



Experiment title: High-resolution polarisation dependent x-ray absorption fine structure (HR-P-XAFS) study of uranyl complexes	Experiment number: EC- 484	
	Beamline: ID26	Date of experiment: from: 29.04.2009 to: 4.05.2009
Shifts: 18	Local contact(s): Kristina Kvashnina	Date of report: 10.02.2010 <i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): 1) Tonya Vitova* 1) Melissa Denecke* 1) Karlsruhe Institut für Technologie (KIT) Institut für Nukleare Entsorgung (INE) P.O. Box 3640, D-76021 Karlsruhe, Germany		

Report:

Introduction:

X-ray absorption fine structure (XAFS) spectroscopy has proven to be particularly useful in investigations relevant to high-level nuclear waste disposal [1]. The physics and chemistry of uranium plays a central role in assessing the safety disposal of spent fuel rods. However, the complex electronic structure of the mostly present as uranyl ion ($\text{U}^{\text{VI}}\text{O}_2^{2+}$, U(VI)) still remains subject of discussion. The uranyl moiety is a highly symmetric with linear structure with unusually short, strong covalent bonding to two axial O atoms, $[\text{O}=\text{U}=\text{O}]^{2+}$. This lends its anisotropic character with a strong polarization dependency of its X-ray absorption spectroscopic signal [2,3]. The aim of the here presented investigation is to compare theoretically calculated electronic structure of the uranyl ion with experimental high-resolution polarisation dependent XAFS (HR-P-XAFS) spectroscopic data from an oriented cesium uranyl chloride ($\text{Cs}_2\text{UO}_2\text{Cl}_4$) single crystal. The comparison of these results will quantify the extent that the weakly bound ligands affect the valence bond structure, i.e. select the appropriate method for including combined correlation and relativistic effects into theoretical calculations. Measured U LIII edge EXAFS and XANES spectra of uranyl sorbed into the interlayer siloxane surfaces of the clay mineral montmorillonite in Ref. [4] show no strong polarisation dependency. However, Monte Carlo simulations suggest that the uranyl ion is tilted under 45° with respect to the clay surface normal. As this deviates from the “magic angle”, for which no polarization dependence of the signal is expected, we use HR-P-XAFS, and comparison to the single crystal results as a reference system, to confirm this calculated angle of the uranyl ion tilt in the clay.

Experimental details:

The HR-P-XAFS experiments at the U L3 edges of a $\text{Cs}_2\text{UO}_2\text{Cl}_4$ single crystal and a uranyl loaded dried clay were performed at the ID26 beamline at ESRF, Grenoble. The synchrotron radiation was monochromatized by a Si(311) double crystal monochromator. The experimental energy resolution was about 0.7 eV, which is the width of the quazy elastic peak scattered by a Ag foil. The energy of the primary monochromator was scanned from 17151.2 to 17225.2 eV with 0.1 eV step width over the U L3 edge during the experiment. For each excitation energy, the emitted photons from the sample were monochromatized by a spherically bent Ge(777) analyzer crystal and focused on an avalanche photodiode. The sample, crystal and detector were positioned on a circle (Rowland geometry) with diameter 1m equal to the bending radius of the crystal. HR-P-XANES measurements were performed with the incident radiation at 0° , 20° , 45° and 65° to the (-201) crystal habitus, which corresponds to 90° , 70° , 45° and 25° angles between linear uranyl units in the crystal with respect to the polarization vector (ϵ) of the primary beam, respectively. HR-P-XAFS measurements of the uranyl loaded clay (XANES and EXAFS) were performed at 30° and 65° degrees with respect to ϵ . At least three spectra for each angle were collected in order to check the reproducibility of the spectral features and to improve the counting statistics.

Results and discussion:

Polarisation dependent partial fluorescence yield (PD-PFY) U L3-XANES spectra of a $\text{Cs}_2\text{UO}_2\text{Cl}_4$ single crystal are shown in Fig. 1 a). All spectral features in the PD-PFY XANES are sharper and better resolved compared to the simultaneously measured conventional fluorescence XANES spectrum (labelled “ $\text{Cs}_2\text{UO}_2\text{Cl}_4_F$ ” in Fig. 1 a)). As a result, changes in the local atomic environment of the U absorbing atoms are readily detectable in the PFY-XANES spectra. Moreover, a pre-edge feature is clearly visible in all these spectra. This resonance originates from 2p transitions to U 5f states and is observed here for the first time ever in actinide L3 edge XANES spectra. The orientation between the ϵ of the beam and the uranyl ($[\text{UO}_2]^{2+}$) axis is varied during PD-XANES measurements, thereby enhancing transitions to certain molecular orbital states. Transitions to the U $6d_\pi$ or $6d_\delta$ orbitals dominate in the spectrum’s main resonance or ‘white line’ (WL), when ϵ is parallel or perpendicular to the $[\text{UO}_2]^{2+}$ axis, respectively (Fig. 1 a)). The experimental spectra are well reproduced by ADF DFT calculations performed by R. G. Denning (Oxford University) (see Fig. 1 b)). Experimental and theoretical efforts lead to the following results:

1. Theory reproduces the general shape of the experimental spectra;
2. U $6d_\pi$ orbitals strongly interact with O and Cl π -orbitals and U $6d_\sigma$ orbitals with O π -orbitals;

