

Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic

Room B116 - Session LX+AS+BI+HC+SS+TH-MoA

Laboratory-Based AP-XPS:Surface Chemistry and Biological/Pharmaceutical Interfaces

Moderators: **Gregory Herman**, Argonne National Laboratory, **Ashley Head**, Brookhaven National Laboratory

1:40pm **LX+AS+BI+HC+SS+TH-MoA-1 The Role of Co-Adsorbed Water in Decomposition of Oxygenates**, *H. Nguyen, K. Chuckwu, Líney Árnadóttir*, Oregon State University **INVITED**

The decomposition of oxygenates in the presence of water finds various applications in chemical processes, such as biomass conversion. The presence of co-adsorbates and solvents affects both the reaction rate and selectivity. In this study, we used NAP-XPS and DFT to investigate the decomposition of acetic acid on Pd(111) as a model system for the decomposition of small oxygenates in the absence and presence of water. The decomposition of acetic acid occurs through two main reaction pathways, decarboxylation, and decarbonylation, forming CO₂ or CO, respectively. Our DFT calculations indicate that the two pathways have similar barriers without water. However, in the presence of water, the decarboxylation path becomes. Similarly, our AP-XPS experiments show an increase in the CO₂/CO ratio as well as a decrease in the CO/acetate-acetic acid and acetic acid/acetate ratios when water is present. The shift in selectivity is not due to a single reaction step, but rather the decreasing barrier in general for OH scissoring and the increasing barrier for C-O scissoring. This shift favors the formation of CO₂, as demonstrated by our microkinetic model.

2:20pm **LX+AS+BI+HC+SS+TH-MoA-3 Integrating First-principles Modeling and AP-XPS for Understanding Evolving Complex Surface Oxides in Materials for Hydrogen Production and Storage**, *B. Wood, Tuan Anh Pham*, Lawrence Livermore Laboratory **INVITED**

Chemical processes occurring at solid-gas, solid-liquid, and solid-solid interfaces critically determine the performance and durability of hydrogen production and storage technologies. While directly probing behavior of these interfaces under actual operating conditions remains challenging, modern surface science approaches such as ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) can provide insight into the evolution of surface chemistry in approximate environments. However, interpretation of these spectra can be complicated: standards for complex surface chemical moieties are often unavailable, and bulk standards can be unreliable. First-principles computations are emerging as an important companion approach, offering the ability to directly compute spectroscopic fingerprints. This has the advantage of aiding interpretation of the experiments, while simultaneously using the experiment-theory comparison to inform construction of more accurate interface models. In this talk, I will show how computation has been combined with laboratory-based AP-XPS measurements to understand the evolving chemistry of complex native surface oxides. Two examples will be drawn from activities within the U.S. Department of Energy HydroGEN and HyMARC consortia, which focus on renewable hydrogen production and materials-based hydrogen storage, respectively. First, I will discuss the application to surface oxidation of III-V semiconductors for photoelectrochemical hydrogen production, which demonstrates transitions between kinetically and thermodynamically controlled oxidation regimes with implications for device performance. Second, I will also show how the same approach has been applied to understand the rate-determining role of surface oxides in the dehydrogenation performance of NaAlH₄ for solid-state hydrogen storage.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

3:00pm **LX+AS+BI+HC+SS+TH-MoA-5 Particle Encapsulation on Reducible Oxides Under Near-Ambient Pressures**, *F. Kraushofer, M. Krinninger, P. Petzoldt, M. Eder, S. Kaiser, J. Planksky, T. Kratky, S. Günther, M. Tschurl, U. Heiz, F. Esch, Barbara A. J. Lechner*, TUM, Germany **INVITED**

Catalysts on reducible oxide supports often change their activity significantly at elevated temperatures due to the strong metal-support interaction (SMSI), which induces the formation of an encapsulation layer around the noble metal particles. However, the impact of oxidizing and

reducing treatments at elevated pressures on this encapsulation layer remains controversial, partly due to the 'pressure gap' between surface science studies and applied catalysis.

In the present work, we employ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and scanning tunneling microscopy (NAP-STM) to study the effect of reducing and oxidizing atmospheres on the SMSI-state of well-defined oxide-supported Pt catalysts at pressures from UHV up to 1 mbar. On a TiO₂(110) support, we can either selectively oxidize the support or both the support and the Pt particles by tuning the O₂ pressure.^[1] We find that the growth of the encapsulating oxide overlayer is inhibited when Pt is in an oxidic state. Our experiments show that the Pt particles remain embedded in the support once encapsulation has occurred. On Fe₃O₄(001), the encapsulation stabilizes small Pt clusters against sintering.^[2] Moreover, the cluster size and thus footprint lead to a change in diffusivity and can therefore be used to tune the sintering mechanism. Very small clusters of up to 10 atoms even still diffuse intact after encapsulation.

[1] P. Petzoldt, P., M. Eder, S. Mackewicz, M. Blum, T. Kratky, S. Günther, M. Tschurl, U. Heiz, B.A.J. Lechner, Tuning Strong Metal-Support Interaction Kinetics on Pt-Loaded TiO₂ (110) by Choosing the Pressure: A Combined Ultrahigh Vacuum/Near-Ambient Pressure XPS Study, *J. Phys. Chem. C* 126, 16127-16139 (2022).

[2] S. Kaiser, J. Planksky, M. Krinninger, A. Shavorskiy, S. Zhu, U. Heiz, F. Esch, B.A.J. Lechner, Does Cluster Encapsulation Inhibit Sintering? Stabilization of Size-Selected Pt Clusters on Fe₃O₄(001) by SMSI, *ACS Catalysis* 13, 6203-6213 (2023).

4:00pm **LX+AS+BI+HC+SS+TH-MoA-8 Applications of NAP XPS in Pharmaceutical Manufacturing: Surface Analysis, Hydrogen Bonds, and Solute-Solvent Interactions**, *Sven Schroeder*, University of Leeds, UK **INVITED**

The availability of laboratory-based NAP XPS creates novel interface research opportunities for scientific disciplines and technology areas that deal with materials incompatible with traditional ultra-high vacuum XPS. This is, for example, the case for many organic and/or pharmaceutical materials and formulations, whose characterization by XPS has hitherto been restricted by their vapour pressures. NAP XPS permits for the first time systematic and detailed analysis of the light element photoemission lines (especially C/N/O 1s) in these materials. In conjunction with elemental analysis by survey XP spectra they provide quantitative information on composition and speciation both in the bulk and at the surfaces of pure organic solids, in their formulations with other components and in solutions. Especially of interest are studies of the solid/liquid interface with water, which is of high relevance for understanding and controlling drug release profiles from tablets. To illustrate these points I will present various examples of research on pharmaceutical materials. Moreover, near-ambient pressure core level spectroscopy turns out to be an extremely powerful probe for the structure and dynamics of hydrogen bonding and proton transfer in materials, both in the solid state and in solutions. NAP XPS measurements provide unique insight into proton dynamics in noncrystalline solids and liquids, where traditional characterisation by crystallography and nuclear magnetic resonance fails or provides ambiguous information on proton locations.

4:40pm **LX+AS+BI+HC+SS+TH-MoA-10 The Change of DNA and Protein Radiation Damage Upon Hydration: In-Situ Observations by Near-Ambient-Pressure XPS**, *Marc Benjamin Hahn*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

X-ray photoelectron-spectroscopy (XPS) allows simultaneous irradiation and damage monitoring. Although water radiolysis is essential for radiation damage, all previous XPS studies were performed in vacuum. [1] Here we present near-ambient-pressure XPS experiments to directly measure DNA damage under water atmosphere. They permit in-situ monitoring of the effects of radicals on fully hydrated double-stranded DNA. Our results allow us to distinguish direct damage, by photons and secondary low-energy electrons (LEE), from damage by hydroxyl radicals or hydration induced modifications of damage pathways. The exposure of dry DNA to x-rays leads to strand-breaks at the sugar-phosphate backbone, while deoxyribose and nucleobases are less affected. In contrast, a strong increase of DNA damage is observed in water, where OH-radicals are produced. In consequence, base damage and base release become predominant, even though the number of strand-breaks increases further. Furthermore, first data about the degradation of single-stranded DNA binding-proteins (GSP / GV5 and hmtSSB) under vacuum and NAP-XPS conditions are presented.

Monday Afternoon, November 6, 2023

[1] Hahn, M.B., Dietrich, P.M. & Radnik, J. In situ monitoring of the influence of water on DNA radiation damage by near-ambient pressure X-ray photoelectron spectroscopy. *Commun Chem* 4, 50, 1-8 (2021). <https://doi.org/10.1038/s42004-021-00487-1>

Actinides and Rare Earths Focus Topic

Room C124 - Session AC+MI+TH-TuM

Magnetism, Electron Correlation, and Superconductivity in the Actinides/Rare Earths

Moderators: Edgar Buck, PNNL, Tomasz Durakiewicz, Idaho National Laboratory, Krzysztof Gofryk, Idaho National Laboratory

8:00am **AC+MI+TH-TuM-1 Uranium and Cerium Based Systems Probed with High-Pressure XANES and XMCD**, *Fabrice Wilhelm*, A. Roagelv, ESRF, France

INVITED

This talk reviews recent advances in use of polarized x-rays to study local magnetic properties and electronic structure of uranium and cerium based compounds such as the ferromagnetic UGe_2 , the heavy-fermion paramagnet UTe_2 and the nanolamellar ferromagnetic Kondo lattice $Mo_4Ce_4Al_7C_3$ system.

