

MO 18: Poster: Cluster

Time: Wednesday 17:00–19:00

Location: Tent C

MO 18.1 Wed 17:00 Tent C

Nickel L_3 excitation energy shifts and spectroscopic signatures revealing different electronic characteristics within cationic nickel halides — ●MAX FLACH^{1,2}, KONSTANTIN HIRSCH¹, TIM GITZINGER², MARTIN TIMM¹, MAYARA DA SILVA SANTOS^{1,2}, OLESYA ABLYASOVA^{1,2}, MARKUS KUBIN¹, TOBIAS LAU^{1,2}, BERND VON ISSENDORFF², and VICENTE ZAMUDIO-BAYER¹ — ¹Helmholtz-Zentrum Berlin — ²Universität Freiburg

Electronic configurations play an important role for the catalytic abilities of late transition metals. Late first row transition metal halides like nickel halides have been of interest in various studies regarding their possible use in catalytic reactions and reactivity studies reveal differences in their reactivity with respect to the halogen ligand. In this study we use x-ray absorption spectroscopy at the nickel L_3 -edge of $[\text{NiX}]^+$ ($X=\text{F,Cl,Br,I}$) and mono atomic nickel cations in two well defined electronic configuration to show the change from NiF^+ with a predominant $3d8$ configuration to $[\text{NiX}]^+$ ($X=\text{Cl,Br,I}$) with a predominant $3d9$ configuration. Experimentally obtained L_3 -edge shifts of the mono atomic species correspond well to the well established theory for exact one integer change in $3d$ occupation in atomic core level spectroscopy. The obtained L_3 -edge shifts of the $[\text{NiX}]^+$ ($X=\text{F,Cl,Br,I}$) series shows shifts associated with an integer change in oxidation state in literature. Comparison between mono atomic with valence electrons in purely atomic orbitals and the diatomic samples with valence electrons contributing to molecular orbitals provides insight on the influence of $3d$ electrons participating in bonding on L_3 excitation energy shifts.

MO 18.2 Wed 17:00 Tent C

DFT and TD-DFT study of the gas-phase nickel tetracarbonyl complex — ●A. HREBEN^{1,2}, O. S. ABLYASOVA^{2,3}, M. FLACH^{2,3}, M. TIMM², M. DA SILVA SANTOS^{2,3}, V. ZAMUDIO-BAYER², K. HIRSCH², and J. T. LAU^{2,3} — ¹Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany — ²HZB, Albert-Einstein-Straße 15, 12489 Berlin, Germany — ³Universität Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany

Investigations of transition metal carbonyl complexes have a significant role in the rapid development of coordination chemistry. Metal carbonyls are widely used as catalysts in synthesis and industrial processes and also find applications in electrochemistry and laser chemistry as precursors. The first discovered homoleptic carbonyl complex was $\text{Ni}(\text{CO})_4$, whose structure and binding properties are still under discussion. In this research, we focused on calculating the most stable structure of $\text{Ni}(\text{CO})_4^+$ using DFT methods. Four possible multiplicities of the given complex were analyzed using three different functionals (B3LYP, M06L, TPSSH) and two basis sets (def2-TZVP, 6-311+G(3df)). Based on the comparison of the obtained final total energies of optimized geometries, the method giving minimal energy was used for further TD-DFT calculations. The obtained simulated oxygen K-edge of the X-ray absorption spectra (XAS) are compared to experimental data. For that matter, gas-phase $\text{Ni}(\text{CO})_4^+$ complex measurements were performed via XAS in ion yield mode at the oxygen K-edge on mass-selected ions, cryogenically cooled in the Ion-Trap end station located in BESSY II.

MO 18.3 Wed 17:00 Tent C

Detailed investigation of unexpected photoelectron spectra via angle-resolved spectroscopy of Gold clusters — ●STEVE TAKOUAN TCHOUNGA, LUKAS WEISE, and BERND VON ISSENDORFF — Physikalisches Institut der Albert-Ludwigs-Universität Freiburg, 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 angu-

lar 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.

[1] A. Piechaczek, C. Bartels, C. Hock, J.-M. Rost, and B. v. Issendorff, Phys. Rev. Lett. 126, 233201 (2021). [2] C. Bartels, C. Hock, R. Kuhnen, M. Walter, and B. v. Issendorff, Physical Review A 88, 043202 (2013).

