X-RAY PHOTOELECTRON STUDY OF ACTINIDE (Th, U, Pu, Am) NITRATES

by

Yury A. TETERIN[1], **Anton Yu. TETERIN**[1], **Nikolay G. YAKOVLEV**[1], **Igor O. UTKIN**[1], **Kirill E. IVANOV**[1], **Leonid D. SHUSTOV**[1], **Labud Dj. VUKČEVIĆ**[2], **and George N. BEK-UZAROV**[3]

In this work an X-ray photoelectron spectroscopy study of nitrates $Th(NO_3)_4\,4H_2O$, $UO_2(NO_3)_2\,nH_2O$, $Pu(NO_3)_4\,nH_2O$, and $Am(NO_3)_2\,nH_2O$ was done in the binding energy range from 0 to 1000 eV in order to draw a correlation of the fine spectral structure parameters with the actinide ions oxidation states, close environment structure, and chemical bond nature. The linearity of the dependence of the $An5f^n$ line intensity on the number n_{5f} of the $An5f$ electrons was proven to remain up to the Am^{3+} ion with the electron configuration $\{Rn\}\,5f^6$. The spectral structure in the binding energy range from 0 to ~15 eV was associated with the formation of the outer valence molecular orbitals due to the interaction of the $An6d-$, $7s$, $5f-O2p$ electrons, and the fine spectral structure in the binding energy range from ~15 to ~50 eV – with the formation of the inner valence molecular orbitals due to the interaction of the $An6p-O2s$ electrons from the filled neighboring atomic orbitals of actinide and oxygen in the studied compounds. The fine structure of the core level electron spectra in the binding energy range from ~50 to 1000 eV was shown to correlate with the actinide ion oxidation state.

Key words: actinide nitrates, XPS, outer valence (OVMO) and inner valence (IVMO) molecular orbitals

INTRODUCTION

Understanding the mechanisms of the fine X-ray photoelectron spectral structure and establishment of the correlation of its parameters with the physical and chemical properties of actinide compounds is a topical problem [1-5]. Solving this problem expands significantly the range of X-ray photoelectron spectroscopy (XPS) for the study of actinide materials. It is essential to the nuclear industry technologies employed on all the stages from

ore processing to the spent fuel transmutation, as well as to the corresponding ecological problems [6-11].

The XPS method enables determination of the relative radionuclide contents, oxidation states of the included radionuclides, their ionic compositions, the structure of their close environments, the type of ligands and the nature of the chemical bond [1, 4, 11].

The present work examined the samples of thorium $Th(NO_3)_4\,4H_2O$, uranium $UO_2(NO_3)_2$ $2H_2O$, plutonium $Pu(NO_3)_4\,nH_2O$ and americium $Am(NO_3)_3\,n\ _2O$ nitrates in the binding energy range from 0 to 1000 eV in order to study the correlation of the fine X-ray photoelectron spectral structure parameters with the oxidation states of the actinide ions, the structure of their close environment and the nature of the chemical bond.

Authors' addresses:
[1] Russian Research Center "Kurchatov Institute",
   1, Kurchatov sq., Moscov 123182, Russia
[2] Faculty of Natural Sciences and Mathematics,
   University of Montenegro, P. O. Box 211, 81001 Podgorica,
   Serbia and Montenegro
[3] VINČA Institute of Nuclear Sciences
   P. O. Box 522, 11001 Belgrade, Serbia and Montenegro

E-mail address of corresponding author:
teterin@ignph.kiae.ru (Y. A. Teterin)

EXPERIMENT

XPS spectra of the studied solid-state samples were taken with an HP-5950A spectrometer using

monochromatized Al K $_{1,2}$ (hv = 1486.6 eV) X-rays utilizing a low energy electron flood gun for charge compensation under 1.3·10^{-7} Pa at a room temperature. Overall resolution measured as the Au4f$_{7/2}$ electron line full width half maximum (FWHM) was 0.8 eV. Electron binding energies (E_b) are given relative to the E_b of the C1s electrons from adventitious hydrocarbons at the sample surface defined as 285.0 eV. On the gold substrate E_b(C1s) = 284.7 eV at E_b(Au4f$_{7/2}$) = 83.8 eV. The line widths are given relative to that of the C1s line (C1s) = 1.3 eV. The measurement errors of line position and widths were 0.1 eV, whereas relative line intensities errors were about 10%.

