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Abstract

We present XANES at the L_{III} edge for four plutonium solid phases: $Pu(III)F_3$, $Pu(IV)O_2$, $NaPu(V)O_2CO_3$, and $Ba_3Pu(VI)O_6$. These correspond to the four important oxidation states in the process chemistry and environmental chemistry of plutonium. By a fitting method that uses an arc tangent function and gaussian curves, it was possible to reproducibly determine the edge energy and distinguish among the four oxidation states. These data demonstrate a 1.85 ± 0.20 eV shift per oxidation state.

Keywords: XANES, plutonium, actinide, oxidation state

Background

The environmental and process chemistry of plutonium remains an important area of research as DOE continues to address problems related to the management of nuclear waste (Banaszak et al., 1998; Lieser, 1995; Silva and Nitsche, 1995). The chemistry of plutonium is diverse because it can exist as Pu(III, IV, V, and VI) under environmentally relevant conditions. A key to understanding its environmental chemistry is, for this reason, its oxidation state. In this context, the application of synchrotron-based techniques to identify the oxidation state in complex environmental samples has great utility.

X-ray absorption near edge spectroscopy (XANES) measurements were made at the Pu L edges of four plutonium phases, $Pu(III)F_3$, $Pu(IV)O_2$, $NaPu(V)O_2CO_3$, and $Ba_3Pu(VI)O_6$. Solid phases may be expected to show stronger geometric effects in the near-edge structure. These effects may show up as changed "white line" intensities, shifted edge positions, and changed pre-edge features. If XANES is to be used to determine the Pu oxidation state, it must be determined how reliably these edge features may be measured and identified. The edge energy is an attractive means of measuring the oxidation state because of its intrinsic simplicity. However, the use of edge energy to identify oxidation state is only meaningful if the distortions introduced by differing environments may be modeled and eliminated. To this end, we are studying Pu compounds in different oxidation states, as well as compounds with the same oxidation state but different local environments (not reported here).

Any method of measuring the edge position that results in a unique determination of the oxidation state is valid; this is a phenomenological approach rather than a theoretical model of the edge features. Herein, several methods are described which attempt to define such a metric. Coupling the quantitative measurement with an evaluation of the spectral features should result in an unambiguous assignment of the oxidation state when primarily one oxidation state exists in unknown systems.

Sample Preparation

The plutonium samples analyzed by XANES were all fine powders dispersed on Kapton tape and encapsulated in a styrene matrix to contain the radioactivity during the analysis. Two layers of Kapton film further encapsulated the sample. Since the actinide L edges were all at a fairly high energy (>15 keV), even relatively large amounts of plastic did not significantly reduce the x-ray flux or measured signal. In addition, only small quantities (<1 μg Pu/mm^2) were necessary to obtain a good signal.

The four types of plutonium solids were synthesized using standard methods with Pu-242 (50% purity by activity, >99% purity by isotope). The PuF$_3$ was synthesized by reducing Pu to Pu(III), taking the product to dryness in hydrobromic acid, adding fluoride after dissolution in water, and precipitating. The plutonium oxide was made from high purity oxide stock, which was provided by Oak Ridge National Laboratory. This was high-fired to ~1000°C. The NaPuO$_2$CO$_3$ was precipitated from Pu(V) stock [made by electrolytic reduction of Pu(VI)] by titrating with sodium carbonate solution to pH ~ 7. The Ba$_3$PuO$_6$ was used as received from stock previously synthesized at Argonne National Laboratory.

Analysis Methods

Several methods of measuring the edge position were studied to determine which procedure would produce the most reliable measurement and which would produce the largest difference among oxidation states. The most common method, finding the second-derivative zero crossing, is sensitive to noise in the data and is therefore not adequately accurate. All of the following fitting methods use a larger portion of the data.

Noise in the data can be reduced significantly by performing a polynomial fit of the edge data (fourth order generally works well), and then finding the second-derivative zero crossing of the fit function. As shown in the second column of Table 1, this edge measurement is accurate but does not produce a signature energy for each oxidation state.

In addition, this method is somewhat influenced by the exact choice of end points. Noise in the data is not of much concern when evaluating these standard compounds, but for unknowns in which the Pu concentration may be in the 1 ppm range, noise would be an important consideration.

Using the same polynomial as for the above method, and then calculating the energy at 25% of the edge step, produces smaller errors (not shown here). After a pre-edge fit line is subtracted, the data are normalized by the standard techniques employed in x-ray absorption fine-structure (XAFS) spectroscopy; a fit through the data from about 50 to 300 eV above the edge is extrapolated to the edge. The measured edge position is fairly insensitive to both the normalization and the end points of the polynomial fit. Unfortunately, this method also results in an ambiguous oxidation-state determination due to shape effects.

