Glenn T. Seaborg Center Special Seminar

5th Annual
Burris Cunningham
Actinide Science Seminar

"Computational Studies of Actinide Hydrolysis and High Oxidation States"

David A. Dixon

Department of Chemistry, The University of Alabama

Wednesday, November 02, 2016
4:00 pm – 5:00 pm
Bldg. 50, Auditorium

There is substantial interest in understanding the reactions of water with complexes containing actinides to better understand their chemistry, especially in aqueous solution. We are using computational chemical approaches The hydrolysis reactions of AnO_2^+ for An = Pa to Cf as well as for ThO_2 and UO_2^{2+} were studied to examine the role of filling the f shell in the An(V) oxidation state. The potential energy surfaces show that the reaction proceeds initially via a Lewis acid-base interaction followed by a proton transfer step to form the $MO(OH)_2^+$ intermediate which may or may not be symmetric. These calculations were done at the CCSD(T) level with large basis sets. The acidities of Th, Pa, U, Np, and Pu for the +III and +IV oxidation states have been calculated with multiple solvation shells with different numbers of water molecules in the first solvation shell using density functional theory and an implicit self-consistent reaction field approach for the bulk solvent. The tetravalent actinides also exhibit extensive hydrolysis and condensation behavior due to their high charge density and acidity and polynuclear species are known to play a significant role in their overall chemistry. Electronic structure calculations of thorium oxide clusters with carboxylate, sulfate and selenate ligands provide new insights into their stability, reactivity, and role as nucleation site precursors. Finally, the structures and vibrational frequencies of neutral and anionic actinide fluorides AnF_x are being calculated to determine the maximum formal oxidation state of the actinide. Energetic properties including electron affinities, ionization energies, fluoride and fluorocation affinities, and bond dissociation energies are calculated to provide further insights into periodic trends.

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