



ORGANIZERS

Ingo Barke Thomas Fennel Bernd v. Issendorff Christian Klinke Karl-Heinz Meiwes-Broer Christian Peltz Josef Tiggesbäumker

		Sunday,	October 6th	
19:00			dinner	
		Monday,	October 7th	
$\begin{array}{c} 08{:}45\\ 09{:}00\\ 09{:}40\\ 10{:}05 \end{array}$	KL T T	Asmis Breier Torres Boy	Welcome ^{1,2,3} H: The Research Training Group on Hydrogen Isotopes Exploring $\operatorname{Si}_n \mathbb{C}_m^+$ molecules: First laboratory detection of $\operatorname{Si}\mathbb{C}^+$ via EPD H-Bonding in Ionic Complexes: Insights from Infrared Action Spectroscopy in Helium Droplets	
10:30			coffee break	
11:00 11:40 12:05	KL HT T	von Helden Demianenko Jongchan	Spectroscopy of Mass/Charge Selected Ions in Helium Droplets Time- and energy-resolved fluorescence measurements of collective effects in polyacene aggregates attached to rare gas clusters Investigating the Valence Electronic Structure of Sub-micrometer	
		-	Aqueous Droplets	
12:30			lunch	
16:45	KL	Schweikhard	Production, Identification and Investigation of Actinide Clusters by	
17:25	Т	Penna	Laser-Ablation Multi-Reflection Time-of-Flight Mass Spectrometry IRPD Spectroscopy of [Fe ₂ AlO ₄] ⁺ and [Co ₂ AlO ₄] ⁺ Unexpected Structural Isomers upon Transition Metal Substitution Imaging Plasmons of Individual Supported Nanoparticles: Energetics, Mode Geometry, and Photoelectron Momentum	
17:50	KL	Barke		
19:00			dinner	
20:00			poster session	
		Tuesday,	October 8th	
9:00 9:40	KL T	Bernhardt Ablyasova	Femtosecond XUV-Spectroscopy on Nano-Structured Surfaces Electronic state of a manganese oxide clusters revealed by Soft X-ray spectroscopy	
10:05	ΗT	Mikolaj	Activation of CO_2 by free metal oxide clusters	
10:30			coffee break	
11:00 11:40	KL T	Schooss Flach	Hydrogen Induced Structure Transitions in Small Platinum Clusters Abrupt Change from Ionic to Covalent Bonding in Nickel Halides	
12:05	Т	Bastian	Accompanied by Ligand Field Inversion Probing the Temperature of Single Quantum Dots Confined in a Nanoparticle Ion Trap by Fluorescence Thermometry	
12:30			lunch	
16:45	KL	Iwe	Size and charge state effects on the plasmonic properties of polyanionic silver clusterss	
17:25	Т	Jin	Probing the Vibrational and Rotational Wave-Packet Dynamics of Mass-selected Neutral Clusters	
17:50	KL	Dopfer	Spectroscopy and Dynamics of Diamondoid Ions and Their Clusters	
19:00			dinner	
20:00			poster session (bear sponsored by Hiden Analytical Europe GmbH)	

		Wednesday,	October 9th
09:00	KL	Christen	Rayleigh scattering study of the formation of propane clusters
			in supersonic jet experiments
09:40	Т	Tang	X-ray coherent diffractive imaging of nanoplasma generated from liquid submission
			droplets by irradiation with intense UV light
10:05	HT	Raspe	Size effects in the Coulomb explosion of mass-selected silver clusters
10:30			coffee break
11:00	KL	von Issendorff	Dynamics of superheated silver nanoparticles
11:40	HT	Ovcharenko	X-ray pump – X-ray probe induced dynamics
12:05	HT	Sindelar	Source and laser technologies for matter-wave interferometry
			with large metal clusters
12:30			lunch
10.15		Ŧ	
16:45 17:25	KL T	Lau Studomund	Small Cilicon Owide Cations
17:20	T	Studemuna	Small Sincon-Oxide Cations: Photodissociation and Ontical Absorption Properties
17:50	KL	Fielicke	Action spectroscopy in the infrared: from photodissociation
			to photo-induced Rydberg ionization
19:00			barbecue
		Thursday.	October 10th
		21101000039	
9:45	\mathbf{KL}	Vajda	Controlling Selectivity in Oxidative Dehydrogenation Reactions
			with Mono- and Bimetallic Clusters
			by Changing Composition Atom by Atom
10:30			coffee break
11.00	т	Arildii	IP spectroscopy of larger Purrole action elustors (Purt ⁺):
11.00	1	Amun	Evolution of charge resonance interaction
11:25	\mathbf{KL}	Niedner-Schatteburg	N_2 activation by size selected transition metal clusters
			- why should I care and how do I optimize it?
12:05			Concluding remarks
12:30			lunch
			doparturo
			ucharme

Poster	
Ablyasova	Electronic state of a manganese oxide clusters
	revealed by Soft X-ray spectroscopy
Barke	Silver cluster plasmon experiences strongest substrate effect
	when excited farthest away:
	Spooky action at a distance?
Bastian	Controlled charging of single silica nanoparticles
	by electron attachment and charge transfer
Buttkus	Cryogenic Ion Trap Vibrational Spectroscopy of
	$[\mathrm{PF}_6^-, (\mathrm{HFIP})_x, (\mathrm{H2O})_y]$ Complexes:
	Exploring Solvent-Solvent vs. Solvent-Anion Interactions
Diaconescu	Characterization of the Yb ⁺ $[4f^{13}6s^2]$ F ⁻ states of ytterbium fluoride
	using REMPI spectroscopy
Han	Probing the Adsorption and Activation of CO ₂ Molecules
	by Transition Metal Oxides with Infrared Photodissociation Spectroscopy
Harmsen	Coulomb explosion of pure and doped helium droplets
Kazemi	High-resolution photoelectron spectroscopy on Niobium clusters
Kurti	A new setup for synchrotron x-ray photoelectron spectroscopy
	on gas-phase size selected clusters
Lakhanpal	A new setup for Free Electron Laser based photoelectron spectroscopy.
Ober	Ultracool IR Spectroscopy: Carbocations in Helium Nanodroplets
Peltz	Reconstructing the anisotropic expansion of a laser driven nanoplasma
Pervez	Anisotropic photoemission from an individual plasmonic silver nanoparticle
	deposited on silicon
Tchounga	Detailed investigation of unexpected photoelectron spectra
9	via angle-resolved spe+ctroscopy of Gold clusters
Schwarz	Gas phase photoelectron spectroscopy studies on anthracene anions
Servarz	sus phase photoereeren spectroscopy studies on antifacene amons

^{1,2,3}H: The Research Training Group on Hydrogen Isotopes

Knut R. Asmis

Leipzig University, Wilhelm Ostwald Institute for Physical and Theoretical Chemistry, Germany

The Research Training Group (RTG) on Hydrogen Isotopes, centred at Leipzig University, started its business in October 2021. In my presentation, I will give an introduction to the structure and central research aim of the RTG, followed by highlighting recent results of the two projects directly related to research on gas phase clusters.

In the first project, we characterize and model the role of nuclear quantum effects in the adsorption of dihydrogen isotopologues (DHIs) by metal-containing clusters in order to improve design concepts for DHI separation materials. Copper cation DHI complexes are characterized by infrared photodissociation spectroscopy and ion trap mass spectrometry, focusing on cluster ions with sterically tailored electrophilic binding sites that mimic binding environments found in metal organic frameworks.[1] We discuss the role of the environment and the coordination geometry of the adsorption site in achieving a high selectivity and the ramifications for identifying and designing future materials for adsorptive DHI separation.[2]

In the second project, we study the gas phase vibrational spectroscopy of the halide anion ($X^- = CI^-$, Br⁻, I⁻) – 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) complexes. HFIP is a versatile, cost-effective and increasingly popular solvent used in organic synthesis for promoting chemical reactions, which also finds application in chemical biology as well as supramolecular and polymer science. A comparison of the results to those obtained for the corresponding complexes with (d-)isopropanol and water demonstrate that the observed red-shift of the hydrogen-bonded O-H(D) stretching frequency scales with the difference of the anion proton affinity and the deprotonation enthalpy of the neutral molecule. A bonding analysis reveals that the observed vibrational signatures in the HFIP complexes are characteristic for strong hydrogen bonds dominated by electrostatic attraction.

- [1] Ji. Jin, T. Wulf, M. Jorewitz, T. Heine, K.R. Asmis, Phys. Chem. Chem. Phys. (2023), 25, 5262-70.
- [2] E.G. Dongmo, S. Haque, F. Kreuter, T. Wulf, J. Jin, R. Tonner-Zech, T. Heine, K.R. Asmis, *Chem. Sci.* (2024), **15**, 14635-43.

Exploring Si_nC_m⁺ molecules: First laboratory detection of SiC⁺ via EPD

Alexander A. Breier¹, Taarna Studemund¹, Kai Pollow¹, and Otto Dopfer¹

¹ Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

The detection of SiC, a challenging endeavor both in laboratory and space-based settings, saw a breakthrough with collaborative efforts between radio astronomy and laboratory astrophysics, culminating in its definitive identification in the circumstellar shell of the evolved carbon star IRC+10216 [1]. SiC's presence, confirmed through millimeter-wave spectral lines, emphasizes its relevance in cosmic dust formation processes, particularly in carbon-rich environments [2] where photochemistry also plays an important role. Notably, the identification of SiC will likely soon extend to cationic species, offering insights into the ionization- and the non-equilibrium processes within the environment of evolved stars [3].

Nevertheless, SiC and its ionic counterparts can be seen as the starting pieces in siliconcarbide dust formation reactions, serving as crucial precursors in the nucleation and growth of dust grains. This presentation focuses on the experimental investigation of the smallest cationic silicon-carbide molecule, SiC⁺, synthesized in our laboratory by evaporating a solid SiC rod using a pulsed laser in a carbon-enriched buffer gas environment. The adiabatic expansion of the gas jet facilitates the observation of its electronic photodissociation fragments, shedding light on its electronic structure and vibrational motions. This is conducted within a tandem mass spectrometer integrating a quadrupole and a time-of-flight mass spectrometer, alongside a widely tunable UV/VIS-OPO laser [4,5]. Subsequently, the experimental observations are compared and evaluated with computational predictions using high-level quantum chemical calculations [6].

As observational techniques advance and spectroscopic information is recorded in laboratory environments, SiC⁺ may emerge as a significant component, offering valuable insights into key aspects of astrophysical processes and cosmic evolution.

References:

[1] J. Cernicharo, C. A. Gottlieb, M Guélin, P. Thaddeus, and J. M. Vrtilek, ApJ 341, 25 (1989).

- [2] M. Frenklach, C. S. Carmer, and E. D. Feigelson, Nature **339**, 196 (1989).
- [3] D. Gobrecht, Front. Astron. Space Sci. 8, 662545 (2021).

[4] T. Studemund, K. Pollow, S. Verhoeven, E. Mickein, O. Dopfer, and M. Forstel, J. Phys. Chem. Lett. **13**, 33 (2022).

[5] M. Förstel, B. K. A. Jaeger, W. Schewe, P. H. A. Sporkhorst, and O. Dopfer, Rev. Sci. Instrum. **88**, 12 (2017).

[6] D. Zhou, D. Shi, J. Sun, and Z. Zhu, Spectrochim. Acta A **204**, 164 (2018).

H-Bonding in Ionic Complexes: Insights from Infrared Action Spectroscopy in Helium Droplets

 $\frac{\text{América, Y. Torres-Boy}^1, \text{Martín I. Taccone}^1, \text{Carla Kirschbaum}^{1,2}, \text{Katja Ober}^1, \text{Tamar Stein}^3, \text{Gerard Meijer}^1 \text{ and Gert von Helden}^1}$

¹Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany ²nstitute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany ³Institute of Chemistry and Fritz Haber Center for Molecular Dynamics, Hebrew University of Jerusalem, Jerusalem 91904, Israel

IR Action Spectroscopy in Helium Droplets of isolated molecular ions and ionic clusters has been proven to be an effective technique for the experimental characterization of molecular systems.[1] Because the ions are examined at the equilibrium temperature of the helium droplet (0.37 K), this method presents a significant advantage greatly reducing the spectral congestion.

