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Molecular Characterization of Actinide Oxocations from Protactinium to Plutonium

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Abstract. This presentation addresses the structural characterization by EXAFS of actinide cations at oxidation states (V) and (VI) as one walks across the periodic table from $Z = 91$ (protactinium) to $Z = 94$ (plutonium). A structural comparison between Pa, U, Np and Pu oxocations in aqueous solution at formal oxidation states (V) and (VI) is carried out. These results are corroborated by quantum chemical and molecular dynamics calculations.

Keywords: XAS, Actinide

PACS: 82.75.J

INTRODUCTION

Actinide molecular chemistry is surprisingly rich because the "5f" elements have large atomic numbers (from $Z = 89$ for Ac) and their valence electrons are relatively available compared to the lanthanide family. For industrial, environmental and public health purposes, this chemistry has been the subject of considerable efforts since the 50's. Aqueous redox chemistry, ionic selective recognition, uptake by specific biomolecules or compartments of the geosphere are some of the major fields of investigation. The physical-chemical properties of the actinide elements strongly depend on the 5f/6d electronic configuration. Some of them (U, Np, Pu and Am) can form AnO_2^{n+} ($n = 1, 2$) oxocations, so-called actinyls, with two strong An-O covalent bonds. In any case, the cation polyhedron is characterized by large, flexible coordination spheres with various stable and metastable metal oxidation states.

Protactinium, as the first actinide with 5f-electrons involved in bonding, occupies a key position in the actinide series. At formal oxidation state V (its most stable oxidation state in solution as well as in the solid state) Pa(V) corresponds to the formal $5f^0$ electronic configuration. U(VI) also corresponds to the formal oxidation state $5f^0$ and is most often encountered as the

stable oxocationic form UO_2^{2+} . The first stable form of actinide at formal oxidation state (V) under atmospheric conditions is NpO_2^+ with formal $5f^2$ electronic configuration. U(V) is highly unstable under atmospheric conditions and Pu(V) dismutates into Pu(IV) and Pu(VI). On the other hand, the existence of the PaO_2^+ form in solution and in solid state is highly improbable and has never been reported.

Several spectroscopic tools have been technically adapted to actinide chemistry, as Infra Red Spectroscopy and Spectrophotometry. In solution, combined XANES and EXAFS data at the actinide L_{III} edge is an ideal structural probe of the cation coordination sphere. Furthermore, coupling the XAFS data with molecular dynamics calculations leads to a better description of the cation-solvent interactions. In addition, disorder can explicitly be taken into account using time spaced snapshots of the molecule. This is particularly important when large disordered polyhedra are composed of similar ligands as water molecules. The structural comparison between Pa, U, Np and Pu oxocations in aqueous solution at formal oxidation states (V) and (VI) is corroborated by quantum chemical calculations.

EXPERIMENTAL

The following complexes have been investigated : **Pa(V)/HF_C** (Pa(V) in [HF]=12M); **Pa(V)/HF_d** (Pa(V) in [HF]=0.05M); **U(VI)/HClO₄** (U(VI) in [HClO₄]=0.05M); **Np(V)/HClO₄** (Np(V) in [HClO₄]=0.05M) and **Pu(V)/HClO₄** (Pu(V) in [HClO₄]=0.05M). Experimental details are described elsewhere [1]. XAS measurements were performed in 600 μ L cells specifically designed for radioactive samples. All data was acquired at the actinide L_{III} edge. XAS measurements of protactinium and plutonium were carried out on the Rossendorf beam line (ROBL) at ESRF (6.0 GeV at 200 mA) in fluorescence mode, at room temperature, with a Si(111) water cooled monochromator in a channel cut mode. XAS measurements of uranium and neptunium were carried out on the 11-2 beam line at SSRL (3.0 GeV at 100 mA) in fluorescence mode at room temperature, with a Si(220) nitrogen cooled monochromator in a channel cut mode. Energy calibration was carried out with a Y foil (17052 eV at the absorption maximum) and Zr foil (18014 eV at the absorption maximum). Data were extracted with Athena code [2] and fitted in R-space ($k^3\chi(k)$ Kaiser Fourier transformed) between 1 and 4 \AA . Phases, amplitude and inelastic losses were calculated with Feff82 [3] from 10 \AA clusters of UO_2^{2+} obtained with molecular dynamics calculations in a water box. Quantum chemistry calculations were performed using Amsterdam Density Functional (ADF) program package [4]. Relativistic effects were considered through the zeroth-order regular approximation (ZORA).

