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**Actinide Molecular Science:
f-Electronic Structure in Synthesis, Spectroscopy, and Computation.**

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Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The molecular chemistry of actinides has always been of prime importance at Los Alamos, providing the technical basis for process and separation chemistry related to the weapons mission of the Laboratory. The project objective was to increase our understanding of the relative roles of 5f/6d electrons in chemical bonding, the relative roles of ionic and covalent behaviors, and polar and nonpolar solvents in controlling actinide chemical reactivity. The approach combined recent advances in synthesis, spectroscopy, and electronic structure theory to understand and predict the chemical and physical properties of actinide materials at the molecular level. Significant progress toward the objectives was made during the lifetime of the project. Future work at the Laboratory will hopefully build on these results, with implications for the behavior of actinides in waste and spent-fuel repository environments, and in the design of high efficiency recovery processes.

Background and Research Objectives

The molecular science of actinide elements is critical to the Laboratory and DOE missions, and provides the technical basis for process and separations chemistry, the fate and transport of actinides in the environment, the remediation of contaminated soils and groundwaters, and the long term disposition of legacy waste materials. The behavior of actinide ions under these conditions ultimately depends on the nature of the molecular complexes formed, and their resulting electronic and molecular structure. In particular, we now recognize that planning and decision making about environmental remediation and waste management must include knowledge of the molecular-level processes that affect the transformation, release and movement of actinides in the environment.

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However, our present understanding of actinide molecular electronic structure and the nature of the chemical bond in actinide compounds and complexes is insufficient. This is in great contrast to the chemistry of light elements of the periodic table, where our understanding of molecular transformations and the theory of chemical bonding enables us to prepare new pharmaceuticals, polymers, ceramics, and other materials that are expertly tailored to our specific needs. We can exercise such control over the chemistry because we have a detailed understanding of the electronic structure and chemical reactivity of the light elements in the periodic table. Presently, we have no such detailed understanding of the actinides. A fundamental, molecular-level understanding of actinide chemistry will have clear implications for modern improvements in process and separations chemistry, the storage and disposition of legacy waste materials, the fate and transport of plutonium in the environment, and the long-term predictions of nuclear weapons aging and safety. Understanding and predicting the chemistry of actinides will be the key to solving actinide-related problems that have resulted from the past 50 years of nuclear weapons production.

The goal of this project was to increase our understanding of the manifestation of actinide electronic structure on the physical and chemical properties of actinide materials, and advance towards a more intimate understanding of electronic structure and its affect on molecular scale processes.

Importance to LANL's Science and Technology Base and National R&D Needs

A knowledge of actinide science continues to be essential to the US and central to the mission of the DOE, including national defense, energy, environmental restoration, and radioactive waste management. With nuclear weapons technology continuing to play a key role in defense policy for the foreseeable future, knowledge and expertise in the production, processing, purification, characterization, analysis, and disposal of actinide elements is essential to US national security. Moreover, cleaning up the legacy of over 50 years of nuclear weapons production will clearly depend on our ability to understand and control the chemistry of plutonium and its actinide neighbors. This legacy cleanup effort will also extend to aiding efforts to help clean up the legacy wastes in the former Soviet Union, where the magnitude of the waste problem far exceeds that in the US.

Meeting the future goals of our continuing laboratory mission will require modern chemical separation processes and modeling based on molecular level behavior in solution, and interaction of molecular species with surfaces. The environmental fate and transport of

actinides are based to a large extent on the nature of the molecular species, and the interactions of molecular species with mineral surfaces.

Many of the aging processes affecting plutonium disposition and storage are also related to molecular interactions on actinide surfaces. Thus, actinide molecular science will continue to positively impact the goals of Science Based Stockpile Stewardship by enabling advanced, environmentally benign processing, possible degradation processes, and safe disposal of plutonium. Actinide molecular science will impact the goals of Integrated Environmental Science by providing fundamental approaches to understanding actinides in the environment that will enable development of new environmental remediation and restoration programs.

Scientific Approach and Accomplishments

The project was developed with the recognition that there was a real need to shift actinide chemical studies away from traditional investigation of bulk processes to a detailed molecular-level understanding of basic processes that determine the chemical and physical behavior of actinide elements. To accomplish this goal, it was recognized that a multidisciplinary team of experts was essential. The project was therefore developed to coordinate and integrate chemical synthesis, spectroscopy, and electronic structure theory in actinide molecular science. Since the making and breaking of chemical bonds is the essence of chemical reactivity, a major focus of the effort was to better understand the nature of the chemical bond in actinide molecules and relative roles of the valence 5f and 6d atomic orbitals.

The synthetic efforts were designed to develop new methodologies to test for reactivity differences between high valent actinide ions in aqueous and nonaqueous environments. A powerful array of characterization techniques were employed in this project, including Infrared and Raman spectroscopy to study vibrational energies for understanding bond strengths; nuclear magnetic resonance for solution molecular structure and the dynamic behavior of the ligands; electronic absorption and emission spectroscopies to study the energies of electronic transitions between various 5fⁿ configurations; and X-ray diffraction and X-Ray absorption spectroscopy techniques for determination of the molecular structures, and interatomic distances within molecules. This project was also responsible for improving our understanding of the electronic structure and bonding in actinide molecular compounds through the use of relativistic hybrid density functional theory (DFT). Two different approaches to relativistic density functional theory --ECP (effective core potentials) and ADF (Amsterdam density functional) -- were used to compare the differences in structures and properties predicted by these methods.

