

# Investigation of actinide compounds by coupling X-ray absorption spectroscopy and quantum chemistry

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## Abstract

X-ray absorption near edge structure (XANES) is a sensitive probe of the electronic structure, and can provide information about the valency, the unoccupied electronic states and the effective charge of the absorbing atom. In this work, XANES spectra are reported at the uranium  $L_3$ ,  $M_5$  thresholds and used to determine structural and electronic properties of actinide compounds. In addition, ligand K-edge spectra are analysed in order to better characterize the nature of the actinide–ligand bond. Experimental data analysis by simulating the absorption edge allows to compare the coordination polyhedrons, identify the electronic transitions and calculate the density of states associated with the absorption spectra. Moreover, a comparison between simulations of the experimental spectra and quantum chemical calculations is performed, in order to improve the model describing the final states and better understand the bonding properties of the cation with the ligand.

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## 1. Introduction

Both structural and electronic properties of the actinide cations are of fundamental interest in order to describe the intramolecular interactions. The 5f and 6d orbitals are the first partially or totally vacant states of these elements and their properties reflect the nature of the actinide–ligand bond. Because of its chemical and orbital selectivities, XANES spectroscopy is useful to probe the actinides' frontier orbitals and then understand the cation reactivity towards chelating ligands. The  $L_3$ -edge X-ray absorption spectroscopy of uranium (formal 2p–6d transition in the dipolar approximation) has been the most reported one in the literature because of its convenient energy (17.2 keV). Although significant structural information on the coordination polyhedron can be obtained from these electronic transitions because of the important shape resonances [1,2], the very short core hole lifetime broadens the edge signal ( $\sim 7$  eV) resulting in very little extractable electronic information. On the other

hand, the  $M_5$  (3d–5f transition) edge provides a better resolution ( $\sim 4$  eV for  $M_5$  core hole) and allows to achieve quantitative information. Thus a multiple-edge approach has been chosen to study both structural and electronic properties of actinides compounds.

In this paper, we discuss, in a preliminary work, the influence of the uranium effective charge as well as the uranium polyhedron on the edge position and edge features. For this purpose, the data are compared to energy levels and population analysis obtained by quantum chemical calculations.

The studied compounds have been chosen in order to enhance the effect of the uranyl group ( $UO_2^{2+}$ ) on the XANES spectra. Thus we compare a sample belonging to the uranyl (VI) series: uranyl nitrate ( $UO_2(NO_3)_2 \cdot 6H_2O$ ) and perovskite  $Ba_2ZnUO_6$ , that does not exhibit any 'yl' oxygens.

## 2. Experimental and computational methods

### 2.1. XANES spectroscopy

The uranyl compound  $UO_2(NO_3)_2 \cdot 6H_2O$  is from Aldrich Chemicals, used as received. In this molecular compound, the uranyl group ( $UO_2^{2+}$ ) is surrounded

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equatorially by a near-planar oxygen hexagon of four oxygen atoms from two non-equivalent bidentate nitrate groups and two equivalent water oxygens [3]. In the  $\text{Ba}_2\text{ZnUO}_6$  solid state compound, the uranium atom sits in the centre of an oxygen octahedron, the space group being  $Fm\bar{3}m$  [4]. For the preparation of the perovskite see reference [5].

$L_3$  and  $M_5$ -edges data were acquired at the D44 experimental station of DCI ring (former LURE, Orsay, France). The XANES for oxygen and K-edge was conducted at the 11.0.2 beamline of the Advanced Light Source (Lawrence Berkeley National Laboratory, USA), particularly relevant for radioactive materials and soft X-ray experiments [6].

## 2.2. Data simulations

The absorption spectra were simulated by the FDMNES code, using the multiple-scattering theory or the finite-difference method and relativistic calculations [7]. The program allows to calculate the signal for different polarizations, as well as the density of state (DOS) of the atomic orbitals. After a first calculation, the spectra are convoluted with a Lorentzian in order to take into account the core hole lifetime. However, some results are presented before convolution for a better understanding.

## 2.3. Quantum chemical calculation

Electronic populations were obtained from a Mulliken population analysis derived from density functional theory (DFT) calculations. DFT calculations were performed using the Amsterdam density functional (ADF) program package [8]. Relativistic effects were considered through the zeroth-order regular approximation (ZORA) [9]. Spin-orbit effects were not taken into account. Uncontracted triple- $\zeta$  Slater type orbitals valence orbitals with one set of polarization functions were used for all atoms. The frozen-core approximation was used where the core density was obtained from four-component Dirac-Slater calculations on all the atoms and kept frozen during molecular calculations.  $1s^2$  core electrons were frozen for carbon, nitrogen and oxygen. The valence space of the heavy elements includes 6s, 6p, 6d, 5f, 7s shells of actinides. The density functional consists of a local density part using the parametrization of Vosko, Wilk, and Nusair and exchange-correlation gradient corrected parts of Becke.