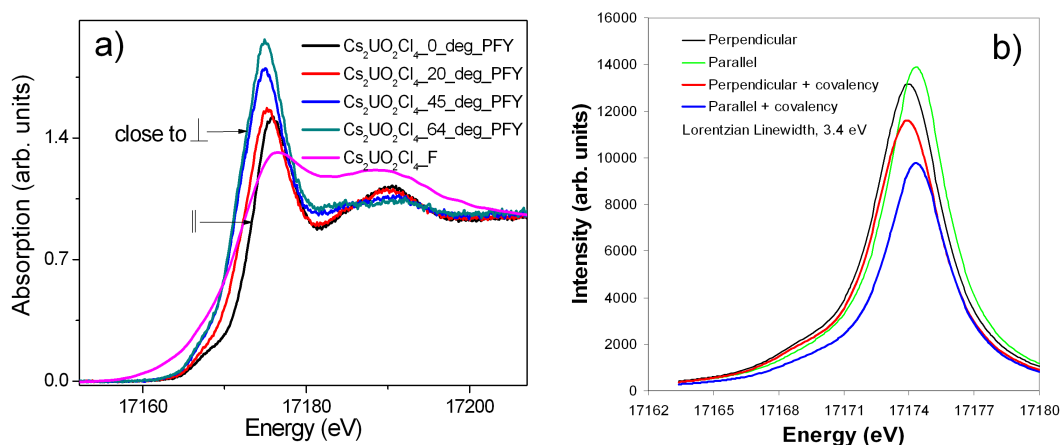


Fig. 1: Experimental a) and theoretical b) $\text{Cs}_2\text{UO}_2\text{Cl}_4$ single crystal HR-P/ PD-PFY XANES U L3 edge spectra.

3. The theoretical difference of 0.5 eV between absorption maxima in parallel and perpendicular orientation is comparable to the experimental value of 0.8 eV;
4. Quadropole 5f transition intensity relative to the 6d dipole transition is well reproduced;
5. Theoretical separation between 5f and 6d absorption peaks (5.2 eV) differs slightly from the experimental separation (7 eV);

The HR-P-XANES spectra of the uranyl loaded clay are shown in Fig. 2. The WL of the spectrum measured with uranyl' orientation 65° with respect to incoming beam has narrower, lower intensity profile compared to the respective of the 30° spectrum (see Fig. 2 b)). The WL width change is better visible in Fig 2 c), where the two spectra are normalized to the maximum WL intensity. This finding clearly indicates that the uranyl ion is tilted with respect to the clay surface normal under angle different than the “magic angle”. By comparing with the single crystal reference measurement in Fig.1 a), we assume that the angle between the uranyl molecule and ϵ is smaller in the “clay_65_deg” case spectrum. More detailed analyzes of the data will determine the tilt angle with respect to the clay surface normal.

HR-P-XAFS spectroscopy provides well-resolved data, which we used to refine theory for calculating

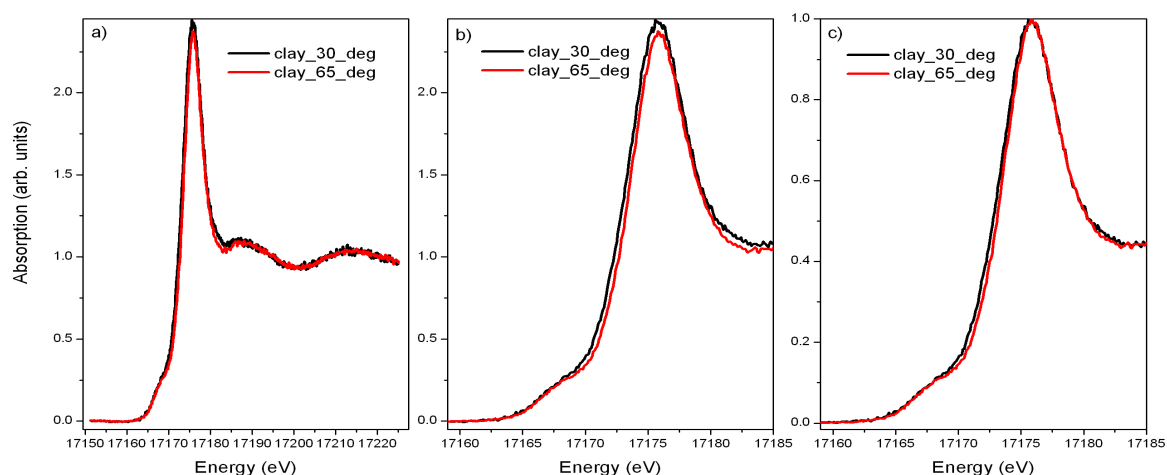


Fig. 2: Experimental HR-P/ PD-PFY XANES U L3 edge spectra a), b) and normalized to the max WL intensity c).

transition intensities to U 5f and 6d orbitals and their energies. This experimental technique unambiguously helped us to gain new general insight into U electronic structures in reference and laboratory prepared natural analog systems. More details will be given in the currently prepared publications.

References:

- [1] M. A. Denecke, (2006), *Coord. Chem. Rev.*, **250**, 730.
- [2] E. A. Hudson, P. G. Allen, L. J. Terminello, M.A. Denecke, T. Reich, (2006), *Phys. Rev. B*, **54**, 156-65.
- [3] D. H. Templeton, L. K. Templeton, (1982), *Acta. Cryst. A*, **38**, 62.
- [4] J. A. Greathouse, H. R. Stellalevinsohn, M. A. Denecke, A. Bauer, R. T. Pabalan, (2005), *Clay and Clay Minerals*, **53**, 278.

Acknowledgement:

We gratefully acknowledge ESRF for the provided beamtime and Kristina Kvashnina for the support during the experiment.