8:40am **AC+MI+TH-TuM-3 Searching for New Uranium-Based Arsenides**, *Eteri Svanidze*, Max Planck Institute for Chemical Physics of Solids, Germany
As new classes of superconducting materials emerge, puzzles of high-temperature superconductivity continue to be one of the pressing issues in condensed matter physics and solid-state chemistry. In particular, iron pnictide superconductors still pose many open questions. Surprisingly, very few actinide-based analogues of iron pnictide high temperature superconductors have been reported so far, perhaps as a result of synthesis complications imposed by toxicity, reactivity, and high vapor pressure of constituent elements. In this work, we revisit the U-Fe-As ternary, in which only one compounds has been reported to exist so far – $UFeAs_2$ ($P4/nmm$ space group) [1]. By implementing flux synthesis, we were able to grow large single crystals of UFe_5As_3 compound, which adopts UCr_5P_3 structure type [2] ($P2_1/m$, $mP18$) with lattice parameters $a = 7.0501(17)$ Å, $b = 3.8582(9)$ Å and $c = 9.6342(13)$ Å, $\beta = 100.2(8)^\circ$ [3]. The refined composition agrees well with the elemental ratio established by the EDX analysis – $U_{9.9(2)}Fe_{58.7(2)}As_{31.4(2)}$. The magnetic behavior of UFe_5As_3 was studied by magnetic susceptibility measurements in the temperature range 1.8 - 600 K and an antiferromagnetic ordering below $T_N = 56$ K was established. The Sommerfeld coefficient $\gamma = 138$ mJ/mol K^2 indicates enhanced effective electron mass. More in-depth investigations of this and other U-Fe-As ternary compounds are currently underway.

References:

- [1] D. Kaczorowski, J. Alloys. Compd. 186, 333-338 (1992).
- [2] W. Jeitschko, R. Brink, P.G. Pollmeier, Z. Naturforsch. (1993) 48b, p. 52-57.
- [3] N.Zaremba, M. Krnel, Yu. Prots, A. Leithe-Jasper, Yu. Grin, E. Svanidze, in preparation (2023)

9:00am **AC+MI+TH-TuM-4 5f Magnetism at an Extreme**, *Ladislav Havela*, Charles University, Faculty of Mathematics and Physics, Czechia; *V. Buturlim*, Idaho National Laboratory; *F. Honda*, Tohoku University, Japan; *D. Kaczorowski*, Institute of Low Temperature and Structure Research, Wrocław, Poland

Specific features of 5f magnetism in U-based systems, namely the strong spin-orbit coupling and very strong magnetic anisotropy or giant magnetoresistance, are degraded by low temperatures of magnetic ordering. The variability of T_C or T_N in intermetallics has been explored and it turns out that involvement of magnetic d -metals such as Fe or Co does not help, unless very high fraction of the transition metals turns a compound in fact a regular d -magnet, in which the unique 5f features are suppressed. The reason is the 5f- d hybridization with a destabilizing action on both d and 5f moments.

Seeking additional degrees of freedom we turned towards compounds with more polar character of bonding, which drives U to the verge of metallicity. Interesting alternative to intermetallics is provided by Zintl phases, typically ternary compounds with one cation (e.g. an f -metal) and a complex covalently bond anion, stabilized by a charge transfer from the cation. An excellent insight is provided by such compounds with layered crystal structures, which leads to strongly anisotropic electronic properties. Our research focuses on Zintl phases with the trigonal $CaAl_2Si_2$ type ($P-3m$), formed by alternating cationic (Ca) and anionic (Al-Si) layers. Those without f -metals or with 4f metals tend to be narrow-gap semiconductors. U-based phases such as UCu_2P_2 are semi-metallic. The prominence of this compound dwells in ferromagnetism with high Curie temperature $T_C = 216$ K, which is

further enhanced by pressure application to the vicinity of room temperature. Ab-initio calculations reveal it this material is actually a half-metal, with spin-split 5f band bringing spin-up only states to the Fermi level. The conduction electron states remain hybridized with the 5f states, which causes also the non-f electrons to be fully spin polarized. The magnetisms is of local moment type, with magnetic entropy exceeding $R \ln 2$, but arising from 5f bands. UCu_2P_2 can be compared with $EuZn_2P_2$. Here the Eu^{2+} moments are organized in an AF structure. The field alignment of the moments impacts the width of the gap seen in transport data, but the material remains semiconducting.

This work was supported by the Grant Agency of the Czech Republic under the grant No. 21-09766S.

9:20am **AC+MI+TH-TuM-5 Valence-to-Core RIXS in Insulating Compounds with 4f and 5f Elements**, *Jindrich Kolorenc*, Institute of Physics, Czech Academy of Sciences, Czechia

In the first part, we investigate the electronic structure of europium sulfide (EuS) with the aim to understand the valence-to-core resonant inelastic x-ray scattering (RIXS) spectra measured at the Eu L_3 edge. We show that the main part of the observed signal comes from the direct RIXS: an Eu 2p core electron is excited to an empty Eu 5d band above the Fermi level, and then another electron from an Eu 5d state hybridized with the S 3p bands (located below the Fermi level and hence occupied) fills back the core hole. Besides this straightforward channel, the measured RIXS spectra display two satellite features. After considering several candidates (such as excitations of the 4f shell excited by indirect RIXS processes, that is, by the interaction with the core hole in the intermediate state), we arrive at the conclusion that the satellites are excitons formed by a 4f hole and an 5d electron localized at the same Eu atom. Such excitons were suggested in the context of optical absorption a long time ago [1], but the concept is not widely accepted. It was argued that existence of these excitons is incompatible with photoconductivity measurements [2]. Our observations indicate that these arguments may need to be revisited.

In the second part, we simulate valence-to-core RIXS at the actinide M_5 edge in selected actinide oxides starting from the dynamical mean-field electronic structure obtained earlier [3] and using techniques similar to [4]. This investigation is motivated by the recent experimental study of UO_2 and UF_4 [5]. Our preliminary results suggest that the feature observed at an energy loss of roughly 10 eV above the white line is likely a charge-transfer excitation, the intensity of which is sensitive to the hybridization between the actinide 5f states and the ligand 2p states.

This work was supported by the Czech Science Foundation under the grant No. 21-09766S.

- [1] T. Kasuya and A. Yanase, Rev. Mod. Phys. 40 (1968) 684, <https://doi.org/10.1103/RevModPhys.40.684>
- [2] P. Wachter and B. Bucher, Physica B 408 (2013) 51, <https://doi.org/10.1016/j.physb.2012.09.018>
- [3] J. Kolorenc, A. Shick, A. I. Lichtenstein, Phys. Rev. B 92 (2015) 085125, <https://doi.org/10.1103/PhysRevB.92.085125>
- [4] J. Kolorenc, Physica B: Condensed Matter 536 (2018) 695, <https://doi.org/10.1016/j.physb.2017.08.069>
- [5] J. G. Tobin et al., J. Phys.: Condens. Matter 34 (2022) 505601, <https://doi.org/10.1088/1361-648X/ac9bbd>

9:40am **AC+MI+TH-TuM-6 Magnetism of Binary Actinide Oxides**, *Binod Rai*, A. Bretaña, Savannah River National Laboratory; *G. Morrison*, University of South Carolina, Columbia; *R. Greer*, Savannah River National Laboratory; *K. Gofryk*, Idaho National Laboratory; *H. zur Loye*, University of South Carolina, Columbia

Historically, the bulk of actinide oxide research has focused on the properties of various uranium and plutonium compounds as they impact their use in the nuclear fuel industry. While the fundamental understanding of compounds such as UO_2 has improved, a fundamental grasp of the physical properties of other actinide oxides remains elusive. In actinide systems, the 5f electrons experience a uniquely delicate balance of effects and interactions having similar energy scales, which are often difficult to properly disentangle. The interplay of factors such as the dual character of 5f-states, competing interactions, and strong spin-orbit coupling results in magnetically unusual and intriguing behavior: multi-k antiferromagnetic ordering, multipolar ordering, mixed valence configurations, and more. In this presentation, I will provide an overview of the available synthesis techniques for selected binary actinide oxides. I will also show the current state of knowledge on their crystal structures and magnetic properties.

Moreover, I will talk about the future opportunities that are vital for a fundamental understanding of these systems.

11:00am **AC+MI+TH-TuM-10 N-Point Saddle-Band Model for the Hidden Order Phase of URu₂Si₂**, *J. D. Denlinger*, Lawrence Berkeley National Laboratory; *J. Kang*, The Catholic University of Korea; *L. Dudy*, SOLEIL, France; *J. Allen*, University of Michigan; *L. Wray*, New York University; *A. Gallagher*, *R. Baumbach*, National High Magnetic Field Laboratory; *N. Butch*, University of Maryland; *M. Maple*, University of California, San Diego

The 5f heavy fermion system of URu₂Si₂ is famous for an unconventional hidden order (HO) phase transition at T₀=17.5K and the various related doping phase diagrams explored to elucidate the nature of this unknown transition. A new model of an extended U 5f saddle-point dispersion at the N-point is proposed for the underlying physics of this 35-year old puzzle. With a 10X DFT energy renormalization suggested by angle resolved photoemission (ARPES) measurements in comparison to DMFT calculations [1], this feature lies only a few meV below E_F and thus is thermally active at T₀. ARPES reveals a distinct temperature-dependent evolution of incommensurate 5f nesting hotspots lying along Z-N-Z [1], whose origins are found in electronic susceptibility calculations of intraband q-scattering for thermal occupations in the temperature range of T₀. Tuning of the N-point region f-band energetics with chemical doping is thus naturally proposed to unify our understanding of the various phase diagrams. ARPES is presented which confirms the existence of N-point spectral and dichroic changes for ferromagnetic Re/Ru-substitution, for (001) antiferromagnetic Fe and Os/Ru-substitution, and for (1/2,1/2,1/2) antiferromagnetic P/Si-substitution, thus further demonstrating experimentally the key relevance of the N-point electronic structure to the HO phase. [1] J. D. Denlinger et al., *Electron. Struct.* 4, 013001 (2022).

11:20am **AC+MI+TH-TuM-11 Magnetoelastic Properties of 5f Ferromagnet UCu₂P₂**, *Volodymyr Buturlim*, Idaho National Laboratory; *P. Doležal*, *O. Koloskova*, *J. Prchal*, Charles University, Czechia; *I. Turek*, Charles university, Czechia; *M. Martinez Celis*, CRISMAT Laboratory, France; *F. Honda*, Kyushu University, Japan; *M. Divis*, Charles University, Czechia; *D. Kaczorowski*, Polish Academy of Sciences, Poland; *K. Gofryk*, Idaho National Laboratory; *L. Havela*, Charles University, Czechia

UCu₂P₂, a Zintl phase with the trigonal CaAl₂Si₂ structure type, is a 5f ferromagnet with a record-high Curie temperature among U compounds, T_c = 216 K [1]. While the size of the magnetic moment 2.0 μ_B/U is not surprising due to U-U spacing exceeding the Hill limit, the reasons for the high T_c are less understood. Ab-initio calculations reveal only very weak hybridization of the U-5f states with the 6d states as well as with electronic states of Cu and P. It seems that a transfer of U-6d states to the P-3p states is an important ingredient, which was highlighted by a rapid increase of T_c under hydrostatic pressure so that a room-temperature 5f ferromagnetism could be demonstrated. Besides magnetization, transport, and heat capacity studies on single crystals we performed also characterization of a polycrystalline material, which has T_c = 219 K. Thermal expansion study revealed a moderate increase of both lattice parameters just below T_c, so we can exclude that the pressure enhancement of T_c is driven simply by thermodynamics (via the Ehrenfest relation). Hence the reasons have to be attributed to the enhancement of specific U-U couplings upon compression. Indeed, ab initio calculations probing the energy enhancement upon moments reversal gave a semi-quantitative account of the observed tendency of T_c.

