



### Tonya Vitova

Dr. Vitova, a Scientist at the Institute for Nuclear Waste Disposal at Karlsruhe Institute of Technology, Germany, presented her invited plenary talk at Pu Futures 2018 during Plenary Session VIII. The talk was titled "Pu Electronic Structure and Speciation Applying Pu  $M_5$  Edge HR-XANES and RIXS."



### Paul Bagus

Dr. Bagus is a Research Professor at the University of North Texas. He was a keynote speaker at Pu Futures 2018 and gave his talk titled "Theoretical Analysis of the Properties of Pu(IV) and Pu(VI) in the Condensed Matter Physics I technical session."

# Probing Actinide Covalency: Plutonium Electronic Structure Studies Using High Energy Resolution X-Ray Spectroscopy

Tonya Vitova,<sup>1</sup> Horst Geckeis,<sup>1</sup> Paul S. Bagus<sup>2</sup>

The nature of chemical bonds in compounds with actinide (An) elements and the role of covalency is a topic of extensive research. Understanding these bonds ultimately allows us to design actinide material properties or predict their behavior in the environment. Covalency is a very important component of bonding that affects the chemical properties of a compound, and can be broadly defined for actinide complexes as the amount of mixing between metal-ligand orbitals in a bonding interaction. Advanced spectroscopic methods can provide new insights into the nature of these chemical bonds and can help the development and optimization of theoretical approaches for predicting chemical and physical properties.

## Principles of X-ray emission and absorption spectroscopy

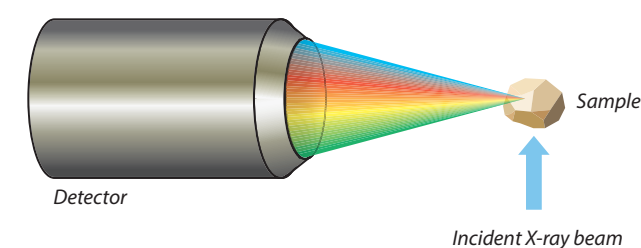
One of the commonly used spectroscopic methods for studies of actinide materials is X-ray absorption spectroscopy (XAS). It is based on the absorption of X-ray radiation by atoms, leading to the excitation of a strongly-bound electron into an empty orbital that is only weakly bound. The resulting excited state decays or relaxes quickly through either the emission of electrons (photo- or Auger-emission) or X-ray fluorescence. The detection of these decay events is important to help us understand the nature of the An 5f and 6d shells, where the chemistry largely occurs.

XAS is element-sensitive because the characteristic electron binding energies are dependent on atomic number ( $Z$ ); it is also angular momentum selective due to Fermi's golden rule. We can probe the amount of An f and d character of the unoccupied valence states by looking at different adsorption edges. Specifically, these include  $3d \rightarrow 5f$  and  $2p \rightarrow 6d$  excitations ( $M_{4,5}$  and  $L_3$  adsorption edges).

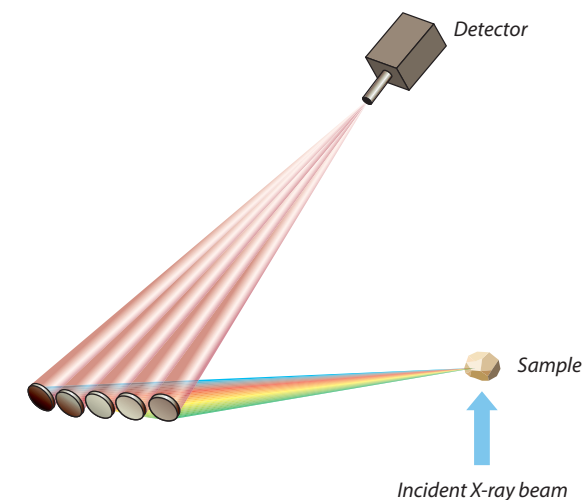
X-ray absorption spectra can be recorded in direct transmission geometry using the Lambert-Beer law to obtain the linear X-ray absorption coefficient while tuning the X-ray energy in the vicinity of an absorption threshold (i.e., the inner shell binding energy). The spectra can also be acquired by recording the intensity of a follow-up (relaxation) process, i.e., emission of electrons or characteristic X-ray fluorescence. Simplified schemes of the latter process for the  $M_5$  absorption edge using the most intense characteristic fluorescence line  $M_\alpha$  are shown in Fig. 2 (lines A and B). We focus herein on the first portion ( $< 200$  eV) of the X-ray absorption spectrum, which is named X-ray absorption near edge structure (XANES; Fig. 1c,d).

