Thursday Morning, November 9, 2023

Light Sources Science Mini-Symposium
Room C124 - Session LS+AC+LX+MI+TH-ThM

Tender X-ray Science and Time Resolved Studies

Moderators: Alison Pugmire, LANL, **David Shuh**, Lawrence Berkeley National Laboratory, **James G. Tobin**, University of Wisconsin-Oshkosh

8:00am **LS+AC+LX+MI+TH-ThM-1 Developments of High Resolution X-Ray Spectroscopic Tools for Probing Structural Properties of Actinide System from the Metal and Ligand Perspective*, Tonya Vitova,*** Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Germany **INVITED**

High energy resolution X-ray absorption and emission spectroscopic techniques became indispensable methods in actinide and radionuclide research.[1-5] One important motivation is studies concerning the mobilization and retention of long-lived actinides and fission products in geochemical processes relevant for safety studies of a potential deep geological nuclear waste repository.[3-4] In-depth insights into the actinide-ligand binding properties is a main application of these novel experimental techniques too.[6] Development at the ACT experimental station of the CAT-ACT wiggler beamline at the Karlsruhe Institute of Technology (KIT) Light Source will be discussed. One experimental technique especially powerful to differentiate oxidation states of actinides (An) is the An $M_{4,5}$-edge high-energy resolution X-ray absorption near-edge structure (HR-XANES).[4] This presentation highlights the latest technological developments at the ACT station enabling the HR-XANES spectroscopic technique for samples with low radionuclide loading down to 1 ppm in combination with a cryogenic sample environment reducing beam-induced sample alterations.[7-8] It paves the way for the examination of coupled redox/solid-liquid interface reactions.[8] Examples of applications of An $M_{4,5}$ edge core-to-core and valence band resonant inelastic X-ray scattering (CC-RIXS and VB-RIXS) for probing the electronic structure and binding properties of the actinide elements will be illustrated.[6] First results obtained using a newly developed versatile chamber for soft X-ray spectroscopy at the X-SPEC beamline at the KIT Light Source will be discussed.

This work has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 847593. We also acknowledge funding from the ERC Consolidator Grant 2020 under the European Union's Horizon 2020 research and innovation program (grant agreement No. 101003292).

References

1. Vitova, T. et al., *Inorganic Chemistry* **2020,***59* (1), 8-22.

2. Vitova, T. et al., *Chem Commun* **2018,***54* (91), 12824-12827.

3. Vitova, T. et al., *Nature Communications* **2017,***8*, 16053.

4. Pidchenko, I. et al., *Environ Sci Technol* **2017,***51* (4), 2217-2225.

5. Bagus, P. S. et al., *Inorganic Chemistry* **2021,***60* (21), 16090-16102.

6. Vitova, T. et al., *Chem Sci* **2022,***13* (37), 11038-11047.

7. Schacherl, B. et al., *J Synchrotron Radiat* **2022,***29* (1), 80-88.

8. Schacherl, B. et al., *Anal Chim Acta* **2022,***1202*, 339636.

8:40am **LS+AC+LX+MI+TH-ThM-3 High-Energy-Resolution X-Ray Spectroscopy and Actinides Research at SLAC*, Dimosthenis Sokaras,*** SLAC National Accelerator Laboratory **INVITED**

Nowadays, high-energy-resolution x-ray spectroscopy is a well-established and powerful tool available in state-of-the art synchrotron facilities. The suppression of the core-hole lifetime contribution within the conventionally broad spectroscopic features of actinide series has revitalized the role of x-ray spectroscopy in the study of actinide complexes and intermetallics. Numerous studies have leveraged the fine structure of M or L absorption edge resonances to sensitively probe and quantify the oxidation state, 5f delocalization, and ligation of the actinides species. The increasing availability of large solid angle instruments coupled with high flux beamlines is quickly enabling such advanced studies for dilute samples or samples under special sample environments. In this presentation we will summarize the high-resolution tender and hard x-ray spectroscopy advances at SLAC and the actinides research program that these capabilities have enabled during the last decade.