While a variety of systems were studied [1-6], perhaps the most revealing were our studies of high oxidation state complexes composed of the well-known trans dioxo ion, shown qualitatively in Figure 1. These molecules consist of four to six ligand positions (L) that reside in an equatorial plane surrounding the actinide metal center (An), with two oxo ligands (O) above and below the plane.

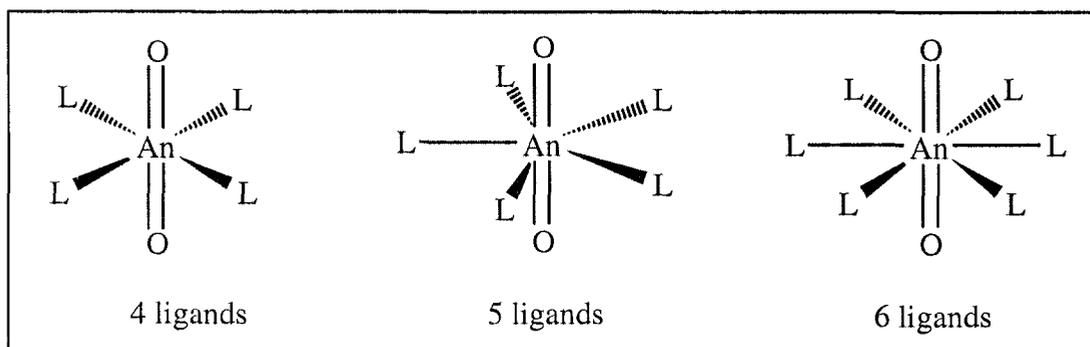


Figure 1.

Experiments were developed to influence a change in the electron donating abilities of equatorial ligands, L. In general we found that these equatorial ligand influences modify the electron density at the axial oxo ligands. In aqueous solution, polar solvents buffer the increasing negative charge at the oxo ligand, blocking chemical reactivity at the terminal oxygen atom. In contrast, in nonaqueous, nonpolar solutions, there is no capacity for the solvent to buffer the negative charge build-up at oxygen. In this case, chemical reactivity at the oxo ligand is generated. As the electron donating power of the equatorial ligand increases, the oxo group of the AnO_2^{2+} unit acts as a ligand and coordinates to an adjacent actinide ion in solution. The result is that in aqueous solution, polymer forming reactions occur in the equatorial plane, whereas in nonaqueous solution, polymer forming reactions occur through the oxo ligand itself.

For discrete molecules we were able to show that strong donor ligands (L) generally produced a weakening and lengthening of the axial $An=O$ bond, which is accompanied by a concomitant decrease in the vibrational energies of the $An=O$ bonds as probed by Raman and IR spectroscopy (see Table 1).[1-6] In a similar fashion, we could show that extremely weak donor ligands would increase the $An=O$ bond strength as revealed by a shortening of the $An=O$ bond and concomitant increase in vibrational energy. These experimental observables provided an excellent opportunity to develop new theoretical tools to understand the electronic structure of the molecules.

The new theoretical tools could calculation the interatomic bond distances and vibrational frequencies for direct comparison with experiment.

Table 1. Comparison of experimental An=O bond lengths and vibrational frequencies for AnO_2^{2+} complexes containing equatorial ligands of varying donating capabilities.

	$AnO_2(OH)_5^{2+}$	$AnO_2Cl_4^{2-}$	$AnO_2(CO_3)_3^{4-}$	$AnO_2(OH)_4^{2-}$
R(U=O), Å	1.76(1)	1.77(1)	1.80(1)	1.83(1)
R(Np=O), Å	1.75(1)	1.76(1)	1.77(1)	1.81(1)
R(Pu=O), Å	1.74(2)	1.74(1)	1.75(1)	1.77(1)
$\nu_1(U=O)$, cm^{-1}	870	833	812	786
$\nu_1(Np=O)$, cm^{-1}	856	793	802	773
$\nu_1(Pu=O)$, cm^{-1}	836	791	788	758

For both aqueous and nonaqueous chemical systems, our theoretical efforts have focused on extending the current capabilities involving density functional theory (DFT) to treat actinide-containing molecules.[7-13] Calculations using DFT approaches at the Laboratory and elsewhere have shown that this technique is capable of providing reliable predictions of molecular geometries, vibrational frequencies, and thermochemical properties at considerably less computational effort than traditional methods. The initial goal was to extend DFT capabilities to be able to treat actinide species. This required development and benchmarking of appropriate basis sets and relativistic effective core potentials for U, Np and Pu, along with further enhancement of current capabilities for geometry optimizations and calculation of vibrational frequencies to address specific issues arising for actinide molecules.[9] A portion of these activities is carried out in collaboration with Prof. Bruce Bursten of Ohio State University.

