

MO 15: Spectroscopy of Metal Clusters

Time: Wednesday 14:30–16:30

Location: HS 3042

Invited Talk

MO 15.1 Wed 14:30 HS 3042

Metal Cluster opportunities — ●GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie, RPTU Kaiserslautern-Landau

Isolated Main group Metal Clusters (MMC) and those of Transition Metals (TMC), both provide for unique physical properties and chemical activities which are neither found in single atoms nor in bulk metals. Variation of cluster sizes provide for a scalable tuning of these properties, with some cluster size and shape related non-scalable exceptions superimposed. Empirical scaling laws often find a descriptive interpretation while the non-scalable exceptions receive or await support by explicit quantum chemical modelling. It is a major prevailing challenge to record and to describe appropriately TMCs electronics and their spin couplings. Upon deposition onto strongly interacting surfaces the properties of MMCs and TMCs may change significantly, and much less by weakly interacting surfaces.

The presentation reviews and exemplifies some of these aspects in complement to the prior Symposium on the Spectroscopy of Metal Clusters (SYMC). It concludes with a short outline of likely applications and limitations.

MO 15.2 Wed 15:00 HS 3042

Ultrafast Dynamics of Mass-selected Neutral Cerium Clusters Probed by Femtosecond NeNePo Spectroscopy — MAX GRELLMANN¹, NIKITA KAVKA², ●JIAYE JIN¹, ROLAND MITRÍČ², and KNUT R. ASMIS¹ — ¹Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Germany

Cerium clusters have unique physical properties, making them a subject of current research. The studies on sizes-selected clusters isolated in the gas phase provides information on the inherent cluster properties in the absence of a perturbing environment. Here, we report our results on electronic-state-selected vibrational wave-packet dynamics for the mass-selected neutral cerium clusters (Ce_{2-4}) in a cryogenic ion trap probed by two-color femtosecond pump-probe spectroscopy involving the negative-neutral-positive excitation scheme (fs-NeNePo). High-level CASSCF calculations and quantum dynamic simulations are performed to disentangle the observed oscillatory nuclear wave-packet dynamics on the dense potential energy surface (PES) for the neutral Ce_2 , which arises mainly from two electronic states containing superconfigurations in Π symmetry. Both of the fs-NeNePo spectra for Ce_3 and Ce_4 show coherent vibrational wave-packet dynamics that decay rapidly within 2 picoseconds, suggesting the presence of crossed PESs. These valuable results demonstrate complex electronic and vibrational structures of neutral cerium clusters and the potential of fs-NeNePo to study femtosecond dynamics of mass-selected, neutral and tag-free lanthanide clusters with high density of states.

MO 15.3 Wed 15:15 HS 3042

Magnetic nanodoping: cobalt doped silver clusters — ●V. ZAMUDIO-BAYER¹, K. HIRSCH¹, L. MA², K. DE KNIJF³, X. XU⁴, A. ŁAWICKI¹, A. TERASAKI⁵, P. FERRARI³, B. VON ISSENDORFF⁶, P. LIEVENS³, W.A. DE HEER⁷, J.T. LAU^{1,6}, and E. JANSSENS³ — ¹HZB, DEU — ²TCNN, CHN — ³KU Leuven, BEL — ⁴UNL, USA — ⁵Kyushu U., JPN — ⁶U. Freiburg, DEU — ⁷Georgia Tech, USA

The magnetic properties of neutral and charged silver metal clusters with a magnetic cobalt atom impurity were investigated experimentally by exploiting the complementary methods of Stern-Gerlach cluster beam deflection and XMCD action spectroscopy and are accompanied by DFT calculations and charge transfer multiplet simulations [*Phys. Rev. Research* **5**, 033103 (2023)]. The influence of the number of valence electrons and the consequences of impurity encapsulation were addressed in free size-selected, singly cobalt-doped silver clusters $CoAg_n^{0,+}$ ($n = 2-15$). Encapsulation of the dopant facilitates the formation of delocalized electronic shells with complete hybridization of the impurity $3d$ - and the host $5s$ -derived orbitals, which results in impurity valence electron delocalization, effective spin relaxation, and a low-spin ground state. Doped clusters with more than nine silver atoms are low-spin systems independent of their charge state, coincident with the increase in stability and decrease in reactivity of endohedrally doped silver clusters. In the exohedral cluster size range, spin pairing in the free electron gas formed by the silver $5s$ electrons is the dominating driving force determining the local $3d$ occupation of

the impurity and thus the cluster's spin multiplicity.

