

XAFS at the edge of the periodic table: Determining the role of 4f- and 5f-orbital delocalization in bonding and electronic structure

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The fundamental properties of the atom are generally thought to be understood. However, bonding involving atoms at the lower edge of the periodic table, i.e. the 4f (lanthanide, Ln) and 5f (actinide, An) elements, remains an enigma, despite their technological relevance and decades of research. In addition to the practical bottlenecks of measuring radioactive samples and their sometimes-short lifetimes, the fundamental challenge of understanding the actinides is that, actinides almost never act like their 4f counterparts, although they share many of their more unusual properties. In particular, most of the actinides can exist in many different valence states, heightening the role of strongly correlated electron interactions. Strong correlations typically dominate when competing interactions are of similar strengths, especially in the ground between ionic and covalent bonding, that is, between localized and delocalized electronic states. Binding actinides to organic ligands offers many advantages toward expanding our knowledge of the late actinides. In particular, the ability to use ligands as building blocks can vastly increasing the number of known compounds and structures. Likewise, these ligands offer some tunability for studying various properties. For these and other reasons, understanding the coordination chemistry of actinides in organic complexes has become an attractive avenue of research.

For the discussion presented here, work on Ce and Yb organometallics will provide context in terms of Ln L_{III}-edge XANES measurements of f-occupancy and in bonding characteristics and the effect on magnetism. The role of strongly correlated electron interactions will be described in terms of configuration interaction (CI) and related calculations. Local structure (EXAFS) measurements demonstrate the final effect on the bonding at the metal center.

XANES measurements of the f-orbital occupancy of actinides is more difficult to interpret and will be discussed. The focus will be, however, on EXAFS measurements across the An series in the presence of strongly oxidizing ligands. Chosen ligands include hydroxypyridonone (HOPO), with less oxidizing ligands, such as diethylenetriaminepentaacetic acid (DTPA) used for comparison. Cations include Th, U, Pu, Am, Cm, Bk, and Cf. Discussions will center on nearest-neighbor bond lengths, using DFT calculations as a guide. The surprising role of covalency in the late actinides will be considered, both in terms of the EXAFS results and in terms of the edge shifts. In addition, the role of radiation damage will also be discussed. Finally, these measurements often require small amounts of material, both for safety and practical reasons, and the sample holders and techniques used will therefore also be presented.

This work was supported by the U.S. Department of Energy (DOE), Office of Science (OS), Office of Basic Energy Sciences (OBES), under Contract No. DE-AC02-05CH1123 (C.H.B., L.M.M., G.D. and R.J.A.) and Contract No. DE-AC52-06NA25396 (M.P.K., E.R.B., and P.Y.).