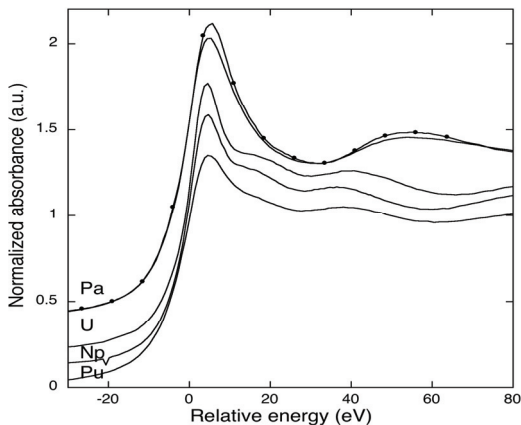


FIGURE 1a: L_{III} edge XANES spectra of **Pa(V)/HF_C** (—), **Pa(V)/HF_d** (—●—), **U(VI)/HClO₄**, **Np(V)/HClO₄** and **Pu(V)/HClO₄**.

Uncontracted triple- ζ Slater type orbitals valence orbitals with one set of polarization functions were used for all atoms. The frozen-core approximation was used. The density functional consists of a local density part using the parameterization of Vosko, Wilk, and Nusair and exchange-correlation gradient corrected parts of Becke. All the results have been obtained using the conductor-like solvation model (COSMO) to take into account solvent effects.

RESULTS

Figure 1a presents the L_{III} edge XANES spectra and first derivative of **Pa(V)/HF_C**, **Pa(V)/HF_d**, **U(VI)/HClO₄**, **Np(V)/HClO₄** and **Pu(V)/HClO₄**. All spectra but that of protactinium exhibit the well known multiple scattering feature around 15 eV above the edge [5, 6] that is attributed to the transdioxo unit of the actinyl species. This is also clearly visible on the absorption derivative of Figure 1b. Qualitatively, these data suggest that none of the two protactinium complexes is a trans dioxo cation. Furthermore, XANES simulations with FDMNES [7] based on model clusters have shown that due to the intrinsic width of the actinide L_{III} edges, the presence or absence of a mono oxo unit does not significantly modified the shape of the edge [1]. This suggests that **Pa(V)/HF_C** and **Pa(V)/HF_d** are either in the form of PaO^{3+} or Pa^{5+} .

Table 1 presents the best fit parameters obtained from the EXAFS data at the actinide L_{III} edge (Figure 2). Analysis of the EXAFS spectrum of **Pa(V)/HF_d** is under investigation. The structural data obtained for

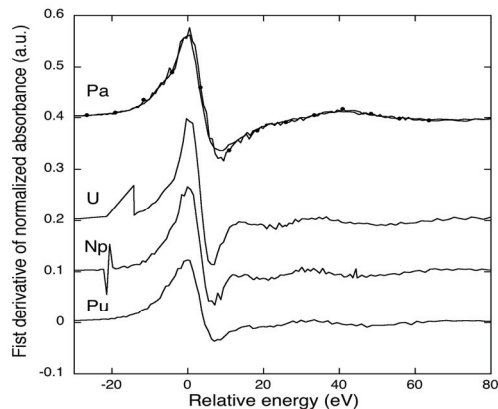


FIGURE 1b: Derivative of the L_{III} edge XANES spectra of **Pa(V)/HF_C** (—), **Pa(V)/HF_d** (—●—), **U(VI)/HClO₄**, **Np(V)/HClO₄** and **Pu(V)/HClO₄**.

