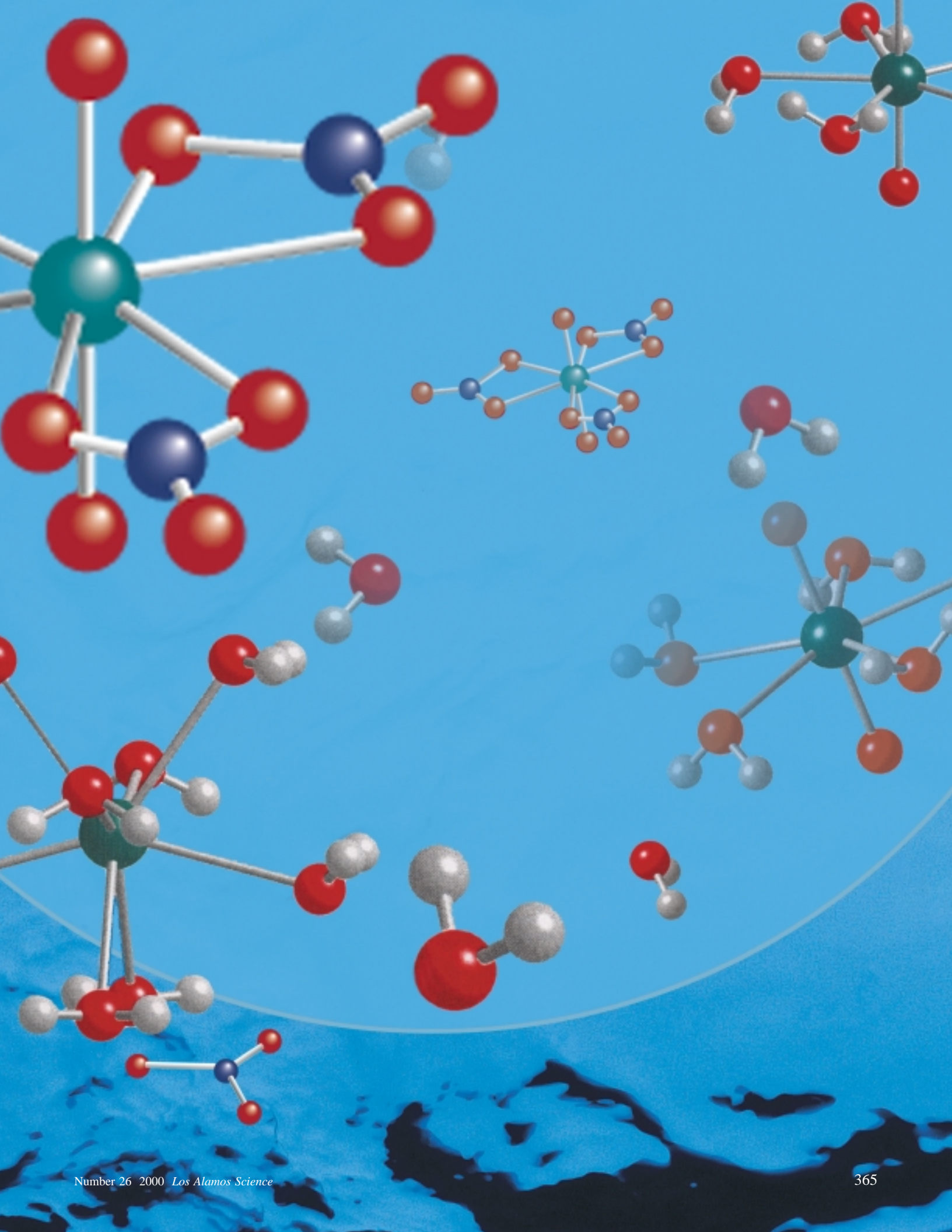# The Chemical Complexities of Plutonium

David L. Clark

Few people have ever seen plutonium, and far fewer have actually handled or manipulated it. Yet this manmade element has arguably altered the course of civilization as much as copper, bronze, iron, or steel. Within five years of its synthesis, the primary use of plutonium was for the release of nuclear energy in weapons of mass destruction, and it seemed that the new element might lead the human race to the brink of self-annihilation. But instead, plutonium has become a stabilizing agent in global politics, forcing the human race to govern itself without resorting to nuclear war. Never before has a simple chemical element had such a profound impact on the consciousness of mankind.

Plutonium has had a similarly humbling impact in the more circumscribed arena of science. Incredibly, it displays physicochemical behaviors that are among the most complex of any element in the periodic table. The pure element exhibits seven distinct crystal phases, is highly reactive, and is known to form compounds, complexes, or alloys with virtually every other element. Molten plutonium is highly corrosive and will slowly react with its container, causing difficulties for handling. When elemental plutonium reacts to give up its valence electrons, it can form a wide variety of positively charged ions with the ability to form up to twelve chemical bonds to other ions or molecules in solution. The element can exhibit five oxidation states, and under certain chemical conditions, four different oxidation states can be present in appreciable amounts simultaneously! No other element displays such a complex chemistry.

Figure 1. Chemical Periodicity and the Periodic Table
The modern periodic table derives principally from the work of Dimitri Mendeleev, who in 1869 enunciated a "periodic law" that the properties of the elements are a periodic function of their atomic weights and arranged the 65 known elements in a "periodic table." Fundamentally, every column in the main body of the table is a group of elements that display similar chemical and physical behavior. Similar properties are therefore exhibited by elements with widely different masses. Chemical periodicity is central to the study of chemistry, and no other generalization comes close to its ability to systematize and rationalize known chemical facts. With the development of atomic theory and an understanding of the electronic structure of atoms, chemical periodicity and the periodic table now find their natural explanation in the electronic structure of atoms. Moving from left to right along any row, the elements are arranged sequentially according to nuclear charge (the atomic number). Electrons balance that charge, hence each successive element has one more electron in its configuration. The electron configuration, or distribution of electrons among atomic orbitals, may be determined by application of the Pauli principle (paired spin in the same orbital) and the Aufbau principle (which outlines the order of filling electrons into shells of orbitals s, p, d, f, etc.) such that in a given atom, no two electrons may have all four quantum numbers identical.

The chemical complexity is a double-edged sword. Plutonium chemistry is rich, varied, and fascinating, but it can also be difficult to control. Its behavior 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 between light atoms is such that we can undertake complex, multistep processes to synthesize 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 comprehension of plutonium. Only recently have we at Los Alamos been able to gain new insight into the molecular- or atomic-scale properties of the element. It is obvious, however, that a fundamental grasp of plutonium chemistry will have clear implications for modern improvements in process and separations chemistry, the storage and disposition of legacy 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 plutonium will be the key to solving plutonium-related problems that have resulted from 50 years of nuclear weapons production.

This article will therefore present plutonium chemistry from a basic, molecular-level perspective. It will start with a discussion of 5f electrons, which define the actinide series and are responsible for the chemical properties of the series. It will end with a summary

Table I. Ground-State Valence Shell Configurations of Lanthanum, the Lanthanides, Actinium, and the Actinides

Lanthanide		Configuration			Actinide		Configuration		
La	lanthanum		$5d^1$	$6s^2$	Ac	actinium		$6d^1$	$7s^2$
Ce	cerium	$4f^1$	$5d^1$	$6s^2$	Th	thorium		$6d$	$7s^2$
Pr	praseodymium	$4f^3$		$6s^2$	Pa	protactinium	$5f^2$	$6d^1$	$7s^2$
Nd	neodymium	$4f^4$		$6s^2$	U	uranium	$5f^3$	$6d^1$	$7s^2$
Pm	promethium	$4f^5$		$6s^2$	Np	neptunium	$5f^4$	$6d^1$	$7s^2$
Sm	samarium	$4f^6$		$6s^2$	Pu	plutonium	$5f^6$		$7s^2$
Eu	europium	$4f^7$		$6s^2$	Am	americium	$5f^7$		$7s^2$
Gd	gadolinium	$4f^7$	$5d^1$	$6s^2$	Cm	curium	$5f^7$	$6d^1$	$7s^2$
Tb	terbium	$4f^9$		$6s^2$	Bk	berkelium	$5f^9$		$7s^2$
Dy	dysprosium	$4f^{10}$		$6s^2$	Cf	californium	$5f^{10}$		$7s^2$
Ho	holmium	$4f^{11}$		$6s^2$	Es	einsteinium	$5f^{11}$		$7s^2$
Er	erbium	$4f^{12}$		$6s^2$	Fm	fermium	$5f^{12}$		$7s^2$
Tm	thulium	$4f^{13}$		$6s^2$	Md	mendelevium	$5f^{13}$		$7s^2$
Yb	ytterbium	$4f^{14}$		$6s^2$	No	nobelium	$5f^{14}$		$7s^2$
Lu	lutetium	$4f^{14}$	$5d^1$	$6s^2$	Lr	lawrencium	$5f^{14}$	$6d^1$	$7s^2$

of some of our most recent structural studies of plutonium carbonate complexes, studies that are relevant for understanding the behavior of plutonium ions in natural groundwaters. Along the way, it will also bring to light some fundamental chemistry of the most fascinating element known.

The Actinide Elements

Plutonium is one of the actinide elements, those fourteen elements with atomic numbers 90 to 103 that follow actinium in the periodic table. The table itself is shown in Figure 1. The figure caption also provides some background material on chemical periodicity and electronic structure. The actinide elements occupy their unique position at the bottom of the periodic table because they contain 5f electrons in their valence shell. Because the valence electrons are the ones that ultimately dictate chemical behavior, we would expect the actinides to be chemically similar to the only other elements that have f electrons in their valence shell—the lanthanides. Those are the fourteen elements with atomic numbers 58 through 71, which sit directly above the actinides in the periodic table and have 4f valence electrons.

Chemically, the lanthanides are characterized by relatively homogeneous behavior (especially in aqueous solution). All members tend to form trivalent ions and form similar chemical compounds. In general, the chemical and physical differences between adjacent elements in the series are small. If placed in the main body of the periodic table (which is organized according to similarities in chemical traits), all fourteen would occupy the single position set aside for the element lanthanum (number 57).