Hydrogen bonds, though weaker than covalent bonds, are widely present in nature and play a significant role in many processes across physics, chemistry, and biology. By studying the structure of hydrogen-bonded clusters, we can gain insights into molecular interactions, stability, and the dynamics of diverse processes.

Investigating hydrogen-bonded systems at cryogenic temperatures allows for a better understanding of their fundamental properties. In this study, we investigate the proton-bound dimer of dihydrogen phosphate and formate ([H2PO3 + H + HCOO]-) using cryogenic action spectroscopy. High-resolution vibrational spectra were obtained for the dimer at different levels of deuteration and compared to both anharmonic and harmonic quantum chemistry predictions. Notably, some H-bending modes of the non-deuterated complex are found to be sensitive to the helium environment. For the partially deuterated complexes, the experiments indicate that internal dynamics lead to an interconversion process between these two isotopomers inside the He droplet after photon excitation. The fundamental aspects regarding the position, energetics, and dynamics of the dimer of the complex are thoroughly examined and discussed. Future experiments involving time resolution are also addressed.



Figure 1: Caption text goes here.

References

[1] A. I. G. Flórez, et al., PCCP (2015), 17(34), 21902-21911.

Infrared Spectroscopy of Mass/Charge Selected Ions in Helium Droplets

<u>Gert von Helden</u>

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Helium droplets can pick up mass/charge selected 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 atoms up to mass/charge selected protein ions containing several thousand atoms.

The figure below shows a schematic of the experimental setup. Ions are generated using a nano



Figure 1: Scheme of the experimental setup.

electrospray source. After mass/charge selection using a quadrupole, ions are injected and stored in an ion trap. Helium nanodroplets, generated by a cooled pulsed valve, are then allowed to traverse the trap. The droplets travel at a beam velocity of ≈ 500 m/s and even relatively small droplets containing only a few hundred helium atoms have a kinetic energy that is higher than the longitudinal trapping potential of the ion trap. When a droplet picks up an ion via mechanical impact, the ion will be cooled to the equilibrium temperature of the droplet (0.4 K), and the ion doped droplet can exit the trap. Doped droplets are irradiated using tunable IR light from the FHI free electron laser. After resonant absorption of multiple photons, droplets evaporate and the bare ion is detected in a time of flight mass spectrometer. Plotting the IR yield as a function of IR frequency gives an IR spectrum. The droplet evaporation process involves the absorption of many IR photons. Results from kinetic modelling of the absorption/evaporation process will be presented.

Time- and energy-resolved fluorescence measurements of collective effects in polyacene aggregates attached to rare gas clusters

<u>Aleksandr Demianenko</u>, Moritz Michelbach, Sebastian Hartweg, Frank Stienkemeier (please underline presenting author)

University of Freiburg, Freiburg im Breisgau, Germany

Collective effects in organic semiconductors affect excited state lifetimes, important for organic optoelectronic and photovoltaic applications. A complete understanding of the energy level structure, and decay mechanisms require high spectral and temporal resolution. We present a setup combining conventional laser-induced fluorescence (LIF) spectroscopy with time-correlated single photon counting (TCSPC) and discuss advantages and implementation challenges. Using wavelength-tunable nanosecond dye laser pulses allows us to measure high-resolution LIF spectra of transitions to highly excited states of tetracene embedded in superfluid helium nanodroplets, or deposited on solid rare-gas clusters. The newly implemented TCSPC detection in combination with a femtosecond laser system is aimed at studying radiative and non-radiative decay mechanisms connected to collective effects in aggregates of polyacenes. This technique allows us to cover the sub-ns lifetime region not previously reachable in our fluorescence measurements.

Investigating the Valence Electronic Structure of Submicrometer Aqueous Droplets

Jong Chan Lee,¹ Jonas Heitland,¹ Loren Ban,¹ Grite L. Abma,¹ William G. Fortune,² Helen H. Fielding,² Bruce L. Yoder,¹ and Ruth Signorell¹ ¹ Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, C.H. ² Department of Chemistry, University College London, London WC1H 0AJ, U.K

ABSTRACT: Many biochemical and atmospheric chemical processes take place in aqueous environments or at aqueous interfaces, where photochemical reaction rates can be dramatically enhanced.1,2 To understand the chemical behavior and photo response of molecules in and on water, it is essential to examine their electronic structure and potential energy landscape, with photoelectron spectroscopy (PES) being an invaluable method.3,4 This research employs photoelectron velocity-map imaging (VMI) following ultraviolet multiphoton ionization of sub-micrometer aqueous droplets to study the valence electronic structure of weakly soluble organics. Liquid phase photoelectron (PE) spectra are affected by the inelastic electron scattering and this makes it complicated to analyze liquid phase photochemical process.5–7 Here, we introduce the droplet photoelectron imaging technique to address this issue. This method allows us to understand low kinetic energy electron scattering and investigate droplet finite size effects.5,8

We present PE spectra of aqueous droplets with varying phenol concentrations, and after resonant and nonresonant photoexcitation. Phenol, previously studied in LJs, is used as a representative organic solute.7,9 Our results show that the vertical binding energies (VBE) of phenol in aqueous droplets are lower than those of isolated phenol, due to stabilization by the polar solvent. For non-resonant measurement, we observe that increasing phenol concentration decreases the VBE. This shift is attributed to a systematic lowering of the energy of the lowest cationic state with increasing concentration, caused by phenol dimer and aggregate formation at the droplet surface. However, in the case of resonant ionization, we do not find any significant correlation between the concentration and VBE. We attribute the constant vertical binding energy of ~8.1 eV upon resonant excitation to ultrafast intermediate state relaxation.

REFERENCE

(1) Li, K.; Gong, K.; Liu, J.; Ohnoutek, L.; Ao, J.; Liu, Y.; Chen, X.; Xu, G.; Ruan, X.; Cheng, H.; Han, J.; Sui, G.; Ji, M.; Valey, V. K.; Zhang, L. Cell Reports Physical Science 2022, 3, 100917. (2) Rovelli, G.; Jacobs, M. I.; ab D Megan Willis; Rapf, R. J.; ab, A. M. P.; Wilson, K. R. 2020, DOI: 10.1039/d0sc04611f. (3) Signorell, R.; Winter, B. *Physical Chemistry Chemical Physics* **2022**, *24*, 13438–13460. (4) Fortune, W. G.; Scholz, M. S.; Fielding, H. H. Accounts of Chemical Research 2022, 55, 3631–3640. (5) Signorell, R.; Goldmann, M.; Yoder, B. L.; Bodi, A.; Chasovskikh, E.; Lang, L.; Luckhaus, D. Chemical Physics Letters 2016, 658, 1-6. (6) Luckhaus, D.; ichi Yamamoto, Y.; Suzuki, T.; Signorell, R. Science Advances 2017, 3, e160322. (7) Scholz, M. S.; Fortune, W. G.; Tau, O.; Fielding, H. H. The Journal of Physical Chemistry Letters 2022, 2022, 6889-6895. (8) Ban, L.; Yoder, B. L.; Signorell, R. Annual Review of Physical Chemistry **2020**, 71, 315–334. (9) Ghosh, D.; Roy, A.; Seidel, R.; Winter, B.; Bradforth, S.; Krylov, A. I. Journal of Physical Chemistry B 2012, 116, 7269-7280.

Production, Identification and Investigation of Actinide Clusters by Laser-Ablation Multi-Reflection Time-of-Flight Mass Spectrometry

Paul Fischer¹, Jonas Stricker^{2,3}, Christoph E. Düllmann^{2,3,4}, Dennis Renisch^{2,3}, Lutz Schweikhard¹

- ¹ Institute of Physics, University of Greifswald, 17487 Greifswald, Germany ² PRISMA+ Cluster of Excellence and Department of Chemistry, Johannes
- Gutenberg University Mainz, 55099 Mainz, Germany
- ³ Helmholtz-Institut Mainz, 55099 Mainz, Germany
- ⁴GSI Helmholtzzentrum für Schwerionenforschung GmbH, 64291 Darmstadt, Germany

Multi-Reflection Time-of-Flight Mass Spectrometry has recently been employed in the search for thorium and uranium clusters produced by laser ablation from target foils in high vacuum (i.e. without aggregation gas). The method is known to produce and investigate molecules and clusters for a number of target materials, see e.g. [1-3], and is now expanded to the realm of the actinides where data on gas-phase compounds is very scarce. In the present uranium-target study only monomers and dimers are found – in addition to various molecules incorporating, e.g., oxygen, nitrogen or fluorine atoms [4]. For the thorium target, however, in addition to such small molecules [5] cationic clusters are observed with up to n = 15 thorium atoms. Two different distributions can be distinguished: The smaller clusters are heavily oxidized, which could be expected as the target is quite old and has been exposed to air for several decades. The larger clusters, however, are found as pure rather than oxygenated species. In addition, their signal intensity as a function of cluster size drops significantly from n = 13 to n = 14, thus indicating a magic number n=13, i.e. a shell closure for the thorium clusters Th_{13}^+ [6].

- [1] P. Fischer et al., Isotope-resolved photodissociation pathways of lead-doped bismuth clusters from tandem multi-reflection time-of-flight mass spectrometry, Phys. Rev. Research 1, 033050 (2019) <u>https://doi.org/10.1103/PhysRevResearch.1.033050</u>
- [2] P. Fischer et al., Decay-rate power-law exponent as link between dissociation energy and temperature, Phys. Rev. Research 2, 043177 (2020) https://doi.org/10.1103/PhysRevResearch.2.043177
- [3] P. Fischer et al., Disentangling poly-cationic fullerenes produced from glassy carbon with multireflection time-of-fight mass spectrometry, Phys. Rev. Research 4, 043187 (2022) <u>https://doi.org/10.1103/PhysRevResearch.4.043187</u>
- [4] P. Fischer et al., publication in preparation.
- [5] P. Fischer et al., publication under review.
- [6] P. Fischer et al., publication in preparation.

IRPD Spectroscopy of $[Fe_2AlO_4]^+$ and $[Co_2AlO_4]^+$: Unexpected Structural Isomers upon Transition Metal Substitution

Tatiana Penna,^{1,2} Francine Horn,^{1,2} Winni Schwedland,³ Fabian Berger,³ Nanako Ishida,⁴ Keijiro Ohshimo,⁴ Fuminori Misaizu,⁴ Joachim Sauer,³ Knut R. Asmis¹

¹Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Germany ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany ³Institut für Chemie, Humboldt-Universität zu Berlin, Germany ⁴Graduate School of Science, Tohoku University, Japan

Studies on metal oxide clusters in the gas phase are aimed at gaining a better atomistic understanding of single-site catalysts. Here, we study the structure and reactivity of cationic model systems using a combination of mass spectrometry, infrared photodissociation (IRPD) spectroscopy, ion mobility and electronic structure calculations ranging from density functional theory to multi-reference electron correlation methods.

The reactivity of the aluminium oxide cations $[Al_3O_4]^+$ is studied upon the substitution of Al atoms by the transition metal ones, Fe or Co. The electronically closed-shell $[Al_3O_4]^+$ has a cone like structure and is unreactive towards methane activation,^[1] while $[FeAl_2O_4]^+$ and $[CoAl_2O_4]^+$ show a planar bicyclic structure with a terminal oxygen radical $(AlO^{\bullet-I})$ that can abstract H from CH_4 .

However, the doubly transition metal substituted species, $[Fe_2AIO_4]^+$ and $[Co_2AIO_4]^+$ are unreactive towards methane, and the structure assignment could not be done solely comparing IRPD spectra to harmonic vibrational spectra for different isomers. Therefore, we used ion mobility spectrometry and ab initio molecular dynamics simulations to unambiguously determine the structure of these systems. They exhibit a "key-like" structure with a planar four-membered ring connected to a nearly linear terminal O–TM^{+III}–O^{-II} unit, that display large amplitude motions that can only be captured by anharmonic simulations. Ion mobility data for the cobalt system, $[Co_2AIO_4]^+$, were also obtained and confirm the assignment made.



Figure 1: Structure of $[Fe_nAl_{(3-n)}O_4]^+$ clusters.

- G. Santambrogio, E. Janssens, S. Li, T. Siebert, G. Meijer, K. R. Asmis, J. Döbler, M. Sierka, J. Sauer, J. Am. Chem. Soc. (2008), 130, 15143.
- [2] F. Müller, J.B. Stückrath, F.A. Bischoff, L. Gagliardi, J. Sauer, S. Debnath, M. Jorewitz, K.R. Asmis, J. Am. Chem. Soc. (2020), 42, 18050–59.

