

Characterizing the Plutonium Aquo Ions by XAFS Spectroscopy

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Plutonium is one of only a handful of elements to exhibit four common oxidation states: Pu(III), Pu(IV), Pu(V), and Pu(VI). In addition, plutonium complexes in aqueous solution can change their oxidation state by undergoing disproportionation or reproporation reactions, or through radiolytic reactions. Because so many plutonium species can form and interact in solution, aqueous plutonium chemistry can be remarkably complex.

In environments where different ligands abound, such as the ground waters of Yucca Mountain or the waste materials (residues) produced during the manufacturing of nuclear weapons, the plutonium species need to be understood beyond simple elemental analysis. We need to have information about the possible oxidation states of the numerous species, along with information about their atomic compositions and molecular structures.

The plutonium aquo ions are the “baseline” plutonium species in aqueous solution because they only have water molecules attached to a central plutonium ion. Other species form as different ligands replace one or more of the water molecules in the coordination sphere of the plutonium ion. Understanding the aquo ions in detail can therefore provide a starting point for understanding other plutonium complexes.

The aquo ions of plutonium in the III and IV oxidation states have the general formula $\text{Pu}(\text{H}_2\text{O})_n^{3+}$ and $\text{Pu}(\text{H}_2\text{O})_n^{4+}$, respectively, which are often designated as $\text{Pu}^{3+}(\text{aq})$ and

$\text{Pu}^{4+}(\text{aq})$. But plutonium in the V or VI oxidation state has such a large positive charge that, in aqueous solution, it reacts with water to form the trans-dioxo (plutonyl) cations PuO_2^+ or PuO_2^{2+} . The corresponding aquo ions therefore have the general formulas $\text{PuO}_2(\text{H}_2\text{O})_n^+$ and $\text{PuO}_2(\text{H}_2\text{O})_n^{2+}$, which are conveniently designated as $\text{PuO}_2^+(\text{aq})$ and $\text{PuO}_2^{2+}(\text{aq})$. Before we conducted our research, the number of water molecules, n , surrounding the plutonium ions was still open to debate.

Several years ago, Los Alamos scientists from three Laboratory divisions began working together to apply x-ray absorption fine-structure (XAFS) spectroscopy to characterize the plutonium aquo ions. (More information about XAFS spectroscopy is found in the article “XAFS” on page 422.) All the measurements were performed at the SPEAR synchrotron x-ray source, which is owned and operated by the Stanford Synchrotron Radiation Laboratory (SSRL).

Solutions containing ions in a single oxidation state were prepared by electrochemical synthesis. These samples allowed us to study each aquo ion independently. We verified the oxidation state integrity of the samples before and after x-ray absorption analysis by measuring the electronic absorption spectra. Because the chemical environment surrounding the plutonium ion in each solution was very consistent (the only ligands were water molecules), we could also look for behavioral or structural trends among the four oxidation states.

Identifying the Plutonium Oxidation States

The x-ray absorption near-edge structure (XANES) of an XAFS spectrum can be used to determine the oxidation state of the target (x-ray absorbing) element in solution or the solid state. The energy at which an absorption edge appears depends on the ionization potential of the ion. This ionization potential increases with the ion’s valence, so in general the absorption edge shifts toward higher energy with increasing oxidation state. This known effect has been observed in some of the actinides, for example, in uranium and neptunium. We have recently observed this shift in the plutonium aquo ions.

Figure 1(a) shows a detailed view of the XANES spectra for the aquo ions of Pu(III), Pu(IV), Pu(V), and Pu(VI). The shift between successive oxidation states is clearly visible, although there is almost no difference in the absorption-edge energy (within experimental error) between Pu(IV) and Pu(V) complexes. Other parts of the XANES, however, can be used to help correlate a spectrum with an oxidation state. For example, the shoulder that appears just after the main absorption peak in the spectra of Pu(V) or Pu(VI) complexes in solution—the “-yl” shoulder—can be used to distinguish those oxidation states from Pu(IV). (Refer to the box “XANES” on page 432 in the article “XAFS”.)

A graph of the edge energy versus oxidation state for the plutonium aquo

ions is shown in Figure 1(b). We have obtained nearly identical graphs for other plutonium species—including plutonium nitrates, carbonates, carboxylates, and oxides—in solution and the solid state. (In fact, other than an overall shift in the edge energy, we obtained nearly identical graphs for uranium and neptunium.) Because the edge energies are independent of the chemical form of the plutonium, they can be used to identify the oxidation state of plutonium complexes in unknown chemical matrices.

There is still speculation about the underlying reason behind the small shift between the IV and V oxidation states. The shift toward higher energies depends on the actual charge of the ion, rather than its “formal” charge, and evidently, the actual charge does not vary much between the two states. One possible explanation is linked to the formation of the plutonyl cations.

