules serve as photochemical model systems. The photodissociation on the surface can initiate subsequent bimolecular reactions of the photofragments with co-adsorbed molecules. Via time-, mass-, and velocity-resolved monitoring of intermediate and product species it is possible to obtain insight into the complex dynamics of the photoinduced surface reaction.

In addition, a new experimental setup is presented in which metal supported graphene layers serve as template to grow regular metal cluster nano-structures for molecular adsorption and photodissociation. The bound unoccupied electronic state structure of an Ir(111)/graphene surface covered by differently sized and spaced Ir clusters was characterized by means of femtosecond two-photon photoemission spectroscopy. The cluster lattice was found to affect the image potential states of the substrate to an extent, which is surprisingly large compared to the graphene area covered by Ir clusters. This effect can be related to the influence of the cluster lattice on the screening of the image state electron trapped in front of the surface. Furthermore, lateral confinement effects could be observed due to the decreasing extension of bare graphene areas. Finally, the adsorption and photoreaction of molecules on these cluster lattices is investigated by scanning tunneling microscopy.

Charge-transfer in the system Pt_n/SiO_2/metal and its effects on the activity of ethylene hydrogenation

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The interplay between a support and an underlying metal, e.g. thin silica films grown on metal single crystals, has proven to play a key factor in the activity of a catalyst, e.g. size-selected clusters, supported on such a system.

The nature of their interaction is determined by parameters as the thickness and stoichiometry of the silica film and the work function of the metal. Depending on these, a charge-transfer can be induced between support and catalyst and result in a change of the local electron density of the supported clusters. Hence, the activity of the clusters towards a particular reaction can be tuned through specifically (de)charging them as a function of the selected proprieties of the support system, i.e. film and metal.

The presence or absence of bonds formed at the metal-silica interface and the local work function of the support, which is a function of the work function of the underlying metal, were found to govern the aforementioned charging effects. A system exhibiting a high local work function and no metal-silica bonds yields clusters of a positive partial charge, while clusters are partially charged negative with a low local work function and formation of metal-silica bonds. In this context, the change in activity of size-selected Pt_n-clusters (n = 10, 13, 14), supported on thin silica films on different metal single-crystals (Pt, Mo) towards the hydrogenation of ethylene has been investigated under steady-state conditions. The catalytic samples were characterized through TPD, vibrational spectroscopy (IRRAS) and electron spectroscopy (MIES/UPS).

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IR spectroscopy of amantadine-water cluster cations: First step of microhydration

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Amantadine is an amino derivative of adamantane, which is the smallest member of the diamondoid family. Diamondoids are a recently established important class of saturated hydrocarbon molecules. They are rigid and stress-free cycloalkanes with well-defined structures and therefore of interest in manufacturing new nanomaterials with applications in materials and polymer sciences, molecular electronics, biomedical sciences, and chemical synthesis [1]. We recently analysed the IR spectrum of the adamantane radical cation and found direct evidence for Jahn-Teller distortion upon ionization [2]. Amantadine is successfully used to treat Parkinson's diseases and the influenza A virus.

To better understand the behavior of amantadine in a polar solvent (here microhydration), we investigate amantadine-water clusters with an increasing number of water molecules. To this end, IR photodissociation (IRPD) spectra are measured in a tandem quadrupole mass spectrometer coupled to an electron ionization source. The cluster cations are produced in a pulsed supersonic plasma expansion by electron and/or chemical ionization of amantadine and water. The combined approach of gas phase spectroscopy with quantum chemical DFT calculations at the B3LYP-D3/cc-pVTZ level provides precise information about structural, vibrational, and electronic properties. Here, we present IRPD spectra of the amantadine cation solvated with up to three water molecules. The structural and electronic changes upon hydration of the amantadine cation are directly reflected by its vibrational spectrum. With the calculations, vibrational modes are assigned and stable isomers are identified.

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Development of a Piezoelectric Detector for Determining Particle Density and Mean Cluster Size in a Pulsed Supersonic Molecular Beam

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In our studies a piezoelectric polyvinylidene fluoride (PVDF) foil is used for the detection of a pulsed supersonic beam. Benefits of this method are a fast detector response, a ruggedized setup and the fact that no ionization is required. Experimental results performed in a wide range of source conditions (source pressures between 3 bar and 20 bar, source temperatures between -40 °C and 70 °C) show that the detector response is proportional to mass, density, and square of the velocity of impinging particles. A simultaneous measurement and evaluation of the background pressure in the vacuum chamber allows a calibration of the detector to the amount of particles. Alternatively, an analytic model describing the electrical and mechanical detector properties for data analysis allows a calibration-free operation. The setup will be extended to determine the mean cluster size by measuring radial density profiles of the skimmed molecular beam.

Structural Properties of $[(Al_2O_3)_n(FeO)]^+$ Clusters Studied by Infared Photodissociation Spectroscopy

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Alumina-based materials are currently attracting much attention due to their industrial use, e.g., as ceramics, abrasives, absorbents, catalysts and catalyst support. They are also known for their structural variability, which raises the question, how the structure of bulk-like aggregates compares with that of thin films, nanoparticles and gas-phase clusters.[1] A detailed understanding of their structure-reactivity relationship at the molecular level is also indispensable for designing oxides with tailored properties. In zeolites, e.g., Fe-impurities can have a dramatic effect on their photocatalytic activity.[2] Here, we study the effect of Fe-impurities in gas phase model systems. Based on our previous study on small, formally electronically closed-shell aluminum oxide cations,[3] we replace a single Al(+III)- with a Fe(+III)- center, forming the binary metal oxide cations $[(Al_2O_3)_n(FeO)]^+$ with n=1-5 and characterize their structure using cryogenic ion vibrational spectroscopy in combination with density functional theory (DFT) calculations. [4,5] We are interested in characterizing

- the effect of Fe-substitution on the cluster structure,
- the change in electronic structure by introducing a redox active metal center, and
- the performance of DFT in predicting the energetics and vibrational spectra.

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Imaging the melting of silver nanoclusters in free flight

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Wide angle x-ray diffraction (WAXD) at free electron lasers (FEL) has been proven a viable tool to determine the 3D structure of single metal clusters in one single shot[1]. This is enabled by the ultrashort (< 100fs) and very intense xray pulses from the FEL that allow sufficient intensity to scatter off the sample before radiation damage sets in and destroys it. Consequently this technique provides the potential to image ultrafast processes which has not been combined with the shape revealing capabilities of WAXD on metal particles in gas phase. 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. To overcome this difficulties a carefully taylored source for clusters was set up. While in previous free flight experiments the dynamics of desintegrating xenon clusters and the subsequently formed nanoplasmas have been studied[3], nondestructive changes in the crystal structure (melting) of metal nanoparticles have so far only been studied on substrate[2]. 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.

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Aromatic Charge Resonance Interaction Probed by Infrared Spectroscopy

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Charge resonance is a strong attractive intermolecular force in aromatic dimer radical ions. For cations, this stabilization arises from sharing a positive charge between two identical or different molecules (A_2^+, AB^+) with comparable ionization energies within the π-stacked dimer. Despite its importance, this fundamental interaction has not been characterized at high resolution by spectroscopy of isolated dimers. Herein, we employ vibrational infrared spectroscopy of cold aromatic pyrrole dimer cations to precisely probe the charge distribution by measuring the frequency of the isolated NH stretch mode (ν_{NH}) [1]. We observe a linear correlation between ν_{NH} and the partial charge q on the pyrrole molecule in different environments. Subtle effects of symmetry reduction, such as substitution of functional groups (here pyrrole → N-methylpyrrole) or asymmetric solvation (here by an inert N_2 ligand), sensitively shifts the charge distribution toward the moiety with lower ionization energy. This general approach provides a precise experimental probe of the asymmetry of the charge distribution in such aromatic homo- and heterodimer cations.

