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Assessing Actinide-Oxygen Covalency by K-edge X-ray Absorption Spectroscopy.

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The development of many essential nuclear technologies requires a comprehensive grasp of the electronic ground and valence states of molecular actinide bonding interactions. Identifying itinerant or delocalized electrons – in molecular nomenclature, ionic or covalent bonds – is a longstanding problem in actinide science. Recent advances have shown that the transition intensities measured by ligand K-edge X-ray absorption spectroscopy (XAS) directly relate to coefficients of covalent orbital mixing. Ligand K-edge XAS has been employed successfully to describe the valence states of materials containing predominantly ionic metal–Cl and metal–S bonds, however, it remains experimentally challenging to obtain quantitative intensity information at the K-edge for light atoms such as C, O, N, and F. Insights regarding the nature and extent of orbital mixing in actinide–O bonds are now within reach through a combination of XAS with a scanning transmission X-ray microscope (STXM) and hybrid density functional theory calculations (DFT). A new effort to employ these techniques for non-conducting molecular systems containing interactions between actinide and oxygen-based ligands will be discussed. Oxygen K-edge XAS measurements and DFT for a series of six structurally related transition metal oxides suggest that metal *nd* and O *2p* orbital mixing increases with increasing *Z*. The actinyl ions were chosen for the first O K-edge XAS measurements with actinides because they represent the most important high-valent actinide species in the environment. Features in the polarized XAS of the actinyls follow anticipated trends based on the *5f* and *6d* orbital energies and occupancies. Results from an ongoing collaboration with theorists ties these experimental trends in actinide–O orbital mixing to changes in *3d*, *4d*, *5d*, and *6d/5f* valence orbital occupancies.