Our theoretical studies examined of aqueous $[UO_2(OH)_4]^{2-}$, $[UO_2F_4]^{2-}$, and $[UO_2Cl_4]^{2-}$ complexes which all show the existence of the traditional trans structure with a linear O=U=O bond as well as a stable cis isomer with a bent O=U=O bond.[10] The intramolecular conversion between cis and trans isomers was also studied in detail for the tetrahydroxo species.[7] Such an intermolecular interaction has been observed experimentally for $[UO_2(OH)_4]^{2-}$. Two different approaches to relativistic density functional theory --ECP (effective core potentials) and ADF (Amsterdam density functional) -- were also used to compare the differences in structures predicted by these methods. The structures and vibrational properties of AnF_6 , $[AnO_2(H_2O)_5]^{2+}$, and $[AnO_2(H_2O)_5]^+$ species were calculated for An = U, Np, and Pu.[13] Representative results for $[AnO_2(H_2O)_5]^{2+}$ are given in Table 2.

Overall the predicted bond lengths and vibrational frequencies are in relatively good agreement with EXAFS and other experimental measurements determined from solution studies.[3] Using an initial allocation of computer time on the SGI Blue Mountain supercomputer at Los Alamos, we have also completed a detailed analysis of the bonding in $\text{AnO}_2(18\text{-crown-6})^+$ species prepared in aqueous solution.[1]

The ADF approach to nuclear magnetic resonance (NMR) chemical shifts was extended to actinide complexes.[11] Examined shifts for F, Cl and O nuclei in U complexes for which there is data from the literature. The BSJ dielectric cavity model was used to compare calculated and experimental free energies for $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ hydrolysis reactions.[8,13] In addition the solvent effects on ionization potentials for the $[\text{AnO}_2(\text{H}_2\text{O})_5]^{2+}$ species (An = U, Np, Pu) were included to obtain calculated redox potentials in solution.[13] The theoretical and experimental redox potentials typically are within 0.3 - 0.5 eV.

Table 2. Comparison of calculated and experimental bond lengths and vibrational frequencies for aquo complexes of AnO_2^{2+} ions.

	$\text{UO}_2(\text{OH}_2)_5^{2+}$			$\text{NpO}_2(\text{OH}_2)_5^{2+}$			$\text{PuO}_2(\text{OH}_2)_5^{2+}$	
	calc	expt		calc	expt		calc	expt
R(U=O), Å	1.76	1.76	R(Np=O), Å	1.75	1.75	R(Pu=O), Å	1.74	1.74
R(Np-OH ₂), Å	2.51	2.42	R(Np-OH ₂), Å	2.50	2.42	R(Pu-OH ₂), Å	2.49	2.41
ν_1 , cm ⁻¹	910	870	ν_1 , cm ⁻¹	854	856	ν_1 , cm ⁻¹	805	836

As described previously, hexavalent actinide ions exist in aqueous solution as the actinyl ion, AnO_2^{2+} . This cation is remarkably stable, showing a high degree of covalency and chemical inertness with respect to the axial An=O bonds, yet a relatively low degree of covalency with respect to the other ligands in the equatorial plane (Figure 1). Our combined studies in both theory and spectroscopy have helped to elucidate the nature of the chemical bond in the linear actinyl ions. Several fundamental differences exist in the spatial extent, orbital energetics, and diffuse nature of valence and nonvalence atomic orbitals in the lighter actinides relative to transition metals that give rise to this unusual chemical bonding. For a transition metal ion in an octahedral ligand field, the metal center can use one valence s (a_{1g}), three p (t_{1u}), and two d (e_g) atomic orbitals to form six metal-ligand σ bonds, while the remaining three d (t_{2g}) orbitals can be used for π -interactions.

In contrast, we now recognize that the valence $7s$ and $7p$ orbitals of the light actinides are far too diffuse for formation of chemical bonds, and this fact accounts for many of the differences in bonding between actinide and transition metal ions.

The linear actinyl ion AnO_2^{2+} has a nominal $\sigma_g^2 \pi_g^4 \sigma_u^2 \pi_u^4$ electronic configuration, and a formal $\text{An}\equiv\text{O}$ triple bond. In the linear configuration, strong, covalent interactions are observed through the formation of $\text{An } 6d\text{-O } 2p$, and $\text{An } 5f\text{-O } 2p$ π bonds, and the underlying $6s$ and $6p$ closed shells are semi-active in σ -bonding. The use of $5f$ orbitals in π bonding only takes place at the very short bond distances seen in $\text{An}=\text{O}$ bonds (Tables 1 and 2) which span $1.74 - 1.83 \text{ \AA}$. Since the virtual $7s$ and $7p$ orbitals are essentially unavailable for bonding, equatorial M-L σ -bonding can only take place through the use of a single $6d$ or $5f$ orbital in the equatorial plane. Hence equatorial bonding is quite weak. This explains the strong covalent multiple bond character in the axial direction, and weak, relatively ionic bonding in the equatorial plane which often manifests itself in the form of complex equilibrium mixtures of molecular complexes in aqueous solutions.

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