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Platinum and Nickel Clusters on TiO_2 in Heterogeneous Photocatalysis

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Sustainable and eco-friendly energy production is a major challenge of the future, as the impact of global warming is aggravated by the dependence on fossil fuels. A promising scientific approach is photocatalysis, whose aim is to utilize (sun)light for the generation of high-value chemicals and renewable fuels. In heterogeneous photocatalysis, semiconductors are commonly used as catalyst material, which are often optimized by associating co-catalysts onto their surface. The later are usually clusters or nanoparticles and may complement the photochemistry by enabling new surface reaction pathways. Whereas the role of semiconductors is relatively well understood, a lack of insights into the properties and role of cluster co-catalysts remains. For this reason, current state-of-the-art systems are difficult to improve in a strategic manner.
As co-catalyst material, noble metals (in particular platinum) were found to be suitable for hydrogen evolution reactions, as shown in numerous studies. Yet, more abundant materials like nickel also represent promising options for photocatalytic applications due to their commonly known activity in carbohydrate chemistry.

Combining surface science and cluster research, our group is moving metal clusters towards catalytic applications. In this presentation, the role of platinum clusters as co-catalysts on a semiconductor in the photocatalytic oxidation of methanol in UHV is shown. This system enables a long-term catalytic stability and selectivity. More importantly, the deposition of platinum clusters is essential to make the reaction truly catalytic. For nickel, our recent results show that similarities but also significant differences result in the reaction behavior.

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Probing electronic properties of cationic metal halides with x-ray absorption spectroscopy

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Information about chemical bonds are crucial for understanding chemical reactions. Interaction between the valence d electrons and p electrons are therefore of major interest. The environment of the sample has a large effect on this interaction. Here we study diatomic metal halide systems in the gas phase. By changing the halide the influence on the valence electrons of the metal can be studied. The metal halides are produced by an electrospray ionization source which brings the sample from solution into the gas phase. After mass selection the metal halides are trapped in a cryogenic linear Paul trap where they can interact with soft x-rays to measure x-ray absorption spectra. The setup is located at the beamline UE52-PGM at Bessy II.

Joining Microfluidics with Infrared Photodissociation Spectroscopy: Structural Characterization of Transient Intermediates

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Chemical microreactors, such as microfluidic chips, are revolutionizing the way we can study transient intermediates in chemical reactions by making them spectroscopically examinable online, which has not been realizable with conventional techniques. Here, we combine microfluidic chips with the structure determining power of infrared photodissociation (IRPD) spectroscopy in combination with quantum chemical calculations to shed light on the in-situ formation and stereochemistry of *ortho*-quinone methides (*o*-QM), a highly reactive, transient species that is not isolatable by conventional methods. *o*-QMs are of relevance in a multitude of chemical reactions in nature. They also exhibit a large potential in organic synthesis, especially in stereoselective reactions.

By coupling microfluidics with IRPD spectroscopy, we are not only able to characterize the structures, but also assess *E*/*Z* ratios of *o*-QMs, which are produced by dehydration of 1,3-diols in-situ on the chip. This information is given by the analysis of the IR fingerprint region of the short-lived species. Control over stereoselectivity is achieved by changing sterical interactions defined in the substrates and monitored by evaluating stereoisomer-selective IR absorption bands which reflect the resulting *E*/*Z* ratio. With this approach, we are able to gain a deeper understanding over the thermodynamics und kinetics of the formation of elusive *o*-QMs and gain control over the *E*/*Z* isomer specificity.

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Proton Buffered Explosion of Methane Clusters

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When nanoscale particles, like biomolecules or clusters, are exposed to intense short-wavelength light pulses, ultrafast ionization dynamics are induced which lead to the disintegration of the sample. Theoretical calculations [1] predict that the ionization dynamics in molecular systems differ strongly from that of mono-atomic specimen, which were often used in previous experimental and theoretical approaches to study ultrafast radiation damage. Since methane molecules and neon atoms have the same number of electrons and similar masses, clusters made from those materials can be used as ideal model systems to study how the presence of multiple atomic species alters ionization dynamics.

In an early user experiment at the SQS endstation of European XFEL, we studied methane as well as neon clusters using light pulses of 1 keV photon energy and pulse energies up to 3 mJ. First results about size- and intensity-dependent effects in time-of-flight ion spectra will be discussed. Our experimental data can become a valuable benchmark for existing theoretical approaches and will help to refine modeling of radiation damage in single-molecule coherent diffraction imaging experiments.

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Structural, plasmonic and magnetic properties of physically prepared iron-silver nanoparticles

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The prospect of combining both magnetic and plasmonic properties in one single nanoparticle promises both valuable insights on the properties of such systems from a fundamental point of view as well as numerous possibilities in technological applications. The combination of two of the most prominent metallic candidates, iron and silver, has, however, presented a lot of experimental difficulties because of their thermodynamic properties impeding miscibility or even coalescence. Here we present the thorough characterization of physically prepared $Fe_{50}Ag_{50}$ nanoparticles embedded in carbon and silica matrices by electron microscopy, optical spectroscopy, magnetometry and synchrotron-based x-ray spectroscopy. Iron and silver segregate completely into structures resembling fried eggs with a nearly spherical, crystallized silver part surrounded by an amorphous structure of iron carbide or oxide, depending on the environment of the particles. Consequently, the particles display both plasmonic absorption corresponding to the silver nanospheres in an oxide environment as well as a reduced but measurable magnetic response. Finally, environmental plasmonic spectroscopy under reactive conditions is used to monitor the reversible oxidation and reduction of the FeAg nanoparticles. The suitability of such nanoparticles for technological applications is discussed in view of their high chemical reactivity with their environment.

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Mass selected iron clusters on thin oxide films

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Clusters are the bridge between atomic and solid-state physics, they show strong size dependent properties. In our cluster beam facility a magnetron sputter gas aggregation source produces a wide range of clusters. Mass selection is performed with a semi-continuous time-of-flight mass selector [1]. For deposition in a load-lock chamber attached directly to the mass selector a new setup of ion optics was simulated with SIMION [2] and has been put into operation. Iron clusters, e.g. $Fe_{1790\pm30}$, are deposited on an indium tin oxide (ITO) substrate which should be usable for magneto-optical studies. Afterwards ex situ UV/vis spectroscopy measurements were carried out. The deposition of a reasonable cluster coverage on ITO was achieved. UV/vis spectroscopy of the cluster absorption is challenging. Up until now, the sensitivity of optical measurement was of the same order of magnitude as the expected cluster absorption signal - due to light source intensity fluctuations and substrate inhomogeneities. Planned improvements of the experiments are discussed.

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Coulomb interaction in the photoemission of polyanionic silver clusters

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Not only the size, but also the charge state is an important parameter of free, nanoscopic particles. Previous studies concentrated mainly on neutral as well as singly positively and negatively charged species [1]. For multiply negatively charged clusters, the Coulomb interaction between the two or more excess electrons strongly influences the cluster properties. So far, the involved Coulomb potential could only be studied indirectly and their detailed properties are largely unknown [2].

This contribution presents photoelectron-spectroscopy studies on mass-selected polyanionic silver clusters [3]. The emitted electron interacts with the remaining negatively charged cluster, which leads to a Coulomb cut-off in the photoelectron spectra, as known from molecular polyanions [4]. In order to extract details of the Coulomb barrier, photoelectron spectra are recorded for different photon energies. Photoemission from large polyanionic metal clusters can be qualitatively described by electrons, coming from a Fermi distribution in a jellium-like potential. For modeling, direct emission as well as tunneling through the Coulomb barrier are taken into account.