[1] D. Kaczorowski, R. Troc, Magnetic and transport properties of a strongly anisotropic ferromagnet UCu₂P₂, *J. Phys. Condens. Matter*, 1990, 2, 4185.

*This work was supported by the Czech Science Foundation under the grant No. 21-09766S.

11:40am **AC+MI+TH-TuM-12 Density Functional Theory Calculations of the Phonons in Gamma and Delta Phase Pu**, *Sven P. Rudin*, Los Alamos National Laboratory

The thermodynamics of plutonium challenges both theory and experiment. The challenge arises from the multiple structural phase transitions, the nature of the 5f electrons, and the effects due to the material's self-irradiation. Density functional theory calculations have made steady progress toward clarifying experimental measurements. Recently, for the delta phase a non-collinear 3Q spin structure was shown to make all structurally equivalent bonds equivalent in their bonding character. This results in elastic constants and phonons with the correct symmetry, and the calculated phonon dispersion agrees well with experiment. Extending the calculations into the gamma phase of Pu now provides a prediction for the

phonons of that phase.

12:00pm **AC+MI+TH-TuM-13 The 5f UDOS of the Actinide Dioxides: Why Pu is n = 5 in PuO₂**, *James Tobin*, University of Wisconsin-Oshkosh; *H. Ramanantoanina*, KIT, Germany; *C. Daul*, U. Fribourg, Switzerland; *S. Yu*, LLNL; *P. Roussel*, AWE, UK; *S. Nowak*, *R. Alonso-Mori*, *T. Kroll*, *D. Nordlund*, *T. Weng*, *D. Sokaras*, SSRL

The Unoccupied Density of States (UDOS) of ThO₂, UO₂ and PuO₂ have been investigated with a combined experimental and theoretical approach.^{1,2}Ligand field density functional theory calculations of the dioxides of thorium, uranium, and plutonium have been combined with high-energy-resolution fluorescence detection (HERFD) in x-ray absorption spectroscopy and inverse photoelectron spectroscopy (IPES) measurements to provide powerful insight into the underlying composition of the unoccupied 5f electronic structure in these 5f localized systems. Fine structure in the 5f_{5/2} transitions in HERFD can be directly correlated with the fine structure in the leading edge of the IPES. The shapes, intensities, and systematics in HERFD and IPES are explained in a consistent and rigorous fashion in terms of the j-specific 5f electronic structure. Additionally, an actinide N_{4,5} branching ratio analysis of PuO₂ and UO₂ has been performed, including measurements with a scanning transmission electron microscope at the Advanced Light Source and simulation with FEFF. It is shown that the 5f occupation of the Pu in plutonium dioxide is n = 5.

References

1. J. G. Tobin, H. Ramanantoanina, C. Daul, S.-W. Yu, P. Roussel, S. Nowak, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, D. Sokaras, "The Unoccupied Electronic Structure of Actinide Dioxides," *Phys. Rev. B* 2022, **105**, 125129. <https://doi.org/10.1103/PhysRevB.105.125129>
2. J. G. Tobin and S.-W. Yu, "Pu 5f Occupation in Plutonium Dioxide," *Inorg. Chem.* 2023, **62**, 6, 2592–2598, <https://doi.org/10.1021/acs.inorgchem.2c03202>

Theory for Surface Processes and Spectroscopies Focus Topic

Room B116 - Session TH1+AS+SS-TuM

Introduction and Core-Level Spectroscopies I

Moderators: *Gianfranco Pacchioni*, Università 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 discuss 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 CeO₂(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

Tuesday Morning, November 7, 2023

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 origin 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).

(1) Vitova, T.; Pidchenko, I.; Fellhauer, D.; Bagus, P. S.; Joly, Y.; Prüßmann, T.; Bahl, S.; Gonzalez-Robles, E.; Rothe, J.; Altmaier, M.; Denecke, M. A.; Geckeis, H. *Nat. Commun.* **2017**, *8* (May), 1–9.

(2) Vitova, T.; Pidchenko, I.; Fellhauer, D.; Prüßmann, T.; Bahl, S.; Dardenne, K.; Yokosawa, T.; Schimmelpennig, B.; Altmaier, M.; Denecke, M.; Rothe, J.; Geckeis, H. *Chem. Commun.* **2018**, *54* (91), 12824–12827.

(3) Polly, R.; Schacherl, B.; Rothe, J.; Vitova, T. *Inorg. Chem.* **2021**, *60* (24), 18764–18776.

(4) Bagus, P. S.; Schacherl, B.; Vitova, T. *Inorg. Chem.* **2021**, *60* (21), 16090–16102.

(5) Schacherl, B.; Trumm, M.; Beck, A.; Vitova, T. **2024**, *submitted*.

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(7) Schacherl, B.; Tagliavini, M.; Popa, K.; Beck, A.; Walter, O.; Pruessmann, T.; Vollmer, C.; Kaufmann, H.; Mazzanti, M.; Haverkort, M.; Vitova, T. **2023**, *submitted*.

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(H₂O)₉]³⁺, [La(TRIS)(H₂O)₆]³⁺, [La(TRIS)₂(H₂O)₃]³⁺ (buffer media), [La(DOTA)(H₂O)]²⁺, [La(MACROPA)]¹⁺ and [La(PSMA-617)(H₂O)] have been prepared and characterized. We measured La L₂-edge HR-XANES spectra at the Synchrotron Laboratory for Environmental Studies (SUL-X) beamline and La L₃-edge extended X-ray absorption fine structure spectroscopy (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.

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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 UO₂²⁺ 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, UO₂²⁺. 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.

[1] C. J. Nelin et al., *Angew. Chem. Int. Ed.*, 2011, **50**, 10174-10177.

[2] P. S. Bagus and C. J. Nelin, "Computation of Vibrational Excitations in XPS Spectroscopy", in *Rare Earth Elements and Actinides: Progress in Computational Science Applications*, edited by D. A. Penchoff, et al. (American Chemical Society, 2021), Vol. 1388, p. 181.

[3] T. Vitova et al., *Nat. Commun.*, 2017, **8**, 16053.

[4] R. Polly et al., *Inorg. Chem.*, 2021, **60**, 18764-18776.

[5] P. S. Bagus et al., *Inorg. Chem.*, 2021, **60**, 16090.

Theory for Surface Processes and Spectroscopies Focus

Topic

Room B116 - Session TH2+AS+SS-TuM

Core-Level Spectroscopies II

Moderators: Ria Broer, University of Groningen, Bianca Schacherl, Karlsruhe Institute of Technology

11:00am **TH2+AS+SS-TuM-10 Cumulant Green's Function Approaches for Satellites and Multiplets in X-Ray Spectra**, *John J. Rehr*, Dept of Physics, University of Washington; *J. Kas*, Department of Physics, University of Washington

INVITED

The treatment of electronic correlations in open-shell systems is one of the most challenging problems in atomic, molecular, and condensed matter physics. Their importance is particularly evident in x-ray spectra, where the single particle theory breaks down and many-body effects such as satellites and atomic multiplet effects are observed. Conventional approximations are only partly successful. Ligand-field multiplet theory and dynamical mean field theory can describe intra-atomic correlation effects well but typically ignore long range correlation effects. The real-time cumulant Green's function method can describe shake-up effects well [1] but ignores multiplets. We have found, however, that separating the dynamic Coulomb interactions into local and longer-range parts with *ab initio* parameters yields a combined multiplet-plus-cumulant approach that can account for both local atomic multiplets and satellite excitations [2]. The approach is illustrated for transition metal oxides and explains the multiplet peaks, charge-transfer satellites, and distributed background features observed in XPS experiment. In an alternative approach for molecular systems, we have found that a real-time equation of motion coupled-cluster (RT-EOM-CC) cumulant approach can also describe both correlation effects at the CCSD level and intrinsic losses in x-ray spectra, including orthogonality corrections that enhance XAS at the edge [3]. Comparisons with other approaches [4] are also discussed.

[1] Strengths of plasmon satellites in XPS: Real-time cumulant approach: J. J. Rehr and J. J. Kas, *J. Vac. Sci. Technol. A* **39**, 060401 (2021).

[2] Ab Initio Multiplet-Plus-Cumulant Approach for Correlation Effects in X-Ray Photoelectron Spectroscopy, J. J. Kas, J. J. Rehr, and T. P. Devereaux, *Phys. Rev. Lett.* **128**, 216401 (2022).

[3] Equation of motion coupled-cluster cumulant approach for intrinsic losses in x-ray spectra, J. Chem. Phys. J.J. Rehr, F.D. Vila, J.J. Kas, N.Y. Hirshberg, K. Kowalski, and B. Peng **152**, 174113 (2020).

[4] Analysis of the Fe 2p XPS for hematite Fe₂O₃: Consequences of covalent bonding and orbital splittings on multiplet splittings, P.S. Bagus, C. J. Nelin, C. R. Brundle, N. Lahiri, E. S. Ilton, and K. M. Rosso, *J. Chem. Phys.* **152**, 014704 (2020).