MO 18.4 Wed 17:00 Tent C

New setup for synchrotron x-ray photoelectron spectroscopy on gas-phase size selected clusters — ●LOTAR KURTI, PHILLIP STÖCKS, FABIAN BÄR, LUKAS WEISE, and BERND V. ISSENDORFF — Physikalisches Institut der Albert-Ludwigs-Universität Freiburg, Germany

A new apparatus has been constructed which will allow performing X-ray photoelectron spectroscopy on mass selected cluster ions at synchrotrons for the first time. The core of the setup is a liquid nitrogen cooled linear Paul trap, in which stored cluster ions will interact with synchrotron radiation. Emitted electrons will be guided by a specially designed magnetic field into a Hemispherical Energy Analyser, where photoelectron spectra are recorded. The clusters will be produced in a magnetron cluster source and mass selected by a quadrupole mass spectrometer before insertion into the linear ion trap. Measuring element specific binding energies of core levels is expected to yield specific information about the chemical bonding in pure and mixed metal and semiconductor clusters.

MO 18.5 Wed 17:00 Tent C

High-resolution photoelectron spectroscopy on tantalum and gold clusters — ●MAZIYAR KAZEMI, FABIAN BÄR, and BERND V. ISSENDORFF — Institute of Physics University of Freiburg

The characteristics of deeply cold tantalum clusters (Ta_4^* to Ta_{23}^*) and gold clusters (Au_3^* to Au_{40}^*) have been studied using high-resolution photoelectron spectroscopy at 3.9K. Our magnetic bottle time-of-flight photoelectron spectrometer, which employs a time-dependent deceleration for electron package focusing, possesses an energy resolution of $\Delta E/E = 0.22\%$ (5.5 meV at 2.0 eV kinetic energy for Pt ions). This is five times better than a conventional magnetic bottle spectrometer and competitive with hemispherical energy analyzers, which have the disadvantage of a significantly smaller collection efficiency. Combining the improved spectrometer with a low-jitter, short-pulse picosecond laser operating at 211 nm enables us to inspect states bound with up to 5.9eV binding energy with unprecedented resolution. This allows us to observe features like vibrational progressions or contributions from different isomers that have not been resolved before.

MO 18.6 Wed 17:00 Tent C

Single-shot electron and ion coincidence spectroscopy of rare gas clusters. — ●FREDERIC USSLING, YVES ACREMANN, ALESSANDRO COLOMBO, LINOS HECHT, KATHARINA KOLATZKI, MARIO SAUPPE, JOSÉ GÓMEZ TORRES, ALEXANDRE ROSILLO VORSIN, and DANIELA RUPP — ETH Zurich, Laboratory for Solid State Physics, John-von-Neumann-Weg 9, 8093 Zurich, Switzerland

Intense short-wavelength pulses from free-electron lasers (FELs) or lab-based high harmonic generation (HHG) sources enable structural investigation of individual nanometre-sized specimens like viruses [1] or clusters [2] via diffraction imaging (CDI). The intense short-wavelength pulses lead to a highly ionized system followed by complex dynamics covering many different time scales. In this context, atomic and molecular clusters can serve as ideal model systems to study light-matter interaction on the nanoscale. Each interaction residual, such as ejected electrons or ions, gives insights into different processes inside the cluster: Direct electron measurement allows to probe (sub-)femtosecond dynamics, including ionization and nanoplasma formation [3]. Cluster dissociation dynamics, proceeding on longer timescales, can typically be studied via ion time-of-flight spectroscopy [3]. Consequently, the simultaneous measurement of ejected electrons and ions through coincidence spectroscopy is a powerful tool to study light-matter interaction. We present first tests towards single-shot electron and ion coincidence spectroscopy combined with CDI of large rare-gas clusters. [1] M. Seib-

ert et al., Nature 470,(2011) [2] D. Rupp et al., Nat Commun 8, 493 (2017) [3] M. Arbeiter and T. Fennel, New J. Phys. 13 053022 (2011)

MO 18.7 Wed 17:00 Tent C

A new helium droplet source setup for nanoparticle deposition — ●FABIO ZAPPA, ANNA-MARIA REIDER, THOMAS POHL, JAN MAYERHOFER, MASOOMEH MAHMOODI-DARIAN, ELISABETH GRUBER, and PAUL SCHEIER — Institut für Ionenphysik und Angewandte Physik - Universität Innsbruck