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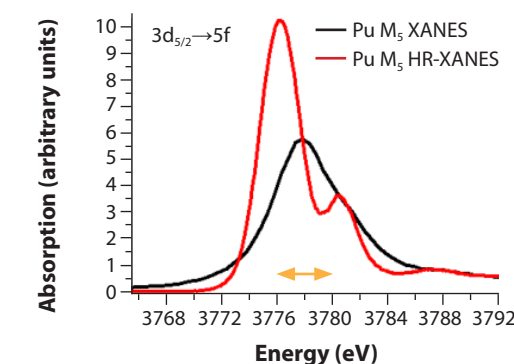
(a) Solid-state detector used for XANES



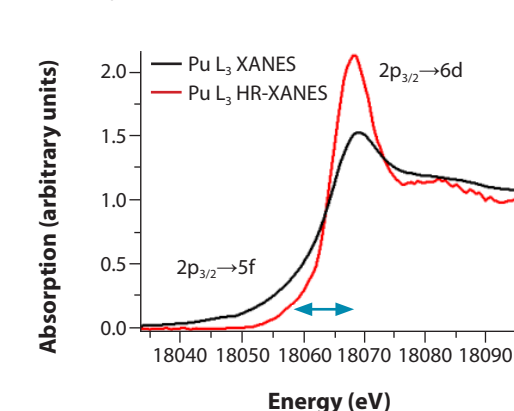
(b) Wavelength dispersive device used for HR-XANES



(c) Pu  $M_5$  absorption edge



(d) Pu  $L_3$  absorption edge



## Limitations to spectroscopic resolution

The resolution of core-level spectroscopies such as XAS is limited by two factors: spectral broadening caused by the experimental setup and the lifetime of the ionized form of the atom (the core-hole state), which, from the quantum mechanical uncertainty principle, leads to an uncertainty in the energy of short-lived core-hole states.

The experimental energy resolution of XAS is tremendously improved if the emitted X-ray fluorescence (element-specific fluorescence line) is detected by a wavelength dispersive device following diffraction (i.e., analyzer crystals for hard to tender X-rays, 20–2 keV; Fig. 1b) instead of directly from a standard solid-state device with low energy resolution (such as a silicon-lithium or high-purity germanium detector; Fig. 1a). In this way, the  $L_3$  and  $M_{4,5}$  high-resolution XANES (HR-XANES) spectra are dramatically improved and exhibit a rich fine structure that cannot be resolved with conventional XAS detection setups (Figs. 1c,d). The lifetime of the core-hole in the final state is intrinsic and determines the spectral broadening.

An X-ray emission spectrometer also allows us to record resonant inelastic X-ray scattering (RIXS) maps. These maps depict a 2D representation of X-ray fluorescence emission measured as a function of excitation X-ray energy scanned across an absorption edge (Fig. 3, left). They allow us to detect energy shifts between emission lines measured at different excitation energies (see lines A and B in Fig. 2). It can be useful to compare HR-XANES spectra of different materials extracted from a RIXS map at specific emission energies.

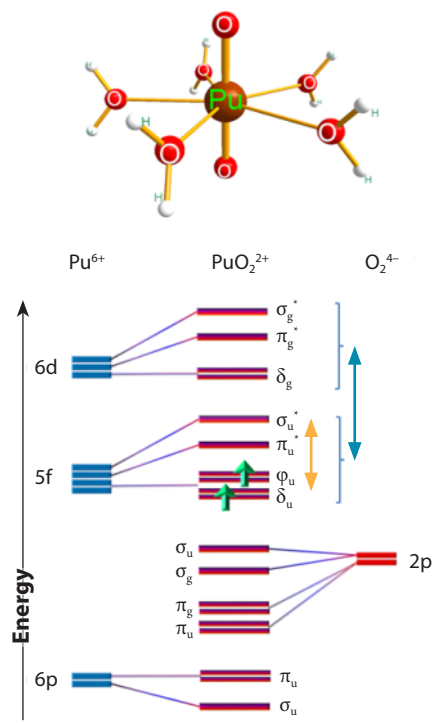
**Figure 1.** Instrumental setups for (a) XANES and superior (b) high-resolution (HR) XANES. The latter employs a wavelength dispersive detector following diffraction rather than a standard solid-state device. The differences in the spectra obtained are shown in (c) Pu  $M_5$  and (d) Pu  $L_3$  absorption edge spectra—the black lines show data from the standard instrument, where the red lines give greater detail using the high resolution setup. The blue and orange arrows correspond to energy differences in Fig. 2. Spectra are for Pu(VI) in aqueous 1M perchloric acid ( $\text{HClO}_4$ ) solution ( $\text{PuO}_2^{2+}$ ).