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Electron and photon interactions with size- and charge-state-selected anionic tin clusters

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Following recent studies on lead clusters [1-4], the dissociation pattern of exited (poly-)anionic tin clusters is currently investigated at ClusterTrap [5]. The exposure of size-selected monoanionic tin clusters to an electron beam leads to dissociation as well as electron attachment, as already reported [6]. In the meantime, photodissociation experiments have been performed on the mono- as well as the polyanions. The mass spectra of the reaction products reveal a transition from a non-metallic to a metallic behavior similar to that of lead. The most prominently observed fragmentation products Sn_{n-7}^-, Sn_{n-10}^-, Sn_{10}^- and Sn_{15}^-, where n is the parent cluster size, are in line with previously-observed stable configurations for small tin clusters [7]. Similar to the studies on lead, fission processes can be observed for tin dianions below the cluster size $n < 45$, resulting in two monoanionic fragment clusters. In contrast to lead however, a further decay path for mono- and dianionic tin clusters has been found to be the breakoff of a neutral heptamer, even up to the largest clusters observed ($n = 70$).

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Infrared Spectroscopy of Gas Phase Subnanometer Particles

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Infrared spectroscopy is tool for characterization of geometrical configuration of atoms in subnanometer particles. This information is important for understanding their physical and chemical properties along the way to establish structure - function relationships. Here we present the principles of a method, which can be used to obtain infrared absorption spectra of gas phase small charged species in their vibrational ground state, on the example of a charged molecule.

The applied experimental approach, so called Infrared Pre-Dissociation (IRPD) Spectroscopy, is based on the dissociation of mass selected tagged ions triggered by an infrared photon followed by the measurement of the depletion of the tagged ion signal on a mass spectrometer allowing single ion detection. The absorption of photons is not detected as such, but rather translated to change of mass. As a tag, here we use loosely bonded helium atom that is removed by absorption of one photon. Typically, helium tagging is accomplished in radiofrequency ion trap by collisions with helium buffer gas cooled to 3 K. At such temperature the molecule is relaxed to its ground vibrational state and its infrared pre-dissociation spectrum is free of hot bands thus it simplifies interpretation. The heart of the experiments is a cryogenic ion trap of the instrument ISORI (Infrared Spectroscopy Of Reactive Ions) [1], an ideal tool for spectroscopic characterization of gas-phase subnanometer charged species up to 4000 u/e, where broadband infrared radiation from an OPO (range 600 – 4700 cm^{-1}, linewidth 1.6 cm^{-1}) is used for vibrational ion spectroscopy experiments. Optionally, two-color spectroscopy can be applied to probe various structural isomers [2].

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How do Pd clusters move in the pore of a hexagonal boron nitride mesh?

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We present examples of cluster dynamics observed via fast scanning tunneling microscopy (FastSTM). To that purpose, we have boosted the temporal resolution of our commercial STM up to 16 frames per second with a specially developed add-on electronics module [1], allowing us to match the frame rate to surface dynamics observed at elevated temperatures. On the example of small Pd clusters supported on a hexagonal boron nitride nanomesh on Rh(111), we observed a range of different dynamics [2]. Cluster diffusion within a nanomesh pore changes with adsorbate size: While atoms diffuse along the rim of the pore, a small cluster experiences a corrugation in the potential energy landscape and jumps between six sites around the pore center. The difference can be explained by the additional internal degrees of freedoms of a cluster. Furthermore, we monitored the reversible switching between two structural isomers of Pd clusters in situ.

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Cryo kinetics and IR spectroscopy of N_2 adsorbed to size selected Tantalum clusters

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Catalytic N_2 activation by active transition metal surfaces has always been a topic of interest. We investigate the effects of transition metal cluster surface structures (Fe, Co, Ni, Rh, Ru) on the vibrational and kinetic behavior of N_2 and H_2 adsorbates [1-5]. Currently, we investigate the N_2 adsorption to small size selected Ta_i^+ $_i$ = 2-5 clusters. Recent studies on the tantalum dimer cation have analyzed the catalytic formation of ammonia from N_2 and H_2 [6]. Our current cryo IR¬PD spectroscopy as well as cryo adsorption kinetics may provide for further spectroscopic and kinetic information about reaction precursors and intermediates.

We chose to examine the Ta_4^+ and Ta_5^+ clusters in more detail. Comparison of experimental and calculated IR spectra of the Ta_4^+ cluster reveals a rearrangement of the adsorbate shell upon stepwise N_2 adsorption. The adsorption kinetics suggest a complex adsorption behavior for large adsorption shells including a slow isomerization followed by a desorption. A pseudo-first-order kinetic fit fails in this case. The adsorption kinetics of the Ta_5+ cluster are reproducible by such a fit.

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Setup and characterization of a helium liquid jet for diffractive imaging experiments

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State-of-the-art XUV and X-ray facilities enable the in-depth investigation of light-matter interaction via novel methods like time-resolved single-particle coherent diffractive imaging (CDI). In particular, high harmonic generation sources have gained popularity due to their very short pulses, which make attosecond temporal resolution feasible [1]. Nevertheless, these light sources exhibit lower photon fluxes than free-electron lasers. This makes it necessary to average over multiple single shots when conducting CDI. To get meaningful results, a constant target is essential. Large helium droplets meet this requirement: Compared to other types of clusters or droplets, they exhibit a very narrow size distribution. They also have a simple electronic structure, show interesting properties like superfluidity, and can be used as a cooling matrix for embedded atoms and molecules [2].

One way of creating these droplets is a helium liquid jet. Adjusting the stagnation conditions, such a source can produce different regimes of helium droplets, where they are either ejected as spray, as a bundle of several side jets with irregularly sized droplets, or in a very uniform single jet with Rayleigh-type breakup. Droplets produced from this Rayleigh-type disintegration are relatively large with diameters of a few microns and exhibit the necessary narrow size distribution mentioned above.

Recently, we have constructed and characterized a source for a helium liquid jet, which is available for user experiments at the SQS endstation at European XFEL. Via shadowgraphy methods, we have analyzed the jet's shape and the droplet size distributions. Complementary, our characterization setup allows to determine the average droplet size via collision with external gas particles. Results from the characterization measurements will be presented.

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Comparison of Electron and Ion Emission from Xenon Cluster Induced Ignition of Helium Nanodroplets

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The charging dynamics of helium droplets driven by embedded xenon cluster ignition in strong laser fields is studied by comparing the abundances of helium and highly charged Xe ions to the electron signal. Femtosecond pump−probe experiments show that near the optimal delay for highly charged xenon the electron yield increases, especially at low energies. The electron signature can be traced back to the ionization of the helium environment by Xe seed electrons. Accompanying molecular dynamic simulations suggest a two-step ionization scenario in the Xe−He core−shell system. In contrast to xenon, the experimental signal of the helium ions, as well as low-energy electron emission show a deviating delay dependence, indicating differences in the temporal and spacial development of the charge state distribution of Xe core and He surrounding. From the pump−probe dependence of the electron emission, effective temperatures can be extracted, indicating the nanoplasma decay.

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Plasmonic information transport in monocrystalline pentagonal ag wires

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Metallic nanowires can be helpful in complex electronic nano- and nano-bio-structures. Usually they are produced by lithographic deposition on flat substrates, mostly with mediocre structural properties, which are deteriorated by irregular polycrystalline structures and only vaguely known electronic film-substrate interactions leading to reduced plasmon coherency.

We present, as an alternative solution, *free*, single, monocrystalline nanowires , separated from stabilization-detergent-free aqueous Ag- electrolytes. Large share of our research fields were, since 1968, concentrated on colloidal systems of noble metal nanoparticles. By a blunt during the chemical sample preparation , in 1995, A. Graff produced some Ag nanowires instead of particles. After finishing his diploma work he changed to the University of Halle, so, his invention remained untreated, until it became the topic of the thesis of D. Wagner (*Thesis "Eigenschaften von Silber-Nanodrähten", RWTH Aachen 2010*) .