Helium droplets have been extensively used in the last years to produce Taylor-made clusters of various atomic and molecular species, which can be analysed both in *in flight* or deposited on surfaces. Surface deposition with helium droplets presents various challenges as well as opportunities which our group is presently exploring. The present communication gives an overview of a new setup that is being developed in our group, which will allow the deposition of doped helium droplets both in neutral or multiply charged state. Various benchmarks and comparisons with other instruments in our lab will be presented, as well as preliminary deposition results with gold as dopant of the droplets.

The work was supported by the Standort Agentur Tirol, K-Regio Project SupremeByNano

MO 18.8 Wed 17:00 Tent C

Density optimization of a pure indole-water molecular beam for thermal-energy studies — ●HOSSEIN SABERIANI^{1,2,3}, MATTHEW SCOTT ROBINSON^{1,2,3}, MUKHTAR SINGH^{1,2,3}, HUBERTUS BROMBERGER^{1,2}, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Center for Ultrafast Imaging, Universität Hamburg — ³Department of Physics, Universität Hamburg

Microsolvated systems, wherein a small number of solvent molecules are clustered around a solute, provide a unique window into solvation effects present in the bulk [1]. In particular, the interaction of biomolecules such as indole with water provides ideal model systems for ultrafast dynamics studies of ambient-temperature/thermal-energy chemistry [2]. To study such systems, we need to start with a pure and high-density molecular beam. Using high-pressure supersonic expansions and the electrostatic deflector, we are able to produce such samples [3]. Here, I will detail how our molecular beam was optimized by tuning valve conditions, and how the absolute density measurements were done using strong-field ionization techniques.

[1] L. He, *et int.*(6 authors), J. Küpper, S. Trippel, *J. Phys. Chem. Lett.* **14**, 10499 (2023)

[2] M. S. Robinson and J. Küpper, *Phys. Chem. Chem. Phys.* **20**, 20205 (2023)

[3] Y.-P. Chang, *et int.*(2 authors), J. Küpper, *Int. Rev. Phys. Chem.* **34**, 557 (2015)

MO 18.9 Wed 17:00 Tent C

Time-resolved laser photodissociation investigation of a cationic Iridium(III) complex in an ion trap — ●PHILIPP WEBER¹, MARCEL J. P. SCHMITT¹, CHRISTOPH RIEHN¹, and CHRISTOPH LAMBERT² — ¹Department of Chemistry, RPTU Kaiserslautern — ²Institute for Organic Chemistry, Universität Würzburg

Iridium complexes are well known for their exceptional photophysical properties, which lead to their application in the fields of OLEDs and photovoltaics. [1] Transient laser photodissociation experiments were conducted on an isolated Ir(III) complex in the ion trap of an electrospray ionization mass spectrometer, giving dynamics on time scales from sub-ps to μ s. We present preliminary results for intrinsic gas phase dynamics of an Iridium(III) two donor- one acceptor (D₂-A) system based on a substituted triarylamine as electron donor (D, ppz-TAA) and tetramethyl-phenanthroline (A, tmp) as electron acceptor, which showed a long-lived (tens of ns) non-fluorescing charge-separated state in solution. [2] We observed, both, fragmentation and photoionization (generating the dication) upon photoexcitation, with the latter dominating the signal for pump-probe investigations. The observed dynamics (~ 0.2 ps, ~ 9 μ s) point more towards the fast formation of a long-lived triplet electronic state rather than a charge-separated state, with the latter possibly destabilized with respect to solution. We discuss different scenarios of electronic state dynamics for gas phase and solution.

[1] Longhi; De Cola. Iridium(III) Complexes for OLED Application. John Wiley & Sons, 2017. [2] Chem. Commun., 2009, 1670-1672.

