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Defining orbital mixing standards for quantitative studies of covalency in actinide ligand bonds

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The exact nature of chemical bonds between actinides and light atoms such as carbon, nitrogen, oxygen, and fluorine is of widespread interest because these interactions control the physics and chemistry of many technologically important processes. Among approaches explored previously, ligand K-edge X-ray absorption spectroscopy (XAS) has emerged as an effective method for quantitatively probing electronic structure and orbital mixing. The presence of covalent mixing is observed as a pre-edge feature in the ligand K-edge XAS, which only has transition intensity if the final state metal orbital contains a component of ligand p orbital character. For actinide–chloride bonds, the Cl K-edge pre-edge intensity is related to percentage covalency by using a copper tetrachloride intensity standard. Recent advances have shown that quantitative pre-edge peak intensities can be measured at the K-edges for light atoms through a combination of XAS with a scanning transmission X-ray microscope (STXM), non-resonant inelastic X-ray scattering (NIXS), and hybrid density functional theory calculations (DFT). However, corresponding intensity standards have not been developed.

Herein, a new effort is discussed that employs these techniques to define experimental intensity standards and garner a quantitative understanding of bonding interactions with d- and f-block coordination compounds. Oxygen K-edge XAS measurements and DFT studies began with the lanthanide dioxides and sesquioxides, LnO₂ and Ln₂O₃ (Ln = Ce, Pr, Tb), which were chosen because 4f covalency in the Ln–O bonds is already well-established from L₃-edge X-ray spectroscopies. Features in the O K-edge XAS increase in intensity in analogy to the L₃-edge measurements, suggesting that both techniques provide equivalent information regarding covalency. Results from an ongoing collaboration with theorists tie these experimental trends to changes in orbital mixing with the σ and π -bonding 4f orbitals. Following a similar approach, ytterbocene, (C₅H₅)₂Yb, was chosen to standardize intensities at the carbon K-edge. Preliminary efforts to use these benchmarks in quantitative determinations of covalency for a variety of actinide molecules and materials will be discussed.

Primary author: Dr MINASIAN, Stefan (Lawrence Berkeley National Laboratory)

Co-authors: Dr BOOTH, Corwin (Lawrence Berkeley National Laboratory); Dr CLARK, David (Los Alamos National Laboratory); Dr SHUH, David (LBNL); Dr NORDLUND, Dennis (SLAC National Accelerator Facility); SOKARAS, Dimosthenis (SLAC National Accelerator Facility); Dr BATISTA, Enrique (Los Alamos National Laboratory); Dr KEITH, Jason (Colgate University); Dr MARTIN, Richard (Los Alamos National Laboratory); Dr KOZIMOR, Stosh (Los Alamos National Laboratory); Dr TYLISZCZAK, Tolek (Lawrence Berkeley National Laboratory); WENG, Tsu-Chein (SLAC National Accelerator Facility); Dr LUKENS, Wayne (Lawrence Berkeley National Laboratory); Dr WEN, Xiao-Dong (Los Alamos National Laboratory)

Presenter: Dr MINASIAN, Stefan (Lawrence Berkeley National Laboratory)

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