By extensive preparative and analytical efforts, isolated wires with lengths up to 0.1 mm in a limited thickness range between about 10 and 100 nm diameter could be created. The single wire consists of five triangular, monocristallinely ordered rods connected regularly at (probably coherent) (111)-grain boundaries, thus forming pentagonal wire cross-sections. Geometric shapes and atomic structures of single wires were analyzed by high resolution TEM. Optical properties were investigated by Zsigmondy-Siedentopf dark-field microscopy extended to polarization dependent scattering.

Main purpose of the project was to investigate the surprising electrical and optical and particularly the plasmonic properties of *free* wires.

Results of several of the , in part not yet sufficiently successful, highly difficult experiments are presented in this talk:

(1) DC- conductivity of end-tip-contacted single free wires at temperatures down to 4 K.

(2) The spectra of combination of local and expanding plasmon modes. They were compared to electrodynamic calculations by Dr. habil. M. Quinten.

(3) The plasmon conductivity along the wire and its application for information transport.

This idea was first formulated on the occation of a workshop in Obernai in 1995. The research presented here, was based on the direct visual observation of field distributions of the longitudinal plasmon mode.

It was mainly performed at the Physics Department of Franzens-University in Graz. (see: H. Ditlbacher:
Thesis "Dunkelfeld- und Fluoreszenz-Mikroskopie an metallischen Nanostrukturen", 2003).

Probably the latter results open novel methods for information transport by guided waves in nanosized fibres of enormous reductions of guide thickness, compared to optical glass fibres.

Essential drawbacks are small free propagation lengths of information signals due to high plasmonic damping in metals. At present they are restricted to about 20 micrometers, hence they are limited to small nano-structures.

Finally, we want to express our gratitude to all colleagues which contributed by various support to the present longterm work.

A cationic oxide cluster with Fe-oxo. Insight from theory and experiment.

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We explore the active sites of potential heterogeneous catalytic materials with mass selected gas phase clusters as representative models. In concert with theory, exact structural assignment is possible allowing for investigation of the site in the absence of bulk phase complexity. Analysis of the cluster $FeAl_7O_{12}^+$ (Figure 1) with infrared photo-dissociation vibrational spectroscopy and DFT reveals the presence of Fe-oxo $[Fe{=}O_t]^{2+}$. The terminal O atom (O_t) bonded to a 4-coordinated Fe(IV) cation shows low reactivity with respect to hydrogen atom transfer (HAT) from CH_4. This is contrary to the high HAT reactivity of the equivalent Al oxide cation $Al_8O_{12}^+$.[1] We use theory to explore the origin of this effect and to gain insight about the spin state of Fe in the cluster.

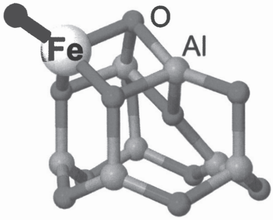

Figure 1. Structure of cation $FeAl_7O_{12}^+$

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Gas-Liquid Interface Studies by Molecular Beam Scattering on Water Surfaces

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Gas-liquid interfacial interactions are central to many research fields, such as catalytic, environmental and atmospheric chemistry. Previous techniques involving wetted-wheels[1] and cylindrical microjets[2] are unsuitable for studying scattering from volatile liquids. For example, wetted-wheels are limited to non-volatile samples due to the large evaporating surface. Cylindrical microjets have low signal-to-noise ratios because of the small scattering area, and the scattering angle from the curved surface is not well-defined[3].

We propose to use a new liquid flat jet design[4] which overcomes the disadvantages of both previous techniques. The nozzle can form water sheets with ~1mm^2 areas. This is similar in size to a molecular beam and will provide us with a better signal-to-noise ratio. The flat surface is also ideal for identifying the scattered particle angular distributions. Another benefit of the jet is the greater evaporative cooling. By cooling down the jet, we can get a lower liquid temperature and therefore lower the liquid vapor pressure.

We have combined a molecular beam scattering experiment with this new liquid source to study interfacial reactions on water surfaces. This apparatus will be used to study the scattering dynamics of noble gases, stable polyatomic molecules, and reactive radical and closed-shell species.

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Catalytic coupling of methane on $Ta_8O_2^+$

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Being the most abundant natural gas and the smallest hydrocarbon, methane represents a promising feedstock for synthesis of industrially valuable products. However, the large C-H bond strength of methane as well as its small polarizability and low pK_a makes its activation challenging. In view of ever-growing demand to develop sustainable industrial conversion of methane into value-added products, a catalyst, able to selectively activate, dehydrogenate and couple methane under mild conditions, is actively sought after. Free metal clusters and their oxides provide an ideal model to study kinetics and energetics of methane reactivity in gas phase.

The reactivity of $Ta_8O_2^+$ clusters towards methane was studied in the ring electrode ion trap (RET) [1]. Ta-clusters and their oxides were generated in a Smalley-type laser vaporization cluster source [2]; $Ta_8O_2^+$ ions were mass-selected in a quadrupole mass filter and stored for the controlled amount of time under multicollisional conditions in the RET, cooled down for the specified temperatures and filled with 200 ppm mixture of CH_4 or CD_4 in He (total pressure 0.88 Pa). Normalized ion intensities were plotted against the storage time, and kinetic traces as well as pseudo-first order rate constants were obtained through the numeric fitting of data points to the proposed reaction mechanism.

The reaction of $Ta_8O_2^+$ ions with methane leads to the formation of a cluster-methylene complex $Ta_8O_2CH_2^+$. The distribution of ion intensities over storage time can formally be described as steady state between $Ta_8O_2^+$ and $Ta_8O_2CH_2^+$. The isotopic effect on the ratio of equilibrium concentrations of methylene complex to bare $Ta_8O_2^+$, as well as the distribution of sums of normalized intensities of those ions, that contain a carbene moiety and those that do not, favor the catalytic nature of this reaction over the presence of the unreactive isomer.

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Simulation of dissociation and caging inside helium clusters

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The dissociation dynamics of molecules embedded in a condensed matter matrix is theoretically and experimentally well studied for macroscopic situations. Generally, excitation above a molecular fragmentation limit can lead to two scenarios depending on the details of the energy dissipation dynamics. The first one is fast recombination (the cage effect, see for example [1]) and the second the long time survival of separated fragments. In a cluster environment a third scenario becomes possible, namely fragments leaving the cluster with or without attached cluster particles. Helium clusters are a very cold (about 0.5 K) but still liquid and dense environment with particularly challenging properties due to the pronounced collective quantum behavior of helium leading to unusual energy dissipation dynamics. We present first results of simulations of the photo dissociation of molecular iodine, I_2, at various excitation energies inside helium clusters with several thousand atoms using a technique based on quantum effective potentials [2] to account for the quantum effects. We obtain cluster size dependent threshold energies for caging, velocity distributions of photo fragments exiting from the clusters and statistics about the number of helium solvent atoms carried along by the iodine atoms similar to experimental results obtained for CH_3I [3].

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Experimental identification of the active site in the heteronuclear reaction (VPO_4^+/C_2H_4) by gas-phase IR spectroscopy

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To identify the active site in the oxygen atom transfer reaction $[VPO_4]^{+\cdot}$ + C_2H_4 → $[VPO_3]^{+\cdot}$ + C_2H_4O conducted at room temperature before, [1] cryogenic ion vibrational spectroscopy[2–3] in combination with electronic structure calculations was used. Under multiple collisions condition, only tiny generation of $[VPO_3]^{+\cdot}$ was observed, while the intermediate $[VPO_4,C_2H_4]^+$ before $[VPO_3]^{+\cdot}$ generated was formed efficiently. So the infrared photodissociation (IRPD) spectrum of CH_2=CH_2 tagged $[VPO_4,C_2H_4]^+$ ions were measured. Compared with the IRPD spectrum of He tagged $[VPO_4]^{+\cdot}$ ions,[1] the band $\nu(P=O_t)$ in $[VPO_4]^{+\cdot}$ at 1445 cm^{-1} vanishes in the IRPD spectrum of CH_2=CH_2 tagged $[VPO_4,C_2H_4]^+$ ions. This preliminarily confirms the previously predicted mechanism that the P atom represents the active site of the heteronuclear cluster $[VPO_4]^{+\cdot}$ for reaction of $[VPO_4]^{+\cdot}$ with C_2H_4. The further excellent agreement between experimental and computational results makes an unambiguous identification.