## 3. Results and discussion

### 3.1. U $M_5$ -edge XANES spectra

Normalized  $M_5$ -edge spectra of the two U(VI) compounds are presented in Fig. 1, shifted in ordinate. Both absorption spectra exhibit an intense white line (A), due to  $3d \rightarrow 5f$  transition, and weak scattering features at higher energy. The main difference is the absence of feature B on the spectrum of  $\text{Ba}_2\text{ZnUO}_6$ .

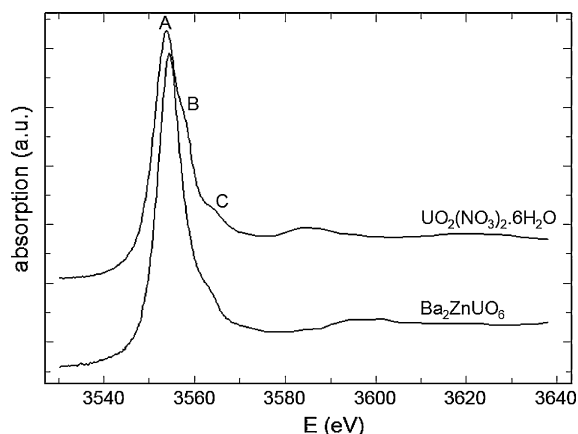


Fig. 1. Experimental U  $M_5$ -edge XANES spectra of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ba}_2\text{ZnUO}_6$ .

Table 1  
Mulliken populations for  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Atom	Charge	s	p	d	f
U	+2.0	0.1	5.7	1.5	2.7
$\text{O}_{\text{yl}}$	-0.6	2.0	4.6	0.0	
$\text{O}_{\text{UN}}$	-0.6	1.9	4.6	0.1	
$\text{O}_{\text{N}}$	-0.4	1.9	4.4	0.1	
N	+1.0	1.0	2.7	0.3	
$\text{O}_{\text{H}_2\text{O}}$	-0.5	1.8	4.6	0.1	
H	+0.3	0.6	0.1		

$\text{O}_{\text{H}_2\text{O}}$ : water oxygens,  $\text{O}_{\text{UN}}$ : oxygen atoms from nitrate groups bound to uranium,  $\text{O}_{\text{N}}$ : oxygen atoms from nitrate groups unbound to uranium.

We assign this feature to the 'yl' oxygens present in the uranyl nitrate and not in the perovskite. In order to confirm this assumption and get other structural and electronic information on the studied compounds, the spectra have been simulated with FDMNES code.

Two calculations, with two different electronic configurations, have been performed for the uranyl compound: one with the uranium ground state configuration and the other with the electronic configuration obtained by quantum chemical calculations. Mulliken population analysis gives an effective charge of  $2+$  for the uranium atom (Table 1) which is far from the formal charge  $6+$  and is in agreement with the occurrence of a high covalency in the uranyl rod [5] (the charge obtained from a natural population analysis is slightly larger:  $2.8+$ ). As we can see in Fig. 2, electronic populations have a huge impact on the uranium  $M_5$ -edge XANES spectrum of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

For the simulation with  $\text{U}^{2+}$ , shoulder B appears and peak C is at the correct energy, compared to the calculation with  $\text{U}^0$ . This result gives evidence that the features of the U  $M_5$ -edge XANES spectrum depend on the effective charge of the actinide, which reflects the electronic structure of the compound. Furthermore, polarized calculations allow us to assign peak B to the presence of the 'yl' oxygens. Indeed, Fig. 2 shows that the major part of feature B comes from the signal polarized along the  $z$  axis, parallel to the 'yl' oxygen rod.