### Tools for studying covalency of the actinide chemical bond

Neidig and co-workers described in their 2013 article “Covalency in f-element complexes” (published in *Coordination Chemistry Reviews*) that the covalency of an actinide-ligand chemical bond can be significant when there is either a strong overlap or good energy match of metal and ligand valence orbitals. These two cases are known as orbital overlap- or energy-driven covalency of the actinide-ligand chemical bond.

In order to explore chemical bond covalency in Pu complexes we studied a well-investigated material, Pu(VI) in aqueous 1M perchloric acid ( $\text{HClO}_4$ ), using the  $M_5$  edge HR-XANES and RIXS techniques. All experiments were performed at the INE-Beamline and ACT station of the CAT-ACT-Beamline at the Karlsruhe Research Accelerator (KARA) at the Karlsruhe Institute of Technology (KIT) in Germany.

Pu(VI) in  $\text{HClO}_4$  forms strong, covalent trans-dioxo linear bonds (trans refers to the location of the oxygen atoms, on opposite sides of the metal ion; Fig. 2), termed plutonyl ( $\text{PuO}_2^{2+}$ ) bonding. Five loosely-bound water molecules are also located in the equatorial plane of the plutonyl cation. A qualitative molecular orbital scheme of  $\text{PuO}_2^{2+}$  is depicted in Fig. 2; this also shows the orbital energy levels which are detected using the HR-XANES technique by observing the electronic transitions between the Pu 3d and 5f/6d orbitals. The linear structure of the  $\text{PuO}_2^{2+}$  ion means that the Pu valence orbitals are most usefully described in terms of their sigma, pi, delta, and phi character (with respect to rotation about the axial Pu–O<sub>ax</sub> z-axis).



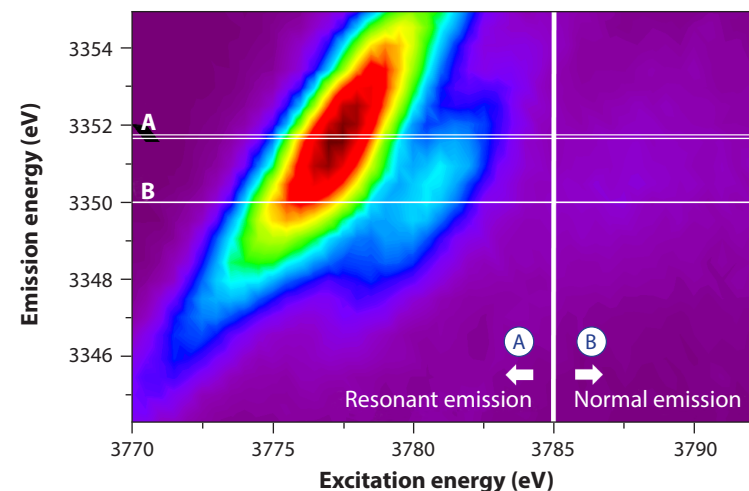
**Figure 2.** Schematic view (top) and molecular orbital scheme of plutonyl (bottom). The orange and blue arrows show the energy shifts between the different unoccupied orbitals measured in the spectra, as indicated in Fig. 1c,d.

### Overlap-driven covalency

The seven empty or partially-occupied 5f orbitals of the  $\text{PuO}_2^{2+}$  cation (Fig. 2) are split by spin-orbit coupling and the ligand field of the axial and equatorial ligands. When there is more than one electron in the 5f shell, Coulomb repulsions between the electrons become important. The spin-orbit splitting of the 5f electrons is approximately 1 eV while the ligand-field splitting can be as large as 7 eV for actinyl species. Matsika described in “Electronic structure and spectra of actinyl ions”, published in the *Journal of Physical Chemistry A* in 2001, that the influence of these effects can be ordered as follows: axial ligand field effects on 5f-based sigma and pi anti-bonding orbitals > Coulomb repulsion > spin-orbit coupling > summed effects of axial and equatorial ligand fields on the 5f-based delta and phi orbitals.