The samples of thorium and uranium nitrates for the XPS measurements were prepared by pressing powder ground in the agate mortar into indium on the metallic substrate as a thick layer with flat surface. The samples of plutonium and americium nitrates were precipitated as thing layers from the nitrate solutions [12].

The qualitative elemental analysis was done for all the studied samples using the formula:

$$\frac{n_i}{n_j} \quad \frac{S_i \sigma_j}{S_j \sigma_i} \sqrt{\frac{hv \quad E_{bj}}{hv \quad E_{bi}}}$$

where n_i/n_j is the relative concentration of the studied atoms, S_i/S_j – relative intensity (area) of the core spectral lines, $_i$ and $_j$, E_{bi} and E_{bj} – corresponding photoemission cross-sections [13] and binding energies, respectively.

RESULTS AND DISCUSSIONS

The XPS spectra from actinide nitrates in the binding energy range from 0 to   eV exhibit the complex structure due to the An5f electrons, as well as the An6d   7s, and O(N)2p electrons from the outer valence molecular orbitals (OVMO) (fig. 1) [5, 8]. The spectral structures of plutonium and americium nitrates in this energy range are mostly due to the An5f electrons since their photoemission cross-sections are significantly higher than those for the valency An6d–, 7s, and O(N)2p electrons [13]. The spectra of thorium and uranium nitrates do not show the similar narrow lines around the zero binding energy. This agrees with the formal valency of Th^{4+} and U^{6+}. The OVMO line widths are 2.5 eV for thorium, 3.5 eV for uranium, 3.4 for plutonium, and 2.4 eV for americium compounds (fig. 1). The electron binding energies for the studied actinide nitrates are given in the tab. 1. The An5f line intensity grows with the actinide atomic number Z. This correlates with the formal number n$_{5f}$ of the weakly bound An5f^n electrons in these compounds.

In the ionic approximation, the spectral structure of the studied actinide nitrates depends on the ac-
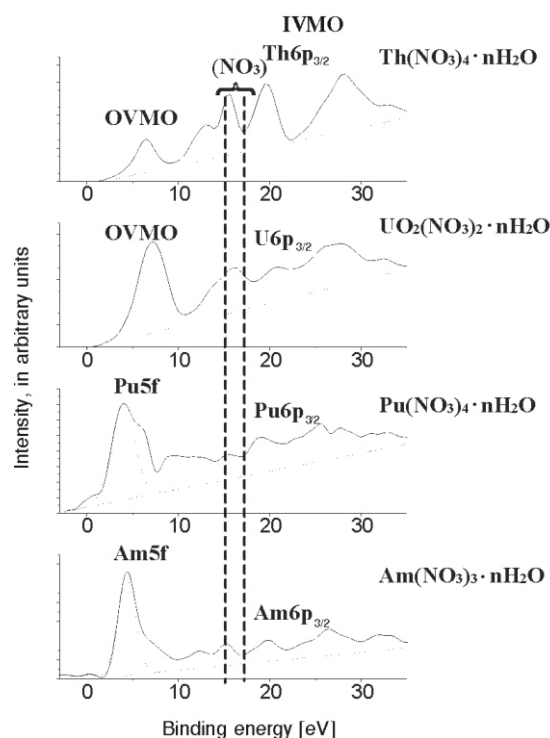

Figure 1. XPS spectra of the OVMO and IVMO binding energy regions of actinide (Th, U, Pu, Am) nitrates

tinide ion final state after the electron photoemission [5]. The An5f binding energy grows with the actinide atomic number Z while the binding energies of the OVMOs due to the An6d–, 7s, and O(N)2p electrons remain constant (see table). Earlier, the experimental dependence of the relative An5f intensity on the formal number n$_{5f}$ of the An5f^n electrons, obtained as an An5f/An4f$_{7/2}$ area ratio for actinide compounds was shown to be linear [8]. The experimental dependence of the relative An5f intesity on the formal number n$_{5f}$ of the An5f^n electrons for actinide nitrates is given in fig. 2. This figure also shows the data for uranium UO$_2$, thorium ThO$_2$, plutonium PuO$_2$, and americium AmO$_2$ oxides [8, 14]. This dependence is linear within the measurement errors and can be used in determination of actinide oxidation states in compounds.