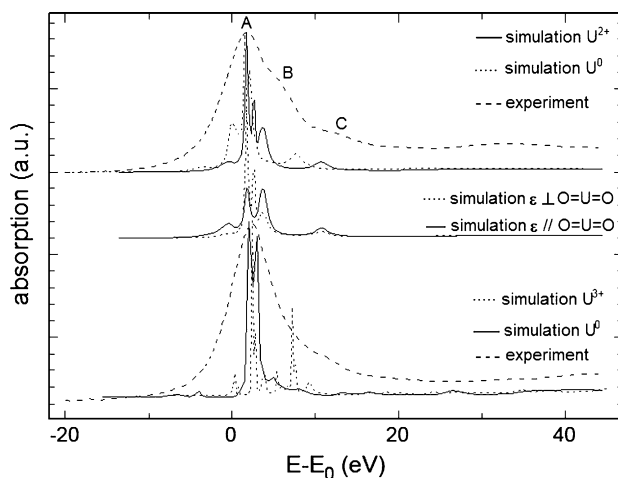


Fig. 2. Experimental and calculated U  $M_5$ -edge XANES spectra of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ba}_2\text{ZnUO}_6$  with different electronic configurations and along different polarization directions. Simulations are shown before convolution.

Calculations including different charges obtained by other methods than Mulliken population analysis are currently being performed in order to determine the sensitivity of XANES spectra toward the electronic configuration and get precise information about the real charge of the actinide.

The perovskite system is periodic and cannot be handled with the same calculation methods than the ones which have been used for the molecular compounds and its electronic structure has not been determined through quantum chemistry calculations in the present study. However, the uranium cation in  $\text{Ba}_2\text{ZnUO}_6$  is supposed to be more ionic than in  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  so the effective charge of uranium in the perovskite is assumed to be higher than  $2+$ . In Fig. 2, FDMNES XANES simulations are presented, for the ground state electronic configuration and for the following one:  $\text{U}^{3+}\text{O}^- \text{Ba}^+\text{Zn}^+$ . As for the uranyl compound, all the features are not well reproduced for the perovskite having neutral atoms (simulation with  $\text{U}^0$ ). Particularly, we can see no feature above the white line. On the other hand, the calculation with  $\text{U}^{3+}$  exhibits two main peaks, the more intense corresponding to the white line (A). The second peak is at lower energy than peak (C), however the simulation of the XANES spectrum of the perovskite is better with  $\text{U}^{3+}$  than with  $\text{U}^0$ .

In order to better characterize the actinide-ligand bond and confirm first results, XANES experiments have been done at the ligand K-edge.

### 3.2. Ligand K-edge XANES spectra

Oxygen K-edge XANES is an excellent probe of the covalency of an actinide oxide bond, since actinide  $5f/6d$  with O  $2p$  orbitals form an antibonding orbital. However, doing oxygen K-edge experiments require all oxygens to be equivalent, that is not the case for  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Thus only O K-edge XANES spectrum for  $\text{Ba}_2\text{ZnUO}_6$  was measured at the 11.0.2 beamline of the ALS. Oxygen K-edge XANES spectra could not be adequately modelled through the full multiple scattering approach, but the finite-difference method approach combined with quantum chemical population analysis gives good results, as we can see in Fig. 3. O K-edge XANES spectrum exhibits one peak (D) at low energy, which is well reproduced with  $\text{U}^{3+}$  electronic configuration. This confirms the assumption, in previous section, that  $\text{U}^{3+}\text{O}^- \text{Ba}^+\text{Zn}^+$  is a better electronic configuration than the one with neutral atoms.

This preliminary work shows that, as for the uranium  $M_5$ -edge, the ligand K-edge XANES spectrum is really sensitive to the electronic configuration of the compound. However, in a future work, a calculation method for periodic system should be used to determine the electronic structure of  $\text{Ba}_2\text{ZnUO}_6$  through quantum chemistry calculations. Then the oxygen charge and the covalency of the actinide–ligand bond could be further discussed.

### 3.3. U $L_3$ -edge XANES spectra

Fig. 4 presents the experimental U  $L_3$  absorption edge of both compounds. It is formally assign to the electronic transi-

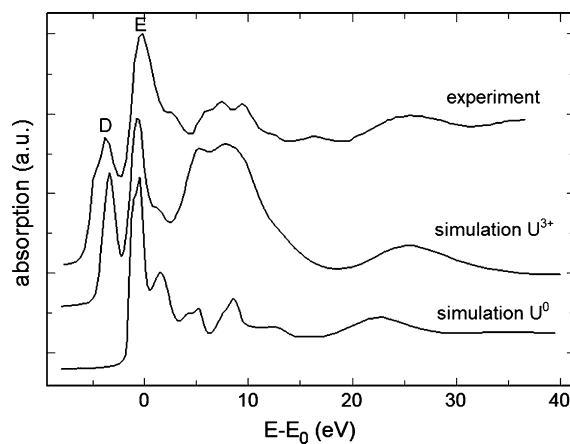


Fig. 3. Experimental and calculated O K-edge XANES spectra of  $\text{Ba}_2\text{ZnUO}_6$  with different electronic configurations.

tion  $2p^6 \rightarrow 6d^1$ . The XANES spectrum of  $\text{Ba}_2\text{ZnUO}_6$  exhibits a broad white line (G) and a shoulder (F) at lower energy, whereas the uranyl nitrate spectrum exhibits one intense white line (H) and feature (I) which is well known to be due to resonant scattering along the linear transdioxo unit [10].

