Reliable Electronic Structure Calculations for Heavy Element Chemistry: Molecules Containing Actinides, Lanthanides, and Transition Metals

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The goal of this project is to study the chemistry of heavy elements through the use of *ab initio* electronic structure calculations, to improve the understanding of the behaviour of the actinides, lanthanides, and heavy transition metals, molecules critical to DOE missions including environmental remediation and nuclear reactors.

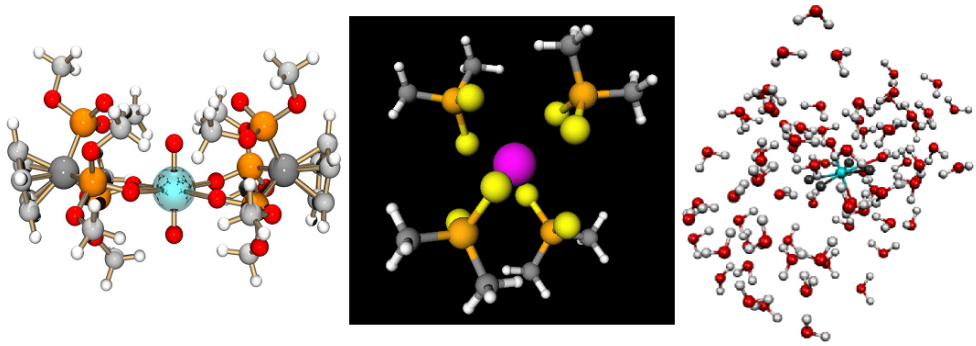
In the first two years of the project a wide variety of quantum chemical methods, based on molecular orbital theory and density functional theory with the proper treatment of relativistic effects, were used to interpret experimental data and to predict the chemistry of actinide, lanthanide, and transition metal compounds. Our results provide a firm theoretical basis for this area of chemistry, extending expensive experimental results into new areas of parameter space. The information obtained from calculations on actinide containing molecules includes, but is not limited to, molecular structure, spectroscopic properties (IR, NMR, UV-vis, ESR), complexation binding energies, and redox chemistry. The results of the calculations help enable the characterization of the interaction of the actinide, lanthanide and heavy transition metal ions with organic complexing agents present in nuclear processing waste tanks and with anion ligands present in natural aqueous systems (e.g., carbonates). This work is leading to a better understanding of the fate and transport of actinides in the environment and of their interactions with new complexants such as phosphates and amides, leading to the design of new innovative *in situ* remediation technologies and novel separation systems. The results obtained from the calculations are an invaluable supplement to current, very expensive experimental studies of the radioactive actinides, lanthanides, and radioactive heavy transition metal elements, allowing limited experimental data to be extrapolated to many other regimes of interest.

The radioactive actinide elements Am and Cm are chemically similar to their lanthanide counterparts. Both are present in nuclear wastes and thus present a challenge for actinide separation. Organodithiophosphinates (middle figure) have great selectivity for Am over the lanthanide elements. We are using calculations to analyze the structural differences in Am-complexation relative to the lanthanides. This difference has been observed experimentally and suggested as the basis for this selectivity. Another compound with a potential application in actinide separation chemistry is the Kläui ligand, currently being studied experimentally at PNNL. Our calculations provide insight into the binding ability of various derivatives of these ligands, for example the binding of one or two Kläui ligands with uranyl (left figure), uranium and thorium, to guide the design of new and better separation agents.

Understanding of the potential reactions of uranyl (UO_2^{2+}) and carbon tetrachloride is critical for the remediation of radioactive wastes at the Hanford site. Our calculations are focused on determining the solvent phase energetics to provide the data for reliable fate and transport models for uranyl species. We have performed similar studies on the formation and solvation of uranyl halides (right figure) and various other actinide-water complexes.

Experiments performed at the University of Virginia, and our calculations, on CUO molecules in noble gas (argon and neon) matrices led to the discovery of actinide-noble gas complexes, published in Science (Li, Bursten, Andrews, Liang, *Science*, **2002**, *295*, 2243) last year. Another combined computational/experimental effort is the development of nuclear magnetic resonance (NMR) as a tool for determining the speciation of nuclear waste in the Hanford tanks Our calculations on the NMR properties of uranyl carbonate and nitrate crystals predicted record wide signals for the uranium–bonded oxygen atoms, subsequently confirmed by experiments at PNNL.

This brief summary provides insight in the research performed in this project over the past two years. The project is a collaborative effort of leading researchers in the field of computational heavy element chemistry, with 22 scientists from PNNL, Ohio State University, the Free University of Amsterdam, and various other universities.



Some molecular actinide systems studied in this project: Uranyl binding with two Kläui ligands (left), americium binding to organodithiophosphinate derivatives (middle), and uranyl fluoride molecule solvated in water (right).