9:20am **LS+AC+LX+MI+TH-ThM-5 New Insight Into Excited-State Chemical Dynamics Using Ultrafast X-Rays:Recent Highlights, Future Opportunities & Development Plans at LCLS*, Robert Schoenlein,*** Linac Coherent Light Source - SLAC National Accelerator Laboratory **INVITED**

Ultrafast X-rays from free-electron lasers (XFELs) are driving a qualitative advance in our understanding of condensed-phase chemical dynamics and catalysis. Ultrafast soft X-rays provide element-specific mapping of chemical bonds, charge distributions, oxidation states and frontier orbitals. Ultrafast hard X-ray pulses reveal the atomic scale structural dynamics of excited-state dynamics – revealing relaxation pathways, and the coupling of atomic structure, electronic structure, and solvent dynamics. This talk will highlight recent results from the Linac Coherent Light source (LCLS) using advanced ultrafast X-ray methods to track excited-state charge-transfer and relaxation pathways, and reveal the influence of molecular structural dynamics, and solvent coupling. Notably, multi-modal methods combining time-resolved X-ray scattering and spectroscopy represent a powerful approach for linking X-ray experimental observables with theory to achieve a deeper understanding of excited-state dynamics to advance the development of design principles for creating molecules, complexes, and assemblies with desired functions.

In addition, new science opportunities enabled by the nearly-completed upgrade of LCLS (LCLS-II) coupled with advanced instrumentation and methods will be discussed. LCLS-II will provide tunable soft X-ray pulses (0.25 to 5.0 keV) at high repetition rate (up to 1 MHz) and hard X-rays up to 25 keV (at 120 Hz). This unprecedented capability will support powerful new methods such as time-resolved resonant inelastic X-ray scattering (RIXS). The new ChemRIXS instrument is optimized for studying solvated complexes with C, N, O (K-edges), 3*d* transition metals (L-edges), and rare-earth elements (M-edges) – where 2D RIXS maps of excited-state dynamics coupled with quantum chemical calculations will reveal the evolution of frontier orbitals. The Tender X-ray Instrument (TXI, 2.1-5.0 keV), now under development for LCLS-II, will support time-resolved tender X-ray spectroscopy (spanning the 4*d* transition metal L-edges and key functional ligands including P, S, and Cl), coherent scattering, and novel nonlinear X-ray pump / X-ray probe methods - combining X-rays from two independently tunable XFEL sources.

11:00am **LS+AC+LX+MI+TH-ThM-10 Attosecond Studies of Radiolysis at XFELs*, Linda Young,*** Argonne National Laboratory **INVITED**

We report the first attosecond x-ray pump/x-ray probe transient absorption study in condensed phases using a pure liquid water target. With tunable two-color attosecond x-ray pulses, the pump ionizes the valence band of water and the probe scans the oxygen K-edge absorption region. Theory establishes the nature of the detected transient absorption and models the observed signal for sub-femtosecond delay times.

Acknowledgements: This work supported in part by by the US Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division under award # DEAC02-06CH11357. Use of the Linac Coherent Light Source (LCLS), SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515.

critical importance for fields ranging from cancer therapy to the longevity of nuclear reactors to space travel. In these applications, radiolysis is initiated by a high-energy particle that leads to the ejection of energetic primary electrons followed by inelastic and non-adiabatic processes that produce damaging low energy electrons and reactive radical species. A microscopic understanding of reaction mechanisms, especially in complex systems, is missing as typical techniques used to detect prominent species, EPR and UV spectroscopies, lack either time resolution or spectral clarity. Tunable ultrafast x rays can dissect the radiolysis process. That is, x-ray pump/x-ray probe studies can systematically either peel electrons from valence, or, eject them from core orbitals and follow the ensuing dynamics on a site-specific basis.

11:40am **LS+AC+LX+MI+TH-ThM-12 First Real-Time Tracking of Oxidation States During Fast Redox of UO_2 Using a Microfluidic Electrochemical Cell and HR-XANES***, Jennifer Yao,* Pacific Northwest National Laboratory*; B. Schacherl,* Karlsruhe Institute of Technology (KIT), Germany*; B. McNamara,* Pacific Northwest National Laboratory*; C. Vollmer,* Karlsruhe Institute of Technology (KIT), Germany*; N. Lahiri, E. Ilton, E. Buck,* Pacific Northwest National Laboratory*; T. Vitova,* Karlsruhe Institute of Technology (KIT), Germany