The chemical homogeneity of the lanthanides results from the relatively small radial extension of the 4f valence orbitals, which are buried beneath the spatially more extended 5d and 6s orbitals. Since 4f electrons are buried so deep within the atom, they have little opportunity to participate in chemical bonding, hence the addition of another f electron to the valence shell has little effect on the overall bonding character or reactivity of the element. Thus, all of the lanthanides tend to behave chemically the same.

To a large degree, the actinides exhibit this same tendency toward homogeneous chemical behavior. The chemistry of plutonium, for example, is similar to the chemistry of uranium and neptunium. Lanthanide-like behavior, in fact, was the main prediction of Glenn Seaborg's "actinide concept" (Seaborg 1984). Seaborg asserted that the 5f subshell begins to fill after actinium, and so the electron configurations of the actinides and lanthanides should be completely analogous, and the two series should behave in a chemically homologous manner. (See the box "The Actinide Concept" on page 368.)

The 5f orbitals are very close in energy to the 6d's. In the early part of the actinide series, electrons find it relatively easy to switch between 5f and 6d configurations, and some of the "light" actinides—actinium through americium—exhibit traits that are reminiscent of elements that have at least one unpaired d electron in their valence shell—namely the transition elements.

The transition elements, also called the transition metals, comprise the d-block elements in columns 3 through 11 of the periodic table. They are the classical hard metals, such as iron,

The Actinide Concept

In 1941, the actinide elements from thorium to plutonium were incorrectly placed in the periodic table under the 5d elements from hafnium to osmium.

In 1939, only three elements were known to be heavier than actinium: thorium, protactinium, and uranium. These elements were assumed to be d transition metals and were placed in the periodic table under hafnium, tantalum, and tungsten, respectively. By 1940, McMillan and Abelson had bombarded uranium atoms with slow neutrons and successfully identified atoms of element 93, which they named neptunium after the planet Neptune. This rapidly set the stage for the discovery of the next succeeding element, plutonium (Seaborg, McMillan, Kennedy, and Wahl 1940), named after the next planet away from the Sun, Pluto. The newly discovered elements were presumed to fit comfortably in the periodic table under rhenium and osmium, respectively, as seen in the 1941 table.

However, subsequent tracer chemical experiments showed that neptunium and plutonium were closer in their chemical properties to uranium than to their presumed homologues, rhenium and osmium. Spectroscopic evidence also indicated that the new elements were not typical d transition elements but had f electrons in their valence shell. Thus, several researchers, including McMillan and Wahl, and Zachariasen at Los Alamos, suggested that these elements might be part of a second inner transition series in which the 5f electron subshell was being filled. It was not clear, however, where the new series would begin. McMillian had proposed a "uraninide series" that started with neptunium, but attempts to isolate

titanium, or tungsten. Many transition elements display a relatively complex chemical behavior that arises because their valence d orbitals extend out to the boundary of the atoms or ions. Electrons in those orbitals are relatively exposed, more accessible for chemical bonding, and are influenced greatly by the surrounding chemical environment. Chemical properties vary significantly between adjacent elements, since the specific chemistry of a transition element is tied strongly to the number of d electrons in its valence shell.

The light actinides show some transition-like behavior. They exhibit higher oxidation states (up to oxidation state VII) and as a subgroup display more chemical variety than the more

lanthanide-like "heavy" actinides from curium through lawrencium. This behavioral split between light and heavy actinides is also evident in the solid-state properties of the series. (See the article "Plutonium Condensed-Matter Physics" on page 90.)

The division between light and heavy actinides is further evident in the electronic configurations of the individual members of the series. As seen in Table I (Katz et al. 1986), the ground-state (or lowest-energy) configuration of the thorium atom is $6d^27s^2$, indicating that the 6d orbital is actually lower in energy than the 5f orbital in the ground-state neutral atom. As one progresses through the series, the orbital energies invert, with the 5f's

becoming lower in energy than the 6d's, and the gap between the 5f and 6d orbitals begins to widen. It is still energetically favorable to keep an electron in a d orbital, however, and so the configurations of protactinium through neptunium are all $5f^n6d^17s^2$ ($n = 2$ to 4). The presence of the d electron and the competition between the $5f^n7s^2$ and $5f^{n-1}6d^17s^2$ electronic configurations means that the light actinides tend to supply more bonding electrons in chemical reactions and thus exhibit a more complex chemistry akin to that seen for transition elements.

In the latter part of the actinide series, the gap between the 5f and 6d orbitals is wide enough that the ground-state configuration stabilizes[1] to $5f^n7s^2$,

elements with atomic numbers 95 and 96 based on assumed similarities to uranium were unsuccessful. Both Wahl and Zachariasen had proposed a thoride series that started with protactinium.

In 1944, Seaborg proposed that the series started with thorium and that all of the elements heavier than actinium constituted an "actinide" series similar to the lanthanides (see the 1945 table). Because the 5f shell began filling in the same relative position as the 4f shell, the electronic configuration of elements in the two series would be similar. Guided by the hypothesis that elements 95 and 96 were homologues of europium and gadolinium, new experiments were designed, and the elements were uniquely separated from all others. The new elements were subsequently named americium and curium.

Seaborg's "actinide concept" thus played a major role in the discovery of the transplutonium elements. It provided the framework that supported synthesis, isolation, and identification of the succeeding actinide elements berkelium through lawrencium and beyond to the element with atomic number 118! But as research has progressed in the study of the actinide elements, it has become clear that the 5f series has a unique chemistry that is distinct from that of the 4f series. One of the focal points of study in actinide research has been to better define the scope and limitations of the actinide concept.

In 1945, the actinide elements from thorium through curium were correctly placed under the 4f elements in the periodic table. The table reflects the now famous "actinide concept."

where $n = 6$ to 14. This is exactly analogous to the standard $4f^n6s^2$ configuration of the lanthanides, and like the lanthanides, the chemistry of the heavy actinides exhibits fewer oxidation states and simpler behavior. The reason for the differences in the light actinide elements relative to the light lanthanide elements has to do with the greater radial extension of 5f orbitals compared with 4f orbitals, and with relativistic effects that are increasingly important for heavy elements.

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[1]An exception is curium, which has electronic configuration $5f^76d^17s^2$, owing to the enhanced stability of a partially filled 5f shell. The f subshell can accommodate seven unpaired electrons, and it is energetically favorable to place the eighth in the d orbital rather than create an electron pair.

Shape and Radial Extension of f Orbitals

The spatial distribution of the electron density in an atom is often described by means of hydrogen-like atomic orbitals, which are obtained by solving the one-electron Schrödinger equation in a spherically symmetric Coulomb potential. The assumption of spherical symmetry allows the electron wave function to be mathematically separated into radial and angular parts.

The angular part of the wave function is independent of distance from the nucleus, and it determines the shape of the electron cloud. The shape varies depending on the type of orbital (s, p, d, f) and hence the orbital's orientation

in space. The orbital shapes of the s, p, and d atomic orbitals are well known and can be found in most undergraduate textbooks, but the shapes of the f orbitals are not commonly discussed. These are illustrated qualitatively in Figure 2. It is seen that the individual f orbitals are nonspherical and lie within specific planes and along specific axes. Thus, bonding to f electrons is often considered to be highly directional.

The radial part of the wave function depends only on the distance of an electron from the nucleus, often displayed as a probability distribution. A radial probability distribution is a plot of the statistical probability that a particular electron could be found as a function of distance from the center of
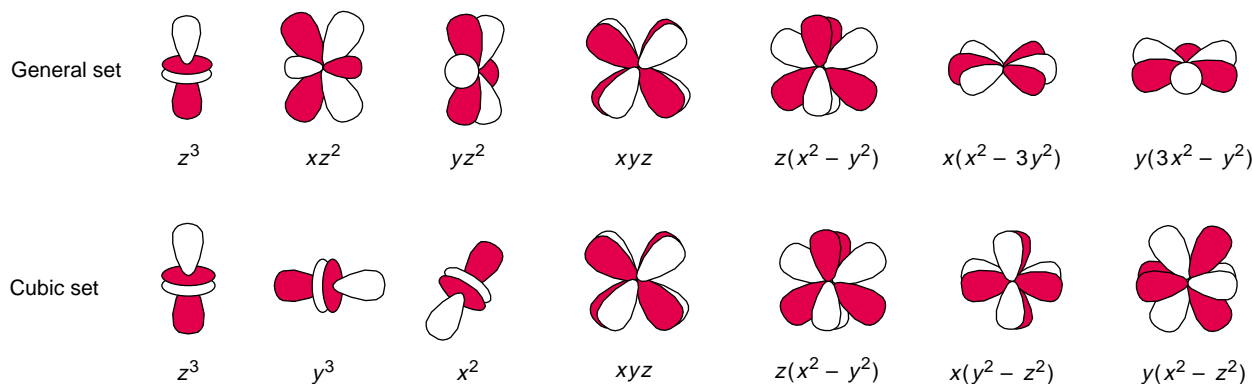
Figure 2. Angular Properties of f Orbitals
The seven f orbitals that arise from solving the Schrödinger equation for a hydrogen-like atom have specific shapes, shown above along with their simplified polynomial designations. The general set of orbitals (top) is useful for understanding molecular complexes or solid structures that contain a single high-order axis of symmetry (where one often finds doubly degenerate orbitals). However, this set is not very useful for solving problems in cubic symmetry because it is not easy to see how these orbitals can be combined to give triply degenerate sets that span the space of cubic point groups. Instead, a cubic set (bottom) can be derived from linear combinations of the general set of orbitals.

the nucleus. In Figure 3, the radial probability distributions of the outer valence electrons for the samarium ion Sm^{3+} (the most common charge of samarium in solution) are plotted and compared with the corresponding radial distributions of Pu^{3+}. These distributions were derived from rigorous, state-of-the-art relativistic calculations performed by Los Alamos researchers (P. Jeffery Hay, unpublished results).