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Some aspects of nitrogen incorporation in metal ions' co-doped titania films used as catalysts in heterogeneous photocatalysis

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Heterogeneous photocatalysis is considered as one of the approaches for ecological purification from anthropogenic pollutants. The presented research is directed to investigation of the mutual effect of nitrogen types (substitutional (Ns) and interstitial (Ni)) and d-block metal ions (zinc, iron or zirconium) incorporated in titania on the photocatalytic activity in the process of dichromate ions reduction. The catalysts in the form of solid thin (650-700 nm) films have been obtained by Pulse Laser Deposition method. The optimal conditions for active photocatalysts' synthesis (film composition, gas atmosphere and pressure, calcination temperature, and other technical parameters of deposition) have been identified. Among numerous tested films, the most efficient catalysts under both UV and visible light is found to be the films obtained from 10 wt.% ZrO_2/TiO_2 and 5 wt.% Fe_3O_4/TiO_2 targets in N_2:CH_4=5:1 atmosphere and calcined at 450 and 550 °C, respectively. The photocatalytic conversion is increased in 2 and 1.5-2 times under UV and visible irradiation, respectively, compare to nitrogen doped titania. In the case of 10 wt.% ZrO_2/TiO_2, crystallization of anatase (25%) and rutile (75 %) mixture caused by the presence of zirconium ions and effective Ns incorporation are the main items of high activity. Contrary to zirconia contained films, nitrogen and iron doped materials are XRD amorphous, the crystallization of rutile phase is started at 450 °C as detected by Raman measurements. The atomic content of nitrogen on the surface of 5 wt.% iron contained TiO_2 treated at 550 °C is the highest compare to the others iron doped films. As shown by XPS results, nitrogen can be bonded not only with titanium atom but also with iron one. Only Ni type has been detected on the surface of zinc doped films that can be a reason of their low activity. It is also observed the relationship between optical band gap values and Ns content. Thus, the direct correlation between i) efficiency of Ns incorporation, ii) ratio of Ns and Ti_{Ns}, iii) metals' nature, iv) metal content and catalytic activity of semiconducting structures is established. The mechanism of nitrogen incorporation during PLD synthesis of the materials with different properties is proposed.

IR action spectroscopy of Cu clusters with small-molecule adsorbed

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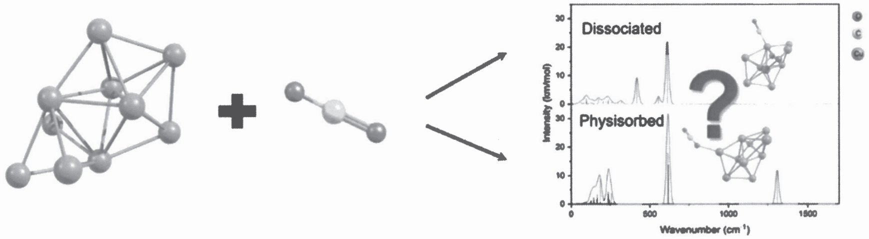
The atmospheric concentration of greenhouse gases (GHGs), such as CO_2 and CH_4, has dramatically increased over the past decades. One of the possibilities to mitigate this is to chemically transform GHG molecules into more valuable chemicals. However, these molecules are very stable and, therefore, a catalyst is required to initiate reactions. CO_2 is, for instance, commercially recycled to methanol in a hydrogenation reaction over a $Cu/ZnO/Al_2O_3$ catalyst, but this requires high temperature and pressure conditions. To make this reaction more sustainable, improved catalysts are required. To develop these an understanding of the reaction mechanism on the fundamental level is required.

In this research, we mimic the active sites of copper catalysts with Cu clusters. We react them with small molecules (CO_2, methane, etc.) and study the structure of the formed complexes via IR action spectroscopy using a tunable IR Free-Electron Laser (70-2000 cm^{-1}). The experimental spectra are compared to DFT calculations to reveal structural information, which allows for a better understanding of the nature of metal-molecule interactions.



Probing plasma evolution and atomic recombination in XUV-induced nanoplasma in ammonia clusters

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Clusters irradiated with high intensity radiation from free electron lasers undergo complex dynamical processes. In an XUV-UV pump-probe scheme using the FERMI FEL we obtain a time-resolved picture of the resulting fragments and their electronic states. Recombination and molecular dissociation lead to a great variety of electron energies and ionic fragments that give insight into the underlying dynamics. With the 266nm probe laser we can selectively ionize excited states that are created in the nanoplasma. The highest intensity of electrons and ions ionized by the UV-probe laser originates from excited hydrogen in the n = 2 state. We use a combined approach observing a pump-probe delay- dependent blue-shift in the electron kinetic energies, and deriving proton kinetic energies from time-of-flight broadening, to characterize the nanoplasma evolution (see figure). We see that the ejection of fast protons and a correlated reduction of the overall charge state of the cluster plays a significant role and evolves on a sub-picosecond timescale. Proton ejection has been predicted to strongly influence the plasma evolution and the inner charge state of hydrogen containing molecular clusters [1].

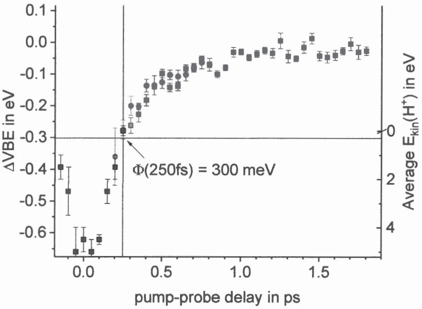

Figure 1. The red and blue curve (right) show the VBE shift in the observed probe photoelectrons for two different FEL pump wavelengths. The black dots are the average probe H^+ ion kinetic energy derived from the time-of-flight broadening. Please note the different scales for ΔVBE and H^+ kinetic energy. The two scales are adjusted in a way that the y-axis

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Infrared Spectroscopy of $CO3^{\bullet -}(H2O)_{1,2}$ and $CO4^{\bullet -}(H2O)_{1,2}$

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Both $CO3^{\bullet -}$ and $CO4^{\bullet -}$ are anions present in the atmosphere, $CO3^{\bullet -}$ is an abundant molecule in the troposphere, $CO4^{\bullet -}$ can be found closer to the Earth's surface. [1] The formation of both ions under atmospheric conditions has been explained by Fehsenfeld et al. [2] UV-Vis spectra have already been recorded previously in our group. Now we added IR spectra in order to get a more complete overview of the ions' properties and their structures.

The measured IR spectra show several features more than are predicted by DFT based quantum chemical calculations for both hydrated $CO3^{\bullet -}$ and $CO4^{\bullet -}$ anions, indicating that harmonic minimum energy calculations of the vibrational frequencies are not sufficient to fully describe the ongoing processes. Therefore, temperature likely has to be considered in the calculations. First attempts in using molecular dynamic calculations to produce the infrared spectra show promising results.

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Delayed electron detachment and fragmentation of laser-excited metal cluster anions

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Delayed Electron Detachment (DED) was employed studying Co_4^- ions [1] stored in the Cryogenic Trap for Fast ion beams (CTF) [2], an electrostatic ion beam trap operated at the Max Planck Institute for Nuclear Physics (MPIK) in Heidelberg. In this trap, stored ions oscillate in the linear, field-free spacing (~30 cm) between the electrostatic mirrors at about 6 keV kinetic energy. Up to 1 ms after irradiation with a crossed nanosecond laser pulse of an optical parametric oscillator, neutrals due to electron detachment were detected with a MicroChannel Plate (MCP) detector. Scanning the laser frequency allowed us to continuously monitor the internal energy distribution of Co_4^- and observe how both hot and cold cluster ensembles thermally equilibrate with the trap environment.