Imaging Plasmons of Individual Supported Nanoparticles: Energetics, Mode Geometry, and Photoelectron Momentum

Kevin Oldenburg, Waqas Pervez, Sylvia Speller, Karl-Heinz Meiwes-Broer, Ingo Barke

Institute of Physics and Center for Interdisciplinary Electron Microscopy (ELMI-MV), Department "Life, Light and Matter", Universität Rostock, 18059 Rostock, Germany

Localized plasmon-polaritons of deposited clusters and nanoparticles are highly sensitive to the optical properties and local geometry of the substrate, down to the atomic scale. Here we present spatially resolved mapping of single-particle plasmon energies using photoemission electron microscopy (PEEM) and electron energy loss spectroscopy (EELS), focusing on the role of the substrate. For size-selected silver clusters deposited on Si(111)-(7x7), the formation of image dipoles in the silicon results in a breakdown of the quasistatic limit, despite small (≈ 10 nm) particles [1]. The photoelectron momentum distribution can be controlled via the laser polarization (left Figure), as observed in k-space mode by selecting an individual particle on a native oxide layer of silicon.

Insight into the detailed geometry of involved plasmon modes is enabled by EELS conducted in a scanning transmission electron microscope (STEM). To access the substrate's effect, silver particles are deposited from a beam on a narrow rim of a carbon support and investigated along a plane perpendicular to the support (cross-sectional view). We observe pronounced symmetry breaking, partially lifting the threefold degeneracy of the dominant dipole modes. In combination with simulations based on the boundary element method (BEM), the full mode structure is revealed, enabling assignment of spectral features. Intuitively, the most pronounced substrate effect, i.e., the strongest red shift, is expected for excitation of modes close to the support, as previously reported for more complex nanostructures. Surprisingly, we find the strongest effect for silver clusters, when the plasmon is excited farthest away (right Figure). As will be discussed, such a non-local substrate influence is a consequence of the simple system under investigation: for silver clusters the intramode geometry dominates over intermode differences of the spatial excitation probability distribution. Our results also suggest that substrate-induced degeneracy lifting plays an important role in long-standing discrepancies of reported size-dependent "true" plasmon energies of a variety of silver clusters [2], since anisotropic mechanisms are not properly taken into account in commonly applied effective-medium corrections.



Left: Momentum distribution of excess photoelectrons from a single Ag cluster on a silicon surface with a native oxide layer, excited near its plasmon resonance.

Right: Spatial distribution of the plasmon energy of a silver cluster (circle) supported by a narrow rim of carbon (bottom).

- [1] K. Oldenburg et al., J. Phys. Chem.C (2019), 123, 1379
- [2] H. Haberland, Nature (2013), 494 E1-E2; A. Campos et al., Nature Physics (2019), 15, 275

Probing the Temperature of Single Quantum Dots Confined in a Nanoparticle Ion Trap by Fluorescence Thermometry

<u>Sophia C. Leippe¹, Florian Johst², Benjamin Hoffmann¹, Sonja Zeller³, Kleopatra Papagrigoriou¹, Knut R. Asmis¹ Alf Mews² and Björn Bastian¹</u>

¹ Wilhelm Ostwald Institute for Physical and Theoretical Chemistry, University of Leipzig, Linnéstraße 2, 04103 Leipzig, Germany

² Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany

³ Fraunhofer IAP-CAN, Grindelallee 117, 20146 Hamburg, Germany

To obtain unaltered information on the intrinsic, size-dependent properties of nanoparticles, it is essential to characterize individual nanoparticles isolated in the gas phase to avoid heterogeneity of a nanoparticle ensemble and prevent perturbing interactions with the environment. Single nanoparticle mass spectrometry (NPMS) allows for the non-destructive monitoring of the absolute mass of a single, charged particle isolated in the gas phase using light scattering.^[1]

Understand the processes taking place on single nanoparticles inside the temperaturecontrollable NPMS ion trap requires knowledge of the nanoparticle. We determined the temperature of a single trapped CdSe/CdS quantum dot (QD) using fluorescence thermometry after laser excitation at 532 nm. The QD temperature is then derived from the fluorescence wavelength using the empirical Varshni relation. A linear correlation between the temperatures of the QD and ion trap is observed, with a slope of one and an offset of 100 K. These experimental findings align well with a simple power balance model and allow for detailed insights into the significance of various heating and cooling mechanisms acting on the trapped particles, the most dominant of which are laser light absorption, fluorescence and collisional cooling.^[2]

- [1] Esser, T. K.; Hoffmann, B.; Anderson, S. L.; Asmis, K. R. A cryogenic single nanoparticle action spectrometer. *Rev. Sci. Instrum.* **2019**, *90*, 125110.
- [2] Howder, C. R.; Bell, D. M.; Anderson, S. L. Optically detected, single nanoparticle mass spectrometer with pre-filtered electrospray nanoparticle source. *Rev. Sci. Instrum.* 2014, *85*, 14104.

Femtosecond XUV-Spectroscopy on Nano-Structured Surfaces

Christian Weigelt,¹ Mihai E. Vaida,^{2,3} Thorsten M. Bernhardt¹

¹Institute of Surface Chemistry and Catalysis, University of Ulm, 89069 Ulm, Germany ²Department of Physics, University of Central Florida, Orlando, Florida 32816, United States ³Renewable Energy and Chemical Transformations Cluster, University of Central Florida, Orlando, Florida 32816, United States thorsten.bernhardt@uni-ulm.de

A new experimental setup for extreme-ultraviolet (XUV) photoemission spectroscopy is presented. With surface sensitive XUV femtosecond pump-probe spectroscopy we aim to characterize the electronic properties of nano-structured surfaces and of molecules adsorbed on such substrates. One recent example focused on the electronic structure of gold nano-clusters on an MgO/Mo(100) substrate. Changes in the photoemission signature are corelated with the electronic structure of Au as it evolves from monomers to small nonmetallic clusters to larger nanoparticles with a metallic character. This work paves a new avenue to a detailed understanding of how surface photoinduced chemical reactions are influenced by the composition and electronic structure of the surface.

- [1] Vaida, M. E.; Bernhardt, T. M., Surface-aligned femtochemistry: Real-time dynamics of photoinduced I₂ formation from CD₃I on MgO(100). *ChemPhysChem* **2010**, *11*, 804-807.
- [2] Vaida, M. E.; Bernhardt, T. M., Tuning the ultrafast photodissociation dynamics of CH₃Br on ultrathin MgO films by reducing the layer thickness to the 2D limit. *Chem. Phys. Lett.* **2017**, *688*, 106–111.
- [3] Vaida, M. E.; Marsh, B. M.; Leone, S. R., Nonmetal to metal transition and ultrafast charge carrier dynamics of Zn clusters on p-Si(100) by fs-XUV photoemission spectroscopy. *Nano Lett.* **2018**, *18*, 4107-4114.
- [4] Vaida, M. E., Rawall, T., Bernhardt, T. M., Marsh, B. M., Rahman, T. S., Leone, S. R., Non-metal to metal transition of magnesia supported Au clusters affects the ultrafast dissociation dynamics of adsorbed CH₃Br molecules, *J. Phys. Chem. Lett.* **2022**, *13*, 4747-4753.

Electronic state of a manganese oxide clusters revealed by Soft X-ray spectroscopy

Olesya S. Ablyasova^{1,2}, Mihkel Ugandi³, Esma Birsen Boydas³, Mayara da Silva Santos^{1,2}, Max Flach^{1,2}, Vicente Zamudio-Bayer¹, Michael Römelt³, J. Tobias Lau^{1,2}, Konstantin Hirsch¹

¹Abteilung für Hochempfindliche Röntgenspektroskopie, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Straße 15, 12489 Berlin, Germany.

²Physikalisches Institut, Universität Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany ³Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

The CaMn₄O₅ cluster's electronic structure plays a crucial role in understanding dioxygen formation in the Kok cycle. The S₄ state, responsible for O₂ formation, is difficult to observe because of the millisecond time scale of the S₃-S₀ transition [1]. Two main widely discussed models for the S₄ state feature different oxidation states of +4 and +5 of the manganese atom at the reaction site [2]. Despite the fact that the spin states of the manganese atoms in state S₄ are still under debate, the reactivity of the CaMn₄O₅ cluster is believed to be spin-dependent [3].

We report on the characterization of cold cationic gas-phase manganese oxide complexes via X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). We identify oxidation and spin states by comparison with reference spectra of manganese compounds with known oxidation states, accompanied by multireference and density functional theory calculations. We demonstrate that cationic $Mn(V)O_2^+$, recently identified as a species with the high oxidation state of manganese atom [4], is only the second manganese oxo complex to exist in a high-spin state. Our most important result is the identification of a $Mn_2O_3^+$ species with Mn(V) in a high-spin state. This is the first observation of the elusive manganese(V) high-spin state in a polymagnanese oxido complex [5, 7]. The observed result might have implications for the oxidation and spin states of the $CaMn_4O_5$ complex in the S₄ state.



- [1] N. Cox et al, *Science* (2014), **345**, 804.
- [2] J. Barber, Nature Plants (2017), **3(4)**, 17041.
- [3] V. Krewald et al, *Inorganic Chemistry* (2016), **55(2)**, 488.
- [4] M. G. Delcey, et al, Phys. Chem. Chem. Phys (2022), 24, 3598.
- [5] R. Gupta, Proceedings of the National Academy of Sciences (2015), 112, 53
- [6] T. Taguchi, et al, Journal of the American Chemical Society (2012), 134(4), 1996.

Activation of CO₂ by free metal oxide clusters

Pavol Mikolaj, Sandra M. Lang, Thorsten M. Bernhardt

Institute of Surface Chemistry and Catalysis, Ulm University, Ulm, Germany

Motivated by the performance of the industrially employed Cu/ZnO catalyst for direct CO₂ hydrogenation [1], the European training network CATCHY [2] seeks to develop new and high-performance cluster-based catalysts. As part of this project, we utilize transition metal oxide clusters in the gas phase as model systems to study the fundamental driving forces that determine the reactive and catalytic properties of such catalysts.

So far, we have investigated the interaction of CO₂ with small copper oxide, cobalt oxide and yttrium oxide clusters via infrared multiple-photon dissociation (IR-MPD) spectroscopy (collaboration with J. Bakker, FELIX laboratory). Clusters were produced by laser ablation of a metal target in the presence of He carrier gas seeded with O₂. Independent of the metal, cluster formation appears to be strongly charge dependent, with cations preferably forming oxygen-rich clusters, while anions tend to form stoichiometric and oxygen-deficient clusters. To study the cluster-CO₂ interaction, a CO₂/He mixture was subsequently introduced in an adjacent flow tube reactor and the resulting reaction products were investigated via infrared spectroscopy.

In the case of cationic copper and cobalt oxide complexes, the characteristic Fermi dyad of CO_2 is observed, indicating the presence of physisorbed, unactivated linear CO_2 . In contrast, all anionic cluster complexes show bands which are characteristic for an activated bent CO_2 molecule (cf. Figure 1). Density functional theory calculations allowed us to assign structures of $Cu_2O_4(CO_2)^-$ and $Cu_3O_4(CO_2)^-$, which revealed that the presence of oxygen leads to the exclusive formation of a stable CO_3 unit, preventing CO_2 dissociation. Most interestingly, the IR-MPD spectra of yttrium oxide- CO_2 complexes appear to be more complex than the spectra of the copper and cobalt oxide complexes, potentially indicating different CO_2 binding motifs.

Additionally, we employed guided ion beam technique, where mass-selected cluster ions generated by sputtering are stored in a radiofrequency octopole ion trap filled with helium buffer gas and small partial pressures of reactant gases to investigate reaction kinetics of copper oxide clusters. Experiments have demonstrated the influence of oxygen on the cluster's capacity to adsorb CO_2 , H_2O , and CO.