For the samarium ion, the region of space occupied by the 4f electrons is buried deep within the atom. The calculations illustrate in a very qualitative fashion why the 4f electrons of lanthanide elements do not participate in chemical bonding to any great extent; they simply do not extend out far enough from the nucleus to participate in bonding interactions.

The 5f electron density of the plutonium ion, although also concentrated within the principal parts of the valence electron distributions, shows a significant tail. The broad extent of this tail is due in part to relativistic effects. The root-mean-square speed of an orbiting electron scales with the nuclear charge, and electrons in heavy elements (especially the inner s and p electrons in the core of the atom) can have speeds that approach an appreciable fraction of the speed of light. According to the theory of relativity, such electrons have an effective mass that is heavier than that of a nonrelativistic electron. As a result, the core s and p electrons in heavier elements contract closer to the nucleus compared with those in lighter elements. These contracted s and p electrons are now more effective at shielding some of the nuclear charge from electrons in outer d and f orbitals. Those electrons move farther out from the nucleus. This contraction/expansion influences even the valence electrons.

When relativistic effects are taken into account for Pu^{3+} (the solid curves in Figure 3), we see that the 5f electron density extends well into the region occupied by the 6d electrons. This greater extension from the nucleus is perhaps the major difference between the light actinides and the light lanthanides, for it allows the 5f electrons to participate (in some cases) in covalent bonding interactions.

We can also infer what happens to the f orbitals as more nuclear charge is added, that is, as we move from left to right in the periodic table across a 4f or 5f subshell. Because the 5f orbitals are not spherically symmetric, the nuclear charge is not completely screened by the additional electron. Each successive element, in effect, exhibits a slightly greater charge, with the result that the outer valence orbitals contract. Thus, the ionic radius should gradually decrease as one moves through the actinide series. Such a contraction is observed for the lanthanides and is known as the lanthanide contraction. It amounts to approximately 0.2 angstrom over the entire series, or on average about 0.014 angstrom between elements.

Following the development of Seaborg's actinide concept, it was long thought that the actinides should exhibit a similar contraction. Up until a few years ago, only indirect evidence supported this conjecture (Seth et al. 1995), but we have recently been able to measure the actinide contraction directly. It is approximately 0.04 angstrom from uranium to plutonium, or about 0.02 angstrom between elements. This observation of the actinide contraction is perhaps the most famous example of the actinide concept.

Chemistry of Plutonium in Aqueous Solution

The chemistry of plutonium is important for many reasons, including the processing and purification of plutonium for preparation of the pure metal, for managing our nation's nuclear wastes, for predicting its behavior in the environment, and for predicting the effects of aging on and the safety of nuclear weapons. For example, as discussed in the article "The Chemical Interactions of Actinides in the Environment" beginning on page 392, if plutonium is accidentally released into the environment, its chemical properties will determine to a large extent whether its transport will be retarded by precipitation from solution or sorption to a mineral surface or whether it will migrate freely as a soluble molecular species. During process chemical operations, we control the chemistry in concentrated nitric acid solutions or molten halide salts to obtain the desired oxidation state for further chemical manipulation or the desired chemical purity for manufacturing purposes. (See the article "A Vision for Environmentally Conscious Plutonium Processing" on page 436.) These rather "forced" chemical conditions were historically required for chemical processing because of the complexity of plutonium chemistry.

Because of its electropositive nature, a plutonium atom in aqueous solution will readily lose between three and seven of its outer electrons to form positively charged cations in five formal oxidation states, Pu(III), Pu(IV), Pu(V), Pu(VI), and Pu(VII). (The roman numeral in parentheses refers to the "formal" charge exhibited by the central positive ion.[2]) Much of the solution chemical behavior of plutonium

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[2]Formal charges can be assigned to each element or ion in a compound. For example, both oxygen, O^{2-}, and the carbonate ion, CO_3^{2-}, are assigned a formal charge of –2 in any compound. Thus, $Pu(CO_3)_5^{6-}$ is a Pu(IV) species, since the plutonium ion has a formal charge of +4, and PuO_2^+ is a Pu(V) species, since the plutonium ion has a formal charge of +5.
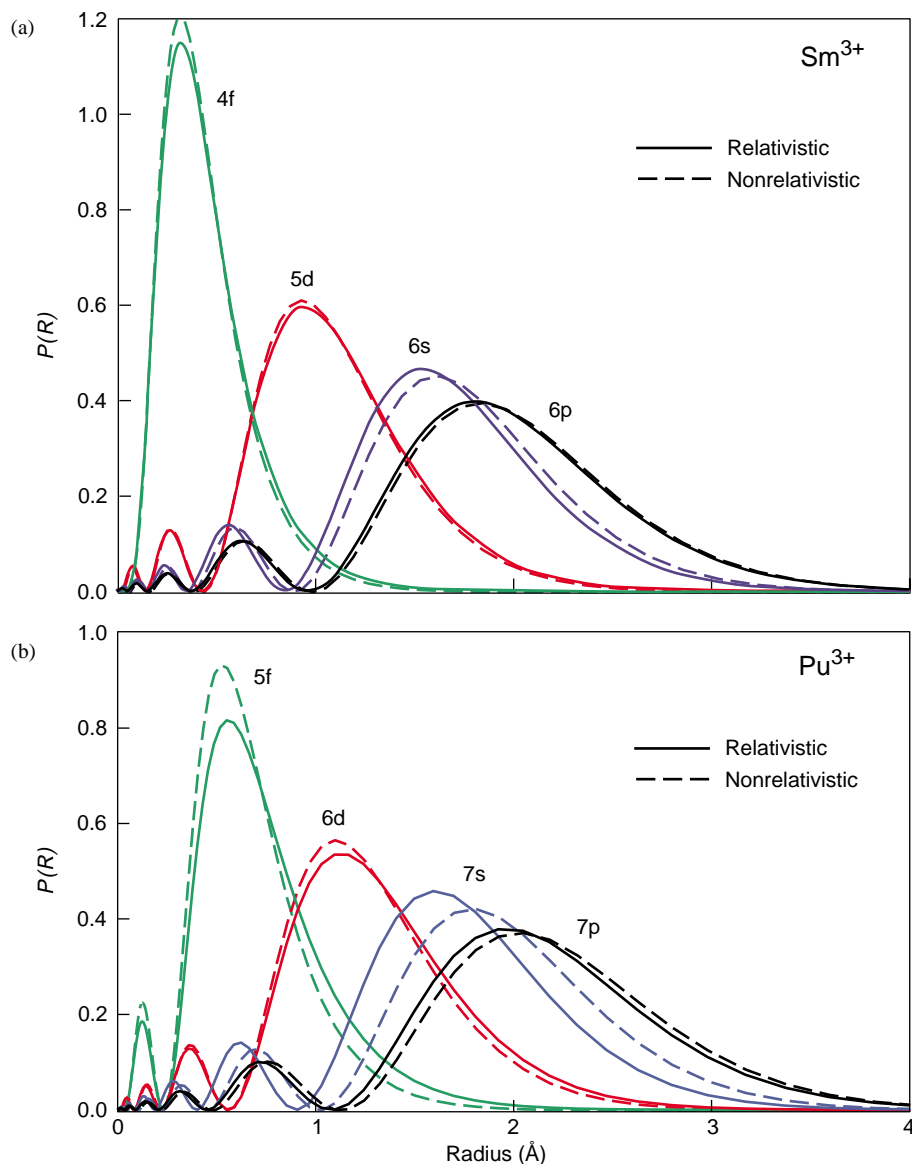

Figure 3. Radial Extent of 4f and 5f Valence Electrons
(a) The radial probability $P(R) = 4\pi r^2 R_{nl}^2$ of finding an electron at a distance r from the nucleus is shown for the valence 4f, 5d, 6s, and 6p orbitals of Sm^{3+}. The solid lines show the probabilities after the inclusion of relativistic effects. The relativistic corrections are of minor importance for 4f elements, and most of the 4f electron density lies close to the nucleus. Bonding to the Sm^{3+} ion takes place by means of electrons occupying the 5d, 6s, or 6p orbitals, and so 4f electrons only marginally influence the chemistry. (b) The analogous figure for Pu^{3+} shows that the tail of the relativistically correct 5f electron distribution extends out much farther from the nucleus than a 4f electron does. In addition, the valence 7s and 7p electrons contract closer to the nucleus when relativistic effects are taken into account. The net effect is that the 5f electrons of the actinides can much more readily participate in bonding than the 4f electrons of the lanthanides. (Calculations courtesy of P. Jeffrey Hay.)
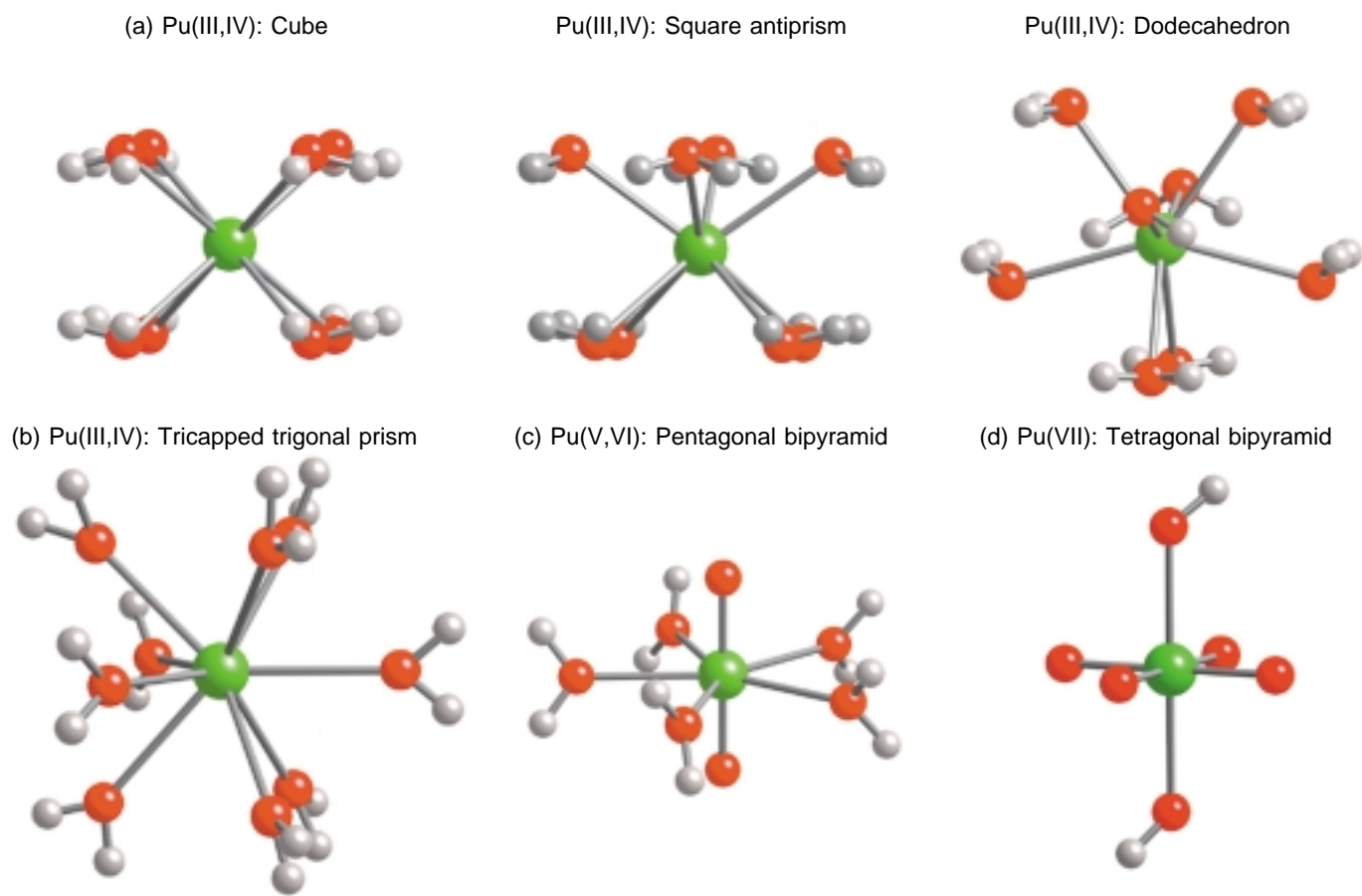
(a) Pu(III,IV): Cube