The axial field exerts the greatest effect—this is caused by the strongly covalent nature of the An–O<sub>ax</sub> (An = U, Np, or Pu) bond manifested by the large overlap of the An (5f, 6p) and O (2p) orbitals. As a result, the 5f sigma and pi anti-bonding orbitals are shifted with respect to the 5f delta and phi orbitals (delta ≈ phi < pi anti-bonding << sigma anti-bonding; Fig. 4); this effect is called “pushing from below”. Pu  $M_{4,5}$  absorption edge HR-XANES and RIXS spectra display electronic transitions of 3d electrons to those 5f delta/phi, 5f pi anti-bonding, and 5f sigma anti-bonding orbitals in the same spectrum (Figs. 1c, 3, and 4).

Due to the improved instrumental resolution it was possible to measure energy differences between the 5f delta/phi and the 5f pi/sigma anti-bonding peaks. We propose using changes in these energy shifts, specifically between the 5f delta/phi and the 5f sigma anti-bonding peaks, as a qualitative measure of changes in the overlap-driven covalency of the actinyl bond. We found that these energy differences decrease in the order  $\text{UO}_2^{2+} > \text{NpO}_2^{2+} > \text{PuO}_2^{2+}$  (Fig. 4), suggesting that the overlap-driven covalency of the An–O<sub>ax</sub> bond decreases similarly. This is consistent with the intuitive view that the 5f orbital size decreases as the nuclear charge increases from U to Pu.



**Figure 3.** Resonant inelastic X-ray scattering (RIXS) map, left, depicts characteristic Pu  $M_\alpha$  fluorescence at the Pu  $M_5$  absorption edge. Horizontal lines A and B show maximum intensities of the most intense resonance and normal emissions; the shift between these lines reflects the gaps between the  $4f_{7/2}$  and  $3d_{5/2}$  states (right). Schemes A and B show resonant and normal emission, respectively, when the electron is excited into either unoccupied 5f orbitals or the continuum (i.e., the atom is ionized); circles represent core holes.

### Energy-driven covalency

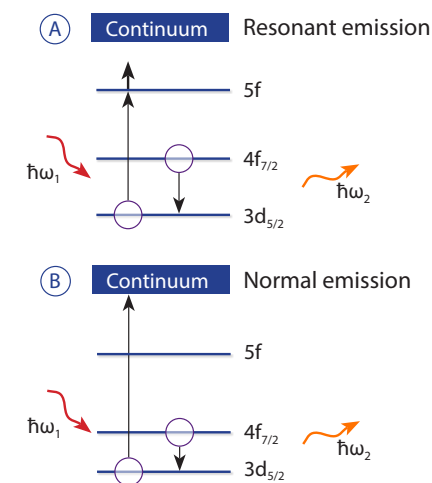
Changes in energy-driven covalency can be estimated by comparing the degree of An 5f orbital localization within a series of materials using RIXS maps. The  $\text{PuO}_2^{2+}$  map and a simplified one-electron scheme describing the emission process are shown in Fig. 3. The 3d electrons are predominantly excited to unoccupied states with substantial 5f character. The RIXS map can be divided into resonant emission and non-resonant (normal) emission (vertical line in Fig. 3); these describe processes in which the electron is excited to bound unoccupied states and to the continuum, respectively, both with subsequent  $4f \rightarrow 3d$  Pu  $M_\alpha$  emission (Fig. 3 A and B).

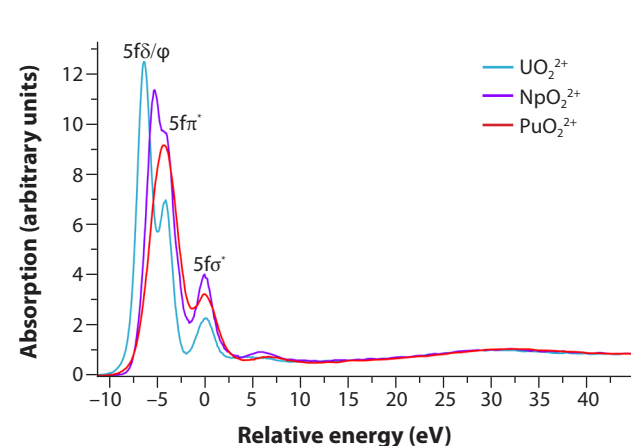
This shift in emission energy of the resonant peaks with respect to normal emission (shift between horizontal lines A and B in Fig. 3) accounts for the strong interaction between the excited electron in the lowest unoccupied bound electronic states and the created core-hole, which differs from the ionized case. The energy shift between lines A and B therefore probes the localization of those lowest unoccupied 5f states on the absorbing atom; this effect is described schematically in Fig. 3. We found an increase in energy shift going from U to Pu in the actinyl system suggesting that the 5f orbitals undergo stronger localization in the order  $\text{UO}_2^{2+} < \text{NpO}_2^{2+} < \text{PuO}_2^{2+}$ .

