Glenn T. Seaborg Center Special Seminar

Quantifying Covalency in d- and f-Block Organometallics Using Carbon K-Edge X-ray Absorption Spectroscopy

Stefan G. Minasian

Lawrence Berkeley National Laboratory
Actinide Chemistry Group, Chemical Sciences Division

Wednesday, 20 November 2013
11:00 am – 12:00 pm
Bldg. 62, Rm. 203

The development of many essential industrial technologies requires a comprehensive grasp of the electronic ground and valence states of molecular M–C bonding interactions. Recent advances have shown that the 1s to np transition intensities measured by ligand K-edge X-ray absorption spectroscopy (XAS) directly relate to coefficients of orbital mixing. However, it has been difficult to obtain quantitative intensity information at the K-edge for carbon. Fortunately, recent upgrades at synchrotron facilities, advancements in beamline instrumentation, and sample preparation methods suggest that these insights are now within reach. Efforts with Group IV metallocene dichlorides, $(C_5H_5)_2MCl_2$ (M = Ti, Zr, Hf), show that C 2p orbital mixing is enhanced for the diffuse Hf (5d) and Zr (4d) atomic orbitals in relation to the more contracted Ti (3d) orbitals. Furthermore, the results provide insight into how changes in orbital mixing within the metallocene wedge are correlated with periodic trends in covalent bonding between the metal and the $C_5H_5^{1-}$ ancillary ligands. Carbon K-edge XAS and DFT of the actinocenes, $(C_8H_8)_2An$ (An = Th, U), showed that the 5f orbitals engage in significant δ-type mixing with the $C_8H_8^{2-}$ ligands, which increased as the 5f orbitals dropped in energy on moving from Th^{4+} to U^{4+}. Experimental evidence for an unusual ϕ-orbital mixing interaction in $(C_8H_8)_2Th$ will also be discussed.

Host: David Shuh (510) 486-6937 DKShuh@lbl.gov Admin. Asst: Catherine Mendez (510) 486-5587
Ernest Orlando Lawrence Berkeley National Laboratory One Cyclotron Road, Berkeley, California 94720