 J. Artz, T.E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow & W. Leitner, Chem. Rev. 118(2) (2018) 434-504.

[2] <u>https://www.catchy-etn.eu/</u>

Hydrogen Induced Structure Transitions in Small Platinum Clusters

Dennis Bumüller¹, Asfaw G. Yohannes¹, Stephan Kohaut¹, Siddhi Gojare¹, Manuel Kraft¹, Ivan Kondov², Manfred M. Kappes^{1,3}, Karin Fink¹ and <u>Detlef Schooss¹</u>

¹ Institute of Nanotechnology, Karlsruhe Institute of Technology ²Steinbuch Centre for Computing, Karlsruhe Institute of Technology ³Institute of Physical Chemistry, Karlsruhe Institute of Technology

Platinum cluster and nanoparticles are the catalytically active species in a large number of important chemical processes. In many of these processes' hydrogen is directly or indirectly involved. While hydrogen adsorption on extended surfaces is well studied, much less is known about the interaction of hydrogen and platinum clusters.

Here we report an investigation of structures of small platinum clusters anions and their hydrides by a combination of trapped ion electron diffraction and density functional computations. For the bare clusters we find a structural evolution from planar (Pte⁻) and amorphous-like (Pt₇⁻ - Pt₉⁻) structures to structures based on distorted tetrahedra (Pt₉⁻ - Pt₁₁⁻). Finally, Pt₁₂⁻ and Pt₁₃⁻ are based on hcp fragments.¹ While the structural parameters are well described by density functional theory computations, the lowest energy structure is found in the experiment only for Pt₆⁻.When exposed to a hydrogen atmosphere, platinum cluster anions readily adsorb hydrogen (deuterium). The TIED measurements indicate a structural transformation induced by deuterium adsorption ranging from a polyhedral structure for Pd₆D_{12±1}⁻ to a cuboctahedral structure for Pd₁₃D_{25±1}⁻.²

- 1. D. Bumüller, A. G. Yohannes, S. Kohaut, I. Kondov, M. M. Kappes, K. Fink, and D. Schooss, *J. Phys. Chem. A* **2022** 126, 3502-3510
- 2. S. Gojare, D. Bumüller, S. Kohaut, M. Kraft, U. Heiz, M. M. Kappes, K. Fink, D. Schooss, *ChemPhysChem* **2024**, submitted.

Abrupt Change from Ionic to Covalent Bonding in Nickel Halides Accompanied by Ligand Field Inversion

<u>Max Flach</u>^{1,2}, Konstantin Hirsch¹, Tim Gitzinger², Martin Timm¹, Mayara da Silva Santos^{1,2},

Olesya Ablyasova^{1,2}, Markus Kubin¹, Bernd von Issendorff², J. Tobias Lau^{1,2}, Vicente

Zamudio-Bayer¹

(please underline presenting author)

¹Abteilung für hochempfindliche Röntgenspektroskopie/Helmholtz-Zentrum Berlin für Materialien and Energie, Berlin, Germany

²Physikalisches Institut/Albert-Ludwigs-Universität Freiburg, Freiburg, Germany

The electronic configuration of transition metal centers and their ligands is crucial for redox reactions in metal catalysis and electrochemistry. We characterize the electronic structure of gas phase nickel monohalide cations via nickel L_{2,3}-edge x-ray absorption spectroscopy. Comparison with multiplet charge-transfer simulations and experimental spectra of selectively prepared nickel monocations in both ground- and excited-state configurations are used to facilitate our analysis. Only for [NiF]⁺ with an assigned ground state of ³II can the bonding be described as predominantly ionic, while the heavier halides with assigned ground states of ³II or ³ Δ exhibit a predominantly covalent contribution. The increase in covalency is accompanied by a transition from classical to inverted ligand-field for [NiCl]⁺, [NiBr]⁺, and [NiI]⁺, resulting in a leading 3d⁹ <u>L</u> configuration with a ligand hole (<u>L</u>) and a 3d occupation indicative of nickel(I) compounds. Hence, the absence of a ligand hole in [NiF]⁺ precludes any ligand-based redox reactions. Additionally, we demonstrate that the shift in energy of the L₃ resonance is reduced compared to that of isolated atoms upon formation of covalent compounds.



Figure 1: Abrupt pronounced difference in electronic structure of nickel monohalides from a classical ligand field in $[NiF]^+$ to inverted ligand field in $[NiX]^+$ (X=Cl,Br,I).

Size and charge state effects on the plasmonic properties of polyanionic silver clusters

 $\underline{N. Iwe}^1$, K. Raspe¹, F. Martinez¹,

L. Schweikhard², K.-H. Meiwes-Broer^{1,3}, J. Tiggesbäumker^{1,3}

¹Institute of Physics, University of Rostock, 18059 Rostock, Germany ²Institute of Physics, University of Greifswald, 17489 Greifswald, Germany ³Department of Life, Light and Matter, University of Rostock, 18059 Rostock, Germany

Numerous applications ranging from efficient solar cells to cancer treatment profit from the interaction between nanoparticles and light. In the case of metal clusters, one often takes advantage of collective resonances of the valence electrons, which lead to a strong increase of the cross section at a certain wavelength. Previous studies have already shown that the resonance energy can be tuned via size and charge state of the nanoparticles [1]. However, systematic measurements to investigate the evolution of the plasmonic resonance in metal clusters concentrate on small sizes. In the case of free silver particles only few experimental results are available for systems larger than N = 20 atoms [2,3]. Furthermore, those collective excitations have not been shown yet for multiply negatively charged species.

We conduct photoelectron spectroscopy on polyanionic silver clusters Ag_N^{z-} in a size range of N = 7-800 and with z = 1-7 excess electrons. By extracting photodetachment cross sections (Fig. 1) from energy resolved photoemission, we do not only get insight into the overall plasmon resonance, but also into the coupling of the collective excitation to electrons previously bound in different electronic levels. For monoanions, we see a transition at N = 55 from the scalable regime of larger clusters showing a 1/R blueshift of the plasmon resonance energy to the nonscalable regime with a general redshift. On top, a splitting of the resonance is observed at few smaller cluster sizes (e.g. Ag_{29}^- , Fig. 1b), hinting on a deformation of the particle. For higher polyanonic charge states, we observe a redshift of the plasmon energy and a broadening of the resonance width, which are both more pronounced for smaller particles.



Figure 1: Photodetachment cross sections of silver clusters Ag_N^- with N = 19,29 and 137 (blue circles). The experimental data are fitted by either a single Lorentz function (black line, a and c) or by a combination of three Lorentzians with equal area and width (black line, b).

- [1] J. Tiggesbäumker et al., Chem. Phys. Lett. (1996), 260, 428.
- [2] N. Iwe et al., Phys. Chem. Chem. Phys. (2023), 25, 1677.
- [3] H. Hövel et al., *Phys. Rev. B* (1993), **48**, 18178–18188.

Probing the Vibrational and Rotational Wave-Packet Dynamics of Mass-selected Neutral Clusters

Jiaye Jin¹, Max Grellmann¹, Knut R. Asmis¹

¹Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Leipzig, Deutschland

Studying the spectroscopy and dynamics of size-selected neutral clusters remains challenging due to the difficulties associated with mass-selection for these clusters and the lack of intense and easily accessible radiation sources. Here, we report our setup and results on vibrational and rotational wavepacket dynamics for mass-selected neutral clusters which allow us to obtain detailed vibrational and rotational information. We employ a cryogenic ion-trap tandem mass spectrometer in combination with a femtosecond laser system to perform femtosecond pump-probe spectroscopy involving with the negative-neutral-positive excitation scheme (fs-NeNePo). We have obtained detailed and accurate information on the molecular vibrations for the ground electronic states of neutral silver clusters via probing their vibrational wave-packet dynamics. Additionally, we have recently investigated the rotational coherence in the mass-selected small boron clusters in the time-domain.

- [1] Jiaye Jin, Max Grellmann and Knut R. Asmis, Phys. Chem. Chem. Phys. (2023), 25, 24313.
- [2] Max Grellmann, Martin DeWitt, Daniel M. Neumark, Knut R. Asmis and Jiaye Jin Phys. Chem. Chem. Phys. (2024), 26, 6600.

Spectroscopy and Dynamics of Diamondoid Ions and Their Clusters

Otto Dopfer

Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Germany

Diamondoids are a class of aliphatic molecules arranged in cage-like structures and serve as a link between small, cyclic hydrocarbons and bulk nanodiamonds. They are well-known for their interesting optical properties, as they typically exhibit large optical band gaps of around 6 eV or higher. Their radical cations, however, are predicted to display transitions in the visible and, due to their favorable structural and optical properties, may be viable candidates as carriers of the diffuse interstellar bands. Here, we present the electronic spectra of the simplest diamondoid cations (adamantane [1], diamantane [2]) recorded in a cryogenic ion trap (BerlinTrap) [3]. Despite ion temperatures below 20 K, these optical spectra show rather broad absorptions in the whole optical range (from near infrared to ultraviolet), arising from rich vibronic activity (Franck-Condon congestion) and/or short excited state lifetime. To explore the effects of functionalization and modification of the diamondoid cage, we characterized the optical spectra of N-substituted adamantanes, namely 1-cyanoadamantane and urotropine. While substitution with the CN group has little impact on the optical response [4], the modification of the diamondoid cage by replacing all four CH groups by isoelectronic N atoms results in highly-resolved vibronic spectra. The optical spectra are obtained by photodissociation of massselected ions in a cryogenic ion trap (5 K) coupled to an electron ionization source and quadrupole/timeof-flight tandem mass spectrometer. The experimental results are compared to photoelectron spectra⁵ and time-dependent DFT calculations. The assignment of the PES spectra with TD-DFT methods illustrates the evolution of the electronic structure and the corresponding molecular orbitals as a function of (i) number of cages (i.e., size of the diamondoid), (ii) type and location of functional groups, and (iii) substitution with heteroatoms in the cage [5]. In addition to bare diamondoid cations, we probe the geometry and reactivity of mass-selected solvated cluster ions by infrared photodissociation in a quadrupole tandem mass spectrometer coupled to an electron impact supersonic plasma expansion. The analysis of these spectra reveals the impact of ionization and protonation, solvation, and functional groups on the structure and reactivity of the diamondoid cations, including cage opening and proton transfer to solvent [6-9].

References

[1] P.B. Crandall et al., Astrophys. J. Lett. (2020) 900 L20. [2] P.B. Crandall et al., Astrophys. J. (2022) 940 104. [3] A. Günter et al., J. Mol. Spectr. (2017) 332 8. [4] P.B. Crandall et al., Mol. Phys. (2024) 122 e2231566. [5] P.B. Crandall et al., Phys. Chem. Chem. Phys. (2024) 26, DOI: 10.1039/d4cp02425g. [6] M.A.R. George et al., Angew. Chem. Int. Ed. (2020), 59, 12098. [7] M.A.R. George et al., J. Phys. Chem. Lett. (2022), 13, 449. [8] M.A.R. George et al., Chem. Eur. J. (2022), 28, e202200577. [9] M.A.R. George et al., Phys. Chem. Chem. Phys. (2023), 25, 13593.

Rayleigh scattering study of the formation of propane clusters in supersonic jet experiments

<u>Wolfgang Christen</u>, Yazmin Garcia Frausto, Maria Fernanda Valle Sejo, Xue Yin Tan, Zhishen Wu

Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2 12489 Berlin, Germany, https://clusterlab.de

In the past molecular clusters have been generated in supersonic jets from a variety of molecules. One special case seems to be propane. Although it is said to nucleate more easily than carbon dioxide under otherwise similar conditions [1], C_3H_8 does not form clusters if expanded as a pure gas [2,3].

We present a comprehensive experimental investigation of the generation of propane clusters by a pulsed high-pressure supersonic jet expansion of the pure fluid through a parabolic nozzle into vacuum. In these experiments source pressure is varied between 6 bar and 110 bar and source temperature between 240 K and 410 K, covering the gaseous, liquid, and supercritical states. The mean cluster size is characterized by time and space resolved Rayleigh scattering measurements, in combination with time resolved residual gas pressure measurements.

Our experiments performed so far indicate that the onset of cluster formation follows the gasliquid phase boundary [4]: no signal is detected from expansions from gaseous propane, even at high source pressures, whereas liquid jet expansions result in a Rayleigh signal that increases with source pressure. Above the critical temperature the dependence of the Rayleigh scattering signal on source conditions shows a more complex behavior.

