Theory for Surface Processes and Spectroscopies Focus Topic

Room B116 - Session TH1+AS+SS-TuM

Introduction and Core-Level Spectroscopies I

Moderators: Gianfranco Pacchioni, Universita' degli Studi di Milano-Bicocca, **John Rehr**, University of Washington

8:00am **TH1+AS+SS-TuM-1 X-Ray Photoelectron Spectroscopy as a Useful Tool to Study Surfaces and Model Systems for Heterogeneous Catalysts***, **Hans-Joachim Freund**,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

After a brief introduction into the concepts of photoemission, including multielectron excitations, and a discussion of ways how to extract information on the chemical state of atoms in the non-ionized ground state from the chemical shift in XPS spectra, as well as from the evaluation of the so-called Auger parameter, we present several examples on how appropriate theoretical calculations may be crucial to properly interpret the spectra in terms of initial and final state effects. Four studies on systems representing model systems for heterogeneous catalysts are discussed. The first two refer to simple thin film oxide systems of MgO(100)/Ag(100) supported on metal single crystals.We interpret line widths in terms of vibrational excitations, depending on the thickness of the oxide film, and compare surface core level chemical shifts with those in the bulk, and discus the differences on the basis of ab-initio cluster calculations. The third example refers to chemical shifts of metal/(Pd) atoms adsorbed on bilayer silica films on Ru(0001), and illustrates the use of the Auger parameter to extract initial state chemical shifts. The last example deals with $CeO_2(111)$ surfaces and exemplifies the influence of open shell on the complexity of core level spectra.

8:40am **TH1+AS+SS-TuM-3 X-Ray Absorption and Emission Spectroscopy of Actinide Materials: Electronic Structure Questions from the Experimental Viewpoint***, **Bianca Schacherl**,* Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany **INVITED**

Understanding the electronic structure of one of the most complex element groups in the periodic table, the actinides, has been topic of extensive research in the last decades.

Spectroscopic tools for these investigations are provided by X-ray absorption spectra. Especially the An $M_{4,5}$-edge high-resolution X-ray absorption and emission spectroscopy has proven to be a powerful tool for electronic structure investigations.[1,2]

In this talk it will be demonstrated how newly revealed spectral features can be used for in-depth analyses of the actinide-ligand chemical bond. For model systems, one focus will lie on how the spectra change upon changes in the electronic structure of the actinide compound. It will be highlighted how several theoretical methods can give a valuable input to understand the orgin of the spectral features.[3–7]

This work is supported by the ERC Consolidator Grant "The Actinide Bond" (N°101003292) under the European Union's Horizon 2020 research and innovation program. The Institute for Beam Physics and Technology (IBPT), KIT is acknowledged for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA).

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9:20am **TH1+AS+SS-TuM-5 Towards New Spectroscopic Tools for Detection of Bonding Properties in Radiopharmaceuticals: Application on La Used as a Homolog of Ac***, **Tonya Vitova**,* Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal, Germany*; B. Schacherl, H. Ramanantoanina,* Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany*; M. Benesova,* German Cancer Research Center, Im Neuenheimer Feld 280, 69120 Heidelberg, Germany*; J. Göttlicher,* Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation (IPS), P.O. Box 3640, D-76021 Karlsruhe, Germany*; R. Steininger,* Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation (IPS), Germany*; M. Haverkort,* Heidelberg University, Institute for Theoretical Physics, P.O. Box 105760, 69047 Heidelberg, Germany*; A. Kovac,* European Commission, Joint Research Centre Karlsruhe, P.O. Box 2340, 76125 Karlsruhe, Germany

In recent years the use of radiopharmaceuticals based on alpha-particle emitting radionuclides has seen a considerable growth. In pre-clinical research and first clinical trials targeted alpha therapy has shown great potential. However, there are still many challenges in this field, one being the need for tight chelating of the alpha-emitting radionuclides and their daughters. We aim to understand relations between bonding properties and bond stability of such compounds.