11:40am **TH2+AS+SS-TuM-12 Understanding Multiplets in the XPS of Transition Metal Oxides: Experiment and Theory and the Effects on Quantitation Procedures**, *Christopher Richard Brundle*, C. R. Brundle and Associates; *B. Christ*, XPS library; *P. Bagus*, Center for Advanced Scientific Computing and Modeling (CASCAM) Department of Chemistry University of North Texas

INVITED

Atoms with open valence shells suffer splitting to their XPS core-levels owing to the different spin-spin coupling possibility between the remaining unpaired core electron and the electrons in the open shell (1). This results in a spectrum with two components of unequal intensity, separated by an eV or two. Gupta and Sen (2) expanded the multiplet splitting theory to include spin-orbit coupling (angular momentum coupling), providing highly cited predictions for the 2p spectra of TM cations (eg Ni²⁺). Bagus, et al (3), and others, using rigorous *ab initio* MO calculations on clusters, have expanded theory further to allow XPS predictions for solid TM compounds (eg Ni²⁺ in NiO, Fe³⁺ in Fe₂O₃) which include both ligand field and bonding effects. Finally, they included shake-up effects (excitation of valence electrons in addition to core level ionization), which can substantially alter the distribution of intensities across the complete core-level spectrum, for example Ni 2p for NiO (4). This progression in the understanding of the origin of the features of TM core-level spectra is discussed, as is also the effects on requirements for providing quantitation of TM compounds using core level intensity ratios or peak fitting. Comparison is then made to alternative theory approaches to modeling the spectra, such as the freely available semi-empirical charge transfer method, CTM4XAS, (5), and the many-body cumulative theory of Rehr and Kass (6). We examine how these agree/differ in the interpretation/understanding of the XPS features, usefulness in ascribing chemical states, and quantitation aspects.

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2. R. P. Gupta and S. K. Sen, *Phys. Rev. B*, 1974, **10**, 71-77; P. Gupta and S. K. Sen, *Phys. Rev. B*, 1975, **12**, 15-19.
3. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, N. Lahiri, and K. M. Rosso, *Phys. Chem. Chem. Phys.*, 2022, **24**, 4562-4575.
4. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, E. S. Ilton, N. Lahiri, and K. M. Rosso, *Inorganic Chemistry*, 2022, **61**, 18077
5. F. De Groot and A. Kotani, *Core level spectroscopy of solids*. CRC Press, Boca Raton, 2008.
6. J. J. Kas, J. J. Rehr and T. P. Devereaux, *Phys. Rev. Lett.* 2022, **128**, 216401

Actinides and Rare Earths Focus Topic

Room C124 - Session AC+MI+TH-TuA

Chemistry and Physics of the Actinides/Rare Earths

Moderators: Ladislav Havela, Charles University, Czech Republic, Eteri Svanidze, Max Planck Institute for Chemical Physics of Solids, Gertrud Zwicknagl, Technical University Braunschweig

2:20pm **AC+MI+TH-TuA-1 Electronic Structure Methods for f-Block Elements: Are We There Yet?**, X. Li, Chad Hoyer, University of Washington
INVITED

The computational modeling of rare-earth and heavy-element complexes requires an accurate treatment of spin-orbit and electron correlation effects to fully understand the physical underpinnings of their chemical properties. The fully correlated frequency-independent Dirac-Coulomb-Breit Hamiltonian in a multireference framework provides the most accurate description of electron-electron interaction before going to a genuine relativistic quantum electrodynamics theory of many-electron systems. Our recent studies using many-body multireference methods suggest that there is a significant correlation effect of inner-valence electrons in rare-earth and heavy-element complexes. Ignoring this effect could lead to inaccurate descriptions of molecular properties, such as covalency, bonding, and spectroscopic response. In this talk, we will examine how the correlation effect of inner-valence electrons is manifested in molecular properties with a focus on the covalency in rare-earth and heavy-element complexes.

3:00pm **AC+MI+TH-TuA-3 Structures and Electronic States of Actinide and Lanthanide Complexes with Phenanthroline Derivatives**, Tsuyoshi Yaita, Japan Atomic Energy Agency, Japan
INVITED

Actinides and lanthanides are f-electron elements, and thus their chemical behavior is very similar if they have the same valence. Recently, the demand for lanthanides, especially specific lanthanides such as Nd, Tb, and Dy, is increasing with the realization of a carbon-neutral society and the shift to EVs for vehicle, and there is a growing need to find new resources and recycle them from urban mines. On the other hand, in the case of geological disposal of radioactive waste generated from nuclear power generation, separation of minor actinides such as Am, which are long-lived α -nuclides, is very important from the viewpoint of recycling in a geological repository in a small country like Japan, and the establishment of separation and transmutation technology is desired. This means that the need for separation of specific f elements from solutions such as high-level liquid waste containing a wide variety of lanthanides and actinides will, needless to say, increase more and more.

Here, we have been new synthesized phenanthroline amide derivatives (phenanthroline amide: PTA) with N and O as donor elements for these purposes. These ligands achieve separation of a special f-element by recognize slight size differences or utilize differences in their interactions with the donor elements.

In this talk, the chemical bonding properties of phenanthroline ligands to actinides and lanthanides by XAS/XES and RIXS using soft X-rays, the structural properties of tridentate and tetradentate PTA derivatives by single crystal structural analysis and EXAFS, respectively, will be presented. Taken together, the mechanisms governing ion recognition of PTA derivatives will be reported.

4:20pm **AC+MI+TH-TuA-7 Unraveling the Unique Properties of f-Element Terpyridyl Complexes**, Alyssa Gaiser, Michigan State University; C. Celis-Barras, Colorado School of Mines; F. White, Oak Ridge National Laboratory; T. Albrecht-Schoenert, Colorado School of Mines
INVITED

A terpyridine derivative was synthesized with the lanthanides and several trivalent actinides targeted at probing differences between americium and curium. In addition to investigating high quality structural data on both the americium and curium concluding in a slight increase in covalent character in the americium system, the cerium and berkelium analogs proved to be even more interesting, exhibiting enhanced covalent character in the system. This terpyridyl system continues to provide novel behavior throughout the f-elements exemplifying the inverse trans influence throughout the series with the interaction between the terpyridyl and the nitrate molecule in the same plane.

5:00pm **AC+MI+TH-TuA-9 Electronic Properties of Plutonium Oxycarbide**, Paul Roussel, AWE plc, UK

Plutonium is both electropositive and highly reactive, such that an oxide film of varying thickness is always present on metal samples. It is of interest from a safety point of view (reduced handling/processing) to investigate methods that either prevent or slow down the rate of the corrosion reaction of the metal. This can be achieved by alloying with a suitable quantity of gallium [1] or via the formation of a surface film of plutonium oxycarbide, PuO_xC_y (where $x+y \leq 1$) [2]. Plutonium oxycarbide films have the NaCl structure and were initially called plutonium monoxide, PuO . Plutonium oxycarbide films are formed from the bulk to surface diffusion of the ubiquitous carbon impurity in the metal [3]. However, to date, there is little understanding of the electronic properties of plutonium oxycarbide films. The aim of this work is to investigate the electronic structure of plutonium oxycarbide surface films using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). XPS measurements have been acquired at elevated temperature following the Pu 4f, O 1s and C 1s / Pu 5p_{1/2} spectral regions on both alloyed and pure plutonium samples following sputter cleaning and oxidation at room temperature. UPS and IPES were acquired at room temperature following the formation of the surface plutonium oxycarbide film. All three spectroscopic measurements display a two peak structure consistent with a partially localized and itinerant 5f electronic structure for plutonium oxycarbide. Finally, the Auger parameter (Pu N₇O₅V - Pu 4f_{7/2}) for plutonium oxycarbide films of varying carbon and oxygen stoichiometries are compared to the recently reported values for plutonium metal and the homoleptic plutonium oxides [1].

[1] XPS characterization of a PuGa-7 at. % alloy, P. Roussel, S. C. Hernandez, J. J. Joyce, K. S. Graham, T. Venhaus, J. Vac. Sci. Technol. A 41, 023204 (2023).

[2] Retardation of plutonium oxidation by a PuO surface film, D. T. Larson, D. L. Cash, J. Vac. Sci. Technol. 9, 800 (1972).

[3] Initial studies of plutonium corrosion, P. Roussel, D. S. Shaw, D. A. Geeson, J. Nucl. Sci. Technol. 39:sup3, 78 (2002).

5:20pm **AC+MI+TH-TuA-10 Exploring the Surface and Subsurface Behavior of Hydrogen in δ -Pu(100) and Bulk δ -Pu Through Density Functional Theory**, Charles Fricke, S. Hernandez, Los Alamos National Laboratory

The corrosion of plutonium to form its hydride creates significant challenges in handling, researching, and storing of the metal. Plutonium hydrides rapidly, much faster than most metals, and the kinetics are less well understood. Significant questions remain, including the energetics of hydrogen formation in different lattice sites, such as the tetrahedral, octahedral, and vacancy sites, as well as its reactive behavior on and in the surface of metallic plutonium. As such, this work aims to explore how hydrogen behaves within face-centered-cubic δ -plutonium from the surface into the subsurface and into the bulk through density functional theory. We find that hydrogen is energetically favored to remain on the surface, but that the energetics of hydrogen in the first subsurface remains thermodynamically favorable for both the subsurface tetrahedral and octahedral sites when compared to the referenced gas-phase hydrogen molecule. We also find that the octahedral site remains thermodynamically favorable for hydrogen species to fill from the 2nd subsurface to the bulk in δ -Pu(100). In addition, we find we have subsurface to bulk formation energy convergence at the 3rd sublayer of δ -Pu(100). Finally, we will discuss the energetic differences of hydrogen between the surface, subsurface, and bulk within δ -Pu.

5:40pm **AC+MI+TH-TuA-11 Nanoscale Nuclear Materials: Synthesis and Advanced X-Ray Characterization of Uranium Oxide Nanoparticles**, Liane Moreau, Washington State University, US

Nanostructures (particularly with sizes below 10 nm) are inherently challenging to characterize on the atomic scale, due to broadening which occurs in diffraction-based characterization methods, and the high concentration of surface defects and energy-minimization effects. Characterization challenges compound when investigating nanoscale actinide oxides, such as uranium oxide, due to radioactive sample constraints and rich electronic structure which can potentially stabilize a wide range of crystallographic arrangements. To address these challenges, x-ray spectroscopic and scattering based methods are used to probe challenging nanoscale systems in detail over multiple length scales. In particular, synthetic developments are paired with robust characterization, in order to improve knowledge of nanoparticle growth and transformation,

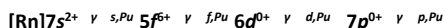
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as well as develop ways to make advanced x-ray characterization analysis more informed and accessible, in tandem.