- [1] J. Krohn, M. Lippe, C. Li, R. Signorell, Phys. Chem. Chem. Phys. 22, 15986, 2020.
- [2] E. S. Toma, H. G. Muller, Phys. Rev. A 66, 013204, 2002.
- [3] J. J. Ferreiro, S. Chakrabarty, B. Schläppi, R. Signorell, J. Chem. Phys. 145, 211907, 2016.
- [4] E. W. Lemmon, M. O. McLinden, W. Wagner, J. Chem. Eng. Data 54, 3141, 2009.

X-ray coherent diffractive imaging of nanoplasma generated in submicron liquid droplets with intense UV light

Hanchao Tang⁽¹⁾, Loren Ban⁽¹⁾, Alessandro Colombo⁽²⁾, Bruce Yoder⁽¹⁾, Mario Sauppe⁽²⁾, Christian Pelz⁽³⁾, Paul Tuemmler⁽³⁾, Andre Al Haddad⁽⁴⁾, Linos Hecht⁽²⁾, Jonas Heitland⁽¹⁾, Katharina Kolatzki⁽²⁾, Gregor Knopp⁽⁴⁾, Ana Sofia Morillo Candas⁽⁴⁾, Marie Louise Schubert⁽²⁾, Kirsten Schnorr⁽⁴⁾, Arezu Sehati⁽²⁾, Zhibin Sun⁽⁴⁾, Frederic Ussling⁽²⁾, Xinhua Xie⁽⁴⁾, Hankai Zhang⁽⁴⁾, Christoph Bostedt^(4,5), Thomas Fennel⁽³⁾, Daniela Rupp⁽²⁾, Ruth Signorell⁽¹⁾

(1) Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland, (2) Department of Physics, ETH Zurich, Switzerland (3) Institute of Physics, University of Rostock, Germany (4) Center for Photon Sciences, Paul Scherrer Institute, Switzerland (5) LUXS Laboratory for Ultrafast X-Ray Sciences, EPFL, Switzerland

The extremely bright and short light pulses provided by X-ray Free Electron Lasers allow one to spatially and temporally resolve light-induced nanoplasma formation and its dynamics in sub-micrometer particles via Coherent Diffraction Imaging (CDI) technique [1–6]. In previous CDI studies [5,7,8], nanoplasma formed with pristine noble gas clusters and solid nanoparticles pumped by NIR (800 nm) has been probed. Softening and asymmetric broadening of the particle surface have been observed along the polarisation axis of pump laser pulses. No clear size-dependent effects have been explored and found for nanoplasma generation nor expansion with CDI. This was due to the small size parameter of the studied particles, resulting in a homogeneous internal and a symmetric outer near field distribution.

In this study, we use time-dependent X-ray (661 eV, 3.5 mJ) CDI to follow nanoplasma formation in liquid squalane droplets of various particle diameters (100 – 400 nm) irradiated with UV (266 nm, 7e13 W/cm²) light at Maloja endstation of SwissFeL in Switzerland [9]. This experiment enables us to probe size-dependent dynamics of nanoplasma, and follow how inhomogeneous light distributions develop as a function of particles size. Particles with diameters of 100 nm exhibit asymmetric expansion dynamics along the polarisation axis of the light as was predicted previously [7] and reported for He droplets experimentally [8]. As particle size increases, the internal light distribution forms an intense region in the particle due to nano-focusing [10,11] and the expansion evolves increasingly into the forward scattering direction. Rarefaction waves become visible in the diffraction images due to the inhomogeneous light field produced in the particle. Simulations on plasma expansion give a detailed understanding of the plasma expansion dynamics and their size dependence. With the first systematic study to report nanoplasma formation in liquid particles, we observe and explain the strong influence that particle size has on nanoplasma formation and dynamics.

Acknowledgement: We acknowledge the Paul Scherrer Institute, Villigen, Switzerland for provision of free-electron laser beamtime at the Maloja instrument of the SwissFEL ATHOS branch. This project has received funding from the European Union Horizon 2020 research and innovation program from the European Research Council under the Grant Agreement No. 786636 and from the DFG via Collaborative Research Center 1477 "Light-Matter Interactions at Interfaces" (project no. 441234705). C.B. and H.Z. acknowledge support from the Swiss National Science Foundation SNSF. The Maloja instrument was funded through a R'equip grant from the Swiss National Science Foundation SNSF.

References:

[1] T. Gorkhover et al., Nanoplasma Dynamics of Single Large Xenon Clusters Irradiated with Superintense X-Ray Pulses from the Linac Coherent Light Source Free-Electron Laser, Phys. Rev. Lett. 108, 1 (2012).

- [2] D. Rupp et al., *Imaging Plasma Formation in Isolated Nanoparticles with Ultrafast Resonant Scattering*, Struct. Dyn. **7**, (2020).
- [3] C. Peltz et al., *Few-Femtosecond Resolved Imaging of Laser-Driven Nanoplasma Expansion*, New J. Phys. **24**, (2022).
- [4] L. Flückiger et al., *Time-Resolved x-Ray Imaging of a Laser-Induced Nanoplasma and Its Neutral Residuals*, New J. Phys. **18**, 043017 (2016).
- [5] T. Gorkhover et al., *Femtosecond and Nanometre Visualization of Structural Dynamics in Superheated Nanoparticles*, Nat. Photonics **10**, 93 (2016).
- [6] D. Rupp et al., *Recombination-Enhanced Surface Expansion of Clusters in Intense Soft X-Ray Laser Pulses*, Phys. Rev. Lett. **117**, (2016).
- [7] C. Peltz, C. Varin, T. Brabec, and T. Fennel, *Time-Resolved x-Ray Imaging of Anisotropic Nanoplasma Expansion*, Phys. Rev. Lett. **113**, 133401 (2014).
- [8] C. Bacellar et al., Anisotropic Surface Broadening and Core Depletion during the Evolution of a Strong-Field Induced Nanoplasma, Phys. Rev. Lett. **129**, 073201 (2022).
- R. Abela et al., *The SwissFEL Soft X-Ray Free-Electron Laser Beamline: Athos*, J. Synchrotron Radiat. 26, 1073 (2019).
- [10] R. Signorell, M. Goldmann, B. L. Yoder, A. Bodi, E. Chasovskikh, L. Lang, and D. Luckhaus, Nanofocusing, Shadowing, and Electron Mean Free Path in the Photoemission from Aerosol Droplets, Chem. Phys. Lett. 658, 1 (2016).
- [11] L. Ban, B. L. Yoder, and R. Signorell, *Photoemission from Free Particles and Droplets*, Annu. Rev. Phys. Chem. **71**, 315 (2020).

Size effects in the Coulomb explosion of mass-selected silver clusters

 $\frac{\text{K. Raspe}^1, \text{ L. Kazak}^{1,2}, \text{ N. Iwe}^1, \text{ B. Krebs}^1, \text{ F. Martinez}^1,}{\text{K.-H. Meiwes-Broer}^{1,3}, \text{ and J. Tiggesbäumker}^{1,3}}$

¹ Institute of Physics, University of Rostock, 18059 Rostock, Germany
 ² Institute for Quantum Optics, Ulm University, 89081 Ulm, Germany
 ³ Department of Life, Light and Matter, University of Rostock, 18059 Rostock, Germany

Single-sized clusters are accumulated within a digital Paul trap [1] and exposed to intense optical laser pulses, leading to the formation of nanoplasmas of known initial conditions, not yet feasible. Using field-free diagnostics, the resulting Coulomb explosion is analyzed, giving electron distributions and charge-state resolved ion energy spectra [2], see Fig. 1. Experiments on the well-defined target result in comprehensive information on the particle emission and reveals details of nanoplasma dynamics not available before. These are for example the particle size-specific intensity-dependent transition towards a fully ionized plasma state. In addition, extending the experiments by pump-probe measurments and addressing the plasmon resonance, the ion recoil energy spectra show pronounced peaks, which stem from the emission of ions from different geometrical shells.



Figure 1: Time-of-flight-deflection histogram of the Coulomb explosion of size-selected silver clusters (Ag_{309}^-) after exposure to strong femtosecond laser fields $(I_L = 2.4 \cdot 10^{15} \text{ W/cm}^2)$. The different atomic charge states and their corresponding recoil energy distribution are indicated by diagonal lines in the histogram. Representative ion recoil energies are shown.

- K. Raspe, M. Müller, N. Iwe, R. N. Wolf, P. Oelßner, F. Martinez, L. Schweikhard, K.-H. Meiwes-Broer, and J. Tiggesbäumker, *Rev. Sci. Instrum.* (2022), 93, 043301.
- [2] D. Komar, K.-H. Meiwes-Broer, and J. Tiggesbäumker, Rev. Sci. Instrum. (2016), 87, 103110.

Dynamics of superheated silver nanoparticles

 $\frac{\text{Bernd v. Issendorff}^{1}}{\text{(please underline presenting author)}}$

¹Physics Institute, Freiburg University, Freiburg, Germany

The properties of materials at very high temperatures and pressures is of interest for many fields, ranging from astrophysics to laser ablation applications. Isolated clusters can serve as ideal test cases for the study of such excited matter. Here I report on time-resolved x-ray imaging experiments performed at the FELs FLASH and Swiss-FEL by a large consortium, including, among others, the ETH Zurich, the TU Berlin, and Rostock University.

Large silver nanoparticles were excited by fs-laser pulses at 400 nm, close to the plasmon resonance, and then imaged by a time-delayed x-ray pulse (image reconstructions: Daniela Rupp, Alessandro Colombo, ETH Zurich). The particles exhibit a strong expansion, which for intermediate laser intensities leads to the formation of large liquid bubbles via a cavitation effect - in the case of heated nanocubes even to the formation of hexapods, smaller bubbles with six long extensions. The observed effects are in excellent agreement with MD simulations (Thomas Reichenbach, Michael Moseler, IWM/Uni Freiburg). These can be used to describe the particle dynamics within the phase diagram of silver, demonstrating that the strong cavitation effects set in when the system crosses the so-called spinodal, the phase boundary were overheated liquids become unstable [1]. New fluid dynamic simulations (Claas Bierwisch, Michael Moseler, IWM/Uni Freiburg) demonstrate that the results can for example be used to determine the viscosity and surface tension of the superheated liquid silver.

References

[1] Dold, Reichenbach, Colombo et al., Melting, inflation and explosion of superheated plasmonic nanoparticles, *PRL*, in review. arXiv: 2309.00433

X-ray induced dynamics in single free nanoparticles studied by X-ray pump - X-ray probe CDI techniques

Yevheniy Ovcharenko¹, Jakob Asmussen², Bjoern Bastian³, Thomas Baumann¹, Alessandro Colombo⁴, Simon Dold¹, Alberto De Fanis¹, Robert Hartmann⁵, Linos Hecht⁴, Bruno Langbehn⁶, Asbjørn Lægdsmand², Ltaief Ben Ltaief², Sivarama Krishnan⁷, Björn Kruse⁸, Daniela Rupp⁴, Keshav Sishodia⁷, Bjoern Senfftleben¹, Frank Stienkemeier⁹, Rico Mayro Tanyag¹⁰, Paul Tuemmler⁸, Sergey Usenko¹, Michael Meyer¹, Marcel Mudrich²

¹European XFEL GmbH, Holzkoppel 4 22869 Schenefeld, Germany

²Aarhus University, Department of Physics and Astronomy, Ny Munkegade 8000 Aarhus C, Denmark

³Universität Leipzig, Fakultät für Chemie und Mineralogie, Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Linnéstr. 2 D-04103 Leipzig, Germany

⁴ETH Zurich, Department of Physics, Laboratory for Solid State Physics, John-von-Neumann-Weg 9 8093 Zürich, Switzerland

⁵PNSensor GmbH, Otto-Hahn-Ring 6 81739 München, Germany

⁶Technische Universität Berlin, Institut für Optik und Atomare Physik, Hardenbergstrasse 36 D-10623 Berlin, Germany

⁷Indian Institute of Technology Madras, Department of Physics, Chennai 600 036 INDIA, India

⁸Universität Rostock, Institut für Physik, Albert-Einstein-Straße 23 - 24 18059 Rostock, Germany

⁹Albert-Ludwigs University of Freiburg, Faculty of Mathematics and Physics Institute of Physics, Hermann-Herder-Str. 3 79104 Freiburg, Germany

¹⁰Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Department Atomic-Scale Dynamics in Light-Energy Conversion, Magnusstraße 2 12489 Berlin, Germany, Germany

The rapid development of short-wavelength free-electron lasers (FELs) [1] over recent decades has stimulated the investigation of the interaction between intense, high-energy light pulses and matter, and has become a very active field of research. FEL pulses allow to perform the structural characterization of clusters, nanoparticles or bio-molecules by means of single-shot coherent diffraction imaging (CDI). This technique is expected to revolutionize the investigation of nano-scale objects structures or thier dynamics, which are otherwise lost in the statistical sampling of time- and ensemble-averaged measurements.