Pu(III,IV): Square antiprism

Pu(III,IV): Dodecahedron

(b) Pu(III,IV): Tricapped trigonal prism

(c) Pu(V,VI): Pentagonal bipyramid

(d) Pu(VII): Tetragonal bipyramid

Figure 4. Possible Molecular Geometries for the Plutonium Aquo Ions

(a) Three common geometric arrangements are possible for eight water ligands around a central Pu(III) or Pu(IV) ion: a cube, a square antiprism, and a dodecahedron. A cubic arrangement of ligands is rather rare in molecular chemistry because a simple twist of one square face by 45 degrees gives the square antiprism, which is known to minimize ligand–ligand repulsive forces. The dodecahedron can be viewed as two interpenetrating tetrahedra, one flattened and one elongated with respect to the cube. (b) With nine water ligands, Pu(III,IV) can form the tricapped trigonal prism. Six water molecules are arranged on the top and bottom planes of the vertically oriented right prism. Each of the three molecules in the equatorial plane are centered about one face of the prism. (c) Both the Pu(V) and Pu(VI) aquo ions exist as actinyl ions. Two oxygen atoms form strong covalent bonds with the plutonium to form a linear plutonyl unit, O=Pu=O. All the water molecules bond in the equatorial plane. The actinyl aquo ions typically have five water ligands, and the common geometry is a pentagonal bipyramid. (d) Plutonium VII can form under extreme oxidizing conditions. The $PuO_4(OH)_2^{3-}$ molecule shown here has a tetragonal bipyramid arrangement; four oxygen atoms form double bonds in the equatorial plane, while the two OH ligands bond along the axis of the bipyramid.

Hydrogen

Oxygen

Plutonium

depends on the nature of its oxidation state. The metal ion in each of those states can form a variety of molecular complexes, each with a characteristic solubility and chemical reactivity. In addition, we shall see later that plutonium is the only element in the periodic table that can have appreciable amounts of four different oxidation states existing in aqueous acidic solutions simultaneously.

Under noncomplexing acid conditions (such as perchloric or triflic acid), both Pu(III) and Pu(IV) exist as the simple hydrated (or aquo) ions. Water molecules are coordinated around the metal ion, resulting in the molecular cations $Pu(H_2O)_n^{3+}$ and $Pu(H_2O)_n^{4+}$, where n can vary depending on the concentration of other ions (the ionic strength). Common values for n are 8, 9, and 10. Aquo ions with eight ligands

are shown in Figure 4(a), while a structure with nine ligands is shown in Figure 4(b).

Both Pu(V) and Pu(VI), have such large positive charges that in aqueous solution they readily strip oxygen atoms from water molecules to form a unique class of *trans*-dioxo cations, PuO_2^+ or PuO_2^{2+}. The plutonium atom is aligned between the two oxygen atoms in a linear structure, O=Pu=O, known as an
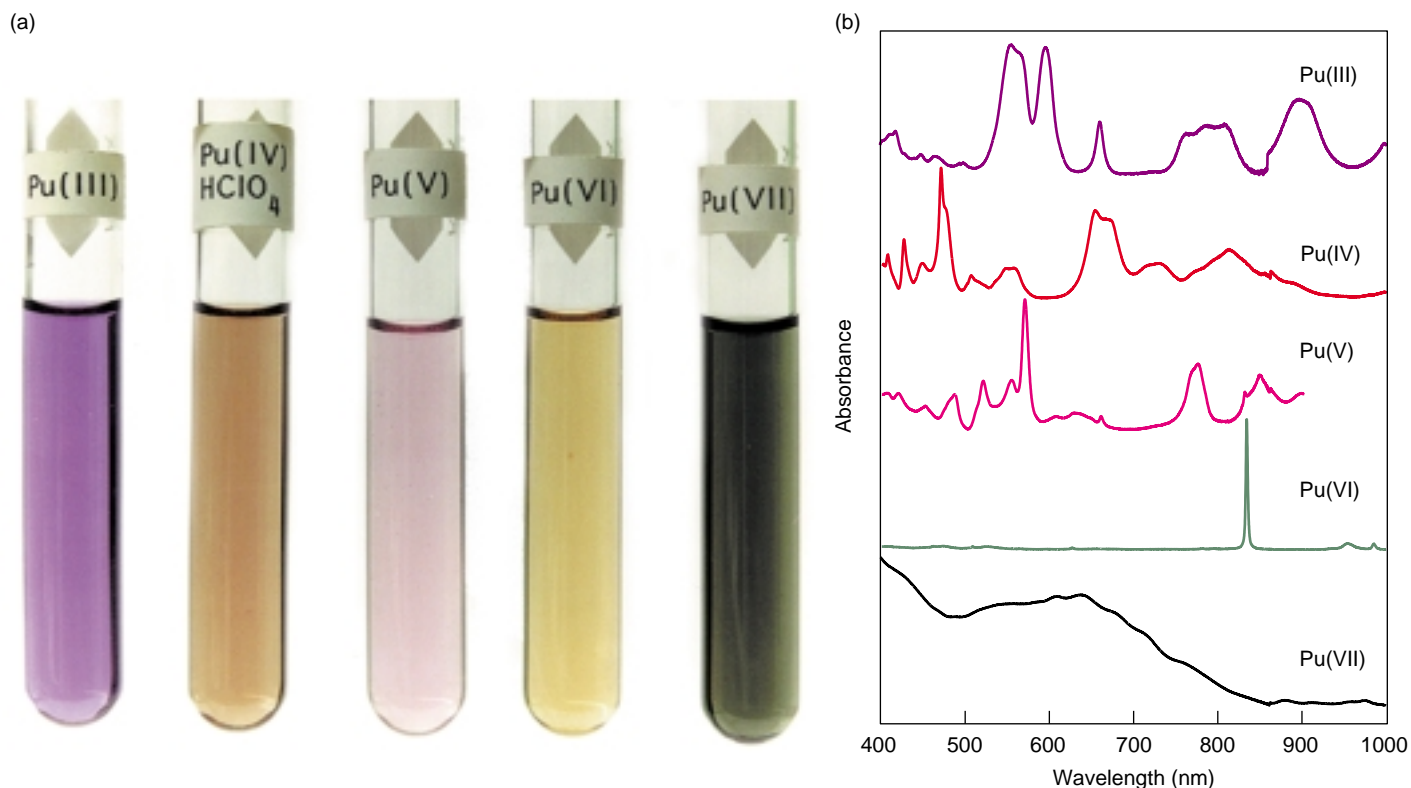
(a)

(b)

Figure 5. The Color of Plutonium
(a) Each of the plutonium oxidation states has a characteristic color in solution. The colors are specific and depend on the type and number of ligands. The photograph shows the aquo ions in 1 M perchlorate ($HClO_4$) solution. (Pu(V) is in $NaClO_4$ at pH = 7, Pu(VII) is in 2.5 M NaOH.) (b) The electronic absorption spectra of the plutonium aquo ions are compared here. (The relative absorbance values are not to scale.) The solution conditions are the same as in (a). Pu(VII) is a relatively rare oxidation state, but it can be formed under alkaline solution conditions. Each oxidation state can be identified by its characteristic absorption fingerprint.

actinyl[3], and all ligands (molecules or ions that donate at least one electron pair to a central metal ion) bond in the equatorial plane of this structure. The actinyl geometry is ubiquitous for the V or VI complexes of uranium, neptunium, plutonium, and americium. As discussed later, this geometry is known to be a result of a balance between valence 5f, 6d, and "shallow core" 6p electron interactions within the framework of the linear actinyl ion (O=An=O) bonds, where An represents either U, Np, Pu, or Am.