The method of fitting the edge to an arc-tangent step function and a number of gaussian curves results in a correlation between the measured edge energy and the oxidation state. The errors are somewhat larger than the previously described methods. But as in the previous method, the exact data range is relatively unimportant since a large amount of data is used to determine the edge energy.

First the background slope is removed using a line to fit the pre-edge region. Then, the data are fit to the following equation, which is based on the function presented by Conradson et al. (1998a):

$$\mu(E) = A + B \times \tan^{-1}\left(C \times (E - E_0)\right) + \sum_{n=1}^{N} D_n \times \exp\left(-\left(\frac{E - F_n}{G_n}\right)^2\right) + H \times (E - E_0) \times \Theta(E - E_0)$$

(1)

A line is added to the post-edge region to account for the slope remaining after the pre-edge background removal. The edge position, E_0, is defined as the inflection point of the arc-tangent component. N is the number of gaussian curves. The variables *A-D* and *F-H* are the parameters in the fit, while E is the incident x-ray energy. Since this is a

nonlinear least-squares fit, careful attention must be paid to avoid false minima in the final fit parameters. An example using Eq. (1) to fit the Pu(IV) data is shown in Fig. 1.

There are other criteria that must be applied to the analysis of the fit results. First, the arc-tangent step function must accurately reproduce the edge step, neither under- nor over-shooting the actual step. The physical basis for this requirement is that we are using the arc tangent as a crude model for the atomic absorption; the EXAFS oscillations are plus or minus this function. Second, the data range was taken to be from about -30 eV to +450 eV relative to E_0. Since the EXAFS oscillations are not modeled by the fit, and so far an adequate method of de-emphasizing this region has not been found, one must qualitatively evaluate the fit. In practice, this means that the pre-edge portion from −30 eV to the edge is more important than the EXAFS region and must be fit well, even at the expense of the quantitative best fit.

Taken together, these criteria mean that one must find the arc-tangent inflection point that has the lowest energy resulting in a good fit. A fit that passes quantitative inspection can easily have a higher energy edge position than the actual edge, but a fit that has too low an edge energy will result in neither a qualitatively nor a quantitatively good fit.

Results

The edge positions from both the second-derivative method and arc-tangent/gaussian method are shown in Table 1. The change in the edge position with oxidation state is much clearer in the arc-tangent fit. A line drawn through the L_{III} edge results (Fig. 2) gives a change in the edge energy of 1.85 ± 0.20 eV per unit change in formal oxidation state. However, there is no *a priori* reason to expect that the change be linear.

An important difference is evident in the aqueous vs. the solid phase Pu data for the Pu(V) and Pu(VI) oxidation states. In the aqueous data, the white line intensity is reduced and a pronounced shoulder appears above the edge (Conradson et al., 1998a).

This has been attributed to the two short-distance apical oxygen atoms of the plutonyl species. In the solid compounds (Fig. 3), the Pu(V) does have the '-yl' group, but the associated features are not as distinct. In fact, the solid Pu(V) data above the edge is qualitatively more similar to Pu(IV) than Pu(VI).

In addition, small differences in the measured edge position are observed in the fluorescence and transmission spectra, which cannot be accounted for by self-absorption in the fluorescence spectra. This aspect of the XANES data will be investigated further to determine the extent of the systematic effect.

Conclusions

The results of this study and the other studies referenced show that the edge energy may be used as an oxidation-state identifier for Pu materials, demonstrating the utility of synchrotron-based techniques for the study of Pu chemistry. As is conventional with x-ray spectroscopies, a sample with mixed species (oxidation state and/or phase) will remain difficult to unequivocally identify. However, other techniques which rely more on the spectral shape may be brought to bear on this problem (Conradson, 1998b).

Acknowledgments

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Table 1. Table of fit results for the Pu L_{III} edges. The second-derivative zero crossing was determined by fitting the edge data to a polynomial as described in the text, with the end points taken at 20% and 90% of the white line height. The remaining columns detail the results for the arc-tangent/gaussian function. Errors are shown in parentheses.

Figure 1. Example fit of L_{III} XANES data for Pu(IV) sample using Eq. (1) with gaussian curves (N=2). Data (crosses) are shown with the fit (solid line) and the fit components (dashed lines).