In addition, various interesting phenomena such as absorption enhancement, bleaching, modification, suppression of electron emission as well as others mechanisms are expected to play a key role in plasma dynamics. Detailed understanding of these processes in nano-scale objects considering plasma dynamics is of fundamental interest.

In this context, recently commissioned opportunity for two-color experiment in the soft X-ray regime at the European XFEL facility [2] in combination with the advanced version of the pnCCD detector [3] from pnSensor opens the way to a novel two-color CDI technique. Spectral sensitivity of the pnCCD camera allow us to resolve two simultaneously recorded CDI images from the pump and probe X-ray pulses. In this case both the initial configuration and the state of expansion of the same nano-object can be identified and monitored for delay times of up to 1ps. Simulation and first experimental results on pure and Xe doped He nanodroplets will be presented.

- [1] Decking W et al, Nat. Photonics (2020), 14, 391–397.
- [2] Serkez S et al, Appl. Sci. (2020), 8, 10.
- [3] Kuster M et al, J. Synchrotron Rad. (2021), 28, 576–587.

Source and laser technologies for matter-wave interferometry with large metal clusters

Bruno E. Ramírez-Galindo¹, <u>Severin Sindelar</u>¹, Richard Ferstl¹, Sebastian Pedalino¹, Tomás de Sousa¹, Stefan Gerlich¹, and Markus Arndt¹

University of Vienna, Faculty of Physics, VDS & VCQ, Boltzmanngasse 5, 1090 Vienna

Metal nanoparticles are currently the main candidates for direct interferometric tests of the quantum superposition principle within the 1MDa mass range, providing not only a considerable improvement upon the current 28kDa milestone¹ but also opening a promising window for interferometric studies on the properties of metals in the interface to the bulk². Among the experimental challenges that must be tackled to observe the interference of 1MDa metal nanoparticles, developing an adequate source plays a key role. Such a source must produce a long-duration, high-brilliance beam of MNPs with masses up to 1MDa and velocities below 40m/s to be suited for the next generation of near-field matter-wave interferometers.

Here, we present our work towards a suitable nanoparticle source; an approach based on an LN2-cooled source and an aerodynamic lens array allows us to produce a stable beam of nanoparticles with masses up to 2MDa and velocities of down to 70m/s.

To increase the range of accessible metals beyond what can be ionized with our 266nm laser, we are working on the high harmonic generation of a DPSS pumped TiSa laser, to achieve intense deep ultraviolet light below 220nm. This light shall enable photodepletion gratings in the interferometer and facilitate the mass-selective detection after DUV ionization.

These technologies are setting us one step closer to a source tailored specifically for the needs of high-mass interference. Additionally, we explore the current limitations and prospects for nanoparticle generation, slowing, and cooling to bridge the gap to the required values.

References

¹ Fein, Y. Y., et al (2019). Quantum superposition of molecules beyond 25kDa. Nature Physics, 15(12).

² Pedalino, S., et al. (2022). Exploring metal nanoparticles for matter-wave interferometry. Physical Review A, 106(2).

Small Silicon-Oxide Cations: Photodissociation & Optical Absorption Properties

<u>T. Studemund</u>, K. Pollow, M. Förstel, A. A.Breier, and O. Dopfer IOAP, Technische Universität Berlin, Hardenbergstraße 36, 10623 Berlin, Germany

The evolution of solar systems, planets such as Earth and other celestial bodies is significantly influenced by interstellar dust, predominantly composed of μ m-sized silica and metallic silicates.¹ Among the potential precursors for macroscopic dust particles in interstellar regions and interstellar disks, only molecular SiO has been identified hitherto.² Thus, further intermediate steps in the formation of dust particles remain unresolved. Combining experimental measurements of polyatomic Si_nO_m⁺ cations with quantum-chemical calculations offers a promising strategy towards providing insights into these unanswered questions. Accordingly, this study presents the initial optical spectra of Si_nO_m⁺ cations exceeding SiO⁺ and Si₂⁺ in size.^{2,3} The characterization of the electronic and optical properties of the investigated clusters generated via laser vaporization relies on photodissociation of mass-selected ions in a tandem mass spectrometer coupled to a laser excitation source.⁴ Thereafter, the action spectroscopy-derived electronic photodissociation data are compared and interpreted using TD-DFT calculations.

- ¹ K. Nagashima et al., Nat. 428, 921 (2004).
- ² R. W. Wilson *et al.*, *ApJ*, *167*, L97 (1971).
- ³T. Studemund *et al.*, *J. Phys. Chem. Lett.*, **13**, 7624 (2022).
- ⁴ M. Förstel et al., Rev. Sci. Instrum. 88, 12 (2017).

Control of Catalytic Activity and Selectivity by Changing Cluster Size and Composition One Atom a Time

S. Vajda^a

^a J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences, Prague, Czech Republic stefan.vajda@jh-inst.cas.cz

The presentation will address the tuning knobs available at the subnanometer scale to control the catalytic performance of the catalytic sites made of subnanometer clusters by changing their metal components, interaction with the support and reaction conditions., using the examples of the oxidative dehydrogenation of cyclohexane [1-2], and cyclohexene [3-5], (see the schematics below for the latter)

on size- and composition selected Co, Cu, Pd and CuPd clusters, supported on oxideand carbon-based supports.

In addition to leveraging the atomic precision control of the size and composition of the mono- and bimetallic clusters for controlling their catalytic propensities, also support effects, including the thickness of e.g. zirconia



support and the morphology or doping and surface termination of nanocrystalline diamond supports were also explored as additional variables for the design of catalysts with optimized performance. The obtained results show that in these systems the catalytic activity could be increased by up to two orders of a magnitude and selectivity switched between the products made.

[1] Halder, A.; Ha, M.-A.; Zhai, H.; Yang, B.; Pellin, M.J.; Seifert, S.; Alexandrova, A.N.; Vajda, S. Oxidative Dehydrogenation of Cyclohexane by Cu vs Pd Clusters: Selectivity Control by Specific Cluster Dynamics. *ChemCatChem.* **2020**, *12*, 1307–1315. DOI: 10.1002/cctc.201901795, *front cover*, <u>link</u>

[2] Lee, S.; Halder, A.; Ferguson, G.A.; S. Seifert, Winans, R.E.; Teschner, D.; Schlögl, R.; Papaefthimiou, V.; Greeley, J.; Curtiss, L.A.; Vajda, S. "Subnanometer Cobalt Oxide Clusters as Selective Low Temperature Oxidative Dehydrogenation Catalysts", *Nat. Commun.* **10**, Article number: 954, p. 1-9, published on line February 27, 2019, DOI: 10.1038/s41467-019-08819-5, *Communication, Editors' Highlight*, link

[3] Jašík, J.; Valtera, S.; Vaidulych, M.; Bunian, M.; Lei, Y.; Halder, A.; Tarábková, H.; Jindra, M.; Kavan, L.; Frank, O.; Bartling, S.; Vajda, Š. Oxidative dehydrogenation of cyclohexene on atomically precise subnanometer $Cu_{4-n}Pd_n$ ($0 \le n \le 4$) tetramer clusters: The effect of cluster composition and support on performance. *Faraday Discuss.* **2023**, *242*, 70-93. DOI: 10.1039/D2FD00108J, link

[4] Valtera, S.; Jašík, J.; Vaidulych, M.; Olszówka, J.E.; Zlámalová, M.; Tarábková, H.; Kavan, L.; Vajda, Š. Atom by Atom Built Subnanometer Copper Cluster Catalyst for the Highly Selective Oxidative Dehydrogenation of Cyclohexene. *J. Chem. Phys.* 2022, *156*, 114302-114310. DOI: 10.1063/5.0065350, <u>link</u>
[5] unpublished

IR spectroscopy of larger Pyrrole cation clusters (Py_n^+) : Evolution of charge resonance interaction

<u>Dashjargal Arildii</u>^a, Otto Dopfer^{a,b*} ^aTechnische Universität Berlin, Berlin, Germany ^bTokyo Institute of Technology, Tokyo, Japan

Aside from π H-bonding, cation/anion- π , and π - π stacking interactions, the charge resonance (CR) is a fundamental and strong force in charged arene dimers.¹ In aromatic dimer cations, the positive charge is shared between the molecules depending on their ionization energy (IE) differences. Previously, we demonstrated a new high-resolution experimental approach (utilizing infrared photodissociation spectroscopy (IRPD)) to precisely probe the charge distribution and the CR interaction in aromatic dimer cations for the prototypical case of the pyrrole dimer cation (Py_2^+ , Figure 1) in the gas phase. Py (C_4H_5N) is a five-membered heterocyclic ring which has a single isolated and uncoupled NH stretch oscillator ($\nu_{\rm NH}$) whose frequency is strongly dependent on its charge state and proton affinity of ligands.¹⁻⁴ Our further approach focuses on exploring the evolution of charge delocalization in larger Py_n^+ (n>2) clusters. Hence, herein, we produce the Py_n^+ (n=3-7) and their colder Ar-tagged Py_n^+Ar (n=3-6) clusters in the supersonic plasma expansion and determine the structures by IRPD and dispersion-corrected density functional theory calculations. The structuresensitive $v_{\rm NH}$ of Py_n^+ clusters plays an important role in revealing their structures and the evolution of the partial charges. The analysis of IRPD spectra of mass-selected Py_n^+ and its cold Py_n^+Ar clusters combined with geometric parameters of intermolecular structures reveals that Py_n^+ clusters grow through solvating of CR-stabilized Py_2^+ core by additional Py ligands through the formation of NH... π H-bonds rather than by sharing the positive charge between the Py_n⁺ units (Figure 1), unlike the benzene₃⁺ (Bz_3^+) cluster, in which charge delocalizes into the third Bz unit.⁵



Figure 1. Optimized structures of Py_n^+ (*n*=2-6) is obtained at the B3LYP-D3/cc-pVTZ level. The red dashed line represents the CR, and the blue dashed line is the NH... π interaction.

- [1] Chatterjee, K.; Matsumoto, Y.; Dopfer, O. Angew. Chem. Int. Ed. (2019), 58, 3351-3355.
- [2] Schütz, M.; Matsumoto, Y.; Bouchet, A.; Öztürk, M.; Dopfer, O. Phys. Chem. Chem. Phys. (2017), 19, 3970-3986.
- [3] Arildii, D.; Matsumoto, Y.; Dopfer, O. J. Phys. Chem. A (2023), 127, 2523-2535.
- [4] Arildii, D.; Matsumoto, Y.; Dopfer, O. J. Phys. Chem. A (2024), 128, 3993-4006.
- [5] Inokuchi, Y; Nishi N. J. Chem. Phys. (2001), 114, 7059-7065.

N_2 activation by size selected transition metal clusters: Why should I care and how do I optimize it?

Max Luczak¹, Christopher Wiehn², Daniela Fries³, Gereon Niedner-Schatteburg⁴

¹Math2Market, Kaiserslautern ²US Airforce, Kaiserslautern-Vogelweh ³BASF, Ludwigshafen ⁴RPTU Kaiserslautern-Landau, Fachbereich Chemie, Kaiserslautern

Size selected transition metal cluster ions serve to record the cryo kinetics and cryo IR spectra of N_2 adsorption. The DFT modelling of likely cluster structures, adsorption sites and IR spectra elucidates reaction pathways and critical points along these. Choice of transition metal, cluster size and charge state modulate the findings beyond simple predictions, and some vaguely recognizable systematics emerge slowly.



Figure 1: Calculated reaction pathways of N₂ activation by various TM clusters

Future research aims to expand the current findings and in particular to analyze the electronic structure of the rate determining transition state T3SP in more detail.