The plutonyl cations have a linear structure, $\text{O}=\text{Pu}=\text{O}$. Recent calculations have shown that bonding between the plutonium and oxygen atoms in the plutonyl has a substantial covalent character, so that the actual charge of the central plutonium ion is reduced. (See the article “Computational Studies of Actinide Chemistry” on page 382.) The actual charge of the plutonium ion in the Pu(V) complex $\text{PuO}_2^+(\text{aq})$ may therefore be very similar to the actual charge of the plutonium ion in $\text{Pu}^{4+}(\text{aq})$.

The Structure of the Plutonium Aquo Ions

Data from the high-energy side of the x-ray absorption spectrum (the EXAFS region) provides information about the local atomic-scale environment. A Fourier transform of the data results in a radial distribution function that can be interpreted as shells of near-neighbor atoms surrounding the central ion. The position and intensity of the peaks in the Fourier transform are related to the atomic identity, distance, and number of atoms in each shell.

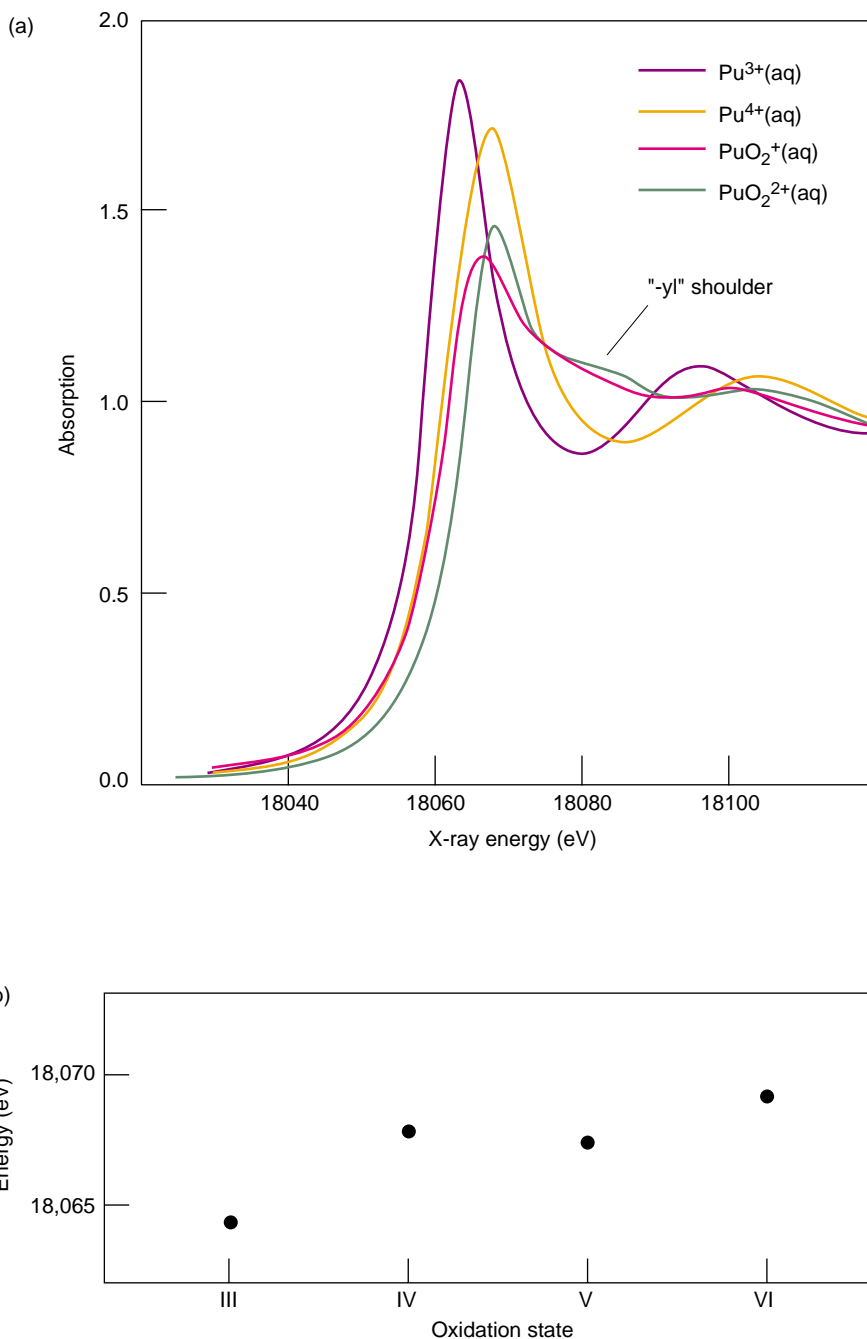
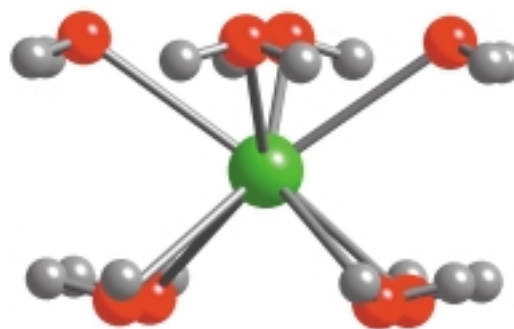
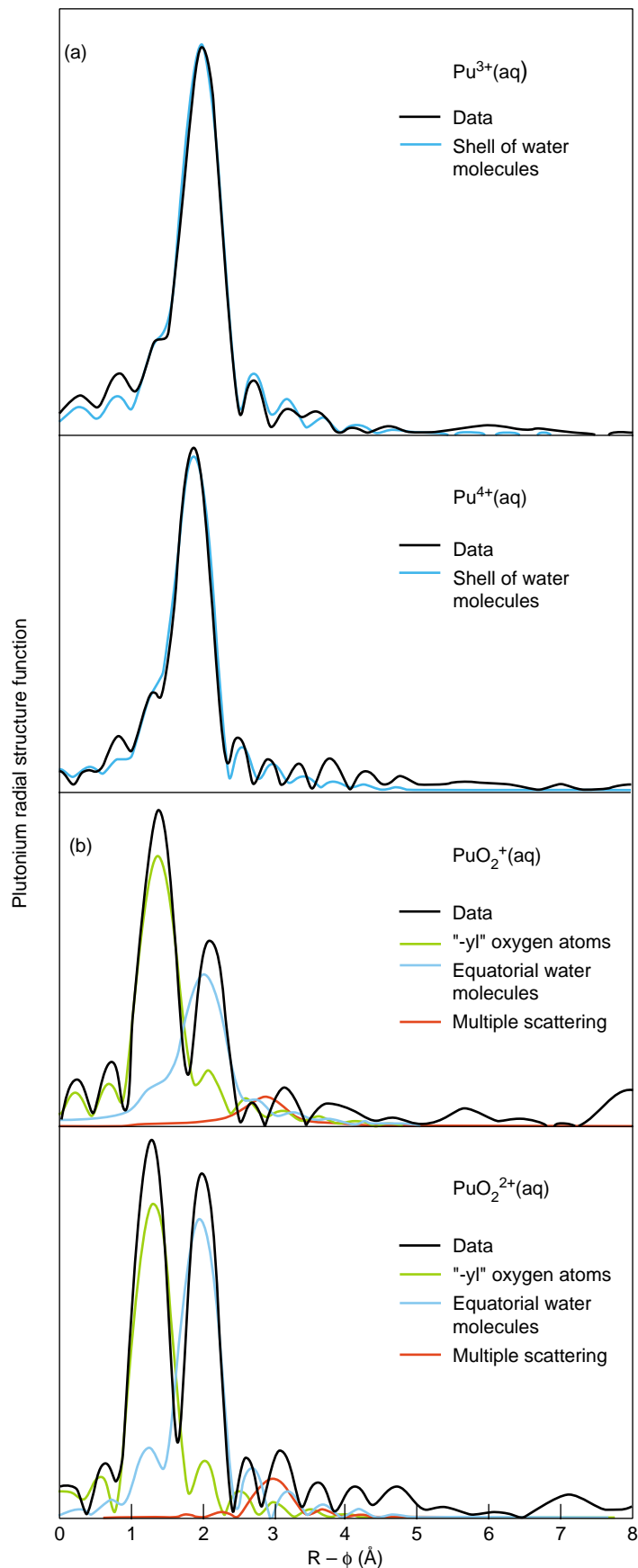


Figure 1. XANES Spectra of the Aquo Species of Pu(III) to Pu(VI)

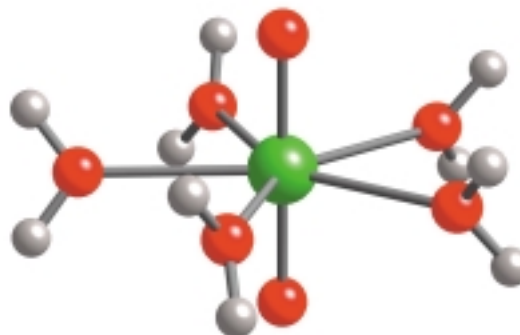
(a) The absorption edge shifts toward higher energy and increases almost linearly as a function of oxidation state. The change in energy between $\text{Pu}^{4+}(\text{aq})$ and $\text{PuO}_2^+(\text{aq})$ is quite small, but the two oxidation states can be distinguished by other features, such as the “-yl” shoulder in the XANES spectrum. (b) The edge energy is plotted as a function of oxidation state, which helps to illustrate the point that the IV and V oxidation states are in fact indistinguishable based on absorption-edge energy alone.