MO 18.10 Wed 17:00 Tent C

Towards Femtochemistry in a Micro-Solvated Environment — ●DEEPAK K. PANDEY¹, LILIANA M. RAMOS MORENO¹, CLAUS-PETER SCHULZ², and JOCHEN MIKOSCH¹ — ¹Institut für Physik, Universität Kassel, Heinrich Plett Str. 40, 34132 Kassel, Germany — ²Ultrafast XUV-Physics, Max Born Institute (MBI), Max-Born-Straße 2A, 12489 Berlin, Germany

Chemical reactions, intrinsic to both natural processes and technological advancements, exhibit diverse dynamics, particularly within the realm of solution-phase environments. Understanding these dynamics is crucial, especially when employing gas-phase techniques to investigate reactions in solution, a trend that has gained prominence. In contrast to the popular liquid-jet technique, we aim to systematically introduce water molecules to a gas-phase photochemical reaction in a bottom-up approach - one at a time. Our experimental setup utilizes the water cluster technique pioneered by Udo Buck in combination with a Photoelectron Photoion Coincidence (PEPICO) spectrometer. At the University of Kassel, we aim to investigate the impact of micro-solvation on chemical reactions, ultimately using VUV light as a probe. The initial focus is on the steric effects of water on photochemical dynamics, employing a conventional pump-probe experiment to study processes such as photodissociation and photo-induced isomerization reactions. Our poster will focus on the experimental approach, characterization of the water cluster source and the spectrometer, and experimental advance toward studying photochemical reactions.

MO 18.11 Wed 17:00 Tent C

Supramolecular dynamics investigated on hydrogen-bonded pyrrole-water clusters upon site-specific x-ray photoionization — ●WUWEI JIN^{1,2}, IVO VINKLÁREK¹, HUBERTUS BROMBERGER¹, SEBASTIAN TRIPPEL^{1,3}, REBECCA BOLL⁴, MICHAEL MEYER⁴, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Department of Physics, Universität Hamburg — ³Center for Ultrafast Imaging, Universität Hamburg — ⁴European XFEL GmbH, Schenefeld

The solvation of molecules crucially affects their photostability and introduces additional pathways for relaxation dynamics compared to isolated molecules. To gain molecular-level insights into the solvation effects on the photofragmentation dynamics of a supramolecular system, we investigate the dynamics of a spatially separated pure sample of pyrrole-water (pyr-H₂O) clusters prepared by the electric deflector [1-2]. This is achieved through an IR-pump-x-ray-probe experiment at EuXFEL. An ionizing IR pulse triggers the (pyr-H₂O)⁺ fragmentation. The resulting dynamics are site-specifically probed by x-ray free-electron laser pulses [3]. This study of the hydrogen-bonded pyrrole-H₂O system is particularly relevant to pyrrole-containing biomolecules and establishes a new approach to study the key role of intermolecular interactions in supermolecular dynamics.

[1] M. Johny, S. Trippel, and J. Küpper, *Chem. Phys. Lett.* **721**, 149 (2019) [2] YP Chang, D. Horke, S. Trippel, and J. Küpper, *Int. Rev. Phys. Chem.* **557**, 34 (2015) [3] J. Onvlee, S. Trippel, and J. Küpper, *Nat. Commun.* **7462**, 13 (2022)

MO 18.12 Wed 17:00 Tent C

UV photo-induced dissociation dynamics of solvated (bio)molecular complex system — ●MUKHTAR SINGH^{1,2,3}, MATTHEW SCOTT ROBINSON^{1,2,3}, HUBERTUS BROMBERGER^{1,2}, JOLIIN ONVLEE^{1,3}, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Center for Ultrafast Imaging, Universität Hamburg — ³Department of Physics, Universität Hamburg

We present the investigation of ultrafast chemical dynamics induced by UV excitation in a micro-solvated indole-water-complex system probed by time-dependent strong-field ionization, and ion mass spectroscopy [1]. Indole-water is important due to indole's role as the chromophore of tryptophan, the strongest near UV absorber in proteins. The experimental setup contains a molecular beam and the electrostatic deflector to produce a pure gas-phase sample of indole-water [2]. We conducted a UV-IR pump-probe experiment, wherein we excited the system to the electronic excited state using 270 nm light. The dissociation dynamics of the system was monitored using strong-field multiphoton ionization by 1.3 μ m wavelength light from a femtosecond laser, tracking the time-dependent ion signals of the indole and indole-water ions.

[1] J. Onvlee, *et al.*, *Nat Commun.* **13**, 7462 (2022)

[2] S. Trippel, *et al.*, *Rev. Sci. Instrum.* **89**, 096110 (2018)