- D. V. Fries, M. P. Klein, A. Straßner, M. E. Huber, M. Luczak, C. Wiehn, G. Niedner-Schatteburg J. Chem. Phys. (2023), 159, 164303. https://doi.org/10.1063/5.0157217
- [2] D. V. Fries, M. P. Klein, A. Straßner, M. E. Huber, G. Niedner-Schatteburg, J. Chem. Phys. (2023), 159, 164306. https://doi.org/10.1063/5.0157218

Electronic state of a manganese oxide clusters revealed by Soft X-ray spectroscopy

Olesya S. Ablyasova^{1,2}, Mihkel Ugandi³, Esma Birsen Boydas³, Mayara da Silva Santos^{1,2}, Max Flach^{1,2}, Vicente Zamudio-Bayer¹, Michael Römelt³, J. Tobias Lau^{1,2}, Konstantin Hirsch¹

¹Abteilung für Hochempfindliche Röntgenspektroskopie, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Straße 15, 12489 Berlin, Germany.

²Physikalisches Institut, Universität Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany ³Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

The CaMn₄O₅ cluster's electronic structure plays a crucial role in understanding dioxygen formation in the Kok cycle. The S₄ state, responsible for O₂ formation, is difficult to observe because of the millisecond time scale of the S₃-S₀ transition [1]. Two main widely discussed models for the S₄ state feature different oxidation states of +4 and +5 of the manganese atom at the reaction site [2]. Despite the fact that the spin states of the manganese atoms in state S₄ are still under debate, the reactivity of the CaMn₄O₅ cluster is believed to be spin-dependent [3].

We report on the characterization of cold cationic gas-phase manganese oxide complexes via X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). We identify oxidation and spin states by comparison with reference spectra of manganese compounds with known oxidation states, accompanied by multireference and density functional theory calculations. We demonstrate that cationic $Mn(V)O_2^+$, recently identified as a species with the high oxidation state of manganese atom [4], is only the second manganese oxo complex to exist in a high-spin state. Our most important result is the identification of a $Mn_2O_3^+$ species with Mn(V) in a high-spin state. This is the first observation of the elusive manganese(V) high-spin state in a polymagnanese oxido complex [5, 7]. The observed result might have implications for the oxidation and spin states of the $CaMn_4O_5$ complex in the S₄ state.



- [1] N. Cox et al, *Science* (2014), **345**, 804.
- [2] J. Barber, Nature Plants (2017), **3(4)**, 17041.
- [3] V. Krewald et al, *Inorganic Chemistry* (2016), **55(2)**, 488.
- [4] M. G. Delcey, et al, Phys. Chem. Chem. Phys (2022), 24, 3598.
- [5] R. Gupta, Proceedings of the National Academy of Sciences (2015), 112, 53
- [6] T. Taguchi, et al, Journal of the American Chemical Society (2012), 134(4), 1996.

Silver cluster plasmon experiences strongest substrate effect when excited farthest away: Spooky action at a distance?

Kevin Oldenburg, Ingo Barke, Karl-Heinz Meiwes-Broer

Institute of Physics and Center for Interdisciplinary Electron Microscopy (ELMI-MV), Department "Life, Light and Matter", Universität Rostock, 18059 Rostock, Germany

The spatial mode geometry of localized plasmon-polaritons of deposited clusters and nanoparticles is closely connected to the substrate-cluster interaction strength, which can be experimentally accessed by observing the red shift induced by the environment. Here we present spatially resolved mapping of plasmon resonances within and around a single silver nanoparticle, deposited from the gas phase onto a carbon support. To this end we employ electron energy loss spectroscopy (EELS) with a scanning transmission electron microscope (STEM). The particle is supported by a narrow rim of a carbon substrate ("cliffhanger", see left figure), such that it can be investigated in a cross-sectional view, within a plane perpendicular to the local substrate surface. In combination with simulations based on the boundary element method (BEM), the full mode structure is revealed (right figure), enabling assignment of spectral features [1]. We observe pronounced symmetry breaking, manifested as a partial lifting of the threefold degeneracy of the dominant dipole modes and the corresponding mode splitting. The intuitive expectation is that the substrate should most strongly affect plasmon modes having maximal weight close to it, as previously reported for more complex nanostructures, such as cubes and pyramids. In contrast, we here observe an increasingly pronounced red shift the farther away the plasmon is excited. It turns out that this non-local substrate influence is a consequence of the simplicity of the system under investigation: for small, quasi spherical silver particles all modes show substantial spatial overlap, such that the intramode geometry governs the strength of cluster-surface interaction. On the other hand, selection of specific modes via their distinct spatial excitation probability dominates for larger, less simplistic nanostructures.

The observed lifted degeneracy contributes an important ingredient to the long-standing discussion of precise plasmon energies of silver clusters of various sizes [2]: in many cases, the dielectric environment of supported or embedded particles is accounted for by effective-medium corrections which do not include anisotropic effects, lifted degeneracies and mode splitting. This situation calls for a fresh approach to study plasmon excitations, with a focus on the cleanest possible system preparations, devoid of ligands or contamination, and well-defined, minimally interacting substrates.



Left: STEM image of a Ag cluster at the edge of a carbon film.

Right: Spatial maps of the electron loss probability of the plasmon resonance at two different energies. Results of a pixel-wise peak fit of experimental data (top) are compared to calculated maps using the boundary element method (bottom).

- [1] K. Oldenburg et al., submitted
- [2] H. Haberland, Nature (2013), 494 E1-E2; A. Campos et al., Nature Physics (2019), 15, 275

Controlled charging of single silica nanoparticles by electron attachment and charge transfer

Authors:

Björn Bastian, Sophia Leippe, Kleopatra Papagrigoriou, Knut Asmis

Abstract:

To characterize the intrinsic properties of single nanoparticles in the absence of inhomogenous broadening and particle-support interactions, we perform action spectroscopy in a cryogenic Paul trap [1]. Light absorption is indirectly detected as a mass loss by evaporating previously adsorbed messenger molecules from the particle surface. Control of the charge state is important for quantitative mass determination, to establish stable experimental conditions and to probe the effect of charge on the investigated properties. To this end, we have characterized charging and discharging of individual positively charged silica nanoparticles (100 nm diameter) with a cold cathode gauge as electron source. The results provide a guide to the selection of appropriate buffer gas species and pressures and, for the first time, allow us to charge and also discharge a nanoparticle over a wide range from about 300 to 1500 elemental charges.

[1] T.K. Esser, B. Hoffmann, S.L. Anderson, K.R. Asmis, Rev. Sci. Instr. 90 (2019) 125110

Cryogenic Ion Trap Vibrational Spectroscopy of $[PF_6^-, (HFIP)_x, (H_2O)_y]$ Complexes: Exploring Solvent-Solvent vs. Solvent-Anion Interactions

Hannah Buttkus, Milena Barp, Jiaye Jin and Knut R. Asmis

Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstraße 2, D-04103 Leipzig, Germany

The influence of a common fluorinated organic solvent molecule, 1,1,1,3,3,3-hexafluoro-2propanol (HFIP), on the microhydration of a hexafluorophosphate anion (PF_6^-) is examined in order to obtain a better understanding of HFIP's role as a strong hydrogen bond donor^[1] in the microsolvation of PF_6^- . Of particular interest is evaluating the formation of solvent-solvent vs. solvent-anion (solute) interactions. The ion complexes $[PF_6^-, (HFIP)_x, (H_2O)_y]$ with x = 1-3 and y = 1-2, are systematically investigated by IR photodissociation spectroscopy of the corresponding, cryogenically cooled D₂ adducts, in the spectral region between 2200 – 4000 cm⁻¹.

In single-solvent complexes, we observe O-H stretching frequency red-shifts of the solvent molecules of less than 200 cm⁻¹, indicating the formation of rather weak ionic hydrogen bonds. The red-shifts, however, increase in the case of $[PF_6^-, (H_2O)_y]$ with increasing number of solvent molecules whereas for $[PF_6^-, (HFIP)_x]$ they decrease. This suggests the formation of a hydrogen-bonded network upon PF_6^- microhydration (as previously predicted by TSCHUMPER *et al.*),^[2] which is not observed upon HFIP microsolvation. In the mixed-solvent complex (x = y = 1) the observed red-shift of one of the O-H stretching bands is twice as large ($\Delta v = 464 \text{ cm}^{-1}$), suggesting a cooperative solvation effect between HFIP and water. Global minimum-energy structure searches using Density Functional Theory (B3LYP-D3BJ/aug-cc-pVTZ) identify the lowest energy isomer of $[PF_6^-, HFIP, H_2O]$, which also exhibits the best agreement between the computed and experimental vibrational spectrum, to reflect a structure in which HFIP cooperatively strengthens the hydrogen bond between PF_6^- and water by engaging in an inter-solvent hydrogen bond.

Reference

[1] I. Colomer, A. E. R. Chamberlain, M. B. Haughey, T. J. Donohoe, Nat. Rev. Chem. 2017, 1, 1–12.

[2] Y. A. Abdo, G. S. Tschumper, *J. Phys. Chem.* **2020**, *124*, 8744–8752.

Characterization of the Yb⁺ $[4f^{13}6s^2]$ F⁻ hole state of ytterbium fluoride using REMPI spectroscopy

Luca Diaconescu¹, Stefan Popa², Sascha Schaller¹, André Fielicke¹

¹Fritz-Haber-Institut der MPG, Berlin, Germany ²Imperial College London, London, UK

The ytterbium monofluoride molecule YbF, used for measuring the electron's electric dipole moment (eEDM), is capable of entering a "hole" configuration, defined by excitation of one of the inner 4f shell electrons of the constituent Yb⁺ cation into the outer 6s shell^[1,2].

Using resonance enhanced multiphoton ionization spectroscopy (REMPI), we have rotationally characterized the low lying $4f_{7/2,1/2}^{-1}$ hole state, corresponding to the Yb⁺[$4f^{13}6s^2$]F⁻ configuration, for v = 0, 1. This knowledge will help improve laser cooling schemes for YbF, thus enabling more precise eEDM measurements.

Furthermore, using the same technique, we have measured and identified Rydberg series converging to several rotational levels of the ground state of the YbF⁺ cation. This allowed us to precisely determine the ionization energy (IE) of YbF and the rotational constant (B) of YbF⁺.

- [1] X. Alauze, J. Lim, Quantum Sci. Technol. (2021), 6, 044005.
- [2] C. Zhang, C. Zhang, J. Mol. Spectrosc. (2022), 386, 111625.

Probing the Adsorption and Activation of CO₂ Molecules by Transition Metal Oxides with Infrared Photodissociation Spectroscopy

<u>Jia Han^{1,2}</u>, Pengcheng Liu¹, Xiaoguo Zhou¹

¹Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, China

²Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Leipzig, Deutschland

As carbon dioxide emissions rise from fossil fuel consumption and tropical deforestation, the development of CO_2 capture and utilization technologies is seen as crucial in the efforts to mitigate global warming. However, the biggest obstacle to speeding up the exploitation of chemical industry based on CO_2 as a raw material is its low energy level as well as chemical inertness. The first crucial step in the conversion of CO_2 for further industrial applications refers to its adsorption and activation by catalysts. Gas-phase studies on well-defined cluster model systems in a controlled environment provide molecular-level insights into underlying reaction mechanisms and in this way ultimately facilitate the rational design of highly active and selective catalysts. We use infrared photodissociation spectroscopy combined with quantum chemical calculations to probe the structures of ion-molecule complexes comprising CO_2 molecules and model catalysts, providing detailed understanding of the elementary adsorption and activation processes.

- [1] Jia Han, Pengcheng Liu, et al., Dalton Transactions (2024), 53, 171.
- [2] Jia Han, Yang Yang, et al., Physical Chemistry Chemical Physics (2023), 25, 13198-13208.