With a similar laser setup and MCP-based detectors, we studied DED and fragmentation of Al_4^- ions in the Cryogenic Storage Ring (CSR) [3], a novel cryogenic electrostatic storage device at MPIK with an effective radiative temperature of ~10 K [4] and low residual gas densities (<140 cm^{-3}) inside its experimental vacuum chambers. Under these conditions, ion beams with kinetic energies up to 300 keV per elementary charge can be stored for hours on the 35 m closed orbit of CSR. To examine DED near the adiabatic detachment energy (~2.2 eV) of Al_4^-, we varied the photon energy in fine steps from 1.95 eV to 2.25 eV. Monitoring the DED events revealed a vibrational peak pattern below 2.2 eV. The cooling behavior of the stored ions could be observed for up to 30 s. We envisage further DED measurements for determining the adiabatic detachment energy.

We discuss the experiment on Co_4^- at CTF and give an insight into the ongoing studies of Al_4^- at CSR.

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Acid Solvation versus Dissociation at Ultracold Temperatures: Sequence Matters

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Aqueous acid dissociation reactions are at the heart of numerous chemical and biological processes. These reactions also play a significant role in atmospheric chemistry, most importantly, to the processes leading to ozone layer depletion. In the past, many theoretical and experimental studies have been carried out on small HCl-H_2O clusters to understand the fundamentals of acid dissociation. [1-3]

We have built a helium droplet machine at the FELIX laboratory [4], which allows us to study ice particle formation and elementary reactions mimicking the star dust conditions.

Herein, we report the full dissociation of HCl on stepwise addition of ≥ 4 H_2O molecules at ultracold temperatures (0.4 K) of helium droplets. [5] Ultrabright pulsed free electron lasers at FELIX laboratory allowed us to explore the fingerprint region [3], 1000-1700 cm^{-1}, for HCl dissociation. Using mass-selective detection, we could unambiguously assign the spectral bands for the smallest droplet of acid, $H_3O^+(H_2O)_3Cl^-$. We also found that the dissociation of HCl is highly specific to the sequence in which molecular aggregation takes place. Accompanying ab initio-MD simulations demonstrate that not only reaction stoichiometry but in particular the reaction sequence needs to be explicitly considered to rationalize ultracold chemistry.

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Electronic and geometric structure of copper formate clusters probed by IRMPD and UV/Vis spectroscopy

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Copper-based catalysts are widely investigated for carboxylation reactions and hydrogen storage applications. They are already applied in industrial catalysis, e.g. in methanol synthesis [1]. The formation of formate is regarded as a crucial step in the activation and transformation of carbon dioxide to methanol or formic acid [2]. It was shown in the gas phase that copper hydride clusters can react with carbon dioxide barrierlessly to copper formate species [3]. We have recently shown that the formation of formic acid can happen in the decomposition of small Cu(II) formate clusters [4].

In this contribution, well-defined gas phase systems are used to investigate copper formate clusters along with their electronic structure by means of IRMPD and UV/Vis-spectroscopy in an FT-ICR mass spectrometer. Decomposition is initiated through vibrational excitation of C-O and C-H stretching modes, as well as electronic excitation using tunable laser systems. Experiments are supported by quantum chemical calculations.

The decomposition of copper formate anions leads towards copper hydrides in oxidation state +I with one or two copper centers, through a sequence of reactions. The observed electronic transitions hereby mainly depend on the oxidation state of the copper centers along with the orientation of the formate ligands. No copper-copper bonding interaction is observed. For Cu(I) centers, Cu(d) to Cu(s/p) transitions are observed while Cu(II) centers exhibit Cu(d)-Cu(d) transitions along with charge transfer from ligand to metal. The decomposition products depend on the photon energy. Photochemistry following a charge transfer transition may lead to the loss of a HCOO radical.

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Long-Baseline Universal Matter-Wave Interferometry

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We present the novel Long-Baseline Universal Matter-wave Interferometer (LUMI) in Vienna, a near-field, Kapitza-Dirac-Talbot-Lau type interferometer designed for quantum interference of high-mass molecules. It improves on an earlier Kapitza-Dirac-Talbot-Lau interferometer [1] by a factor of 10 in length and a factor 100 in inertial force sensitivity.

The modular design of the experiment permits the in-vacuum exchange between optical and material diffraction gratings as well as the introduction of electric and magnetic fields, collision cells or spectroscopy lasers to explore the electronic, optical, magnetic and structural properties of a very diverse class of particles. We discuss new experiments with atoms, complex molecules and future prospects for high-mass clusters with improved precision over previous devices.

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Measurement of optical spectra of astrophysically relevant Si-bearing molecules

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Si is one of the major constituents of interstellar dust. Based on the star of origin, either silicon carbides (C-rich stars) or silicon oxides (O-rich stars) are believed to be the predominant dust forming species. So far only very small specific molecular SiOs or SiCs have been confirmed via observations. Also observed are large silicate nanoparticles. Assuming simple growth patterns, from these few-atom molecules to nanoparticles, it can be inferred that intermediates must exist. The exact nature of these growth mechanisms and the intermediates themselves are, however, still elusive.

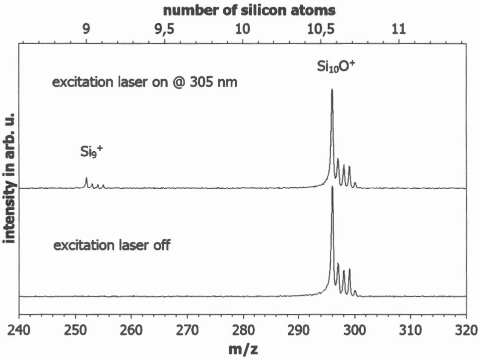

Figure 1: Ion signal of mass selected $Si_{10}O^+$ clusters with and without excitation laser. After absorption of a photon, the cluster fragments into Si_9^+ and SiO. The photon energy dependent dissociation cross section of this process is a measure for the absorption cross section of $Si_{10}O^+$.

Using a laser vaporization source, we produce small to medium sized silicon carbide and silicon oxide cations. These particles are possible intermediates between the observed few atom species and the nanoparticles. Using photoexcitation of these intermediates after mass separation we determine their photon energy dependent fragmentation pathways and their photon energy dependent photodissociation cross sections. The fragmentation pathways reveal stable intermediates that may survive in the radiation fields of stars and from the photodissociation cross section, optical absorption spectra can be inferred, thus enabling an observational search. Additionally, by comparing the results to quantum chemical calculations, we can assign geometries of some of these so far unknown molecules.

In this poster, we will also present a newly applied optimization algorithm that automatically optimizes the electrostatic potentials and the required delay times of the setup to obtain highest transmission of a desired mass selected species.

New setup for core-level and valence-band photoelectron spectroscopy of mass-selected metal clusters at FLASH

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The photon energies of several tens of eV delivered by FLASH allow to conduct core-level photoemission studies on size-selected metal clusters in the gas phase. Interesting aspects are phenomena like core-hole screening which can indicate size-dependent changes in the binding character. However, probing these nanometer-sized targets requires the preparation of a sufficiently high target density in the FEL interaction region.

In this contribution we present a new experimental setup, which includes a high-current cluster source, a quadrupole mass filter and a radio-frequency ion trap. In order to combine high transmission with the capability to conduct angular-resolved studies, the setup consists of two separate interaction regions to perform photoemission experiments. The design allows to record photoelectrons either by a magnetic bottle or by field-free time-of-flight electron spectrometers.

In the last measurement campaign at FLASH II in Hamburg, experiments on mass-selected lead clusters, with sizes down to only 3 atoms, have been conducted. The spectra show a size-dependent shift of the binding energies of the 5d level electrons which can be compared to the metallic sphere model.