Unlike  $M_5$ -edges,  $L_3$ -edges are not as sensitive to electronic configurations. However, the electronic populations giving the best  $M_5$ -edge calculation have been used for the  $L_3$ -edge simulations. In the case of the uranyl nitrate, calculation of the polarized XANES signal (Fig. 4) allows us to assign feature (I) to the presence of the 'yl' oxygens whereas feature (J) originates from atoms in the equatorial plan.

The absence of any feature similar to (I) in the experimental spectra of  $\text{Ba}_2\text{ZnUO}_6$  is consistent with the absence of any uranyl unit in these compounds. The XANES spectrum of  $\text{Ba}_2\text{ZnUO}_6$  exhibits a broad white line (G) and a shoulder (F) at lower energy. In a simple molecular orbital picture, the occurrence of (F) in the U  $L_3$  edge spectrum of  $\text{Ba}_2\text{ZnUO}_6$  can be explained by the atomic orbital diagram of uranium  $6d$

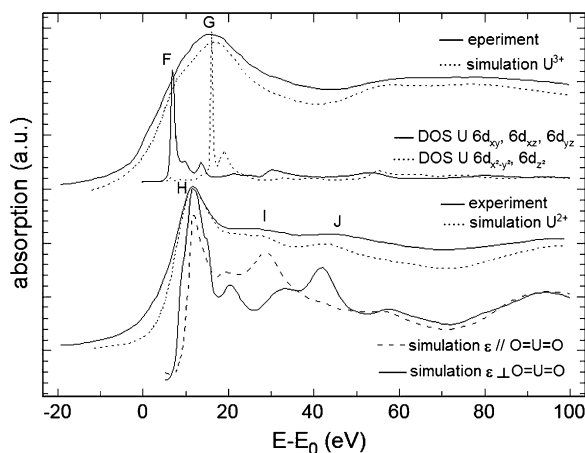


Fig. 4. Experimental and calculated U  $L_3$ -edge XANES spectra of  $\text{Ba}_2\text{ZnUO}_6$  and U  $6d$  DOS calculations (top). Experimental and calculated U  $L_3$ -edge XANES spectra of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and polarized calculations, before convolution (bottom).

orbitals in the  $O_h$  symmetry. The perovskite having octahedral  $UO_6$  units, the shoulder and the white line can be attributed to the electron transitions from  $2p_{3/2}$  states to split 6d states, i.e.,  $t_{2g}$  ( $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ) and  $e_g$  ( $d_{x^2-y^2}$  and  $d_{z^2}$ ). This is confirmed by plotting the DOS of the 6d orbitals obtained with FDMNES code and shown in Fig. 4. On the other hand, there is no visible splitting for the uranyl calculation because of the symmetry of  $UO_2(NO_3)_2 \cdot 6H_2O$  (hexagonal bipyramid).

These results show that in the case of actinide cations, the  $L_3$ -edge, located in the hard X-ray region, provides a useful fingerprint of the cation polyhedron.

#### 4. Conclusions

The present work shows that multiple edge approach for XANES spectroscopy is very promising for electronic and structure studies of uranium and transuranium actinide compounds. The uranium XANES analyses lead to characterize the absorbing atom coordination sphere and its effective charge, by coupling the simulation of the experimental spectroscopic data with quantum chemical calculations. The shape of the threshold in  $L_3$  edge spectra is essentially due to local structure effects but is not well enough resolved to extract electronic information. On the other hand, the  $M_5$  edge provides a better resolution ( $\sim 4$  eV for uranium  $M_5$  core hole) and then is much more sensitive to the electronic structure. The work presented in this paper has proven that  $M_5$  edge XANES simulation combined with electronic structure calculation by quantum chemistry lead to extract quantitative information such as the evolution of the effective

charge of the absorber in a series of compounds. Furthermore, theoretical analysis of low energy ligand K edge XANES spectroscopy is feasible and gives complementary information on the actinide-ligand bond. Overall, to compare experimental and theoretical data is essential to validate and improve the models used for the different calculations.

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