U(VI)/HClO₄, **Np(V)/HClO₄** and **Pu(V)/HClO₄** are in agreement with the literature [8,9]. Fitting the EXAFS spectrum of **U(VI)/HClO₄** with snapshots obtained from molecular dynamics has also been undertaken and will be published shortly. The shortening of the oxygen axial and equatorial distances from Np(V) to Pu(V) (0.02 Å), although close to the uncertainty, is in agreement with the expected actinides contraction from Z to Z+1.

Protactinium(V) is known to behave differently from its neighbors. Indeed, in concentrated HF it is present as a fluoro cation with no evidence of short dioxo bond, as suggested by the XANES spectrum. In concentrated sulphuric acid, Pa(V) has been shown to occur as a mono oxo cation [1].

Quantum chemistry calculations have been performed on the actinyl cation bound to four or five water molecules. Comparison of the EXAFS data with distances obtained

Pa(V)/HF_c : 7 F at 2.16(1) Å $\sigma^2 = 0.0050$ Å²

$S_0^2 = 0.8$, $\Delta e_0 = 3.6$, $R_f = 2.6$ %

U(VI)/HClO₄ : 2 O at 1.76(1) Å $\sigma^2 = 0.0028$ Å²

4.6(6) O at 2.41(2) Å $\sigma^2 = 0.0067$ Å²

$S_0^2 = 0.9$, $\Delta e_0 = 5.9$, $R_f = 3.0$ %

Np(V)/HClO₄ : 2 O at 1.82(1) Å $\sigma^2 = 0.0008$ Å²

4.4(9) O at 2.49(2) Å $\sigma^2 = 0.0043$ Å²

$S_0^2 = 0.9$, $\Delta e_0 = 8.4$, $R_f = 5.5$ %

Pu(V)/HClO₄ : 2 O at 1.81(1) Å $\sigma^2 = 0.0020$ Å²

3.5(8) O at 2.47(2) Å $\sigma^2 = 0.0044$ Å²

$S_0^2 = 0.7$, $\Delta e_0 = 6.6$, $R_f = 5.1$ %

TABLE 1 : Best fit parameters of the experimental $k^3\chi(k)$ data at the actinide L_{III} edge. Figures in italics have been fixed. Uncertainties are in parentheses. Italic numbers are fixed.

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from calculations is very satisfactory if we consider five water molecules coordinated to U(VI) and Np(V) and four water molecules bound to Pu(V) : **U(VI)** (2 O at 1.80 Å and 5 O at 2.43 Å) **Np(V)** (2 O at 1.83 Å and 5 O at 2.51 Å) and **Pu(V)** (2 O at 1.82 Å and 4 O at 2.46 Å). These results are an indication of a change in the number of coordinated water from **Np(V)** to **Pu(V)** from five to four, as already reported [8].

Calculations performed on [PaF₇]³⁻ result in a Pa-F distance of 2.18 Å, in very good agreement with EXAFS data. It should be mentioned that the variation of the number of fluorides in the inner coordination sphere of Pa(V) induces a small change of 0.06 Å in Pa-F distances (2.12 Å in [PaF₆]²⁻ and 2.24 Å in [PaF₈]⁴⁻). At this point of the EXAFS analysis, in absence of any Pa model compound, the number of 7 F atoms has not been fitted.

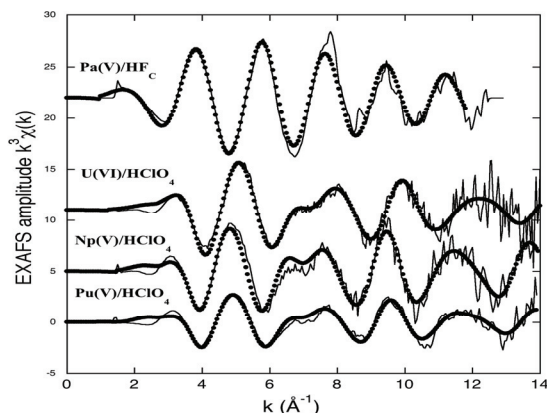


FIGURE 2 : $k^3\chi(k)$ experimental (strait line) and fitted (dots) EXAFS curves of **Pa(V)/HF_c**, **U(VI)/HClO₄**, **Np(V)/HClO₄** and **Pu(V)/HClO₄**.

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