Nanoscale uranium oxides are of interest towards the development of accident-tolerant nuclear fuels and are also relevant to the migration of actinides in environmental systems. Synthetic methods will be presented, which have enabled preliminary investigation into the size and morphology-dependent properties of uranium oxides. Specifically, the synthesis of UO₂ anisotropic nanoparticles and the deposition of uranium onto iron nanoparticles will be highlighted. These synthetic pursuits have been paired with x-ray spectroscopy and x-ray scattering to create new analysis strategies for decoupling surface vs. interior chemistry of nanoparticles and to interrogate the in-depth structural and electronic properties of uranium oxide as a function of particle size and morphology. The studies presented give a glimpse into the interesting fundamental and behavioral differences between actinide nanomaterials and their counterparts elsewhere on the periodic table.

6:00pm **AC+MI+TH-TuA-12 A Statistical Mechanics Treatment of Multiconfigurational Ground States in Isolated Neutral Atoms, Miles Beaux**, Los Alamos National Laboratory

Janoschek, et al. described the ground state of plutonium (Pu) as being, “governed by valence fluctuations, that is, a quantum mechanical superposition of localized and itinerant electronic configurations.” [*Science Advances*, 1, 6 (2015)]. However, a casual internet search of the electronic structure of Pu gives [Rn]7s²5f⁶ which is wholly insufficient to describe the complex nature of its multiconfigurational ground state as described by Janoschek, et al. A better description might be given by



where $\gamma_{s,\text{Pu}}$, $\gamma_{f,\text{Pu}}$, $\gamma_{d,\text{Pu}}$, $\gamma_{p,\text{Pu}}$ represent potentially non-integer deviations from the integer electron occupancies of their respective orbitals. By judiciously selecting bounding conditions for how the eight valence electrons can distribute themselves within the given orbitals, a limited number of occupancy configurations can be identified with an identifiable number of cumulative allowable electron permutations. For example, the bounding conditions

$$-2 \leq \gamma_{s,\text{Pu}} \leq 0,$$

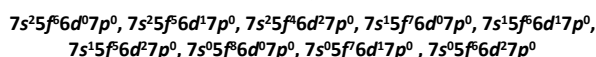
$$-2 \leq \gamma_{f,\text{Pu}} \leq 2,$$

$$0 \leq \gamma_{d,\text{Pu}} \leq 2,$$

$$\gamma_{p,\text{Pu}} = 0, \text{ and}$$

$$\gamma_{s,\text{Pu}} + \gamma_{f,\text{Pu}} + \gamma_{d,\text{Pu}} + \gamma_{p,\text{Pu}} = 0$$

result in nine possible occupancy configurations



with 487,630 cumulative possible electron permutations. With the specific number of permutations identified, principles of statistical mechanics can be applied to multiconfigurational ground states.

Similar generalized representations of ground state electronic structures will be described for each element in the periodic table. Classical Boltzmann's entropies for the respective electronic structures will be calculated by considering the possible electron permutations as statistical mechanics microstates. These entropies will then be compared to known standard molar entropies.

LA-UR-23-24803

Theory for Surface Processes and Spectroscopies Focus Topic

Room B116 - Session TH1-TuA

Electronic Structure Theory

Moderators: Robert Polly, Karlsruhe Institute of Technology, Sefik Suzer, Bilkent University, Turkey

2:20pm **TH1-TuA-1 Non-Orthogonal Configuration Interaction for the Study of Ground and Excited State Properties of Materials, Ria Broer**, University of Groningen, Netherlands; C. de Graaf, Universitat Rovira i Virgili and ICREA, Spain; A. Sanchez-Mansilla, Universitat Rovira i Virgili, Spain; C. Sousa, University of Barcelona, Spain; T. Straatsma, Oak Ridge National Laboratory, USA

INVITED

The properties of materials including their interfaces and surfaces can be studied by a variety of advanced experimental techniques. The technique of

choice depends on the material and on the property of interest. Likewise, a variety of theoretical/computational methods exist for the study of their ground and excited state properties and the method of choice again depends on the specific problem. In many cases progress in the understanding of the properties has leaped forward thanks to productive interaction between experimentalists and theorists. For such understanding the accurate computational reproduction or prediction of data is necessary but not sufficient, we need also interpretation in terms of (preferably simple) physical/chemical concepts.

This presentation introduces the non-orthogonal configuration interaction (NOCI) method, where the wave function of a molecular electronic state is written as an expansion in terms of a small number of many-electron basis functions (MEBFs), each representing a leading electronic configuration that is expressed in terms of its own, optimized orbitals. The MEBFs are single- or multi-configuration self-consistent field (SCF or MCSCF) wave functions. The orbital sets of different MEBFs are neither identical nor mutually orthogonal and this non-orthogonality complicates the computation of off-diagonal hamiltonian elements in the CI matrix. NOCI can be used to study isolated molecules, but also, when combined with the embedded cluster material model, to describe (rather) localized processes, like core excitations, in materials.

In the past decade we have extended the NOCI method to enable application to *ensembles* of molecules or fragments: NOCI-F. [1] The MEBFs are then spin-adapted linear combinations of anti-symmetrised *products* of MCSCF wavefunctions for each molecule/fragment in the ensemble. NOCI-F allows for the study of processes where inter-molecular (or inter-fragment) electron transfer or excitation transfer plays a role.

NOCI and NOCI-F are not computationally simple, but since the final wave functions are short expansions in terms of well-defined molecular states, a clear interpretation in terms of local excitations, charge transfer, etc. can still be given. It is shown how NOCI-F can be used to study multi-exciton generation and magnetic interactions in molecular crystals and electronic excitations involving (molecules on) surfaces.

[1] T. P. Straatsma, R. Broer, A. Sánchez-Mansilla, C. Sousa, and C. de Graaf, GronOR: Scalable and Accelerated Nonorthogonal Configuration Interaction for Molecular Fragment Wave Functions, *J. Chem. Theory Comput.* 18, 3549–3565 (2022)

3:00pm **TH1-TuA-3 Enabling Long Time-scale Quantum Molecular Dynamics Simulation for 5f-elements, P. Yang, Enrique Batista, M. Cawkwell, D. Perez**, Los Alamos National Laboratory

INVITED

5f-element chemistry in solution is very intricate in nature. There is a pressing need to develop molecular dynamics (MD) methods that can describe quantum mechanical behavior, such as bond breaking and forming, at long timescales. Current first-principle MD methods can only reach tens of picoseconds, while classical force fields cannot accurately describe bond breaking and forming. To achieve this goal, we developed semiempirical density functional theory tight-binding (DFTB) parameters for 5f-elements that enable MD simulations at long time scales. Such simulations will be instrumental in understanding the evolution of speciation and reaction mechanisms. In this talk, we will share our recent development on a hybrid model that combines modern machine learning approaches with physics-based methods. We will demonstrate the transferability of this hybrid model on prediction of molecular structural parameters of various molecular clusters and a variety of chemical reaction free energies. Using these parameters, we also demonstrate microsecond-long quantum-MD simulations of nanoparticle systems for complex f-elements, shedding light on their dynamics and kinetics.

Theory for Surface Processes and Spectroscopies Focus Topic

Room B116 - Session TH2-TuA

Electronic Structure and Reactivity

Moderators: Paul S. Bagus, University of North Texas, C. Richard Brundle, CR Brundle and Associates

4:20pm **TH2-TuA-7 Interaction of Hydrogen Species with γ -Al₂O₃ Surfaces, Anne Chaka, K. Khivantsev, T. Ahmed, B. Schmitt, J. Szanyi, L. Kovarik**, Pacific Northwest National Laboratory

INVITED

The interaction of hydrogen species with active sites in transition aluminas such as γ -Al₂O₃ is responsible for performance of these materials in important applications such as heterogeneous catalysis and hydrogen

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permeation barriers. Understanding these active sites and their interactions with hydrogen species has been inhibited by a lack of a clear crystal structure, let alone surface terminations, for these aluminas. Theoretical studies have had to make assumptions regarding surface terminations and the structure of active sites, leading to ambiguous spectroscopic interpretation and uncertainty in reaction mechanisms. Recent experimental investigation of hydrothermally synthesized γ - Al_2O_3 rhombus-platelets utilizing state-of-the-art FTIR, high-field solid state ^{27}Al NMR, high resolution TEM, and CO/N_2 activation probes have clarified the nature of the active sites on (100) segments of highly reconstructed (110) faces and irrational surfaces. (Khivantsev *et al.*, *Angew. Chem. Int. Ed.* 2021, 60, 17522–17530.) High resolution FTIR and *ab initio* thermodynamics and molecular dynamics based on density-functional theory are utilized to characterize the structure and reactivity of these sites as well as surface and bulk transport as a function of temperature and partial pressures of H_2 , D_2 , H_2O , and D_2O .

5:00pm TH2-TuA-9 Elucidating the Effects of Oxygen Vacancies and Electric Fields on the Adsorption of Species on La-Based Perovskites, Ariel Whitten, J. McEwen, Washington State University; E. Nikolla, University of Michigan, Ann Arbor; R. Denecke, University of Leipzig, Germany

Perovskite materials can be used in electrochemical CO_2 reduction processes due to their higher stability than metal catalysts such as Nickel but are limited by their catalytic activity towards CO_2 reduction. For perovskites to be an alternative catalyst for this process, the surface chemistry of perovskites needs to be augmented by the introduction of active sites on the surface such as oxygen vacancies or by applying electric fields. We propose using La-based perovskites (LaNiO_3 , LaCoO_3 and LaFeO_3) which are known to be highly active in CO_2 reduction to reduce CO_2 on the surface and we investigate these surfaces using both experimental and theoretical methods. While this proposal specifically focuses on the theoretical nature of the project, we use experimental methods to ground our theoretical calculations. Our first study explored experimental XPS spectra with theoretical calculations that predict the core level binding energy shifts of various adspecies on the surface (H , O , OH , H_2O and CO_2). Adsorption of species on the surface was favorable with considerable charge transfer occurring between the surface and the adspecies. This study is imperative for understanding the surface chemistry of our system before we augment it with oxygen vacancies and electric fields. We found that the higher energy peak for both LaCoO_3 and LaNiO_3 corresponds to water adsorption while the lower energy peak is due to lattice oxygen. The other species correspond to intermediate satellite peaks. Figure 1 shows the XPS spectra generated for LaNiO_3 . Literature results and temperature dependent XPS spectra confirmed our results were accurate. We will also investigate the effects of coverage and oxygen vacancies on the XPS spectra for several of our surfaces (LaNiO_3 and LaCoO_3). Finally, we investigate the effects of oxygen vacancies and electric fields on the surface activity and adspecies adsorption. Our preliminary studies show that oxygen vacancies can increase the adsorption of CO_2 on the surface and electric fields change the plane wave averaged potential of the surface. We expect that the influence of electric fields will strengthen the adsorption of CO_2 due to the increase electrons stabilizing the surface. Further work will be completed to explore the effects of electric fields on adsorption strength of CO_2 as well as the formation of oxygen vacancies.

