Core-Level Binding Energy Shifts of the Light Actinide Tetrafluorides and Dioxides

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ABSTRACT

The x-ray-induced photoemission spectra for the core and valence levels of PuF_4 and NpF_4 are described. The binding energies observed are compared with previous measurements of the metals, tetrafluorides, and dioxides of other light actinides. Energy shifts from the metal show a nearly linear increase throughout the series Th-Pu as a consequence of the steady increase in the effective nuclear charge. Empirically derived x-ray photoelectron spectroscopy (XPS) sensitivity factors used in quantitative analysis for neptunium and plutonium were obtained.

INTRODUCTION

Many experimental and theoretical XPS studies of the light actinides have been reported in recent years.[1] Although many thorium and uranium compounds have been extensively investigated,[2-6] particularly the metals and oxides, photoemission data exist for only a few transuranic materials. The primary purpose of this investigation was to obtain reliable core-level spectra to be used in the identification of unknown species, mainly Pu-F compounds, for which no previous experimental results exist in the literature. No doubt this lack of information is due to the hazardous nature of these materials and the special facilities needed to safely handle them and protect the environment. The electronic structures of the light actinide tetrafluorides have been calculated,[7] so we have some theory for comparison.

The most useful analytical line for identification of the light actinides is the 4f level. For the tetrafluorides, we observed large binding energy shifts from the metal. These shifts correspond to the classical picture of the chemical shift in which the charge transfer in an ionic compound results in a higher binding energy for the core electrons. PuF_4 and NpF_4 show shake-up satellites about 7 eV above both the 5/2 and 7/2 peaks. These satellites have been seen in uranium, neptunium, and plutonium dioxides by Veal et al.[8] and in many uranium halide and oxyhalide compounds by Thibau, who speculated about their use as indicators of bonding ionicity.[4]

The 5f states in these metals and compounds have attracted much interest because they illustrate the gradual filling and localization of a valence orbital. The chemical state of these elements has a strong influence on the balance between localized and itinerant behavior of the 5f

shell. By looking at various compounds, we can better understand the role of the 5f electrons in bonding.

EXPERIMENTAL PROCEDURE

A PHI Model 549 ESCA/SAM attached to an inert glove box was used for this study. The spectra were collected using a 15-255G double pass cylindrical mirror analyzer (CMA), operating at a resolution of 2% of the pass energy, or about 1.0 eV. Specimens were excited with magnesium $K\alpha$ (1253.6 eV) radiation and were neutralized with low-energy electrons from an electron flood gun. NpF_4 was precipitated from an acid solution with fluoride ions, and following calcination of the oxide, PuF_4 was formed similarly. X-ray diffraction powder patterns confirmed the identity of the compounds. The powders were prepared by gentle grinding with a mortar and pestle to obtain a fresh surface then were pressed into pure indium wafers. A relatively flat surface was produced, and instrument contamination was minimal. Calibration scans were performed near the edge of the specimens, where the lines from the oxidized surface of the indium could be seen through the sample. Several reference energies were used simultaneously to set the electron flood gun conditions and to calibrate the binding energies measured. The adventitious carbon 1s line at 284.6 eV, the indium oxide $3d_{5/2}$ line at 445.3 eV, and the fluorine 1s line at 684.6 eV (the fluorine 1s binding energy is fairly constant between these elements) were all monitored to adjust the electron flood gun current, thereby setting the binding energy scale. Because differential charging can be a problem when analyzing insulators, we observed the carbon 1s energy with respect to the other reference peaks as the flood gun current was raised and lowered. After setting instrumental conditions, spectra were collected from areas on the specimens where the substrate could not be detected. Successive measurements on a single specimen were repeatable to within 0.1 eV. Although these binding energy measurements are reproducible, solid-state problems inherent to the analysis of insulators obscure their accuracy. These measurements represent energies referenced to a floating Fermi edge not coupled with the spectrometer Fermi edge.

RESULTS

Core-Level Spectra

Figure 1 shows the $4f_{7/2}$ and $4f_{5/2}$ regions for PuF_4 and NpF_4. Both regions exhibit the previously mentioned satellite lines about 7 eV above the main peaks. The binding energies measured for the plutonium and neptunium $4f_{7/2}$ peaks were 429.4 and 405.8 eV, respectively. These measurements represent quite large shifts from the values reported for the metals, 422.1 eV for plutonium[9] and 399.5 for neptunium.[10] Shifts reported for the dioxides of plutonium and neptunium are lower, following the expected results simply based on elemental electronegativities. Although the dioxides and tetrafluorides are both tetravalent, the more electronegative anion (fluorine) results in greater charge transfer and thus a higher binding energy.