In the binding energy range from 15 to 40 eV the studied spectra manifest the fine structure due to electrons of the inner valence molecular orbitals (IVMO). These spectra are complex and can be subdivided into the two IVMO groups (fig. 1). One – attributed to the IVMO characterizing the binding actinide-oxygen (An-O), the other one – due to the IVMO of the NO$_3^-$ group. Interpretation of this structure is a topic of a separate study [9]. The considered experimental data [4, 12] taking into account the theoretical results [4] allowed a suggestion that the fine XPS structure in the energy range from ~15 to 50 eV of the studied nitrates shows up due to the effective formation of the inner

Table 1. XPS electron binding energies for valence and core level of actinides in the studied and reference compounds. The data for PuO_2 and AmO_2 are taken from [14]

XPS line	$Th(NO_3)_4$ $4H_2O$	ThO_2	$UO_2(NO_3)_2$ $2H_2O$	UO_2	$Pu(NO_3)_4$ nH_2O	PuO_2	$Am(NO_3)_3$ nH_2O	AmO_2
$An5f_{7/2, 5/2}$				1.9	4.1	4.7	4.5	
$An6p_{3/2}$	18.4	16.5	19.9	18.0	19.5 21.3	18.1	18.1 19.8	18.7
$An6p_{1/2}$		25.5	29.0 31.4	28.5	31.4 33.9	30.3	31.2 32.9	31.7
$An5d_{5/2}$	87.8	86.3	99.2	97.3	106.0	104.7	109.9	109.0
$An5d_{3/2}$	94.8	93.3	107.7	105.5	112.0 118.3			
$An5p_{3/2}$	176.7 180.8 198.9	175.1 178.6	202.2 204.1		217.4		219.6	
$An4f_{7/2}$	335.8	334.3	383.1	380.9	427.1	426.3	449.9	448.8
$An4f_{5/2}$	345.2	343.6	394.0	391.8	439.8	439.0	464.5	463.1
$An4d_{5/2}$	677.1	675.6	741.9	739.3	803.9	801.5	834.0	832.6
$An4d_{3/2}$	714.8	712.7	784.8	781.6	852.4	849.5	884.9	883.7
$O2s_{1/2}$	26.7	22.0	26.0 27.5	23.3	25.8 27.2	22.5	26.5	23.7
$O1s_{1/2}$	533.3	530.2	533.6	530.5	533.0	530.0	533.1	529.6
$N1s_{1/2}$	407.7		407.8		407.6		407.7	

valence molecular orbitals (IVMO) from the An6p and O2s atomic shells. The An6p-O2s interaction complicates the spectral structure (fig. 1).

The An4f spectra from the studied compounds also show fine structure. For example, fig. **3** gives the spectra from plutonium and americium nitrates. The $An4f_{7/2}$ lines are marked. These spectra exhibit shake up satellites on the higher binding energy side from the basic lines. The shake up process means an extra excitation within the molecular orbitals beside the electron photoemission. It results in the satellites on the higher binding energy sides from the basic lies. The distance from the basic
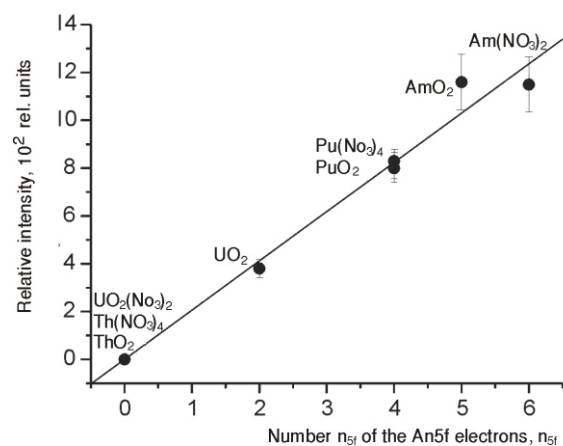
line to the satellite ΔE_{sat} characterizes the oxidation states of actinide ions and the close environment in compounds [1, 5]. These differences were found to be 3-4 eV for An^{6+} and about 7 eV for An^{4+}. The
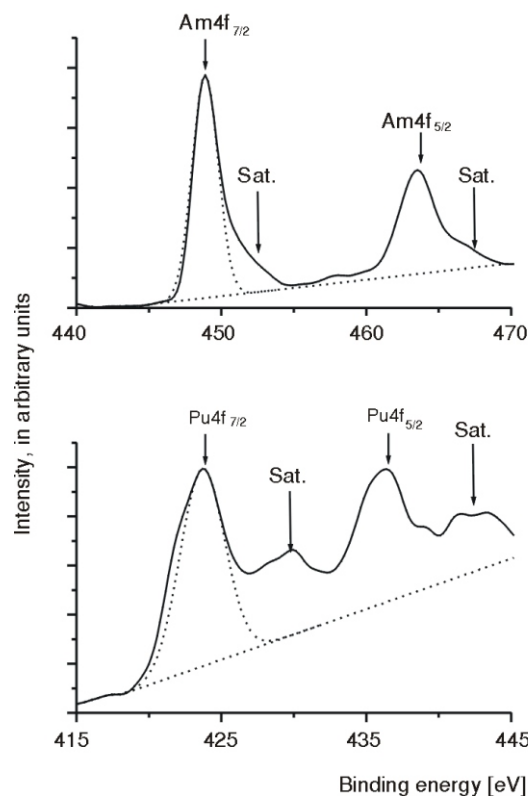