5:20pm TH2-TuA-10 Theory of Magnetic Impurities in Oxides. Complex Problem, Pragmatic Solutions, Gianfranco Pacchioni, Università di Milano-Bicocca, Italy

Dopants in insulating and semiconducting oxides are of fundamental importance for the design of new materials and often lead to the presence of holes or trapped electrons in particular sites. The correct identification of these paramagnetic centers is crucial for understanding the optical, magnetic, photocatalytic and transport properties of oxides. The nature of magnetic impurities can be investigated by comparing DFT calculations using hybrid functionals with electron paramagnetic resonance, EPR, measurements. We will provide a historical perspective on the description of holes in the O 2p valence band of SiO_2 as a paradigmatic example of interaction between theory and experiment. Then we will discuss N-dopants in TiO_2 , ZnO , SnO_2 , ZrO_2 and MgO . A comparison with the EPR data allows one to evaluate the accuracy of the DFT calculations. At high N-dopant concentrations the presence of magnetic ordering in some of these materials has been suggested, implying the existence of magnetic interactions between the isolated defects. The use of hybrid functionals allows to adequately describe the nature of the isolated magnetic defects in the oxides, and shows that no magnetic ordering is expected for the dopant concentrations used in the experiments. Problems related to the theoretical

treatment in DFT of magnetic impurities in insulating and semiconductor oxides are discussed.

5:40pm TH2-TuA-11 Dynamics of Electrical Potential Distribution in Ionic Liquid Based Electrochemical Systems at Extended Time and Length Scales, Observed by Myriad of Experimental Techniques Awaits for Theoretical Attention, Pinar Aydogan Gokturk, Koc University, Turkey; S. Suzer, Bilkent University, Turkey

Ionic liquid systems exhibit rich dynamic responses on electrified surfaces. A long-standing question is why these materials display widely different time constants, ranging from nanoseconds to several hours, which can be attributed to the complex interplay of chemical and physical factors, including steric and molecular interactions. Recent theoretical approaches have concentrated in the faster temporal- and shorter lateral-variations. Although a collection of experimental evidences have been reported the presence of longer length and time-dependent processes, understanding of the molecular nature of them is still elusive. Our group use X-ray photoelectron spectroscopy to directly probe the local electrical potential variations, extracted from the binding energy shifts of the corresponding core levels, for obtaining lateral- and temporal-responses on electrified cells in non-invasive and chemically-resolved fashion¹. Others have used electrochemical, microscopic, terahertz imaging, X-ray and Neutron scattering techniques. Use of electrochemical force microscopy have given new input into the dynamics of charge screening at the solid-aqueous interfaces by identifying multiple time constants and relatively larger length scales of up to 10 microns². But again, such distances are still small to represent real-life electrochemical devices. Moreover, information not only at the interfaces but in the bulk electrolyte covering the entire electrochemical cell is needed. Recent theoretical progress has shed new light on the time dependency, particularly nonlinear response of thin double layer in a parallel plate configuration, where Bazant *et al.*, using a modified version of the Poisson–Nernst–Planck (PNP) equation, had identified different time scales controlled by geometric and ionic diffusion properties of the chemical moieties within such devices³. Most of these approaches have been developed and tested for small electrical potentials and relatively dilute aqueous solutions, while extension to higher voltages and highly concentrated electrolytes, as in the case of ionic liquids, still remains a challenging task due to the high interaction energy and long-range Coulombic forces. We will review some of the recent experimental findings, including those from our own work, and the theoretical work mentioned above and highlight some of issues waiting for attention.

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6:00pm TH2-TuA-12 Sub-eV Electron Inelastic Mean Free Path: A Second Inverted Trend?, Hagai Cohen, The Weizmann Institute, Israel

The dependence on kinetic energy of the electron inelastic mean free path (IMFP) parameter has already been studied extensively, showing a drastic qualitative difference between the high-energy regime (above e.g. 100 eV) and the low-energy regime (below e.g. 40 eV). In fact, definitely opposite energy dependencies are exhibited by the two ‘arms’ of the corresponding $\lambda(\text{Ek})$ universal curve. Extension of these studies to very low energies, below e.g. 5 eV, is by far more challenging experimentally. Hence, only few works have addressed this challenge so far.

Here, a new technique is applied, resulting in an interesting observation. XPS-based experiments with nanometrically thin self-assembled monolayers (SAMs) systematically indicate on a second *inversion* in the derivative of energy dependence, appearing as a common general feature of the sub-eV regime. Using a simple theoretical model, these results are explained and further propose interesting applications for future studies of hot-electron interactions with dielectric layers.

Theory for Surface Processes and Spectroscopies Focus Topic

Room Oregon Ballroom 203-204 - Session TH-TuP

Theory for Surface Processes and Spectroscopies Poster Session

TH-TuP-1 Evaluation of Covalent Bonding In Ionic Compounds, *Paul S. Bagus*, University of North Texas; *C. Nelin*, Consultant; *T. Vitova*, Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Germany; *B. Schacherl*, Karlsruhe Institute of Technology, KIT, INE, Germany

The extent of covalent bonding in ionic compounds like oxides and halides is of considerable importance for their chemical properties; see, for example Refs. [1-2]. It is often estimated from population analyses either based on the original Mulliken formalism [3] or on more modern variants. [4-5] However, population analyses may have artifacts and be misleading. In contrast, we will be using a set of three criteria to estimate covalent character of orbitals in cluster models of compounds. [6] The methods are based on: (1) variation of orbital energies for different symmetry frontier orbitals; (2) estimates of the size of the orbitals as measured by an effective radius; and (3) projection of atomic orbitals. We examine the changes in covalency for two sets of compounds. The first set includes three nominally Ni(II) compounds: NiO, Ni(OH)₂, and NiCO₃. The second set are nominally oxidation state IV actinide dioxides UO₂, NpO₂, and PuO₂. As well as the covalency for ground state WFs, we also consider the different covalent character of cations where a core electron has been ionized or excited. The wavefunctions are obtained as fully relativistic *ab initio* solutions of Dirac Hartree-Fock and many body configuration interaction solutions. It is shown that there are surprising departures from the nominal oxidation states and that the changes are not always consistent with intuitive views of the changes in the covalent character of the different compounds.

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Actinides and Rare Earths Focus Topic Room C124 - Session AC+AS+TH-WeM

Nuclear Safeguards, Forensics, Environmental Science, and Stewardship

Moderators: Paul Roussel, AWE, David Shuh, Lawrence Berkeley National Laboratory, Evgeniya Tereshina-Chitrova, Charles University, Prague, Czech Republic

8:00am AC+AS+TH-WeM-1 Simulation Tools for Improvement of the Fission Track Analysis Method for Nuclear Forensics, *Itzhak Halevy*, Nuclear Engineering, Ben Gurion Uni. Be'er Sheva, Israel **INVITED**

To answer nuclear forensics questions, we are developing new innovative techniques and approaches to make this analysis more reliable and accurate. Currently, only trained researchers can analyze microscope images. Since this analysis is dependent on the researcher's own abilities and skills, it is obvious that different researchers will produce results that are slightly distinct. A new worker's certification period is quite long, and it must cover numerous examples from previously measured data as well as some that we can only predict. A good simulation software can aid with training and provide a tool for grading new researchers.[1] The fission tracks were simulated by Monte-Carlo software, GEANT4, which uses all the physics behind the nuclear fission tracks, such as thermal neutrons flux, fission cross-section, radiation time, particle size, enrichment, etc. In this study, our Trainer2.0 software calculates the tracks on our Lexan detector and its projection, according to the physical parameters like neutron flux, size of the particle, the isotope, and radiation time. The result is a "star" centered on the simulated particle. Our full software is written with MatLab code.

We can simulate an extreme condition and learn new aspect in the fission track technique. From the simulation we can learn about the proper amount of material to use as a sample in the FTA technique.

The simulation can predict and compared to the mini-bulk and the micro-bulk analysis.

New idea of using penetrating fluorescent colors give as the ability to scan our detector in 3D instead of 2D. In this case we used the Dapi marker as a first shoot, this marker is well known for biomedical research.

This new idea to investigate the FT Star more than just by his projection.

Identifying the length of the tracks and their distribution allow us to determine the element source isotope be the shape of "fission products distribution" and the density of the impurities in the source.

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8:40am AC+AS+TH-WeM-3 Characterizing Actinides in Subsurface Sediments for Contaminant Remediation, *Carolyn Pearce*, H. Emerson, Pacific Northwest National Laboratory; C. Delegard, TradeWind Services LLC **INVITED**

The nuclear weapons fuel cycle consists of front-end steps to produce, extract, purify, and engineer plutonium, and back-end steps to safely manage, prepare, and dispose of radioactive wastes. Waste processing has resulted in the release of actinides to the subsurface worldwide, including the release of ~200 kg of plutonium and ~7 Kg of americium from process waste solutions to unconfined soil structures at the Hanford Site in Washington State. The subsurface mobility of actinides is influenced by complex interactions with sediments, groundwater, and any co-contaminants within the waste stream. Developing efficient remediation strategies for released actinides requires a complete understanding of retardation processes and mass flux, including the different mechanisms by which actinides are immobilized in the subsurface, and the effect of localized subsurface conditions. Here, sediments from Hanford waste disposal sites have been selected, based on historical information and sediment composition, for characterization of actinide (plutonium, americium, and uranium) immobilization mechanisms. Results show that the actinides are present in these samples as micron-sized particles, intrinsic and pseudo-colloids, and dissolved species, and that they have been significantly affected by the chemistry of the actinide-bearing waste source term. Spectroscopic characterization of actinides has also proved essential to understand their migration in the deep, unsaturated, vadose

zone sediments at the Hanford Site, due to the significant variability in solubility and mobility with speciation and oxidation state.