Figure 2. XANES spectra for the L_{III} edges of the four Pu oxidation states (offset for clarity).

Figure 3. Edge energy from the arc-tangent/gaussian fit vs. formal oxidation state for four Pu solids.

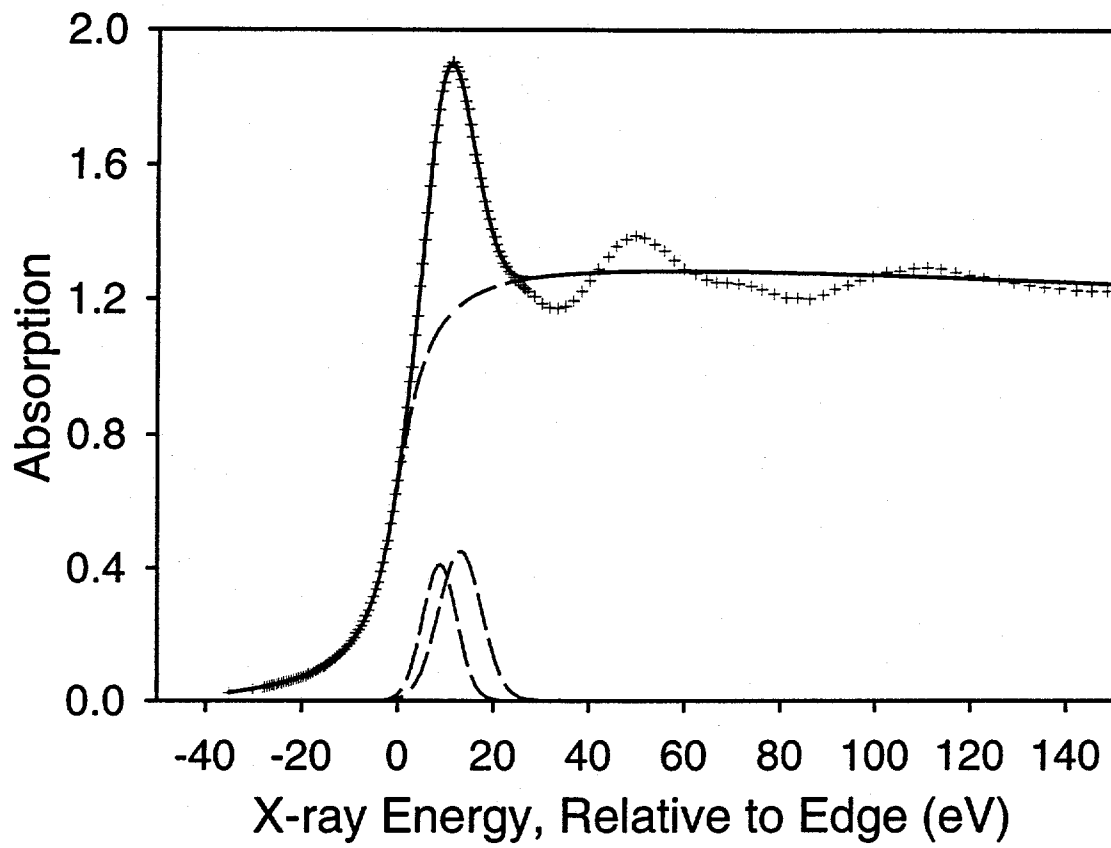| Species	2nd derivative (eV)	Arctangent		Gaussians			
		E_0 (eV)	C (Width)	F_1 (n=1 peak)	G_1 (n=1 width)	F_2 (n=2 peak)	G_2 (n=2 width)
Pu(III)F_3	18059.2(0.3)	18054.9(0.4)	0.19(0.01)	18063.6(0.4)	5.5(0.7)	18068(5)	7.5(2.0)
Pu(IV)O_2	18062.2(0.3)	18057.6(0.3)	0.17(0.02)	18067.3(2.5)	5.9(3.0)	18071(3)	7.3(1.3)
NaPu(V)O_2CO_3	18062.8(0.3)	18059.0(0.4)	0.19(0.01)	18067.0(0.2)	5.2(0.5)	18072(3)	8.4(2.0)
Ba_3Pu(VI)O_6	18065.0(0.3)	18060.6(0.4)	0.20(0.01)	18068.8(0.5)	6.0(0.5)	18075(2)	9.0(1.5)