Figure 2. Experimental dependences of the relative intensity $IAn5f/IAn4f_{7/2}$ on the number n_{5f} of the $An5f^n$- electrons in actinide (Th, U, Pu, Am) nitrates and oxides

Figure 3. XPS An4f spectra from $Am(NO_3)_3$ nH_2O and $Pu(NO_3)_4$ nH_2O

An4f binding energies in actinide nitrates were found to grow with the actinide atomic number Z, and were shown to be higher than those for the corresponding actinide oxides (table). It agrees with the data of fig. 3.

CONCLUSIONS

The X-ray photoelectron spectra of nitrates of actinides (Th, U, Pu, Am) were measured in the binding energy range from 0 to 1200 eV. The relative intensities of the OVMO XPS lines of the studied nitrates were determined.

An experimental dependence of the relative An5f^n intensity $I_{5f}^{Exp} = I(\text{An}5f)/I(\text{An}4f_{7/2})$ on the number n_{5f} of the An5f electrons ($I_{5f}^{Exp} = 0.02\,n_{5f}$) was obtained. It allowed a direct determination of actinide ions oxidation states. This dependence was shown to be linear up to Am^{3+}. The An5f intensity was established to correlate with the number n_{5f} of the An5f^n electrons.

The complex structure in the binding energy range from ~15 to 50 eV due to the An6p-O2s interaction was interpreted. The qualitative evidence for formation of the outer and inner valence molecular orbitals in nitrates of actinides (Th, U, Pu, Am) on the basis of their XPS fine spectral structure parameters in the binding energy range from 0 to 50 eV was obtained. The mechanisms of formation of the fine spectral structure in the core electron spectra of the studied materials were discussed.

ACKNOWLEDGEMENTS

REFERENCES

[1]   Teterin, Yu. A., Kulakov, V. M., Baev, A. S., Nevzorov, N. B., Melnikov, I. V., Streltsov, V. A., Mashirov, L. G., Suglobov, D. N., Zelenkov, A. G., A Study of Synthetic and Natural Uranium Oxides by X-Ray Photoelectron Spectroscopy, *Physics and Chemistry of Minerals, 7* (1981), pp. 151–158

[2]   Gouder, T., Wastin, F., Rebizant, J., Havela, L., 5f-Electron Localization in PuSe and PuSb, *Physical Review Letters, 84* (2000), 15, pp. 3378-3381

[3]   Black, L., Miserque, F., Gouder, T., Havela, L., Rebizant, J., Wastin, F., Preparation and Photoelectron Spectroscopy Study of Un$_x$ Thin Films, *Journal of Alloys and Compounds, 315* (2001), pp. 36-41

[4]   Teterin, Yu. A., Gagarin, S. G., Inner Valence Molecular Orbitals and the Structure of X-Ray Photoelectron Spectra, *Russian Chemical Review, 65* (1996), 10, pp. 825–847

[5]   Teterin, Yu. A., Baev, A. S., Ivanov, K. E., Mashirov, L. G., Suglobov, D. N., X-Ray Photoelectron Spectral Structure of the Low Binding Energy Electrons of Uranium Compounds (in Russian), *Radiokhimiya, 38* (1996), 5. p. 395-402

[6]   Cox, L. E., Ellis, W. P., Cowan, R. D., Allen, J. W., Oh, S.-J., Lindau, I., Pate, B. B., Arko, A. J., Valence-Band Photoemission in UO$_2$(111) Near the 5d Resonant Photon Energy, *Physical Review B., 35* (1987), 11, pp. 5761-5765