### The effect of multiplet splitting and ligand field on plutonyl spectrum

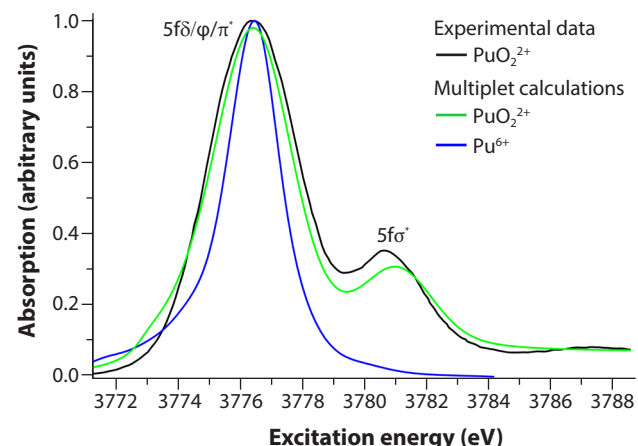
An important contribution to the width of the observed XANES peaks is from coupling between the open shell electrons which show multiplet signals with slightly different energies. These multiplets arise from angular momentum coupling of the open shell electrons, both for the core hole as well as the open 5f shell. Because the small energy differences cannot be resolved experimentally, theoretical calculations can help us understand their presence and how they shape the observed spectra.

Multiplet calculations were implemented for excitations in both an isolated  $\text{Pu}^{6+}$  ion and for the plutonyl ion (Fig. 5, blue and green lines). The first approach did not allow for covalent bonding, but allowed us to study the effect of “ideal” multiplets. The second accounted for both angular momentum coupling and covalent bonding.





**Figure 4.**  $M_{4/5}$  absorption edge HR-XANES spectra showing electronic transitions from An 3d- to 5f-based molecular orbitals. The energy shift between the first peak and the subsequent ones decreases from U to Pu, which can be interpreted as decreasing overlap-driven covalency of the actinide-ligand bond. Due to the increasing number of valence electrons the intensity of the first peak significantly decreases going from U ( $f^0$ ) to Pu ( $f^6$ ).



**Figure 5.** Pu  $M_5$  absorption edge HR-XANES experimental (black) and calculated (green) spectra of  $\text{PuO}_2^{2+}$  and a calculated spectrum of  $\text{Pu}^{6+}$  (blue). We can see a better fit with the calculations in which the Pu–O interaction is explicitly taken into account, as opposed to the more simplistic isolated  $\text{Pu}^{6+}$  ion. The spectral peak labels correspond to orbitals in Fig. 2.

The spectrum calculated for  $\text{Pu}^{6+}$  without any considerations of covalent mixing shows a broad main peak, without the higher energy peak at 3781 eV. The multiplet plutonyl model meanwhile, in which the covalent mixing is taken into account, shows agreement between theory and experiment, and clearly shows that the ligand field is important for a correct theoretical description of the  $\text{PuO}_2^{2+}$  spectrum.

## Acknowledgments

This work is a joint effort from many scientists primarily at the Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), Germany who are authors of the first two publications listed in Further Reading. We acknowledge the Helmholtz Association of German Research Centers for the VH-NG-734 grant and the Karlsruhe Research Accelerator (KARA) for provision of beamtime. PSB acknowledges support from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences (CSGB) Division through the Geosciences program at Pacific Northwest National Laboratory.

## Summary

We have illustrated that HR-XANES and RIXS are very useful tools for characterizing actinide electronic structures and can be applied to any type of materials, under static or dynamic conditions—for example at elevated temperatures, high pressures, or during chemical reactions. RIXS allows direct comparison of the amount of 5f orbital localization. Changes in the relative energy differences between the  $\text{AnO}_2^{2+}$  5f  $\delta/\phi$  and the 5f  $\pi/\sigma$  anti-bonding orbitals, determined from the An  $M_{4,5}$  edge HR-XANES spectra, provide a qualitative measure for the level of overlap-driven covalency in the actinyl bond. The observed trends in these energy differences indicate that U(VI)– $\text{O}_{\text{ax}}$  is more covalent compared to the Np(VI)– $\text{O}_{\text{ax}}$  and Pu(VI)– $\text{O}_{\text{ax}}$  bonds. We have shown that electron-electron interactions lead to broadening but are not the dominant effect in the An  $M_{4,5}$  absorption edge HR-XANES spectra of the actinyl species. The axial ligand field plays the most important role and therefore needs to be considered in calculations.