Real-time tracking of the oxidation states of a UO_2 electrode during electrochemical oxidation and reduction was achieved using operando high-resolution X-ray absorption near-edge structure (HR-XANES) spectroscopy at the ACT station of the CAT-ACT beamline at the KIT Light Source, Karlsruhe, Germany. This was made possible by utilizing a particle-attached microfluidic electrochemical cell (PAMEC) developed at PNNL, and employing KIT's advanced actinide M-edge HR-XANES technique.[1-2] The PAMEC is a three-electrode system consisting of a working electrode (WE) made of the materials of interest a platinum (Pt) reference electrode, and a Pt counter electrode.[3] The electrochemical analyzer connected to the PAMEC device controlled the redox process, e.g., applying constant potential on the UO_2 WE to reduce (-1.1 V vs Pt) or oxidize it (0.5 V vs Pt), while HR-XANES simultaneously scanned its surface chemistry. The U M_4-edge HR-XANES spectra revealed the evolution of U from U(IV) to U(V) and finally to U(VI) during the oxidation process. We were able to demonstrate the reversibility of this process by reducing the same electrode back to pure U(IV), as confirmed by HR-XANES. To our knowledge, this study reports the first in-situ and operando measurement of real-time oxidation state changes of UO_2. The spectra obtained also provided insight into the electronic structure of U(VI) in the UO_2 alteration process. This successful international scientific collaboration showcases the potential of a PAMEC for in-situ and operando experiments with UO_2 and highlights its promising broad application for characterization of spent nuclear fuel systems.

References:

(1) Vitova, T.; Pidchenko, I.; Fellhauer, D.; Bagus, P. S.; Joly, Y.; Pruessmann, T.; Bahl, S.; Gonzalez-Robles, E.; Rothe, J.; Altmaier, M.; Denecke, M. A.; Geckeis, H., The role of the 5f valence orbitals of early actinides in chemical bonding. *Nature Communications* **2017,***8*, 16053. 10.1038/ncomms16053

(2) Schacherl, B.; Prüssmann, T.; Dardenne, K.; Hardock, K.; Krepper, V.; Rothe, J.; Vitova, T.; Geckeis, H., Implementation of cryogenic tender X-ray HR-XANES spectroscopy at the ACT station of the CAT-ACT beamline at the KIT Light Source. *Journal of synchrotron radiation* **2022,***29*, 80-88. 10.1107/s1600577521012650

(3) Yao, J.; Lahiri, N.; Tripathi, S.; Riechers, S. L.; Ilton, E. S.; Chatterjee, S.; Buck, E. C., A microfluidic electrochemical cell for studying the corrosion of uranium dioxide (UO2). *RSC Advances* **2022,***12*, 19350-19358. 10.1039/D2RA02501A

12:00pm **LS+AC+LX+MI+TH-ThM-13 Use of Artificial Intelligence Techniques To Analyze Materials Characterization Data From Actinide Containing Materials***, **Jeff Terry,*** Illinois Institute of Technology

We have developed artificial intelligence (AI) based methodology that can be utilized to reliably analyze experimental results from Extended X-ray Absorption Fine Structure (EXAFS), Nanoindentation, and core level photoemission. Specifically, we use a genetic algorithm to extract the relevant structural parameters through fitting of the measured spectra. The current approach relies on a human analyst to suggest a potential set of chemical compounds in the form of feff.inp input files that may be present. The algorithm then attempts to determine the best structural paths from these compounds that are present in the experimental measurement. The automated analysis looks for the primary EXAFS path contributors from the potential compounds. It calculates a goodness of fit value that can be used to identify the chemical moieties present. The analysis package is called EXAFS Neo and is open source written in Python. I will illustrate the use of this package with fits of actinide species in the barrier layer of Tristructural-isotropic (TRISO) encapsulated nuclear fuel particles. The current particle design consists of a two-phase uranium-oxide/uranium-carbide kernel of 19.74% ^{235}U enrichment, a porous carbon buffer layer, and consecutive layers of pyrolytic carbon, silicon carbide (SiC) and pyrolytic carbon. The SiC layer provides the main barrier to fission product release. Much work has gone towards studying metallic fission product interaction in the SiC containment layer due to the propensity of metallic fission product release as a function of high temperature (safety) testing. Here, I will show how the interaction dynamics of plutonium and uranium within this layer have been determined through EXAFS measurements that have been fit with AI. One of the major benefits of using this technology is that actinide containing materials often have edges from higher Z-elements that limit the usable range of the spectrum. Our method fits momentum space data which does not suffer from transformation artifacts of real space over a small momentum range.

Author Index

Bold page numbers indicate presenter