The Pu(V) and Pu(VI) aquo ions $PuO_2(H_2O)_n^+$ and $PuO_2(H_2O)_n^{2+}$ commonly have five water molecules in the

equatorial plane, as seen in Figure 4(c). Determining the structures of the plutonium aquo ions required a significant, multidisciplinary effort by many Los Alamos researchers. (See the articles "Characterizing the Plutonium Aquo Ions by XAFS Spectroscopy" on page 418 and "Computational Studies of Actinide Chemistry" on page 382.)

The oxidation state of plutonium affects its chemical behavior in solution. For example, Pu(III) and Pu(IV) are, in general, relatively insoluble, whereas Pu(V) and Pu(VI) are, in general, more soluble. These different properties are why knowledge of the oxidation state under environmental conditions is critically important for the long-term performance of underground nuclear waste repositories such as the Waste Isolation Pilot Plant (WIPP) in

New Mexico and the Yucca Mountain Site in Nevada (Hobart 1990). In oxidation state IV, plutonium strongly hydrolyzes (reacts with water), often to form light green "sols," or colloidal solids that behave much like a solution. These intrinsic colloids eventually age, and the solubility decreases over time. These intrinsic colloids can also attach themselves to natural mineral colloids that have important consequences for the migration of plutonium in the natural environment. The importance of colloid-facilitated transport of plutonium in groundwater at the Nevada Test Site in Nevada was recently underscored when plutonium from underground weapons testing were shown to have migrated just over a mile from the location of an underground test performed over 20 years ago (Kersting et al.

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[3]Actinyl is a general term that can refer to the linear *trans*-dioxo cations O=U=O (also called uranyl), O=Np=O (neptunyl), O=Pu=O (plutonyl), or O=Am=O (americyl).

1999). Colloid-facilitated migration is discussed in the article by McGraw. In contrast, Pu(V) hydrolyses the least of all the oxidation states. At trace (nanomolar) concentrations in near-neutral pH solutions, Pu(V) is both reasonably stable and is the dominant oxidation state under many natural environmental conditions, such as in seawater or many groundwaters (Hobart 1990).

Each of the various plutonium oxidation states has a characteristic color in solution and exhibits a distinctive spectral "fingerprint" in its electronic absorption spectrum, as seen in Figure 5. The electronic spectra are the result of the absorption of visible and near-infrared light by the plutonium molecules in the different solutions. The exact frequency of the photons absorbed by a particular plutonium ion corresponds to the energy required to promote an electron from one f electron energy state to another in that particular oxidation state. Thus, the electronic absorption spectrum is a unique diagnostic research tool for identification of the plutonium oxidation state.

The energy required to add or subtract electrons from an ion (and therefore change from one oxidation state to another) is known as the reduction/oxidation (redox) potential. It is normally expressed in volts. For most elements in the periodic table, the redox potentials between oxidation states are sufficiently different that one state is usually favored over all the others. Plutonium is unique among all elements in that the redox potentials that couple the four common oxidation states in acid solution (III, IV, V, and VI) are all remarkably similar, and approximately equal to 1.0 volt (Katz et al. 1986), as seen in Figure 6(a). The plutonium cations therefore have a marked tendency to react with ions of their own kind by means of a *disproportionation* reaction, in which two interacting ions in the same oxidation state are simultaneously oxidized and reduced to higher and lower states. Conversely, under some conditions, two plutonium ions of

different oxidation states can react by means of a *reproportionation* reaction. The two ions are simultaneously oxidized and reduced to form two ions of the same oxidation state. This redistribution of oxidation states is a messy situation, and one that makes aqueous plutonium solution chemistry particularly complex and fascinating.

To further complicate matters, all plutonium isotopes are radioactive. One milligram of plutonium-239 (radioactive half-life of 2.4×10^4 years) emits about 10^6 alpha particles per second, and the radioactive decay is constantly adding energy to any plutonium solution. The radiolytic decomposition of water can generate some rather potent redox agents, including short-lived radicals •H, •OH, and •O, and radical recombination products such as H_2, O_2, and H_2O_2. The result is that radiolysis tends to reduce Pu(VI) and Pu(V) to the Pu(IV) and Pu(III) states.

Interestingly, the reactions involving the making and breaking of Pu=O bonds in the *trans*-dioxo cations of Pu(V) and Pu(VI) are kinetically slow processes. Therefore, it is possible for four oxidation states (III through VI) to coexist with one another in appreciable concentrations in the same solution under certain chemical conditions.

At present, we understand enough about the kinetics of those reactions to predict how rapidly the redox equilibria are reached (Newton 1975). The rate constants and H^+ dependencies for the equilibrium reactions are all known, and if one considers the forward and reverse rates, the rates of disproportionation and reproportionation reactions can be calculated. Figure 6(b) outlines the calculations, Figure 6(c) plots the equilibrium rate constants, and Figure 6(d) shows graphs of the disproportionation of Pu(IV) in a solution of 1 M $NaClO_4$. Appreciable concentrations of the other oxidation states appear after relatively short periods of time, and the rates depend on the total plutonium concentration. At equilibrium, a plutonium solution of approximately pH 1 contains signifi-

cant concentrations of Pu(III), Pu(IV), Pu(V), and Pu(VI).

Clearly, part of the experimental problem faced by plutonium chemists is in obtaining stable, oxidation-state-pure solutions. Years of experience have enabled plutonium scientists to develop electrochemical techniques to prepare such plutonium solutions, which are then used in the synthesis and characterization of molecular complexes (Newton et al. 1986).

The Complexation and Coordination Chemistry

The molecular science of plutonium is critical to the Laboratory and the Department of Energy (DOE) missions because it provides the technical basis for process and separations chemistry, the fate and transport of plutonium in the environment, the remediation of contaminated soils, and the long-term disposition of legacy materials. The behavior of plutonium under these conditions ultimately depends on the nature of the molecular complexes formed and their resulting electronic and molecular structure. For process chemistry, we care about the chemical behavior of plutonium in strong acids with abundant nitrate, chloride, fluoride, or water ligands. For environmental behavior, we care about the interaction of plutonium with the ligands found in natural waters—carbonate, phosphate, sulfate, and silicate—and with natural organic matter such as humic and fulvic acids. For legacy wastes such as those in the aging waste tanks at the DOE Hanford Site in Washington or Savannah River Site in South Carolina, we care about how plutonium interacts with hydroxides, aluminates, organics, and a myriad other chemical agents formed under the highly alkaline conditions of the tanks.
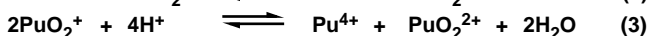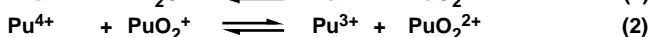
As an example, consider that the molecular behavior of plutonium in nitric acid allows for its chemical purification. In 7 molar nitric acid solution, Pu(IV) exists as a complex

Figure 6. Complications of Plutonium Chemistry
(a) Each of the redox potential differences that separate the primary oxidation states is approximately 1 V. Thus, it is easy for plutonium to change its oxidation state. The figure shows the redox potential differences for the plutonium aquo ions in 1-M perchloric acid, as well as the potential difference between the plutonium aquo ions and the pure metal, Pu(0).
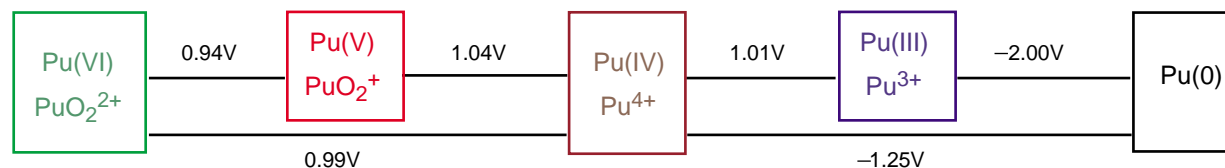

(b) The equations governing the redox reactions for plutonium ions under acidic conditions are

$$2Pu^{4+} + 2H_2O \rightleftharpoons Pu^{3+} + PuO_2^+ + 4H^+ \qquad (1)$$
$$Pu^{4+} + PuO_2^+ \rightleftharpoons Pu^{3+} + PuO_2^{2+} \qquad (2)$$
$$2PuO_2^+ + 4H^+ \rightleftharpoons Pu^{4+} + PuO_2^{2+} + 2H_2O \qquad (3)$$

Note that only two of these reactions are independent, as Equation (3) can be derived from Equations (1) and (2). The redox potentials in 1 M perchlorate solutions have been determined with high precision, and they can be used in calculating the equilibrium constants of these reactions as a function of pH if hydrolysis of Pu(IV) is taken into account. Because the hydrogen ion appears in Equations (1) and (3), the equilibrium constants for these reactions are highly dependent on pH.

(c) The equilibrium constants, corrected for hydrolysis, were used to calculate the equilibrium distribution curves for plutonium ions in 1 M $NaClO_4$ solution (assuming an average oxidation state of IV). In the region between pH 1 and 2, the values of the curves are less certain because the second hydrolysis constant for Pu(IV) has been omitted. (Calculations courtesy of T.W. Newton.)