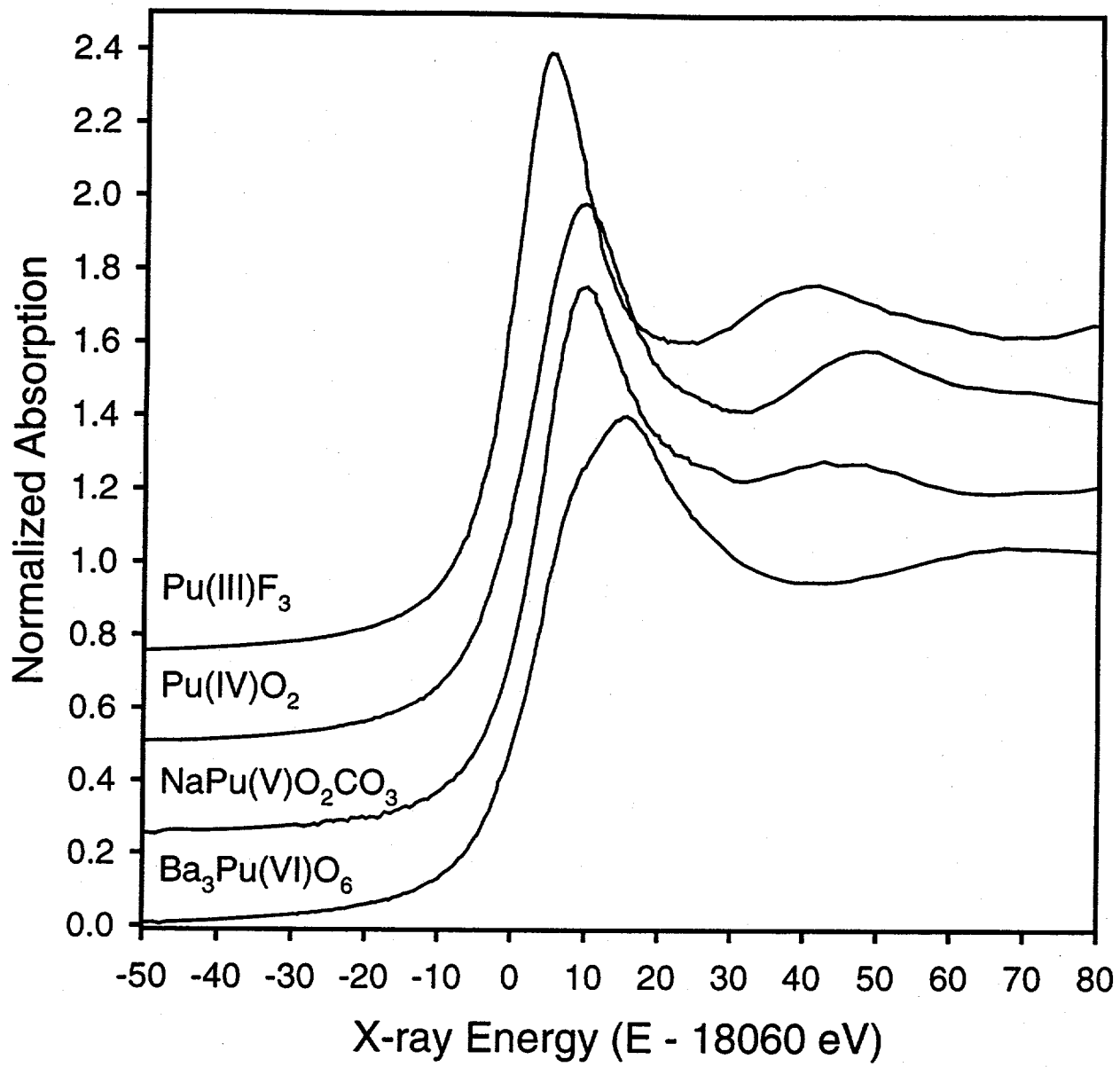Table 1.