Table I lists the core level binding energies measured for both PuF_4 and NpF_4, as well as the binding energies previously reported for the metals, tetrafluorides, and dioxides of thorium, uranium, neptunium, and plutonium for comparison.
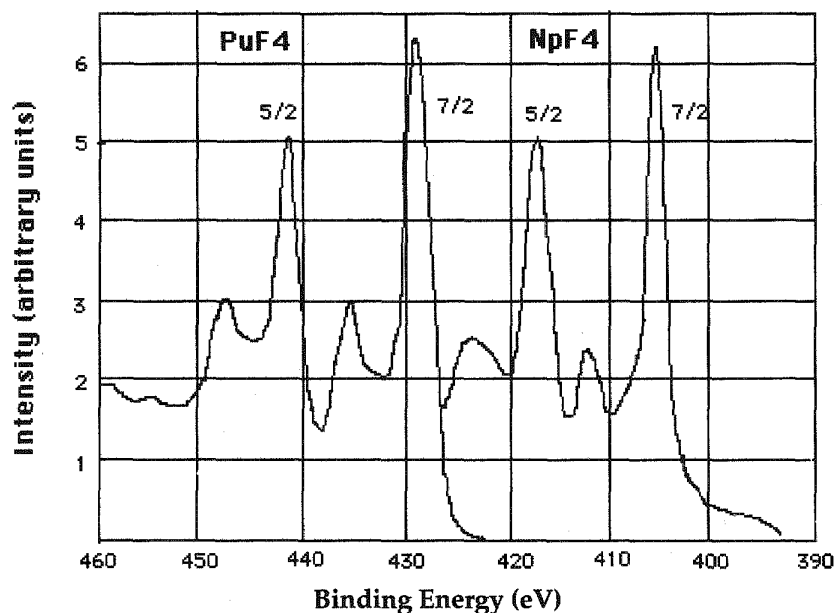

Fig. 1. XPS core-level spectra from NpF_4 and PuF_4 showing the $4f_{7/2}$ and $4f_{5/2}$ regions and associated shake-up satellites.

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TABLE I. Binding Energy Shifts (eV)

Element/Region	4f$_{7/2}$ Binding Energy (eV)			Binding Energy Shifts (eV)	
	Metal	Dioxide	Tetrafluoride	Dioxide	Tetrafluoride
Thorium 4f$_{7/2}$	333.1[a]	334.9[a]	336.3[a]	1.8	3.2
Uranium 4f$_{7/2}$	377.4[a]	380.5[a]	382.1[a]	3.1	4.7
Neptunium 4f$_{7/2}$	399.5[b]	403.6[b]	**405.8**[c]	4.1	6.3
Plutonium 4f$_{7/2}$	422.1[d]	426.5[e]	**429.4**[c]	4.4	7.3

[a]Value from Physical Electronics Handbook of ESCA.
[b]Reference 10.
[c]This work.
[d]Reference 9.
[e]Reference 11.

Core-level shifts from the metal for thorium, uranium, neptunium, and plutonium from Table I are shown graphically in Fig. 2.

Valence-Level Spectra

Figure 3 shows spectra collected from 40 eV below the Fermi level (zero binding energy) show structures similar to those already reported in studies of UF$_4$ by Pireaux et al.[2] The intense peak at about 5 eV is from the localized metal 5f electrons. The broad shoulder of this peak must be attributed to fluorine 2p electrons interacting with those from the metal 5f, 6d, and 7s levels. This shoulder represents a series of unresolved molecular orbitals and is referred to as a "bonding band" in thorium and uranium tetrafluorides by Pireaux. This bonding band is easily resolved from the metal 5f peaks in those elements. As we progress through series Th-Pu, the metal 5f band moves to higher binding energies, nearly merging with the metal-fluorine bonding band. The other two peaks seen at about 30 eV and 20 eV in this
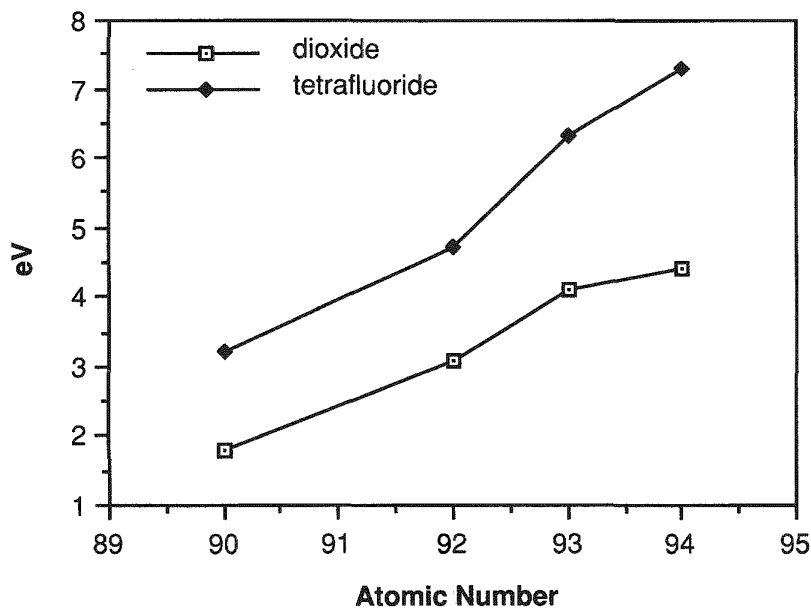