(d) The graph shows the disproportionation of Pu(IV) in 1 M $NaClO_4$, pH = 1, at 25°C as a function of time (units of molar-seconds). Dividing by the total concentration gives the time required to reach any particular distribution. For an initial Pu(IV) concentration of 0.002 M, half of the IV species will be gone in 10,000 s, or about 3 h.
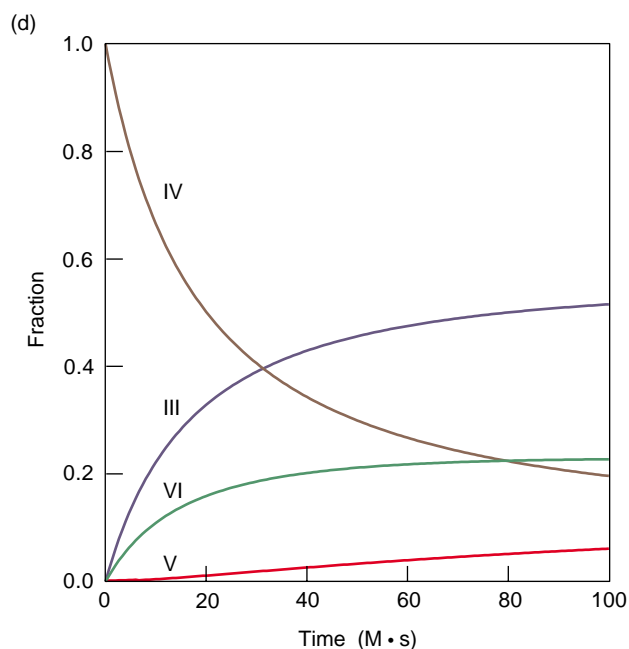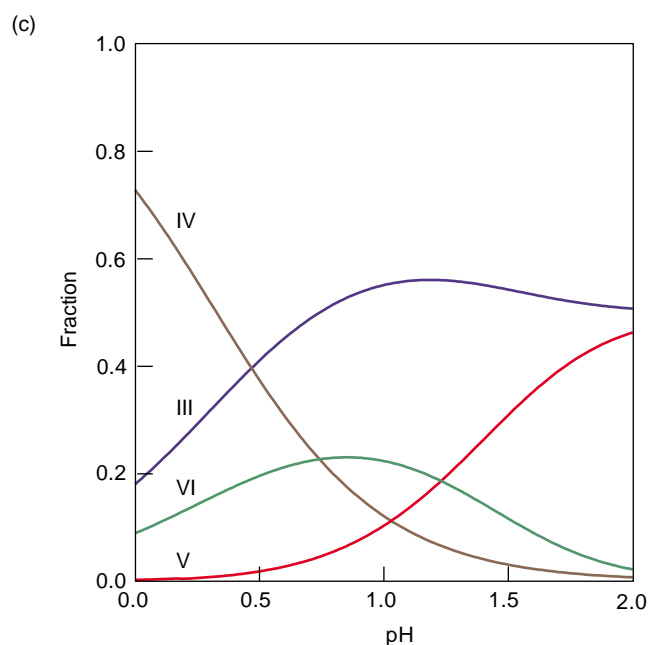
Organoplutonium Complexes

In nonaqueous solutions, where organoplutonium complexes can be stabilized against reaction with air and moisture, other unique kinds of stereochemistry have been observed. Of historical significance is the Pu(IV) "sandwich" compound, $Pu(\eta\text{-}C_8H_8)_2$, known as "plutonocene." The molecular structure has been determined for the uranium analog, and spectroscopic data indicate that a similar structure is present for plutonium. The molecule has rigorous D_{8h} symmetry where the eight-member cyclooctatetraenyl (COT) rings are arranged in an eclipsed conformation. Research at Los Alamos is underway to determine the crystal structure of plutonocene, as part of our "Actinide Molecular Science" competency development project. Other organoplutonium compounds of interest include complexes of the cyclopentadienyl ligand ($\eta\text{-}C_5H_5$), abbreviated Cp. The COT and Cp ligands are considered to occupy three coordination sites on the Pu(IV) metal center, and as such, $Pu(\eta\text{-}C_8H_8)_2$, $Pu(\eta\text{-}C_5H_5)_3Cl$, and $Pu(\eta\text{-}C_5H_5)_4$ can be considered as having coordination numbers of 6, 10, and 12, respectively. The Cp ligands are very large indeed, and actinides are among the few elements in the periodic table large enough to accommodate four Cp rings in a multi-hapto ( ) bonding arrangement.
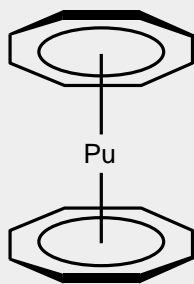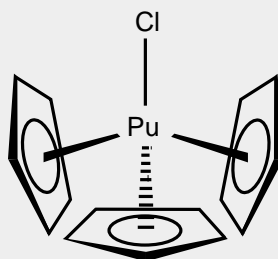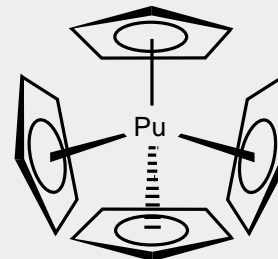
$Pu(\eta\text{-}C_8H_8)_2$ $\qquad$ $Pu(\eta\text{-}C_5H_5)_3Cl$ $\qquad$ $Pu(\eta\text{-}C_5H_5)_4$

equilibrium mixture of plutonium molecules containing two, four, and six nitrate ligands: $Pu(NO_3)_2^{2+}$, $Pu(NO_3)_4$, and $Pu(NO_3)_6^{2-}$ (Allen et al. 1996). The hexanitrato anionic species $Pu(NO_3)_6^{2-}$ sorbs strongly to an anion-exchange column, and anion exchange is used to purify large quantities of plutonium every year.

Once the molecular structure of the hexanitrato species was determined, however, Los Alamos researchers were able to molecularly engineer a revolutionary new anion-exchange resin tailored to its molecular properties (Marsh et al. 1997). The sorption of plutonium to this new resin increased by about an order of magnitude. The new resin allows for a more efficient purification process, with significantly less waste and with a smaller facility footprint (see the article "Molecularly Engineered Resins for Plutonium Recovery" on page 454). This techno-logical advance has been critical to the Laboratory's ability to meet future pit production goals. Obviously, our

continued expertise in the molecular science of plutonium will be critical to our future.

The complexation strength is a measure of how effectively a ligand can compete with water in the coordination shell of the aquo ion. In most cases, complex formation involves an exchange of the water molecules with complexing ligands to form *inner-sphere* complexes. Both the ligand and any remaining water molecules are bound directly to the central metal atom. Those kinds of interactions can form very stable complexes. Weaker complexes result when a ligand is bound to the central metal atom by the waters of hydration. Those are called *outer-sphere* complexes.

Plutonium ions are "hard" acids and consequently form strong, inner-sphere complexes with ligands containing oxygen donor atoms and with highly ionic ligands, such as fluorides, chlo-rides, etc. They also form an extensive series of compounds with oxo anions of nearly every type (CO_3^{2-}, NO_3^-, PO_4^{3-},

etc.), many of which are common in natural waters. Furthermore, plutonium ions form complexes of moderate strength with nitrogen donors and weak, outer-sphere complexes with sulfur donor ligands. They also show a special stability for chelating ligands with oxygen and nitrogen donor atoms.

The relative tendency of plutonium to form complexes is dependent on its charge-to-ionic-radius ratio. Because the ionic radii of the four common oxidation states are of similar magnitude, the stability of the complex parallels the overall charge of the central plutonium ion or of the actinyl ion:

$$Pu^{4+} > Pu^{3+} \simeq PuO_2^{2+} > PuO_2^+ \quad .$$

Pu^{4+} forms the strongest complexes and PuO_2^+ forms the weakest. It should be noted that the actinyl cations, PuO_2^+ and PuO_2^{2+}, form complexes that are stronger than would be expected when compared with monovalent and divalent cations of lighter elements.
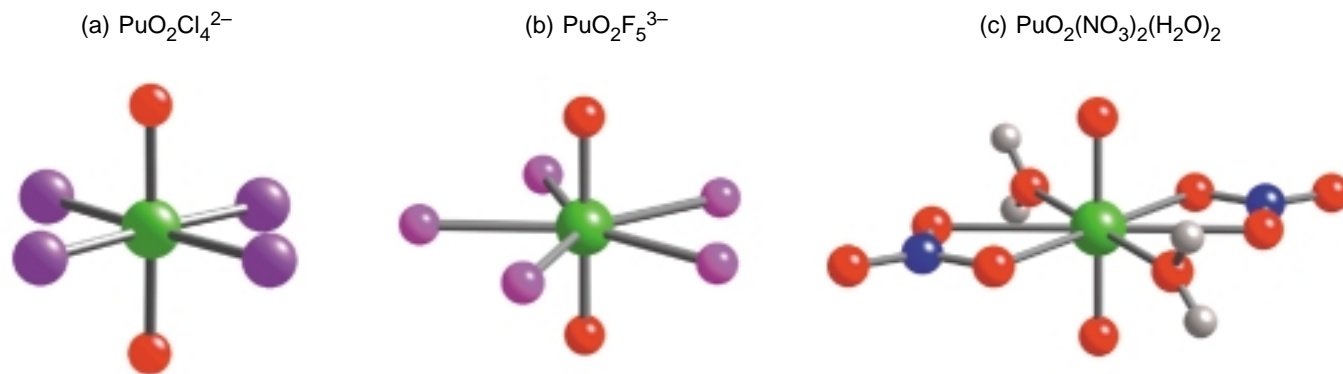
Plutonium ions have relatively large

(a) PuO$_2$Cl$_4$$^{2-}$ (b) PuO$_2$F$_5$$^{3-}$ (c) PuO$_2$(NO$_3$)$_2$(H$_2$O)$_2$

Figure 7. Structural Motifs of Pu(V) and Pu(VI)

In aqueous solution, Pu(V) and Pu(VI) complexes are nearly always actinyl ions. The linear O=Pu=O unit forms the axis of a tetragonal, pentagonal, or hexagonal bipyramid. **(a)** The tetragonal bipyramid structure is usually seen for large, monodentate ligands such as Cl$^-$. The PuO$_2$Cl$_4$$^{2-}$ ion has a coordination number of 6. **(b)** Smaller monodentate ligands such as F$^-$ and OH$_2$ favor the pentagonal bipyramid. The PuO$_2$F$_5$$^{3-}$ ion has a coordination number of 7. **(c)** Hexagonal coordination in an equatorial plane is usually only seen for bidentate ligands. The two nitrate ligands bond in a bidentate fashion in PuO$_2$(NO$_3$)$_2$(H$_2$O)$_2$, while the two water ligands are monodentate. The complex has a coordination number of 8.

ionic radii, so that many ligands can fit around them. They also can exhibit high oxidation states and have a large number of valence shell orbitals available for bonding. As a result, many donor atoms will bond to the central plutonium ion, and so coordination numbers of 8 and 9 appear to be very common in plutonium complexes. However, the actual number of molecular structures that have been determined for plutonium compounds is quite small. Due to the technological importance of water-based solvent extraction, ion-exchange, and precipitation processes needed to prepare plutonium for reduction to the metallic state, almost all of the structures have been deduced in aqueous solution. Some studies, however, have been performed on plutonium complexes in nonaqueous solutions. (See the box "Organoplutonium Complexes.")