Coulomb explosion of pure and doped helium droplets

Frithjof Harmsen,

Institut für Physik, AG Cluster und Nanostrukturen/Universität Rostock, Rostock, Deutschland

High-resolution photoelectron spectroscopy on Niobium clusters

<u>Maziyar Kazemi</u>¹, Fabian Bär¹, and Bernd v. Issendorff ¹ ¹Faculty of physics/University of Freiburg, Freiburg, Germany

Niobium is an element that is famous for its super conductivity properties. Deeply cold Niobium clusters have been studied by high-resolution photoelectron spectroscopy at 6 K, using an optimized magnetic bottle photoelectron spectrometer. This spectrometer, which employs a time dependent deceleration for electron package focusing, currently possesses an energy resolution of $\Delta E/E = 0.19\%$ (3.7 meV at 2.0 eV kinetic energy). This is 10 times better than a conventional magnetic bottle spectrometer and competitive with hemispherical energy analyzers, which have the disadvantage of a significantly smaller collection efficiency. This allows us to observe features like vibrational progressions or contributions from different isomers that have not been resolved before. Another important direction could be the search for evidence of super conductivity (Cooper pairing) in Niobium clusters.



Figure 1: Comparing the result of photoelectron spectroscopy of Niobium clusters after magnetic bottle optimization.

- [1] M.Weigt, PhD thesis, Albert-Ludwigs-Universität Freiburg (2021).
- [2] F.Bär, master thesis, Albert-Ludwigs-Universität Freiburg (2017).

Novel Apparatus for Synchrotron X-ray Photoelectron Spectroscopy of Size-Selected Gas-Phase Clusters

Lotar Kurti¹, Phillip Stöcks¹, Fabian Bär¹, Lukas Weise¹, and Bernd v. Issendorff¹

¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Germany

A newly developed apparatus enables X-ray photoelectron spectroscopy on mass-selected cluster ions at synchrotrons for the first time. The system's centerpiece is a liquid nitrogencooled linear Paul trap, where stored cluster ions interact with synchrotron radiation. The emitted electrons are directed by a specially designed magnetic field into a Hemispherical Energy Analyzer, where photoelectron spectra are captured. Clusters are generated in a magnetron cluster source, mass-selected using a quadrupole mass spectrometer, and then introduced into the linear ion trap. This setup is expected to provide element-specific binding energy measurements of core levels, offering detailed insights into the chemical bonding of pure and mixed metal and semiconductor clusters.

- J Bahn, P Oelßner, M Köther, C Braun, V Senz, S Palutke, M Martins, E Rühl, G Ganteför, T Möller, B von Issendorff, D Bauer, J Tiggesbäumker, and K-H Meiwes-Broer. Pb 4f photoelectron spectroscopy on mass-selected anionic lead clusters at FLASH. New Journal of Physics, 14(7):075008, jul 2012.
- E. Harting, Frank Henry Read, J. N. H.. Brunt, and J. N. H. Brunt. Electrostatic Lenses
 Elsevier Scientific Publishing Company, Amsterdam; Oxford; New York, 1976.
- 3. Fabian Bär. Ultra-high resolution photoelectron spectroscopy on deeply cold niobium clusters. Master's thesis, Albert-Ludwig-University of Freiburg, 2017.

A new setup for Free Electron Laser based photoelectron spectroscopy.

Nishtha Lakhanpal¹, Fabian Bär¹, Kariman Elshimi¹ and Bernd V. Issendorff

¹University of Freiburg, Germany

The development of intense light sources in the XUV and X-ray ranges opens new avenues for the study of free clusters and nanoparticles. A new setup for photoelectron spectroscopy is currently under construction to investigate size-selected, deeply cold clusters, with a focus on characterizing ultrafast electronic processes. This setup will enable the exploitation of the vast potential of FELs in photoelectron spectroscopy. Several components, such as the magnetic bottle photoelectron spectrometer, cluster source, and specialized ion optics, are already in place. Additional components, including a QMS, deflector, and ion trap, are still under development.

Reference:

[1] Bär, F.(2023). High-resolution photoelectron spectroscopy on cold metal clusters. Albert-Ludwigs-Universität Freiburg. https://doi.org/10.6094/UNIFR/237632

Ultracool IR Spectroscopy: Carbocations in Helium Nanodroplets

Katja Ober¹, América Y. Torres-Boy¹, Gerard Meijer¹, Gert von Helden¹

¹Fritz-Haber Institut der Max-Planck Gesellschaft, Berlin, Germany

Gas-phase vibrational spectroscopy has been proven to provide a nearly ideal method for the investigation of ions, unperturbed by solvent effects. In addition, ions can be placed in helium nanodroplets as a matrix, where the interaction with the dopant ion is very weak. As the helium droplets are at very low temperatures (0.37 K), thermal broadening and therefore spectral congestion is significantly reduced. In the experiment, the ions that are embedded in a helium droplet are irradiated with a tuneable infrared free electron laser. Resonant absorption of photons can lead to an evaporation of helium, as the energy of the excitation gets dissipated through the molecule and the droplet, eventually leading to evaporation of helium. Detection of bare ions as a function of infrared wavelength then gives an infrared spectrum. [?] This technique can be used to study a wide variety of molecular ions and ionic clusters, ranging from small carbocations through proton-bound complexes to large organic molecules and biomolecules.

Carbocations are playing an important role in many areas of chemistry. They can be found in the interstellar medium, as the availability of carbon and the long lifetime of gaseous ionic species in astrophysical environments causes a high abundance of ionised carbonaceous molecules, such as polyaromatic molecules and fullerenes. [?] Furthermore, carbocations are intermediates in a variety of organic chemical reactions. Some of those can undergo facile chemical conversions, such as hydride shifts, which can occur due to the overlap of the empty p-orbital and a vicinal CH σ -orbital. [?] Others can form three-center two-electron bonds and are therefore of a more fundamental interest. These so-called non-classical carbocations involve the delocalization of a chemical bond, which results in C-C and C-H bonds of fractional bond order. [?]

Here we show a selection of infrared spectra of carbocations of interest in the spectral range of 800-1600 $\rm cm^{-1}$ to investigate diverse processes such as hydride shifts or the formation of non-classical carbocations.

- [1] Mucha, E. et al. Nat. Commun. (2018), 9(1), 1-5.
- [2] Campbell, E. K. et al. *Nature* (2015), **523**(7560), 322-323.
- [3] Brooks, M. A. et al. J. Am. Chem. Soc. (1999), **121**(23), 5444-5449.
- [4] Mosley, J. D. et al. Angew. Chem. (2014), **126**(23), 5998-6001.

Reconstructing the anisotropic expansion of a laser driven nanoplasma

Paul Tuemmler¹, Felix Gerke², Hendrik Tackenberg¹, Thomas Fennel¹, <u>Christian Peltz</u>¹, Eckart Rühl²

¹ Institute of Physics, University of Rostock, 18051 Rostock, Germany²Physikalische Chemie, Freie Universität Berlin, Berlin 14195, Germany

Coherent diffractive imaging (CDI) at X-ray free-electron lasers (FELs) has evolved into a wellestablished method for the structural investigation of unsupported nanoparticles. This inherently static method can be readily adopted to time-dependent studies by incorporating a second pulse in a pump-probe scheme.

In a recent experiment at LCLS, we utilized this method to study the fundamental process of free plasma expansion into vacuum using the example of large laser-pumped SiO2 clusters [1]. The resulting plasma expansion rapidly and isotropically softens the initial surface density step. This, in turn, increases the radial decay of the scattering signal eventually precluding meaningful measurements due to adiminishing signal-to-noise ratio within only a few hundred femtoseconds.

Here, we present the results of a follow-up experiment at the European XFEL where we revisited SiO2 as a target, but operated in a weaker excitation regime. This approach allowed us to record images over far longer timescales and revealed a strong anisotropic expansion dynamic, as predicted by theory [2].

- [1] C. Peltz et al., New J. Phys. (2022), 24, 043024.
- [2] C. Peltz et al., *Phys. Rev. Lett.* (2014), **113**, 133401.

Anisotropic photoemission from an individual plasmonic silver nanoparticle deposited on silicon

Waqas Pervez,

Institut für Physik, AG Oberflächen- und Grenzflächenphysik/Universität Rostock, Rostock, Deutschland

Detailed investigation of unexpected photoelectron spectra via angle-resolved spectroscopy of Gold clusters

Steve Takouan Tchounga¹, Lucas Weise¹, Bernd von Issendorff¹

¹University of Freiburg, Freiburg im Breisgau, Germany

Angle-resolved spectroscopy provides an important test of the theoretical description of clusters since these spectra carry more information than the bare electron binding energies. Specifically, the anisotropy of photoelectron spectra depends on the angular momentum state [1].

In the experiment cluster anions are produced in a magnetron sputter source, cooled to 7K, and enter a time-of-flight spectrometer for mass selection. Electrons are then detached by linear polarised laser light and projected onto an MCP detector in a velocity map imaging setup.

The presented analysis utilizes the additional information from angle-resolved spectroscopy to gain a better understanding of the electronic structure of the cluster. For Au_{33}^- an electronic shell closing is expected, leading to the opening of a new shell for Au_{34}^- . The angular momentum character of this new shell is not in accordance with a simple shell model. It also differs from the mixed character as observed for Sodium clusters of the same size [2]. Possible influences of the high-lying d-band are discussed.

- A. Piechaczek, C. Bartels, C. Hock, J.-M. Rost, and B. v. Is- sendorff, *Phys. Rev. Lett.* (2021), 126.
- [2] C. Bartels, C. Hock, R. Kuhnen, M. Walter, and B. v. Issendorff, *Physical Review A* (2013), 88.

Name	First name	E-Mail
Ablyasova	Olesya	olesya.ablyasova@helmholtz-berlin.de
Asmis	Knut	knut.asmis@uni-leipzig.de
Barke	Ingo	ingo.barke@uni-rostock.de
Bastian	Björn	bjoern.bastian@uni-leipzig.de
Bernhardt	Thorsten	thorsten.bernhardt@uni-ulm.de
Breier	Alexander	A.breier@physik.tu-berlin.de
Buttkus	Hannah	hannah.buttkus@uni-leipzig.de
Christen	Wolfgang	christen@hu-berlin.de
Christian	Peltz	christian.peltz@uni-rostock.de
Demianenko	Aleksandr	aleksandr.demianenko@physik.uni-freiburg.de
Diaconescu	Luca	lucad@fhi-berlin.mpg.de
Dopfer	Otto	dopfer@physik.tu-berlin.de
Fielicke	Andre	fielicke@fhi-berlin.mpg.de
Flach	Max	max.flach@helmholtz-berlin.de
Harmsen	Frithjof	frithjof.harmsen@uni-rostock.de
lwe	Norman	norman.iwe@uni-rostock.de
Jin	Jiaye	jiaye.jin@uni-leipzig.de
Jongchan	Lee	leejon@ethz.ch
Kayser	André	andre.kayser@hideneurope.de
Kazemi	Maziyar	maziyar.kazemi@physik.uni-freiburg.de
Kurti	Lotar	lotar.kurti@physik.uni-freiburg.de
Lakhanpal	Nishtha	nishthalakhanpal2417@gmail.com
Meiwes-Broer	Karl Heinz	meiwes@uni-rostock.de
Mikolaj	Pavol	pavol.mikolaj@uni-ulm.de
Möller	Thomas	thomas.moeller@physik-tu-berlin.de
Niedner-Schatteburg	Gereon	gns@rptu.de
Ober	Katja	ober@fhi-berlin.mpg.de
Ovcharenko	Yevheniy	yevheniy.ovcharenko@xfel.eu
Penna	Tatiana	tatiana.penna@uni-leipzig.de
Pervez	Waqas	waqas.pervez@uni-rostock.de
Raspe	Klara	klara.raspe@uni-rostock.de
Schooss	Detlef	detlef.schooss@kit.edu
Schwarz	Kevin	kevin.schwarz@physik.uni-freiburg.de
Schweikhard	Lutz	lschweik@physik.uni-greifswald.de
Sindelar	Severin	severin.sindelar@univie.ac.at
Studemund	Taarna	studemund@physik.tu-berlin.de
Takouan Tchounga	Steve	steve.takouan@aims-cameroon.org
Tang	Hanchao	hatang@ethz.ch
Tiggesbäumker	Josef	josef.tiggesbaeumker@uni-rostock.de
Torres Boy	América	torres@fhi-berlin.mpg.de
Vajda	Stefan	stefan.vajda@jh-inst.cas.cz
von Helden	Gert	helden@fhi-berlin.mpg.de
von Issendorff	Bernd	bernd.von.issendorff@uni-freiburg.de
Lau	Tobias	tobias.lau@helmholtz-berlin.de
Han	Jia	jiahan@ustc.edu.cn
Dashjargal	Arildii	arildii@physik.tu-berlin.de