Tuesday Afternoon, November 7, 2023

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 Brauschweig

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-earthy 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-Barros,* Colorado School of Mines; *F. White,* Oak Ridge National Laboratory; *T. Albrecht-Schoenzart,* 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 little understanding 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 N_7O_5V – 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 energetics 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, 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 UO_2 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 $[Rn]7s^2 5f^6$ 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

$$[Rn]7s^{2+\gamma_{s,Pu}} 5f^{6+\gamma_{f,Pu}} 6d^{0+\gamma_{d,Pu}} 7p^{0+\gamma_{p,Pu}}$$

where $\gamma_{s,Pu}$, $\gamma_{f,Pu}$, $\gamma_{d,Pu}$, $\gamma_{p,Pu}$ 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

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

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

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

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

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

result in nine possible occupancy configurations

$$7s^2 5f^6 6d^0 7p^0,\ 7s^2 5f^5 6d^1 7p^0,\ 7s^2 5f^4 6d^2 7p^0,\ 7s^1 5f^7 6d^0 7p^0,\ 7s^1 5f^6 6d^1 7p^0,$$
$$7s^1 5f^5 6d^2 7p^0,\ 7s^0 5f^8 6d^0 7p^0,\ 7s^0 5f^7 6d^1 7p^0,\ 7s^0 5f^6 6d^2 7p^0$$

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.

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