Perhaps the most work to date has been performed on V and VI oxidation states, where the actinyl ions are nearly always observed. The overall pattern is always one in which the linear unit O=Pu=O forms the axis of a tetragonal, pentagonal, or hexagonal bipyramid, as indicated schematically in Figure 7. The tetragonal bipyramid is seen for

large monodentate (single donor) ligands such as Cl$^-$, while smaller monodentate ligands such as F$^-$ and OH$_2$ favor the pentagonal bipyramid. Hexagonal coordination in an equatorial plane is usually seen only for bidentate (two-donor) ligands such as NO$_3$$^-$, CO$_3$$^{2-}$, RCO$_2$$^-$, etc., or where a combination of monodentate and bidentate ligands are used, such as PuO$_2$(NO$_3$)$_2$(OH$_2$)$_2$.

Historically, the molecular structures of plutonium compounds have been inferred based on analogy with uranium, and only a handful of plutonium molecular structures have actually been determined. To help illustrate this point, we bring to your attention that at the time of this writing, the two major international crystal structure databases (The Cambridge Structural Database and the Inorganic Crystal Structure Database) combined contained 1072 molecular structures for uranium and only 81 for plutonium, many of which were duplicates. The structures shown in Figure 7 were only deduced within the past several years.

Advances in our understanding of plutonium molecular science over the last decade can be attributed, in part, to the development and application of

many new techniques that can characterize chemical species, including photoacoustic spectroscopy (PAS), photothermal lensing (PTL), laser-induced fluorescence (LIF) spectroscopy, x-ray absorption fine structure (XAFS) spectroscopy, x-ray and neutron diffraction, laser resonance ionization mass spectroscopy, improved trace analyses, combined extraction methods, and nuclear magnetic resonance (NMR) spectroscopy. Some of these tools will be highlighted in the next section, which discusses an example of our most recent molecular-level structural studies of anionic carbonato complexes of plutonium ions.

Modern Studies in Plutonium Chemistry

To better illustrate how the various chemical properties, modern structural tools, and present understanding of the nature of chemical bonding come into play, I will discuss a current example of molecular studies on carbonate complexes of Pu(VI) and the motivation for the work. Carbonate and bicarbonate are common anions present in significant concentrations in many
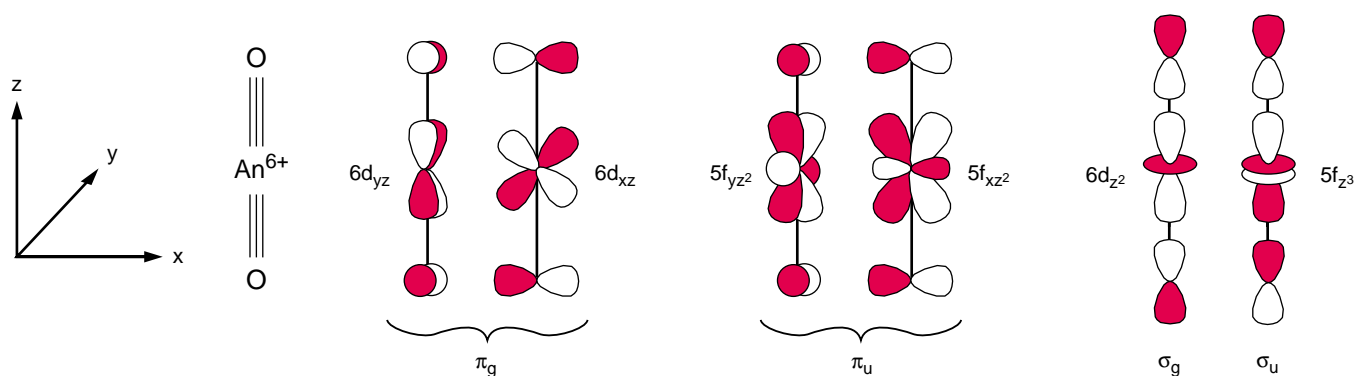
Figure 8. Bonding within the $AnO_2{}^{2+}$ Cation

Twelve valence electrons participate in bonding the central actinide ion to the two oxygen atoms within the actinyl unit. Those electrons occupy six molecular orbitals so that, formally, a triple bond exists between the actinide and each oxygen. Each molecular orbital is a linear combination of either 6d or 5f atomic orbitals of the actinide and the 2p atomic orbitals of the oxygen atoms. The two $_g$ molecular orbitals, for example use the $6d_{yz}$ and $6d_{xz}$ atomic orbitals, respectively, whereas the $_u$ molecular orbitals use the $5f_{yz^2}$ and $5f_{xz^2}$. The designations of the molecular orbitals indicate the electron distribution and parity. The electron density in the orbitals is concentrated on either side of an imaginary line connecting the three nuclei. The subscript g refers to inversion symmetry (positive parity) about the origin, whereas u refers to an antisymmetric (negative parity) state. The electron density in the σ orbitals is concentrated along the line connecting the nuclei.

natural water environments (Clark et al. 1995). They are exceptionally strong complexing agents for plutonium and the actinide ions in general. Ions that normally exhibit quite low solubilities in near-neutral solutions can be complexed by carbonate ligands and (through the formation of anionic complexes) become much more soluble. Therefore, carbonate complexes may play an important role in the migration of plutonium ions from a nuclear waste repository or an accidental site contamination. The environmental behavior of plutonium carbonate complexes will ultimately depend on their molecular scale structure and properties, and as such, it is of intrinsic interest to determine the coordination chemistry and molecular behaviors of these complexes.

As mentioned earlier, Pu(VI) will exist in aqueous solution as an actinyl ion. These cations are remarkably stable. They show 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 ligands in the equatorial plane. Recent developments in both theory and spectroscopy have helped to elucidate the nature of the chemical bond in the linear actinyl ions. Several

fundamental differences exist between the spatial extent, orbital energetics, and diffuse nature of valence and nonvalence atomic orbitals of the light 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, and 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 ions, $AnO_2{}^{2+}$, have a nominal $\sigma_g^2 \pi_g^4 \sigma_u^2 \pi_u^4$ electronic configuration and a formal An≡O triple bond (Denning 1992). In the linear configuration, strong, covalent interactions are observed through the formation of An 6d–O 2p and An 5f–O 2p π bonds, and the underlying 6s and 6p closed shells are semiactive in σ bonding. The An–O π_g and π_u multiple bonding orbitals derived from 6d and 5f atomic orbitals are shown in Figure 8. The use

of 5f orbitals in π bonding only takes place at the very short bond distances seen in An=O bonds, which span 1.74 to 1.80 angstroms. Because the virtual 7s and 7p orbitals are essentially unavailable for bonding, equatorial metal–ligand σ bonding can only take place through the use of the few remaining 6d or 5f orbitals in the equatorial plane. Hence, equatorial bonding is quite weak. This picture of the electronic structure explains the strong, multiple, covalent bonds in the axial direction and the weak, relatively ionic bonds in the equatorial plane.

The plutonyl(VI) carbonate system can also be quite complicated in that it consists of several different complex ions in equilibrium with one another and with the aquo ion or hydrolyzed species, depending on solution conditions. Under dilute solution conditions, compounds of composition $PuO_2(CO_3)$, $PuO_2(CO_3)_2{}^{2-}$, and $PuO_2(CO_3)_3{}^{4-}$ have all been reported (Clark et al. 1995). Our approach toward understanding this problem was to focus our initial attention on the identity of the limiting complexes formed in this system. Understanding the limiting structure can then provide a starting point for identifying the other complexes formed in

the equilibrium. Hence, efforts were focused on solution conditions that favor the limiting anionic $PuO_2(CO_3)_3^{4-}$ complex (Clark, et al. unpublished results).

We used our knowledge of plutonium redox behavior and kinetics to prepare oxidation-state-pure solutions of Pu(VI), and the oxidation state purity was monitored using electronic absorption spectroscopy, by monitoring the intensity of the 830-nanometer absorption band (as seen in Figure 5). Complexation of Pu(VI) by carbonate subsequently stabilizes Pu(VI) against redox disproportionation. Electronic absorption and carbon-13 NMR spectroscopy were used to follow the chemistry and to confirm that our chemical conditions favored a single species in solution. Next, we employed the guanidinium counter cation $C(NH_2)_3^+$ to form hydrogen bonds to the carbonate ligand in solution and thereby grow single crystals of $[C(NH_2)_3]_4[PuO_2(CO_3)_3]$ suitable for x-ray diffraction analysis. One of these single crystals was carefully selected, triply contained for radiological safety, and mounted on the goniometer of an x-ray diffractometer where it was studied by x-ray diffraction. We used a state-of-the-art charge-coupled-device area detector capable of acquiring a full hemisphere of data in only a few hours. This rapid data collection is very helpful for determining the structures of plutonium compounds because the alpha radiolysis of the crystal can damage crystallinity over time, leaving us with an amorphous, nondiffracting solid. The atom positions were determined by routine computational procedures.