Square antiprism

Figure 2. EXAFS of the Plutonium Aquo Ions

(a) The Fourier transforms of the EXAFS of $\text{Pu}^{3+}(\text{aq})$ and $\text{Pu}^{4+}(\text{aq})$ show only one major peak, which indicates that all the oxygen atoms of the water ligands lie in the same coordination shell. The amplitude of the peak indicates between 8 and 9 oxygen atoms per shell. The bond length between III and IV complexes contracts by 4% with the increase in charge, whereas the number of ligands stays roughly the same. The graphic in the upper right shows a possible structure for $n = 8$, the square antiprism. (b) The Fourier transforms of the EXAFS of $\text{PuO}_2^+(\text{aq})$ and $\text{PuO}_2^{2+}(\text{aq})$ show two large peaks, which indicate two well-defined coordination shells. The first peak corresponds to the two oxygen atoms of the plutonyl moiety, which are located at 1.74 Å from the central plutonium ion. The second peak corresponds to the oxygen atoms of the water ligands, which are located about 2.4 Å from the central plutonium ion. The equatorial coordination of the Pu(V) complex compared with the Pu(VI) complex shows a significantly smaller number of water ligands, which are located at a longer distance. This observation is not fully understood. The graphic below shows a possible structure for $n = 5$ water ligands, the pentagonal bipyramid.



Pentagonal bipyramid

Figure 2(a) shows the Fourier transform of the EXAFS data¹. For $\text{Pu}^{3+}(\text{aq})$ and $\text{Pu}^{4+}(\text{aq})$, the data show only a single large peak, which indicates that all the nearest-neighbor atoms (the oxygen atoms of the water ligands) lie at the same distance from the plutonium ion. We obtained a Pu–O distance of approximately 2.49 angstroms for the III state and 2.39 angstroms for the IV state. The number of water molecules bound to the plutonium is similar for both species, with $n = 8$ or 9.

The transform of $\text{PuO}_2^+(\text{aq})$ and $\text{PuO}_2^{2+}(\text{aq})$ data shows two peaks, as seen in Figure 2(b). The first corresponds to the two oxygen atoms in the plutonyl ion. Analysis of the data indicates a Pu=O distance of 1.74 angstroms. The second peak in the Fourier transform corresponds to the oxygen atoms of the water ligands. It is known from other studies that all these oxygen atoms bond in the equatorial plane of the plutonyl moiety, and we deduce Pu–O distances that range from 2.39 to 2.49 angstroms.

The Fourier transform also shows a small peak at about 3 angstroms. This peak is an artifact of the EXAFS technique that results when an electron scatters more than once within the linear geometry of the plutonyl moiety. Thus we include a multiple-scattering peak in our fit to the data.

A significant result of our research is the finding that the $\text{PuO}_2^+(\text{aq})$ has a lower number of water ligands ($n = 4$ to 5), all at a longer distance, than $\text{PuO}_2^{2+}(\text{aq})$, where $n = 5$ to 6. This finding confirms a trend that was seen in studies of the actinyl ions of uranium and neptunium, namely, that actinide(V) species appeared to coordinate fewer ligands than actinide(VI) species. Because plutonium exhibits aquo ions in four oxidation states (and is the only actinide to do so),



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our experiments are the first to observe this trend directly.

When other information is taken into account, the XAFS data are consistent with a bipyramidal coordination geometry for $\text{PuO}_2^+(\text{aq})$ and $\text{PuO}_2^{2+}(\text{aq})$. The plutonyl moiety forms the axis of the bipyramid, and depending on conditions, the geometry may be a tetragonal bipyramid (four ligands in the equatorial plane), a pentagonal bipyramid (five ligands), or a hexagonal bipyramid (six ligands).

We have used the plutonium aquo ions to establish the baseline data and oxidation state trends necessary to determine the oxidation states of plutonium complexes in matrices of unknown composition. With this background data in hand, we are in a position to apply

XAFS spectroscopy to help characterize plutonium or other actinide species in the environment or in the waste that remain after 50 years of nuclear weapons production. ■

¹An EXAFS spectrum is a function of energy, and we take a Fourier transform (FT) of the spectrum to produce a radial structure function that is a function of distance, R . But the transform actually produces a function $\chi(R+\phi)$, where ϕ is a phase shift. In the FT shown in Figure 2, the phase shift causes the peaks to be about -0.5 \AA from the true shell radii. The radial structure function is plotted versus $(R-\phi)$ to emphasize this fact.