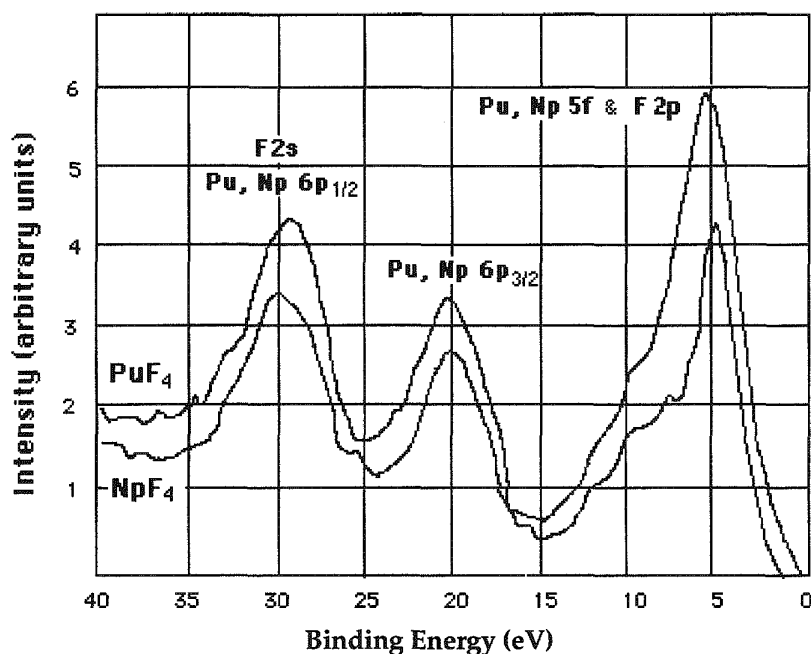*Fig. 2. Binding energy shifts of the light actinides.*

Fig. 3. Valence-level spectra from NpF₄ and PuF₄.

region arise from the fluorine 2s line at 30 eV being superimposed on the less intense metal $6p_{1/2}$ peak and the metal $6p_{3/2}$ line, respectively.

Orbital populations have been calculated for the light actinide tetrafluorides[7] and are shown in Table II. Relatively large differences in the 5f populations are evident as we progress through the series. However, other levels show only slight increases in populations. When the 5f populations for the tetrafluorides are compared with those of the metals (shown in Table III), a trend of increasing differences (Δ 5f) can be seen. Figure 4 shows the 5f populations for both the metals and the tetrafluorides. The 5f occupation for the tetrafluorides does not increase as fast as it does in the metals, so core-level shielding is less effective, resulting in increasing binding energy shifts. The trend seen in binding energy shifts is due largely to the increasing 5f population differences, at least for the series uranium through plutonium. A plot of the tetrafluoride binding energy shifts and the 5f population differences is shown in Fig. 5. The fairly close correlation illustrates how differences in the 5f electron populations between the metals and tetrafluorides for uranium, neptunium, and plutonium are reflected in the binding energy shifts.

Sensitivity Factors for Neptunium and Plutonium

These investigations provided an excellent opportunity for the determination of XPS sensitivity factors to be used in the quantitative analysis of neptunium and plutonium. Because these sensitivity factors are based on fluorine (fluorine 1s intensity) being equal to 1, the ratios of the

Table II. Ground-State Atomic Orbital Populations for AcF₄ Molecules Ac = Uranium, Neptunium, Plutonium

Orbital/Ac	Uranium	Neptunium	Plutonium
$5f_{5/2}$	1.49	1.93	2.44
$f_{7/2}$	0.96	1.45	1.94
	2.45	**3.38**	**4.38**
$6p_{1/2}$	1.99	2.00	2.00
$p_{3/2}$	3.72	3.73	3.75
	5.71	5.73	5.75
$6d_{3/2}$	0.75	0.80	0.81
$d_{5/2}$	0.75	0.78	0.80
	1.50	1.58	1.61
$7s_{1/2}$	0.21	0.18	0.17
$7p_{1/2}$	0.08	0.08	0.08
$p_{3/2}$	0.71	0.75	0.82
	0.79	0.83	0.90

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areas under the respective curves can be used. The intense $4f_{7/2}$ peaks for the metals (including the associated satellites) and the fluorine 1s regions were used to arrive at the sensitivity factors shown below. These values should be applicable to other spectrometers with the same transmission characteristics, i.e., variable retarding voltage and constant pass energy.