A thermal ellipsoid drawing that shows the molecular structure of the $PuO_2(CO_3)_3^{4-}$ ion is shown in Figure 9(a). The central $PuO_2(CO_3)_3^{4-}$ ion displays a hexagonal bipyramidal coordination geometry where three bidentate carbonate ligands lie approximately in a hexagonal plane and two oxo ligands occupy coordination sites above and below the plane. Guanidinium cations (not shown) form outer-sphere hydrogen bonds with the CO_3^{2-} ligands and
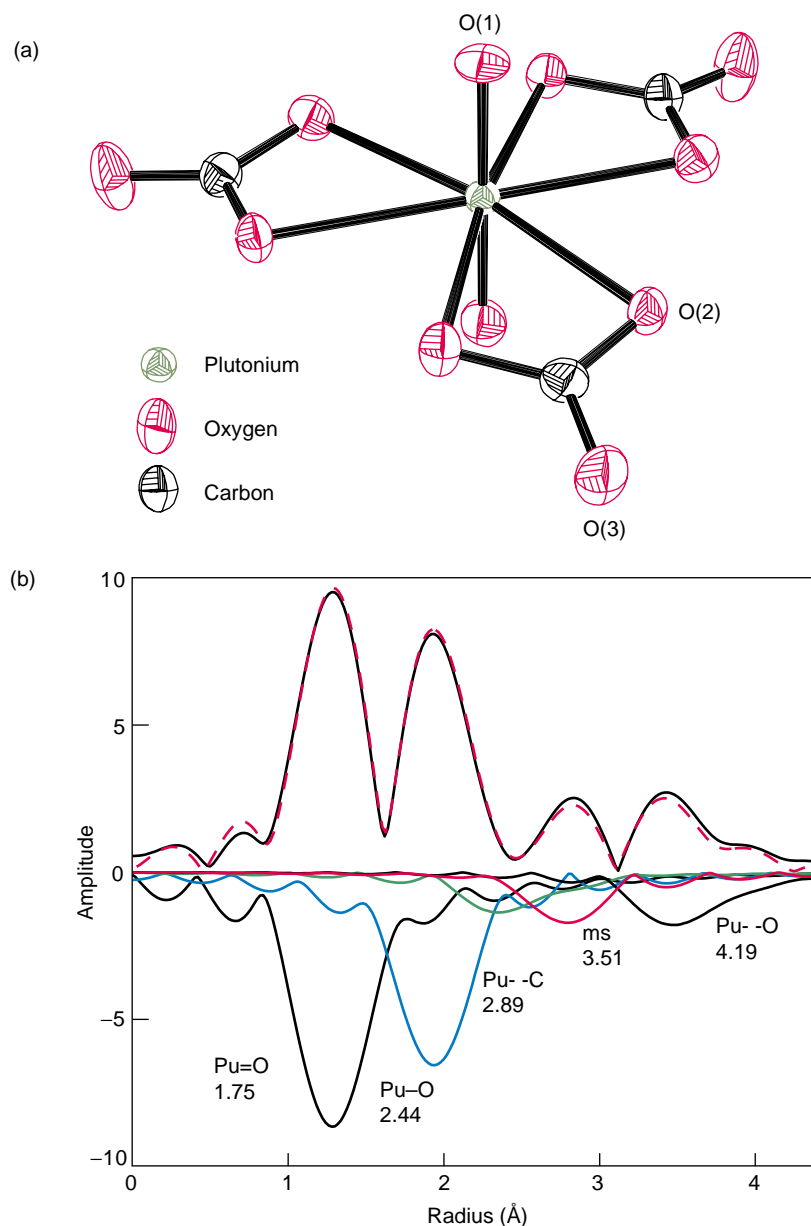

Figure 9. Limiting Structure of Pu(VI) in Carbonate Solution
(a) The structure of the $PuO_2(CO_3)_3^{4-}$ anion in the solid state was determined by x-ray crystallography. This thermal ellipsoid drawing emphasizes the pseudo-hexagonal-bipyramidal coordination geometry about the central plutonium metal ion. (The ellipsoids are indicative of the excursions of the atoms due to thermal motion.) A bond length of 1.75(1) Å was measured to the "-yl" oxygen O(1) and 2.44 Å to the nearest-neighbor oxygen atoms O(2) of the carbonate ligand. (b) The structural parameters of the limiting Pu(VI) complex in 2.5 M Na_2CO_3 solution was determined by XAFS spectroscopy. The figure shows the Fourier transform of the XAFS spectrum (solid black line) and the theoretical fit (dashed red line). The components of the fit, shown beneath the spectrum with negative amplitudes, correspond to individual shells of atoms. (There are no atoms at 3.51 Å [twice the Pu=O distance]. The peak labeled "ms," which is routinely observed in the XAFS data of actinyl ions, is due to multiple scattering of a photoelectron off the oxygen atoms in the linear actinyl unit.) The radii of the coordination shells of the limiting structure in solution match the solid-state structure, and we conclude that the $PuO_2(CO_3)_3^{4-}$ anion is the limiting Pu(VI) species in carbonate solution.

form an extensive hydrogen-bonding network that links the molecules together in a three-dimensional array.

We also determined the structures of the uranium and neptunium analogs. For the axial An=O bonds in isostructural compounds, one can observe a relatively smooth decrease in bond distance from 1.79(1) to 1.77(1) to 1.75(1) angstroms for uranium, neptunium, and plutonium compounds, respectively. This bond length shortening is an experimental manifestation of the actinide contraction. For the equatorial An–O distances to the carbonate ligand, the distances are essentially identical at 2.45(1) angstroms for uranium and 2.44(1) angstroms for neptunium and plutonium.

We then employed solution x-ray absorption fine structure (XAFS) spectroscopy to determine the structural details of the limiting Pu(VI) complex in solution. Samples were synthesized and characterized as before to confirm the sample composition before XAFS analysis. Plutonium solutions were packaged in specially designed sample cells with three layers of radiological containment, then shipped to the Stanford Synchrotron Radiation Laboratory (SSRL). Electronic absorption spectra of the solution examined both before and after XAFS analysis indicated that the same limiting Pu(VI) species was present in excess of 99 percent. The XAFS Fourier transforms show four well-resolved peaks whose qualitative assignment based on the monomeric structure observed in the solid state is straightforward. A representative solution Fourier transform spectrum of $PuO_2(CO_3)_3^{4-}$ is shown in Figure 9(b). Curve fitting revealed peaks at 1.75(1), 2.44(1), 2.89(1), and 4.19(3) angstroms, which may be identified as distances from the plutonium to the plutonyl oxygens, the six carbonate oxygens in the equatorial plane, and the carbonate carbon and distil oxygen atoms, respectively. A well-established O=Pu=O multiple-scattering peak is seen at 3.51 angstroms in both spectra. The close spacing of Pu–O and Pu–C

shells generates the appearance of a single peak in the XAFS Fourier transform.

These studies prove the identity of the $PuO_2(CO_3)_3^{4-}$ ion as the limiting complex in the system and provide structural data for comparison of structural trends across the series uranium, neptunium, and plutonium. Additional studies at more near-neutral pH values indicate that both uranium and neptunium can form monomeric $AnO_2(CO_3)_2^{2-}$ or trimeric $(AnO_2)_3(CO_3)_6^{6-}$ complexes (Clark et al. 1995, Allen et al. 1995). Plutonium, however, does not appear to form the trimeric complex (Mary P. Neu and Sean D. Reilly, unpublished results). That result indicates that there are some fundamental differences between uranium, neptunium, and plutonium chemistry.

Concluding Remarks— Plutonium Chemistry in the New Millennium

In the above discussions I have tried to provide a fairly general overview on the complexities of plutonium chemistry in aqueous solutions. Its radioactivity and redox instabilities give solutions that are constantly changing and evolving. The nature of the oxidation state is crucial for understanding and predicting the behavior of plutonium, with implications for behavior in the environment, in waste matrices, in aging storage tanks, and in our daily process chemical operations. Over the years, we have learned to control these redox states by complexation with a variety of ligands. Some of these ligands, such as the nitrate anion, have played a historically significant role in the processing and purification of plutonium over the last 50 years. Other ligands, such as the carbonate anion, are omnipresent in natural groundwaters and play a dominant role in the fate and transport of plutonium in the natural environment. In more recent times, we have begun to recognize that ligands such as hydroxide and aluminate will

play a significant role in the behavior of plutonium under the conditions present in aging waste tanks. Hence, a fundamental understanding of the molecular behavior of plutonium in its various oxidation states is critical to understanding, predicting, and manipulating plutonium in groundwaters, contaminated soils, nuclear waste repositories, spent nuclear fuels, aging waste tanks, and the large-scale process streams used in reprocessing and purification. Many of our advances in plutonium molecular science were made through the application of new research tools to probe all aspects of the molecular and electronic structure of these complexes. Indeed, in some cases, the development of new tools (such as PAS) was driven by the need to study plutonium under the extremely low concentrations anticipated in the natural environment.

Now that we have obtained this new knowledge about fundamental molecular-level plutonium behavior, we can look forward to a future in which we can apply our improved molecular understanding toward more efficient chemical processes. Imagine a "zero effluent" nuclear facility in the future, based on new, molecularly engineered plutonium compounds and total recycle of environmentally benign designer solvents. This concept is closer to becoming reality than one might think. For example, the French already have a "zero effluent" nuclear facility at Valduc based on molecular waste polishing processes. I imagine that changing regulatory requirements will force the United States to modify its current processes in the near future. Historically, we developed a nitrate anion-exchange process for plutonium purification, then spent decades working out the fundamental understanding of how the process actually worked. Another decade of effort focused on optimizing the process through molecularly engineered ion-exchange processes and through nitric acid recycle or destruction. Is molecular science important for the future of Los Alamos? The answer is a very clear and undeniable

yes! Faced with constantly changing regulatory requirements, I predict that we will be forced to identify better, more efficient, and more environmentally friendly processes as we enter the new millennium.

At this stage, I would like to share my own vision of a futuristic plutonium facility at Los Alamos in the next millennium. My personal view is that we could use our molecular-level understanding of carbonate complexation as the scientific foundation for a brand-new plutonium flowsheet. Imagine a process in which a highly stable anionic carbonate complex is purified on a molecularly engineered ion-exchange resin tailored for the unique molecular structure of the *trans*-dioxo ion. After recovery of the plutonium, the complex can be gently destroyed to release carbon dioxide and water as the only effluent. The carbon dioxide and water can be readily recycled to regenerate the carbonate ligand, thereby eliminating altogether the regulatory issues concerning high-nitrate waste streams leaving the Laboratory. In a subsequent process, I can envision the reduction of purified plutonium to the metallic state, not in a high-temperature molten-salt flux with its associated quantities of radioactive salt waste, but rather at an electrode surface at room temperature using a molecularly engineered room-temperature ionic liquid. I truly believe that such revolutionary approaches in the way we accomplish our mission are coming soon and are limited only by our courage and imagination. ∎

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