### Further Reading:

1. T. Vitova, I. Pidchenko, D. Fellhauer, P.S. Bagus, Y. Joly, T. Pruessmann, S. Bahl, E. Gonzalez-Robles, J. Rothe, M. Altmaier, M.A. Denecke, H. Geckeis; "The role of the 5f valence orbitals of early actinides in chemical bonding"; *Nature Communications*, 2017, 8, 16053.
2. T. Vitova, I. Pidchenko, D. Fellhauer, T. Pruessmann, S. Bahl, K. Dardenne, T. Yokosawa, B. Schimmelpfennig, M. Altmaier, M. A. Denecke, J. Rothe, H. Geckeis; "Exploring the electronic structure and speciation of aqueous and colloidal Pu with high energy resolution XANES and computations"; *Chem. Commun.*, 2018, 54, 12824.
3. P. S. Bagus, C. J. Nelin, D. Hrovat, E. S. Ilton; "Covalent Bonding In Heavy Metal Oxides"; *J. Chem. Phys.*, 2017, 146, 134706.

# Plutonium Metal Corrosion by Water Vapor: An X-Ray Photoelectron Study

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Plutonium metal is particularly susceptible to corrosion, even under ambient conditions. Although this corrosion is controlled industrially, the details of the mechanisms are not well understood and remain controversial, especially in the presence of  $\text{H}_2\text{O}$ . The purpose of this study is to describe the first stages of plutonium metal corrosion mechanisms under water vapor exposure. Understanding these initial stages is important because they drive the corrosion process. X-ray photoelectron spectroscopy (XPS) is useful for studying various properties of surfaces, e.g., composition, chemical and electronic properties, and oxidation state. This technique provides an image of the electronic structure of the surface where corrosion reactions take place.

Plutonium metal has a high chemical reactivity. Two types of oxide form under an oxidizing atmosphere—an inner sesquioxide,  $\text{Pu}_2\text{O}_3$ , in contact with the metal and an outer dioxide layer,  $\text{PuO}_2$ , in contact with the gas. The thickness and the ratio between both oxides depend greatly on the exposure conditions (e.g., temperature, gas pressure, exposure time). Corrosion kinetics experiments (e.g., monitoring weight gain) show that plutonium metal forms a protective oxide layer under oxidant gas. Under certain conditions, this layer can be damaged, sharply enhancing the oxidation rate. Thus, even at room temperature, corrosion may be severe for long-term storage in an atmosphere that is not well controlled.

## X-ray photoelectron spectroscopy and Tougaard analysis

XPS is a technique based on the photoelectric effect that provides information about the nature and valence of atoms related to their chemical environment. Typically, this information is obtained from the chemical shift of the binding energy of elastic photoelectrons, corresponding to the observed peaks in the XPS spectra (Fig. 1).

Recently, a new method has been developed by S. Tougaard (University of South Denmark) which allows surface nanostructure information can be extracted from the background portion of XPS spectra. The transport of photoelectrons in matter depends on the nature of the material, surface geometry, and kinetic energy, which is lost as photoelectrons pass through the solid. Thus, the shape and intensity of the background of the spectra are indicative of surface nanostructure (Fig. 2).

## Experimental considerations

This study consisted of applying low exposures of water vapor to a plutonium metal surface. An initial surface was prepared before each exposure—the challenge was to prepare “perfect” plutonium metal without traces of oxide or carbon contamination (“adventitious” carbon). These traces are due to the extreme reactivity of the metal—plutonium is so reactive that we can expect that the oxidant gas is in contact with an oxide, never with the metal. Therefore, the choice was made to prepare a slightly oxidized metal surface for this first approach which was as clean as possible.



**Lionel Jolly**

Dr. Jolly is a Scientist at the French Alternative Energies and Atomic Energy Commission (CEA) Centre de Valduc. He presented his talk titled "PhotoElectron Spectroscopy Study of  $\text{H}_2\text{O}$  Adsorption and Dissociation on Oxidized Pu Metal" in the Surface Science and Corrosion II session at Pu Futures 2018.