Figure 1.
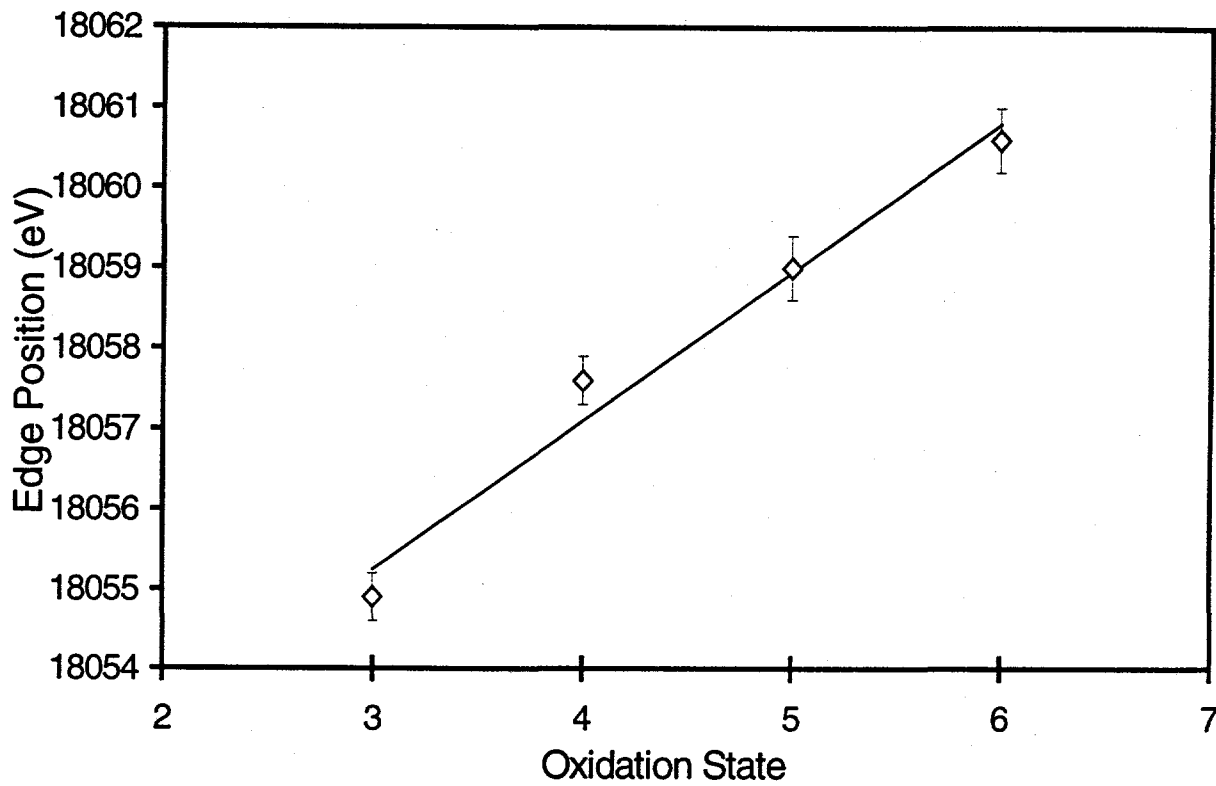
Figure 2.

Figure 3.

Experimental Details

Where was the sample measured:
Materials research – collaborative access team (MRCAT) insertion device line at the Advanced Photon Source (APS)

Ring current and energy:
7 GeV, 50-100 mA

Magnet used (if undulator, tapered or scanned):
Undulator A, tapered and scanned

Type of monochromator (cut, type, fixed exit?):
Double Si(111) crystal non-fixed exit, conventional design with thin web first crystal. At these energies the beam position was essentially fixed.

Details of harmonic rejection:
Rh coated mirror

Detectors used and details:
I_0 filled with nitrogen gas (first run) or mixture of 15%Ar/85%N (later runs)
I_T filled with 15/85 mixture
I_F filled with argon gas (first run) or krypton gas (later runs)
I_{Ref} filled with argon

Energy resolution and how it was determined:
Resolution ~4 eV at 18 keV. Resolution estimated from a measurement of the rocking curve width and the vertical slit size. Beam size 0.4x0.4 mm spot and smaller masked down from full beam.

Sample preparation (particle size, checks on phase purity, uniformity, etc.):
Finely ground powders (no check of size). Particles that were electrostatically attracted to the side of the vial were used.

If relevant, sample thickness μx and $\Delta \mu x$ (if fluorescence, thick/dilute, thin/concentrated):
$\Delta \mu x$, 0.01-0.25

Data Analysis

How was background removed and data normalized:
Pre-edge background line removed. Normalized, when required, to data from 50-300 eV above the edge. A smoothing function was applied to the data to reduce the effect of the chosen lower-energy end point of the normalization fit range.

Identify k=0 location:
Energy reference was a Zr foil with the first inflection point defined as 17999.3 eV.

Describe window function in k- and r-space:
N/A

Window ranges:
N/A .

Reference compounds used and crystallographic data (N, R):
N/A

For theoretical amplitudes an phases, describe structure and give references:
N/A

Other relevant information:
Step size at the edge was ~0.4 eV.