Temperature-induced processes for FexNi1-x nanoparticles on surfaces

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Magnetic nanoparticles have received great attention due to their applications in ultrahigh density magnetic recording and biomedicine. In comparison with pure Fe, Co and Ni, the nanoparticles of binary transition metal alloy can have considerably higher magnetic moments and much more complex phases under different conditions [1]. In order to make devices based on nanoparticles of binary transition metal alloys, it is necessary to investigate the structural phase dependence on the temperature and composition [2].

Two different FeNi alloys nanoparticles are prepared by a magnetron sputtering source. All nanoparticles are prepared under UHV condition on a W (110) surface, therefore contaminations are avoided. We study the response of FeNi alloy nanoparticles to the high temperature. Size and structural properties of nanoparticles are investigated by Scanning Tunneling Microscopy (STM).

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Guided Ion Beam Hydration Energies of $FeOH^+(H_2O)_n$, n = 1 - 4, in Comparison with Theory.

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All $FeOH^+(H_2O)_n$ complexes are observed to undergo water loss under collision induced dissociation experiments. For n = 2 - 4, a sequential water loss is found for higher collision energies while for n = 1, a competitive loss of the neutral hydroxide group is observed. The experimental cross sections are modeled to retrieve 0 K bond dissociation energies (BDEs) which are then compared to quantum chemical calculations. In addition, experimental BDEs for the OH loss from $FeOH^+(H_2O)_n$, with n = 2 – 4 are derived using the experimental BDE of n = 1 and literature data for the water loss from $Fe^+(H_2O)_n$ species. Geometry optimizations were performed at B3LYP/6-311+G(d,p) level of theory and used for single point calculations at B3LYP, B3P86, MP2 and CCSD(T) levels with a 6-311+G(2d,2p) basis set. For cam-B3LYP/def2-TZVP calculations, geometries were re-optimized at this level of theory and dispersion, as well as zero point energy corrections were included for all levels of theory. Theoretically calculated BDEs are in reasonable agreement for water loss from both $FeOH^+(H_2O)_n$ and $Fe^+(H_2O)_n$ complexes, as well as for the OH loss from Fe^+OH but are too low for the loss from larger hydrated complexes.[1]

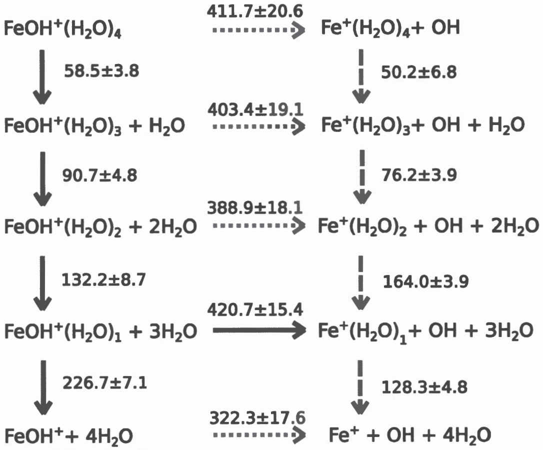

Figure 1: Experimental BDEs in kJ/mol for H_2O or OH loss from $FeOH^+(H_2O)_n$ (solid arrows), derived BDEs for OH loss from $FeOH^+(H_2O)_n$ (dotted arrows) and literature BDEs for H_2O loss from $Fe^+(H_2O)_n$ (dashed arrows) [2].

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Spectroscopy of neutral boron clusters using tunable VUV generated by 4-wave mixing

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Boron clusters have been found to show interesting binding behaviors with delocalized aromatic systems due to the only three valence electrons of the boron atom. According to previous experiments in combination with calculations, anionic boron cluster [1,2] are able to form versatile structures like planar, ring-like and cages. For neutral B_{40} that is suggested to be formed in these experiments by electron detachment from a minor abundant, high energy isomer of the anion a highly stable cage structure has been predicted [2]. Parallels to the carbon fullerenes might be drawn which call for a more direct investigation of the neutral clusters structures.

For this, the neutral clusters can be size-selectively characterized by vibrational spectroscopy using the IR-VUV two color ionization scheme. The resulting infrared spectra are structural fingerprints and, by comparison with calculated IR spectra, can allow for isomer assignment. In IR-VUV two color ionization, VUV photons ionize the clusters near the ionization threshold where the ionization efficiency for cold clusters is low. However, if the clusters can be heated in a preceding resonant IR excitation step a strong increase in the ionization efficiency can be detected. By measuring the ion yield as a function of the IR frequency, cluster size-specific IR spectra can be determined. However, for a given VUV photon energy, there is access to only a limited number of cluster sizes as the ionization energy depends on cluster size. So far, with a commercial VUV laser (F_2 laser, 7.9 eV) very few sizes of boron clusters (B_{11}, B_{16}, B_{17}) could be characterized [3]. To overcome the limitation in photon energy VUV photons are now generated by four-wave mixing in Xenon. In the present configuration which shall cover an energy range of 6.5 eV to 8.2 eV two dye lasers interact in a static gas cell and the resulting 2+1 difference frequency is used for ionization. After creating 7.9 eV photons in that way the spectra reproduce the results obtained via F_2 laser ionization.

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Isolation and Characterization of the Cyanoformate Anion by Infrared Photodissociation Spectroscopy

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Carbon dioxide is known to form complexes with small nucleophile anions, such as halides and pseudohalides (e.g. F^-, Cl^-, OH^-). The reaction of cyanide with carbon dioxide leads to the formation of cyanoformate or $NCCO_2^-$. In nature, cyanoformate is involved in the biosynthesis of ethylene by the enzyme 1-aminocyclopropane-1-carboxylic acid oxidase. Recently, Murphy *et al.* prepared the tetraphenylphosphonium salt of cyanoformate by exposing a concentrated solution of $[PPh_4][CN]$ in acetonitrile to an atmosphere of carbon dioxide.[1] In this work we show that cyanide reacts with carbon dioxide in the atmosphere to form cyanoformate. We isolated the cyanoformate anion and recorded its vibrational spectrum in the spectral region from 700 to 4000 cm^{-1} using infrared photodissociation spectroscopy at cryogenic temperatures. The spectrum can be accurately reproduced using high-level *ab initio* methods.

Moreover, we studied the microhydration of cyanoformate. Cyanoformate is known to be unstable in polar solvents and traces of water lead to the decomposition into cyanide and hydrogen carbonate. However, we show that cyanoformate is stabilized by the first few water molecules. This is consistent with the results obtained for the microhydration of hydrogen carbonate.[2]

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Studying the dynamics and decay channels of C_4O^- in the electrostatic Cryogenic Storage Ring

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The electrostatic Cryogenic Storage Ring (CSR) at the Max-Planck-Institute for Nuclear Physics in Heidelberg offers new possibilities for the study of charged molecules and clusters. The chambers of this large-scale experiment with a circumference of 35 m can be cooled down to 6 K, creating an experimental setup with nearly negligible blackbody radiation [1]. Together with densities corresponding to the equivalent of 10^{-12} mbar or below at room temperature even infrared active systems can lower their internal energies to the few-K level [2]. Ions with sizes varying from small atoms to biomolecules can be stored at energies up to 300 keV in the purely electrostatic ring. As a consequence, new tools for the identification and separation of heavier molecular and cluster systems have to be developed. A comprehensive experimental program aims at investigating ground-state properties of molecular and cluster ions in the gas phase. Photon-induced electron detachment and fragmentation of C_4O^- were studied as a benchmark system. To this end, a tuneable, pulsed OPO laser was used to excite the molecules at various photon energies. Two detectors were employed simultaneously to measure the produced neutrals and fragments in coincidence. Resonant processes could be observed at certain photon energies. Furthermore, by exciting the molecule at different storage times, the radiative cooling of the system inside the cryogenic environment could be studied. The CSR's new analytical tools will be presented along with preliminary results from the study of C_4O^-.