9:20am AC+AS+TH-WeM-5 Changes in Oxidation Mechanism with Relative Humidity: Application to Uranium Dioxide Powders, *Scott Donald*, L. Davisson, Lawrence Livermore National Laboratory **INVITED**

It is of interest in nuclear forensic science to understand the relationship between an interdicted sample's history and the resulting chemical and physical characteristics. It may be possible to glean information on the environmental characteristics experienced by uranium dioxide from variations in the chemistry and structure of a powder sample. The reaction between high purity, stoichiometric UO_2 powder over a range of nominal conditions at room temperature was studied using a range of techniques, including XPS, SEM, and TEM, to interrogate changes to both the surface and bulk properties of the material. Oxidation resulting from the interaction of the surface with the local environment was observed and quantified. A change in the reaction mechanism between low and high relative humidity has been proposed to describe the observed results.

The work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and funded by the Office of Defense Nuclear Nonproliferation Research and Development within the U.S. Department of Energy's National Nuclear Security Administration. LLNL-ABS-848427

11:00am AC+AS+TH-WeM-10 Spatially Resolved Morphological and Chemical Analysis of Nuclear Materials, *Brandon Chung*, A. Baker, S. Donald, T. Li, R. Lim, U. Mehta, D. Rosas, S. Sen-Britain, D. Servando-Williams, N. Cicchetti, Lawrence Livermore National Laboratory; A. Ditter, D. Shuh, Lawrence Berkeley National Laboratory (LBNL)

Nuclear forensics requires accurate identification of distinguishing material characteristics of interdicted nuclear materials. Local morphological and chemical variations in nuclear materials are nearly ubiquitous due to the varying provenance, process, and pathways. We will describe our efforts to strengthen operational and scientific methodologies to employ the focused ion beam-scanning electron microscopy (FIB-SEM) on uranium (U) and plutonium (Pu) materials for direct three-dimensional (3D) morphological analysis or to prepare site-specific material features to obtain spatially resolved characterizations using transmission electron microscopy (TEM) and X-ray synchrotron spectromicroscopy. Both U and Pu materials show variations in the internal chemical composition and morphology from their production processes and storage environments. This information is of potential use in discriminating material signatures to identify the origin and history of interdicted nuclear materials

11:20am AC+AS+TH-WeM-11 Soft and Tender Spectromicroscopy for Nuclear Forensics at the Advanced Light Source, *David Shuh*, A. Ditter, Lawrence Berkeley National Laboratory (LBNL); N. Cicchetti, University of Nevada Las Vegas; R. Lim, S. Sen-Britain, D. Rosas, D. Servando-Williams, A. Baker, S. Donald, B. Chung, Lawrence Livermore National Laboratory

The development of new methods and signatures is crucial to ensure that nuclear forensics activities remain effective. Synchrotron radiation analysis offers one way to extend the scope of forensics investigations in elemental, chemical, and structural analysis which all can be done in imaging modes that in some cases, reaches to the nanoscale. X-ray techniques are particularly useful because of their elemental specificity and non-destructive nature. The ability to use tunable, focused beams makes synchrotron radiation sources a potentially key tool for addition into the array of characterization techniques currently employed, particularly when it comes to the investigation of particles or areas of interest in smaller specimens. Recent efforts at the Advanced Light Source conducting tender and soft spectromicroscopy using x-ray fluorescence (XRF; Beamline 10.3.2) and a scanning transmission x-ray microscope (STXM; Beamline 11.0.2). The XRF measurements provide elemental analysis at the micron scale, whereas the STXM can probe chemical speciation with a spatial resolution of better than 25 nm. Several uranium and plutonium specimens have been investigated using these techniques and the potential signatures from this data, as well as its utility, will be demonstrated. The outlook for synchrotron radiation within nuclear forensics including the strengths and drawbacks of these techniques will also be discussed.

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Actinides and Rare Earths Focus Topic Room C124 - Session AC+AS+MI+TH-WeA

Emerging Topics and Methods in Actinide/Rare Earth Sciences

Moderators: Edgar Buck, PNNL, Krzysztof Gofryk, Idaho National Laboratory, Liane Moreau, Washington State University

2:20pm **AC+AS+MI+TH-WeA-1 Chemical Imaging and Applications Using High Energy Resolution Fluorescence Detection for the Actinides, Samuel Webb, N. Edwards, V. Noel**, SLAC National Accelerator Laboratory **INVITED**
Microscale synchrotron radiation-based x-ray fluorescence (SR-XRF) chemical analyses can provide a unique capability for chemical signature recognition and classification capabilities for actinide micro-particle analysis. SR-XRF is well suited to forensic type analyses of small particles because it is rapid, non-destructive, highly sensitive, has good spatial resolution, and can provide chemical information on the elements that are present when combined with x-ray absorption spectroscopy (XAS). The combination of spatially resolved distribution and chemical information, often known as chemical imaging, effectively provides a “chemical morphology” of the sample of interest and can show how chemical states are distributed within and among a series of particles. This type measurement is critical for understanding particle origin and history, as the spectroscopy, and its spatial distribution, can provide unique and complementary chemical signatures that may not be elucidated with other forms of measurement.

However, the conventional XAS capability in the near edge region as commonly implemented is often inadequate for systems that require high sensitivity or require a higher detail of spectroscopic information. This can be overcome with the combination of traditional micro SR-XRF and XAS, integrated with a high energy resolution fluorescence detector (HERFD) crystal analyzer. This has been recently implemented at BL 6-2b at SSRL and applied in the determination of the micron-scale oxidation state of uranium in particles. A discussion of the image and data processing techniques that can be applied using spatially resolved HERFD to obtain chemical and structural information, as well as the distribution of phases across different particles at the micro-scale, will also be presented.

3:00pm **AC+AS+MI+TH-WeA-3 High Energy X-Ray Characterization of Microstructure at Macroscopic Depths in Pu Alloys, Donald Brown**, Los Alamos National Laboratory; *T. Carver, R. Pokharel*, Los Alamos National Laboratory; *A. Smith, P. Kenesei, J. Park*, Argonne National Laboratory **INVITED**

High energy (95keV) X-rays were utilized to characterize the microstructure of six PuGa alloy samples. The samples had different gallium content, age, and history (i.e. thermos-mechanical processing). The crystallographic textures, phase fractions, lattice parameters and dislocation densities of each sample were evaluated through distinct analysis techniques. The textures of the samples were modest. In each case, the dislocation densities were relatively high, comparable to cold worked metals, with some attributable to mechanical work and some likely due to self-irradiation damage (aging). The lattice parameters determined in the predominantly single-phase samples were larger than expected based on the nominal Ga concentration. The lattice parameter increase is attributed to self-irradiation induced Ga segregation leaving the matrix Ga lean. Finally, measurements of the lattice parameter were completed as a function of temperature to determine the crystallographic thermal expansion of the material.

4:20pm **AC+AS+MI+TH-WeA-7 Native Oxide Growth of Pu—Ga Alloys, Kasey Hanson, S. Hickam, D. Olive, A. Pugmire**, Los Alamos National Laboratory

Plutonium corrosion has proven to be an intricate area of research that garners considerable attention. In particular, understanding plutonium oxidation is significant to the safe handling and storage of plutonium metal, which is known to readily oxidize under ambient conditions. In order to mitigate this, plutonium metal is commonly stored in inert atmospheres. These include gloveboxes as well as ultra-high vacuum (UHV) chambers used for materials characterization.

The objective of this work is to measure oxidation rates of plutonium metal in various storage environments. To achieve this, spectroscopic ellipsometry was selected due to its prevalence in a variety of industries to measure thin-film thickness. A non-destructive technique, ellipsometry exposes the sample to polarized light, and through changes in the amplitude ratio and phase difference of the reflected vs. incident light, one can generate a material's optical properties that can be used to determine oxide thicknesses.

Building upon previous work, this presentation will present the optical constants of plutonium metal, achieved through the use of ion sputtering under UHV, and plutonium oxide formed on plutonium metal in various storage and exposure conditions. These results will then be used to model oxide thickness values directly from ellipsometry measurements as well as provide additional insights into the nature of the oxide films relevant to plutonium storage and handling.

4:40pm **AC+AS+MI+TH-WeA-8 Molecular Beam Epitaxy of Ternary Nitrides: From Transition Metals to Actinoids, Kevin Vallejo**, Idaho National Laboratory; *S. Gutierrez Ojeda*, Universidad Nacional Autonoma de Mexico; *G. Hernandez Cocoltzi*, Benemerita Universidad Autonoma de Puebla, Mexico; *S. Zhou, K. Gofryk, B. May*, Idaho National Laboratory

The exceptional properties of transition metal nitrides for coatings, as well as photo- and electrochemical applications have opened the doors for more detailed studies of their structure and synthesis. Mn- and Cr- nitrides are strong candidates to showcase the application of spintronic and magnetic sensing applications partially because of their ability to form several different metastable phases. Similarly, rare-earth nitrides have been studied for over 50 years due to their optical properties and strong electron correlations, leading to behaviors that range from insulating to metallic. This study uses molecular beam epitaxy to synthesize epitaxial thin films of different Mn-, Cr-, Ga-, and Ce-nitride phases. The electrical and magnetic properties of these films are investigated with the rocksalt MnN and CrN both showing metallic behavior, with the latter showing a magnetic transition ~280K. However, when combining these materials at similar growth conditions, instead of maintaining the rocksalt structure, a new ternary cubic phase of Mn_xCr_yN is obtained which shows narrow-gap semiconducting behavior. Additionally, density functional theory calculations show potential new phases where lanthanoid ternary phases are experimentally realizable. This work presents an avenue for the epitaxial integration of metallic, magnetic, and semiconductor materials via transition metal and lanthanoid compounds, en route to the synthesis of actinoid compounds.

