 ROBL-CRG	Experiment title: Investigation of U(VI)/U(V) carbonato complexes in aqueous solution by spectro-electrochemistry	Experiment number: 20-01-639
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Report:

U L_I- and L_{III}-edge XANES spectra for uranyl(VI)- and uranyl(V) tricarbonato complexes are shown in Figures 1 and 2. The fine structure of the absorption edge comprises structures from electron transitions into atom-like orbitals and multiple-scattering features. The L_{III}-edge shows a strong resonance (P1) that originates mainly from a dipole-allowed transition of the 2p_{3/2} electron to final 6d states. Additional transitions into 8s states are of minor importance. In contrast, the L_I-edge reveals a weak resonance related with the 2s → 7p transition. The difference of the formal charge originates a shift of the absorption edge position.

Several procedures are in use to determine the energy of the absorption edge threshold, E_0 [1]. A common reference is the first maximum of the first derivative of the raising edge. It reveals here a chemical shift of -2.2 eV and -0.6 eV between U(VI) and U(V) at the L_{III} and L_I edges, respectively. However, this approximation is not unambiguous, because the edge position is in superposition with discrete resonances.

The multiple scattering (MS) paths in the XANES region of U(VI) were assigned from polarization-dependent measurements. The similarity of the U(V) and the U(VI) spectra allows to indicate the MS paths in analogy to these references. The peak P1 at the L_I-edge and the peak P2 at the L_{III}-edge arise from multiple scattering with the axial uranyl atoms, the peak P2 at the L_I-edge and P3 at the L_{III}-edge arise from multiple scattering with the equatorial oxygen or more distant atoms [2]. In general, the MS peaks of the

U(V) spectra occur at lower energies than the MS peaks of U(VI). The energy position of the MS peaks are related with the bond lengths R according $\Delta E \sim 1/R^2$, where ΔE is the difference between the MS resonance and the average potential of the interstitial region V_0 . It is interesting to note, that due to this energy shift, the MS U-O_{ax} feature in the L_{III}-edge spectrum of U(V) is covered by the 2p_{3/2} → 6d resonance.

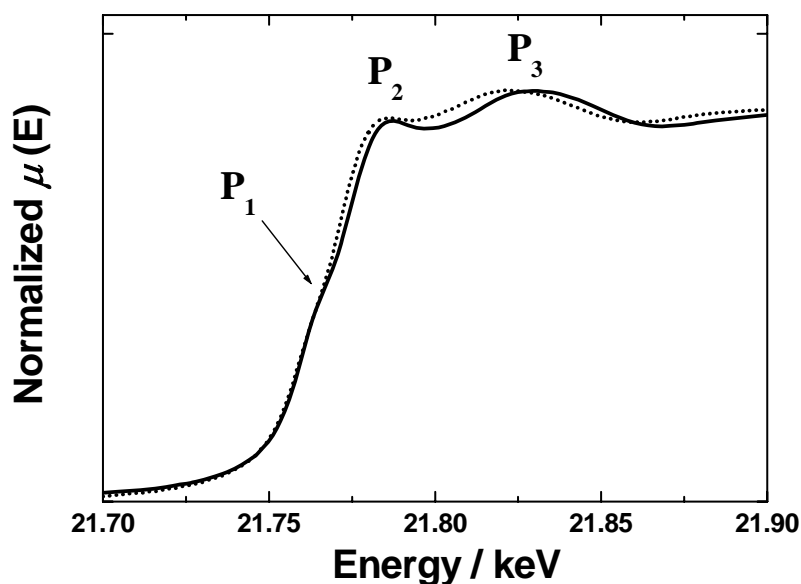


Figure. 1

U L_I-edge XANES spectra of uranyl(VI)- and uranyl(V) tricarbonato complexes: solid line; uranyl(VI) complex, dotted line; uranyl(V) complex.

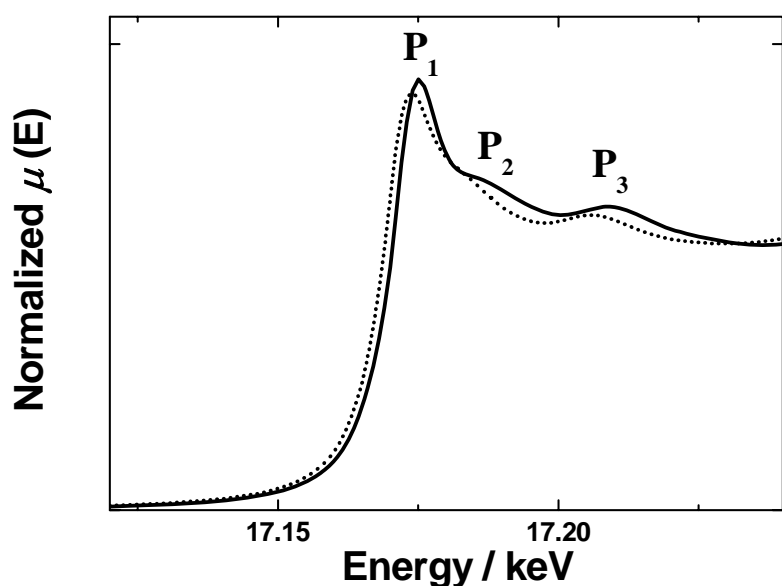


Figure. 2

U L_{III}-edge XANES spectra of uranyl(VI)- and uranyl(V) tricarbonato complexes: solid line; uranyl(VI) complex, dotted line; uranyl(V) complex.

- [1] C. Hennig, Evidence for double-electron excitations in the L₃-edge x-ray absorption spectra of actinides, *Phys. Rev. B*, in press.
- [2] A. Ikeda, C. Hennig, S. Tsushima, K. Takao, Y. Ikeda, A. C. Scheinost, G. Bernhard, A comparative investigation of U(VI) and U(V) carbonato complexes in aqueous solution, *Inorg. Chem.* submitted.