High-energy resolution X-ray absorption near edge structure (HR-XANES) spectroscopy is a valuable tool for the electronic structure study of actinides and lanthanides.[1-2] Here we employ it first to probe the bonding properties of La, a homolog of Ac, with different ligands in discussion as nuclide binding site in radiopharmaceuticals for targeted alpha treatment.

$[La(H_2O)_9]^{3+}$, $[La(TRIS)(H_2O)_6]^{3+}$, $[La(TRIS)_2(H_2O)^3]^{3+}$ (buffer media), $La(DOTA)(H_2O)]^{1-}$, $[La(MACROPA)]^{1+}$ and $[La(PSMA\text{-}617)(H_2O)]$ have been prepared and characterized. We measured La L_2-edge HR-XANES spectra at the Synchrotron Laboratory for Environmental Studies (SUL-X) beamline and La L_3-edge extended X-ray absorption fine structure spectroscopa (EXAFS) at the INE-Beamline at the KIT Light Source. Additionally, density functional theory (DFT) and FDMNES calculations were performed to compute the spectra. Bonding interactions were evaluated using natural orbitals for chemical valence (NOCV) and quantum theory of atoms in molecules (QTAIM) which describes the topology (i.e., shape and magnitude) of the electron density between two bonded atoms.

Several tools (spectroscopic and theoretical) to determine the covalency of the La-ligand bond were developed. One example of this measure can be the comparison of position and shape of the pre- and main absorption edges. EXAFS and HR-XANES analysis gave insights into the coordination environment. With QTAIM bond analysis the covalent from the ionic part of the bonding was differentiated. Combined these results are the first steps towards developing new spectroscopic tools that will help understand the electronic structure and the bonding and will potentially help designing new chelating ligands for use in radiopharmaceuticals for targeted alpha therapy.

References

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9:40am **TH1+AS+SS-TuM-6 Potential Energy Curves of Core-Excited States and Vibrational Broadening of X-Ray Adsorption Spectra of Uranyl***, **Robert Polly**,* Karlsruhe Institute of Technology (KIT), Germany*; P. Bagus,* University of North Texas

It is well known that vibrational excitations lead to an observable broadening of the features in the X-Ray Photoelectron Spectroscopy, XPS, in ionic compounds. This broadening is described as a Franck-Condon, FC, broadening since it arises because there is a change in the equilibrium geometry of the ionized system from that in the initial, ground, state of the system. Studies have shown how the FC broadening is sensitive to coordination of the ionized atom [1] and to the covalent character of the cation – anion interaction [2]. For Uranyl UO_2^{2+} the different potential energy curves of the relevant core-excited states of the U $M_{4,5}$-edge manifold differ significantly and cause different broadenings for the three peaks which characterize the U $M_{4,5}$-edge X-Ray Adsorption Near Edge Spectroscopy, XANES. Thus, FC broadening effects affect the features as they do for XPS. This should be of particular importance in determining the resolution possible with High-Resolution XANES, HR-XANES [3-4]. However, to our knowledge, the possibility of different FC broadening in XANES or HR-XANES has not been considered previously and theoretical modeling of the spectra has used the same geometry for the initial and excited configurations [4-5]. In the present work, we examine vibrational excitations for the representative case of uranyl, UO_2^{2+}. The U $M_{4,5}$-edge HR-XANES spectra reveal three distinct peaks which are assigned to excitations into different 5f valence orbitals. The corresponding core-excited states differ significantly depending on the 5f valence orbital occupation and so does the FC broadening. Based on rigorous ab initio calculations of the wavefunctions, WFs, for the M_4 and M_5-edge XANES, we show that there are considerable changes in the geometry and we provide reliable estimates of the FC broadening due to these geometry changes. We also explain the linear behavior of the observed peak splittings with the internuclear distance, but we can not confirm a relation of the peak splittings with the covalence of the Uranium-Oxygen bond lengths.

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Author Index

Bold page numbers indicate presenter