Empirically Derived Sensitivity
Factors
(relative to fluorine 1s = 1.0)

Plutonium $4f_{7/2}$ = 6.5
Neptunium $4f_{7/2}$ = 6.3

The utility of these measurements was recently demonstrated when an unknown deposit was submitted for analysis. X-ray diffraction results suggested that the deposit was plutonium PuF_4, but since the deposit was so thin, there was some uncertainty and the submitter wanted confirmation. The powder was characterized by obtaining XPS spectra from the plutonium 4f, fluorine 1s, and valence regions. Atomic concentration estimates, based on the previously obtained relative sensitivity factors normalized to 100%, were 19.8% plutonium and 80.1% fluorine. The binding energies determined matched those performed on standard PuF_4, confirming the x-ray diffraction results. Since then, many unknown powders, thin films, precipitates, and deposits have been identified as PuF_4, based on these binding energy values as well as on stoichiometric determinations.

Table III. The 5f Occupation

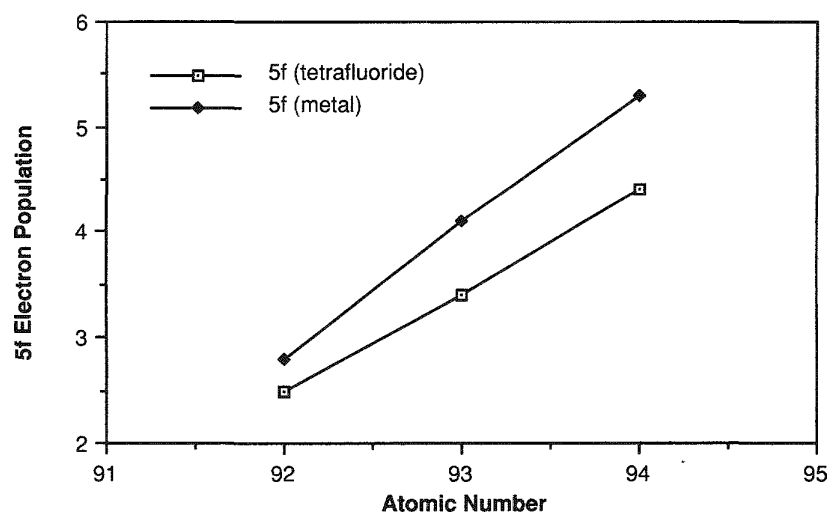|	Metal	Tetrafluoride	Δ 5f
Uranium	2.8	2.45	0.4
Neptunium	4.1	3.38	0.7
Plutonium	5.3	4.38	0.9

Fig. 4. The 5f electron populations for uranium, neptunium, and plutonium metals and tetrafluorides.
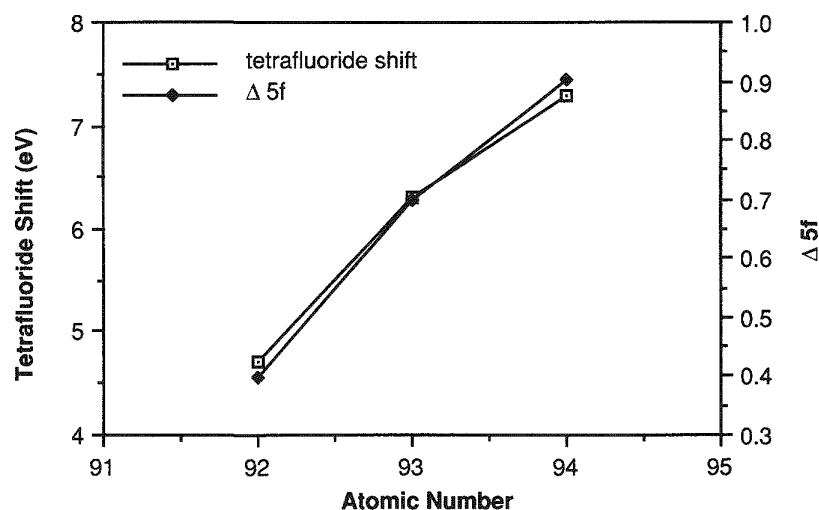

Fig. 5. Plot of the differences in 5f populations and binding energy shifts for uranium, neptunium, and plutonium.

CONCLUSIONS

Core and valence binding energies for NpF_4 and PuF_4 were determined. The large chemical shifts indicate compounds that are more ionic than the oxides, but the valence spectra suggest some covalent characteristics in the interaction of the fluorine 2p band with the metal 5f, 6d, and 7s electrons. Because the 5f, 6d, and 7s energies are about equal throughout the light actinides and because their orbitals overlap, bonding can involve any of them. The linear increase in core-level binding energy shifts is expected to break down at americium where the 5f electrons become more core-like.

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