MO 15.4 Wed 15:30 HS 3042

Electronic structure of reactive transition metal-oxygen cations — ●MAYARA DA SILVA SANTOS^{1,2}, ROBERT MEDEL³, SIMON KRUSE^{2,4}, MAX FLACH^{1,2}, OLESYA S. ABLYASOVA^{1,2}, MARTIN TIMM², BERND VON ISSENDORFF¹, KONSTANTIN HIRSCH², VICENTE ZAMUDIO-BAYER², TONY STÜCKER³, SEBASTIAN RIEDEL³, and TOBIAS LAU^{1,2} — ¹Universität Freiburg, Freiburg, Germany — ²Helmholtz-Zentrum Berlin, Berlin, Germany — ³Freie Universität Berlin, Berlin, Germany — ⁴Humboldt-Universität zu Berlin, Berlin, Germany

Discovering compounds that present transition metals with unusual oxidation states or reactive oxygen species (superoxide, peroxide and oxygen-centered radical) is of great scientific and technological interests, as they have key applications as oxidizing agents, catalysts, or reaction intermediates. Here, we use X-ray absorption spectroscopy (XAS) at the oxygen K and metal M_3 or N_3 edges of gas-phase $[MO_n]^+$ systems ($M =$ transition metal, $n =$ integer), in their ground state, to identify the spectroscopic signatures of oxygen ligands and assign the oxidation state of the metal.[1,2] Experiments were performed at the cryogenic ion trap endstation at the beamline UE52-PGM at the Berlin synchrotron radiation facility BESSY II.[3] The highly oxidized and reactive $[Rh^{VII}O_3]^+$, $[Ru^{VIII}O_4]^{++}$ and $[Re^{VII}O_4]^{++}$ are here investigated via XAS for the first time. References: [1] M. da S. Santos, et al., *Angew. Chem. Int. Ed.* **61**, e202207688 (2022); [2] M. da S. Santos, et al., *ChemPhysChem* **24**, e202300390 (2023); [3] K. Hirsch, et al., *J. Phys. B: At., Mol. Opt. Phys.* **42**, 154029 (2009).

MO 15.5 Wed 15:45 HS 3042

Electronic state of a dioxidomanganese(V) and bis(mu-oxo) di-manganese oxide cluster revealed by XAS and XMCD —

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The $CaMn_4O_5$ cluster's electronic structure plays a crucial role in understanding dioxygen formation in the Kok cycle. The S_4 state, responsible for O_2 formation, is difficult to observe because of the millisecond time scale of the transition. Two main models for the S_4 state feature different oxidation states of +4 and +5 of the manganese atom at the reaction site. We report on the characterization of cold cationic gas-phase manganese oxide complexes via XAS and 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 $Mn(V)O_2^+$ 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 Mn(V) high-spin state in a polymanganese oxido complex, which may have implications for the future study of $CaMn_4O_5$ complex structure.

MO 15.6 Wed 16:00 HS 3042

The highest oxidation states of iridium probed by soft x-ray absorption spectroscopy — ●JOAO P. M. DE ARCANTO¹, M. DA SILVA SANTOS^{1,2}, V. ZAMUDIO-BAYER¹, S. KRUSE^{1,3}, M. TIMM¹, M. FLACH^{1,2}, O. S. ABLYASOVA^{1,2}, K. HIRSCH¹, R. MEDEL⁴, S. RIEDEL⁴, and J. T. LAU^{1,2} — ¹HZB, Berlin, Germany — ²Universität Freiburg, Germany — ³HU, Berlin, Germany — ⁴FU, Berlin, Germany

Iridium stands out prominently in the pursuit of higher oxidation states (OS). Recently, a combined theoretical and experimental effort has confirmed the existence of Ir in the OS +VII, +VIII, and the highest known OS for an element, +IX with $5d^2$, $5d^1$ and $5d^0$ local electron configuration, but only a few compounds are known [1]. Utilizing the potential of the Ion Trap endstation at the beamline UE52-PGM of the BESSY II synchrotron radiation facility, our group has successfully generated a series of cationic iridium oxides $[IrO_n]^+$ ($n = 0-4$) in the gas phase using a magnetron sputtering source. Employing a mass filter, Ir species of interest are selected and cooled in an ion trap.

We performed X-ray absorption spectroscopy at the iridium N_3 -edge allowing to study the 5d derived valence states as well as the oxygen K-edge, facilitating a comparative analysis across the series of iridium-oxo species [2]. [1] Wang et al., Nature 514, 475 (2014) [2] Da Silva Santos et al., Angew. Chem., 61, no. 38, e202207688, 2022

MO 15.7 Wed 16:15 HS 3042

Metal cluster mediated N_2 activation and cleavage — ●GEREON NIEDNER-SCHATTEBURG — Dept. of Chemistry and State Research Center OPTIMAS, RPTU Kaiserslautern-Landau, 67663 Kaiserslautern

Transition metal clusters (TMC) serve a model systems for chemically active surfaces as e.g. of catalytically active nano particles. Size selected TMCs were characterized before to activate and cleave Dinitro-

gen (N_2) spontaneously and under isothermal cryo conditions [1,2,3]. Here, we report on the current state of understanding and on new findings which elaborate the influence of cluster charge state, and which elaborate on cooperative effects amongst multiple adsorbate molecules on the surface of clusters. We discuss the validity of the across-edge above-surface (AEAS) mechanism of N_2 cleavage, and we report on current insights of the underlying interactions. Eventually, we show some results on Dihydrogen (H_2) activation, and we give reference to initial experiments on N_2 - H_2 coadsorption [4].

The presentation concludes with an outline of the current and future experimental schedule of TMC investigation in progress.

[1] <https://doi.org/10.1039/D0CP06208A>

[2] <https://doi.org/10.1063/5.0157217>

[3] <https://doi.org/10.1063/5.0157218>

[4] <http://dx.doi.org/10.1021/acs.jpcclett.8b00093>