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Assembling of gold nanoparticles: main gaps to be filled

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Anisotropic gold nanoparticle/nanorod(Np/Nr) assemblies attract much attention, because they can possess new optoelectronic functions when combined with functional-molecules. Formation of dumbbell AuNps, for instance, by means of different length alkane dithiols leads to the formation of a new absorption-band in the visible wavelength range.[1] AuNps assemblies interconnected by photochromic molecules [2] can be considered as nanoresistors with optically triggered resistance. However, progress in developing of anisotropic gold nano-assemblies is very slow due to various factors governing their formation for instance the specific surface chemistry of Np/Nr compared to the chemistry on flat crystalline surfaces. In addition, a limited number of analytical methods to characterize Np/Nr surfaces are available [1, 3, 4]. Hence, development of semi empirical approaches to monitor specific stages of a nano-assembly formation is required. Therefore, the aim of the presentation is to present some drawbacks of direct strategy for the dumbbells formation and the progress in an optimized pathway for developing Np/Nr dumbbells interconnected by aliphatic molecules directly on a silicon oxide surface for the purpose of molecular electronics and photonics. Some preliminary studies of gold Np functionalized by diarylethene photochromic molecules will be presented as well [5].

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Small silver clusters on porphyrin templates

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Due to promising applications in nanotechnology, the size- and structure-dependent optical properties of noble metal clusters have been studied for many years. In the smallest size regime, both the cluster geometry and optical properties are strongly influenced by size [1]. Recently, first studies on the collective optical characteristics and interactions between silver clusters arranged in an ordered 2D lattice were published [2]. Furthermore, it has been predicted that porphyrin templates may be used to produce such well defined arrangements, e.g. of cationic Ag_3 clusters [3]. As a first step into the direction of cluster arrays we investigated the possibility to combine cationic Ag_3 clusters with single porphyrins in a collision cell in the gasphase and explored first the optical properties of the produced silver-porphyrin-hybrids in the UV/VIS range.

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Angle resolved photoelectron spectra of small copper clusters

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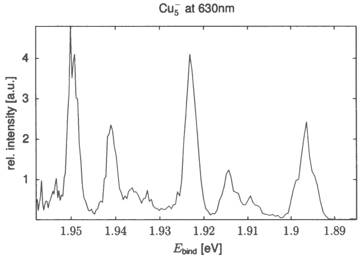
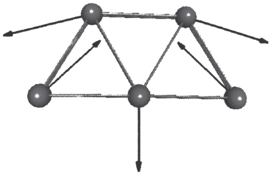
Angle resolved spectra are an important test for the theoretical description of clusters since they carry more information than the bare energy levels. The anisotropy of photoelectron spectra for example depends on the angular momentum state.

The cluster anions are produced in a magnetron sputter source and enter a time-of-flight spectrometer for mass measurement and selection. Afterwards electrons are detached by linear polarized laser light and projected onto a MCP detector in a velocity map imaging setup.

Here the results for small copper cluster are presented. Although copper clusters have been studied intensively, there are still undiscovered features of their photoelectron spectra. For example Cu_5 shows a strong vibrational structure, which is in good agreement with DFT calculations.



(a) Vibrational structure in the photoelectron spectrum of Cu_5^-



(b) Most intense vibration identified by DFT calculations

Towards IR action spectroscopic characterization of CO_2 hydrogenation over metal clusters

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One route to reduce atmospheric CO_2 levels is by regenerating it into a fuel. Hydrogenation of CO_2 to one of the simplest fuels, methanol, is exothermic, but due to the strength of the CO_2 bonds, the reaction requires high temperatures and a catalyst to proceed[1]. The current industrial process is catalyzed using a $Cu/ZnO/Al_2O_3$ catalyst, with strong indications that the active site is formed by Cu nanoparticles with ZnO as promotor[2,3]. The reaction mechanism is, however, poorly understood. To enable the development of novel, more efficient CO_2 hydrogenation catalysts, we aim to model the active site using clusters of Cu and other metals.

We are currently developing experiments where ionic metal clusters are generated in a laser ablation source, mass-selected in a quadrupole mass filter, and stored in a RF ion trap. Here, the clusters are reacted with CO_2 and H_2 under controlled conditions. Products formed are mass-analyzed using a Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer coupled to the Free Electron Laser for IntraCavity Experiments FELICE. Using the latter, we can then structurally characterize clusters, formed complexes and possible intermediate products.

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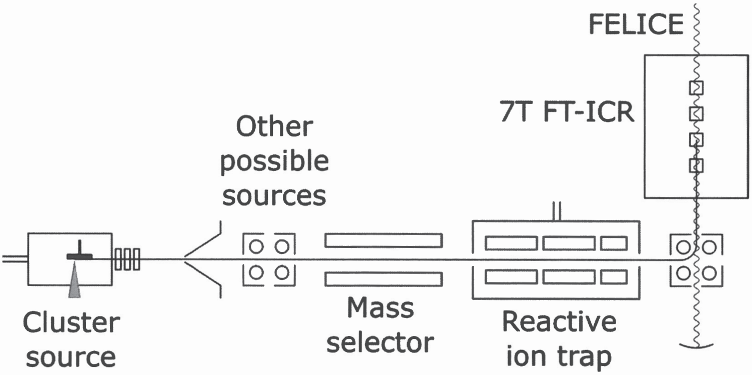

Theoretical DFT Study on the Structure and Reactivity of Selected Cobalt Aluminate Cluster Ions

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Starting from the fully oxidized electronically closed-shell $Al_3O_4^+$ cluster ion[1,2], one or two aluminum atoms were substituted by cobalt atoms to gain the $CoAl_2O_4^+$ and $Co_2AlO_4^+$ cluster ions. Potential global minimum energy isomers and associated spin states were found using genetic algorithms with subsequent refinement on the DFT level. Broken symmetry DFT calculations were conducted to investigate the effect of antiferromagnetical coupling between the transition metal atoms in the $Co_2AlO_4^+$ cluster. In the calculations, a variety of hybrid (TPSSh, B3LYP, PBE0, BHLYP) and non-hybrid (PBE, TPSS) DFT functionals was used in combination with the TZVPP basis set.

As a result, various potential global minimum energy isomers were found for each cluster. Thereby, the energy order differed significantly concerning the used DFT functional in all cases. The calculated harmonic vibrational spectra are well distinguishable for the different isomers and the actual lowest energy isomers could be found when comparing them to experimental spectra. The same two general structural motifs were found for each cluster. Namely, radical structures with one reduced cobalt atom M^{2+} causing a terminal oxygen radical $O^{\cdot-}$ and structures with fully oxidized cobalt atoms M^{3+} and fully reduced oxygen atoms O^{2-}. As for the $Co_2AlO_4^+$ cluster, there are various individual isomers for each of these classes whereas the overall picture is more distinct for the $CoAl_2O_4^+$ cluster. Since considerable differences in reactivity were expected for these differing structural motifs, the reactivity of the most promising isomers towards hydrogen atoms and methane molecules was investigated for both clusters.

References

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Temporal Development of a Fully Ionized Helium Nanoplasma

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Femtosecond pump-probe ion and electron spectroscopy is applied to study the long-time development of strong-field induced helium nanoplasmas. Quasi-free electrons, bound by the deep confining mean field potential, are elevated towards the vacuum level in the nanoplasma expansion. Subsequent electron recombination gives rise for transitions between He^+ states, resulting in Auger emission [1]. Time resolved analysis of the Auger energy transfer to quasi-free electrons allows for a temporal mapping of the distribution of delocalized electrons in the developing mean-field. Furthermore, we use above-threshold ionization as a diagnostic tool to trace the recombination of delocalized electrons near the vacuum-level into highly excited Rydberg states. This process is reflected by an opposing trend between the two helium charge states.

References

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