[7]   Allen, G. C., Holmes, N. R., Mixed Valency Behaviour in Some Uranium Oxides Studies by X-Ray Photoelectron Spectroscopy, *Canadian Journal of Applied Spectroscopy, 38* (1993), 5, pp. 124-130

[8]   Teterin, Yu. A., Baev, A. S., Teterin, A. Yu., Ivanov, K. E., The An5f Intensity and Actinide Oxidation States in Compounds (in Russian), *Doklady Akademii Nauk of RAS, 348* (1996), 2, pp. 213-216

[9]   Hirata, M., Monjyushiro, H., Sekine, R., Onoe, J., Nakaamarsu, H., Mukoyama, T., Adachi, H., Takeuchi, K., Valence Electronic Structure of Uranyl Nitrate UO$_2$(NO$_3$)$_2$ 2H$_2$O, *Journal of Electron Spectroscopy and Related Phenomena, 83* (1997), pp. 59-64

[10]   Teterin, Yu. A., Baev, A. S., Bogatov, S. A., X-Ray Photoelectron Study of Samples Containig Reactor Fuel from "Lava" and Product Groving on it which Formed at Chernobyl NPP due to the Accident, *Journal of Electron Spectroscopy and Related Phenomena, 68* (1994), pp. 685-694

[11]   Teterin, Yu. A., Teterin, A. Yu., Lebedev, A. M., Dementjev, A. P., Utkin, I. O., Nefedov, V. I., Bubner, M., Reich, T., Pompe, S., Heise, K.-H., Nitsche, H., X-Ray Photoelectron Spectroscopy Investigation of U(VI) and Fe(III) with Natural Humic Acid in Aqueous Solutions, *J. Prakt. Chem., 341* (1999), 8, pp. 773-377

[12]   Teterin, Yu. A., Baev, A. S., Yakovlev, N. G., XPS Spectral Structure of Plutonium and Americium Nitrates (in Russian), *Voprosy Atomnoi Nauki i Tekhniki (ser. NuclearPhysical Studies)*, Russian Research Centre "Kurchatov Institute", Moscow, (1992), 3, pp. 58-60

[13]   Scofield, J. H., Hartree-Slater Subshell Photoionization Cross-Sections at 1254 and 1487 eV, *Journal of Electron Spectroscopy and Related Phenomena, 8* (1976), pp. 129-137

[14]   Veal, B. W., Lam, D. J., Diamond, H., Hoekstra, H. R., X-Ray Photoelectron Spectroscopy Study of Oxides of the Transuranium Elements Np, Pu, Am, Cm, Bk, and Cf, *Physical Review B, 15* (1997), 6, pp. 2929-2942

Jурij А. ТЕТЕРИН, Антон Jу. ТЕТЕРИН, Николај Г. JAKOВЛЕВ, Игор О. УТКИН, Кирил Е. ИВАНОВ, Лабуд Ђ. ВУКЧЕВИЋ, Ђорђе Н. БЕК-УЗАРОВ

РЕНДГЕНСКА ФОТОЕЛЕКТРОНСКА АНАЛИЗА АКТИНИДНИХ (Th, U, Pu, Am) НИТРАТА

У овом раду приказани су резултати анализе нитрата $Th(NO_3)_4 \cdot nH_2O$, $UO_2(NO_3)_2 \cdot nH_2O$, $Pu(NO_3)_2 \cdot nH_2O$ и $Am(NO_3)_2 \cdot nH_2O$, чија је енергија везе у опсегу од 0 до 1000 eV, у намери да се нађе корелација између параметара фине спектралне структуре и оксидационих стања јона актинида, затим и структуре њиховог блиског окружења и природе хемијских веза. Доказано је да се линеарност зависности интензитета линије $An5f^n$ од броја n_{5f} електрона $An5f$ одржава све до јона Am^{3+}, чија електронска конфигурација је $Rn\ 5f^6$. Показано је да се структура спектра у области енергије везе од 5 до 50 eV односи на формирање унутрашњих валентних молекулских орбитала, као последица интеракције $An6d$–, $7s$, $5f$ – $O2p$ електрона са попуњених суседних атомских орбитала актинида и кисеоника разматраног једињења. Показано је да структура електронског спектра попуњених љуски које су ближе језгру у области енергија од 50 до 1000 eV и која се јавља као последица ефеката многочестичних интеракција корелира са структуром спољашњих валентних молекуларних орбитала, а да њени параметри корелирају са оксидационим стањем актинидних јона.