5:00pm **AC+AS+MI+TH-WeA-9 Formation and Electronic Properties of Uranium Tellurides: A Thin Films Study, Evgenia Tereshina-Chitrova, S. Alex**, Institute of Physics CAS, Prague, Czechia; *O. Koloskova, L. Horak*, Charles University, Prague, Czechia; *O. Romanyuk, Z. Soban*, Institute of Physics CAS, Prague, Czechia; *T. Gouder, F. Huber*, JRC Karlsruhe, Germany

Understanding the interaction of 5f electrons with other electrons in actinide compounds presents a significant challenge. Factors such as relativistic effects, strong electron correlations, and hybridization with ligands contribute to the complexity of observed effects. This complexity is exemplified in the case of the recently discovered unconventional superconductor UTe_2 [1]. The ongoing debate surrounding UTe_2 revolves around understanding its unconventional superconductivity, the nature of its electronic correlations [2,3], and the character of the 5f electrons. While it's evident that UTe_2 exhibits intermediate occupancy of the 5f states at ambient pressure, there are two opposing interpretations of experimental findings regarding the degree of localization of the 5f electrons: the model based on $5f^26d^1$ states with singlet crystal field states [4,5], and a $5f^3$ -based model with atomic Kramers doublet and greater 5f itinerancy [6,7]. Interestingly enough, ab-initio calculations considering the $4f^2$ U-ion ground state multiplet reproduce bulk experimental observations, such as the Schottky anomaly and magnetic anisotropy at low temperatures [8].

To contribute to this subject, we provide a comprehensive and detailed investigation of thin films of uranium tellurides with various compositions U_xTe_y by means of X-ray Photoelectron Spectroscopy (XPS) and Ultra-violet Photoelectron Spectroscopy (UPS). We also explore the structural and bulk

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properties of the films, including their magnetic and transport characteristics. This comprehensive approach allows us to correlate the changes in XPS spectra across different compositions and crystal structures with resultant bulk properties, contributing to our understanding of the nature of the 5f electrons within uranium tellurides.

The work by E.A. T.-Ch. is supported by the Czech Science Foundation (GAĀr) under the grant number 22-19416S. E.A. Ch.-T. is a recipient of the L'Oreal-UNESCO for Women in Science prize.

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5:20pm **AC+AS+MI+TH-WeA-10 Nanoscale Uranium and Thorium Oxides for Applications in Advanced Nuclear Fuels**, **Matthew Heaney**, L. Moreau, X. Guo, Washington State University

Nanomaterials of uranium and thorium oxides and their mixtures are of significance to the development of advanced nuclear fuels with properties such as self-healing and greater fission gas retention. They also serve as a means for furthering our understanding of spent nuclear fuel behaviors. Furthermore, thorium incorporation into the uranium sublattice induces changes in oxidation behavior, which would be a promising means to provide additional redox resistance. Coupling this with the possible application in fast neutron reactors presents a potential fuel for the Th fuel cycle, which is inherently proliferation resistant. However, these possible applications are purely hypothetical given that, compared to nanomaterials from the rest of the periodic table, actinide nanomaterials are heavily understudied. Therefore, it will be imperative to interrogate the properties of these nanomaterials. This work aims to explore three key areas. (1) How careful kinetic control through variations in synthetic methods can be used to produce particles with different sizes, shapes, and heterogeneities of mixing. (2) Elucidation of the structural and thermodynamic properties of these nanomaterials and how characteristic size, shape, and heterogeneity of mixing affect them through a variety of X-ray characterization and calorimetry techniques. X-ray characterization techniques such as X-ray absorption spectroscopy (XAS) is used to evaluate the heterogeneity of mixing, local structure, and oxidation state of particles while small-angle X-ray scattering (SAXS) is used to determine statistical values on particle size, shape, and polydispersity. Calorimetry techniques like high temperature drop calorimetry are used to determine enthalpies of formation for nanoparticles and the contribution surface effects have on the thermodynamics or thermogravimetric analysis-differential scanning calorimetry (TGA-DSC), which can be used to evaluate oxidation behaviors. (3) How sintered nanoparticles behave in *in-situ* reactor conditions as nuclear fuels and how particle characteristics can be chosen to achieve more desirable radiation-resistance and thermal properties for nuclear fuel, through irradiation studies performed at the 1-MW TRIGA reactor on the campus of Washington State University. Overall, the work presented provides initial evidence for the benefits of nanomaterials in the production of advanced reactor fuels and outlines important fundamental properties of actinides on the nanoscale.

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.

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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), 3d 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 4d 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.

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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.

Thursday Morning, November 9, 2023

11:40am **LS+AC+LX+MI+TH-ThM-12 First Real-Time Tracking of Oxidation States During Fast Redox of UO₂ 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 UO₂ 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 UO₂ 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 M₄-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 UO₂. The spectra obtained also provided insight into the electronic structure of U(VI) in the UO₂ alteration process. This successful international scientific collaboration showcases the potential of a PAMEC for in-situ and operando experiments with UO₂ and highlights its promising broad application for characterization of spent nuclear fuel systems.

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(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% ²³⁵U 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.

Thursday Afternoon, November 9, 2023

Light Sources Science Mini-Symposium

Room C124 - Session LS+AC+AS+LX+MI+TH-ThA

Facility Upgrades and Recent Capability Development

Moderators: David Shuh, Lawrence Berkeley National Laboratory, James G. Tobin, University of Wisconsin-Oshkosh, Gertrud Zwicknagl, Technical University Braunschweig

2:20pm **LS+AC+AS+LX+MI+TH-ThA-1 The Impact of Upgraded High-Brightness Synchrotron Lightsources on the Chemical Speciation of Nanoscale Heterogeneous Aggregates and Transformations, Andreas Scholl**, Advanced Light Source, Lawrence Berkeley National Laboratory

INVITED

ALS-U is an ongoing upgrade of the Advanced Light Source (ALS) at Berkeley Lab that will endow the ALS with revolutionary x-ray capabilities. The new storage ring will enable the production of highly focused beams of soft x-ray light that are at least 100 times brighter than those of the existing ALS. Applying this technology at the ALS will help us better understand and develop new materials and chemical systems needed to advance our research needs in energy science, environmental systems research, and biosciences in the 21st century. This will create a world-leading platform for next-generation soft x-ray and tender x-ray instrumentation.

Four beamlines with new and upgraded capabilities will become available after the upgrade. The FLEXON beamline (FLuctuation and EXcitation of Orders in the Nanoscale), a high-brightness coherent soft x-ray beamline, will provide x-ray photon correlation spectroscopy and diffraction imaging techniques to study electronic, chemical, and magnetic fluctuations in quantum materials with nanosecond temporal and nanometer spatial resolution. A new ALS-U developed tender x-ray beamline is designed to address challenges at the frontiers of diverse scientific areas, ranging from soft condensed matter and biomaterials to energy science and Earth and environmental sciences. It will offer state-of-the-art nanometer-resolved chemical imaging and resonant scattering nanoprobe, enabling operando and in situ studies of materials of K-edges of elements (Na through Ca) and the M and L edges of lanthanides and actinides. These two beamlines will be complemented by two upgraded beamlines for nanometer 3D chemical tomography based on ptychography of light elements and first-row transition metals and for high-resolution ARPES.

The high coherent flux of the upgraded ALS will drastically improve the speed, sensitivity, and spatial resolution of nanoprobe, enabling the speciation and forensic study of nanoscale constituents and contaminants via x-ray absorption spectroscopy and fluorescence detection. Chemical signatures can be correlated with morphology and compared with chemical standards. Operando experiments, for example, of liquid phase systems and studies under ambient conditions, will be enabled by specially designed sample holders and liquid cells using the high penetration of tender x-rays.

3:00pm **LS+AC+AS+LX+MI+TH-ThA-3 The Advanced Photon Source Upgrade: A transformative tool for understanding material structure., Jonathan Lang, J. Lang**, Argonne National Laboratory

INVITED

The APS is currently undergoing a major upgrade of the facility that will increase the brightness of the x-ray beams by factors of up to 500. This upgrade will provide transformational capabilities for examining the nanoscale structure and electronic configuration of materials and their evolution with external stimuli. This presentation will provide an update on the current status of the APS-U project, and discuss the new opportunities for imaging actinide and rare-earth compounds with this new source

3:40pm **LS+AC+AS+LX+MI+TH-ThA-5 Combining Focused Ion Beam Sectioning, Soft X-ray Spectromicroscopy, and Non-Negative Matrix Factorization to Reveal Actinide Chemical Speciation at the Nanoscale, Alexander Ditter, D. Smiles, J. Pacold, D. Lussier**, Lawrence Berkeley National Laboratory; Z. Dai, Lawrence Livermore National Laboratory; A. Altman, Lawrence Berkeley National Laboratory; M. Bachhav, Idaho National Laboratory; B. Chung, Lawrence Livermore National Laboratory; C. Degueldre, Lancaster University, UK; S. Donald, Lawrence Livermore National Laboratory; L. He, Idaho National Laboratory; M. Mara, S. Minasian, D. Shuh, Lawrence Berkeley National Laboratory

INVITED

Spectromicroscopy methods, combining the chemical insight of spectroscopy with microscopy imaging, can give a unique and informative view of a sample of interest. Scanning Transmission X-ray Microscope (STXM) spectromicroscopy is one such method, utilizing synchrotron

radiation to probe electronic structure with a spatial resolution in the tens of nanometers. Specialized methods like ptychography can push the spatial resolution even lower into the single nanometer range.

Discussed here, STXM spectromicroscopy is applied to two actinide samples: spent nuclear fuel, which offers a unique insight into the complex environment of nuclear fuel undergoing burnup, and uranium oxide allowed to age in a humid environment, which serves as a demonstration of the power of this technique for nuclear forensics investigations. These samples are created by focused ion beam (FIB) sectioning to generate cross-sections of ideal thickness for soft x-ray measurements (100-200 nm). The FIB method of sample preparation also allows for the measurement of highly radioactive spent fuel without containment due to the extremely small amount of material present.

Data analysis is a key component to the understanding of spectromicroscopy results for varied samples like these. Non-negative matrix factorization (NMF) is employed to identify key components and recent efforts to improve NMF to work with noisy individual STXM spectra are outlined here. Reproducibility of the analysis is a concern (as with similar methods like multivariate curve regression) and methods to enhance both reproducibility and interpretability of the results are discussed.

Combining STXM spectromicroscopy, FIB sectioning, and NMF analysis has allowed for unique insights into actinide materials. Potential future developments utilizing this method for other samples and with advanced techniques like ptychography are also discussed.

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