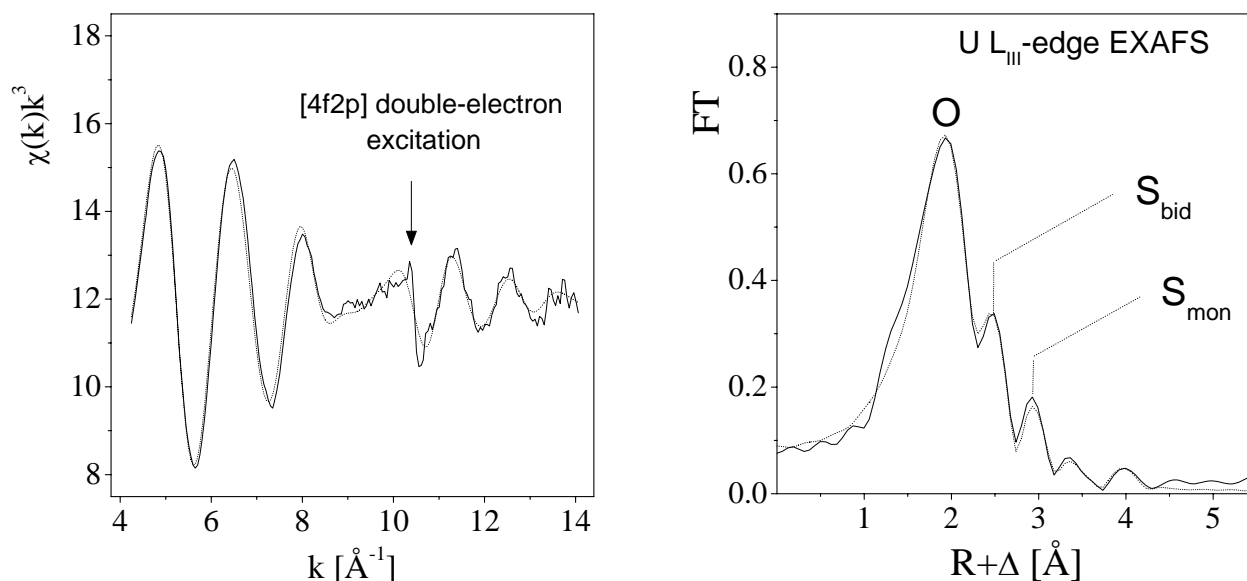
 ROBL-CRG	<b>Experiment title:</b> <b>Spectro-electrochemical cell for in situ XAS measurements of uranium solution species</b>	<b>Experiment number:</b> 20-01-618
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> between: 04. 05. 2005 and 07. 05. 2005 26. 10. 2005 and 30. 10. 2005 08. 02. 2006 13. 06. 2006 and 17. 06. 2006 26. 08. 2006 and 29. 08. 2006 17. 12. 2006	<b>Date of report:</b> 15. 12. 2006
<b>Shifts:</b> 51	<b>Local contact(s):</b> Christoph Hennig	<i>Received at ROBL:</i> 15. 12. 2006
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## Report:

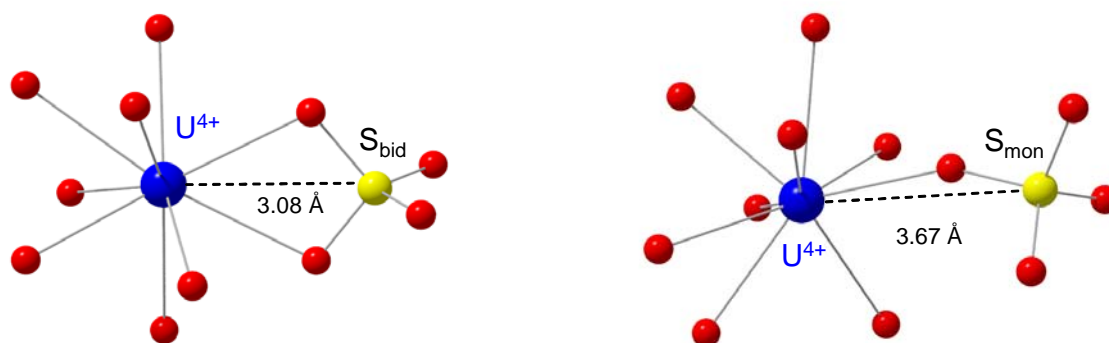
In this project we developed and tested a spectro-electrochemical cell, which allows to study the structure and speciation of aqueous actinide complexes *in situ* by x-ray absorption spectroscopy [1,2]. While *in situ* investigations by combining electrochemical cells with XAS are not new, the prevention of gas-release required for safety reasons needed an appropriate counter electrode reaction. We used an Ag metal electrode as counter electrode, where Ag is oxidized during the actinide reduction, Ag<sup>+</sup> is released and precipitates with Cl<sup>-</sup> from the solution as AgCl. This combination acts as electrode of second kind. The solvated Ag<sup>+</sup> ions are in equilibrium with solid AgCl and the equilibrium potential of the electrode is given by the solubility constant of the precipitate.

As example we show the EXAFS spectrum of U(IV) sulfate in aqueous solution at pH 1 [2]. The EXAFS spectrum shown here is affected by [2p4f] double-electron excitations, an effect that is more pronounced for actinides in oxidation state III and IV [3]. The shell fit of the U(IV) hydrate shows 9 oxygen atoms at a distance of 2.40 Å. The FT shows two additional peaks 3.08 Å and 3.67 Å indicating approximately two bidentate and two monodentate sulfate groups. We found, that the monodentate coordination

generally prevails at low  $[\text{SO}_4^{2-}]:[\text{U(IV)}]$  ratios, whereas the bidentate coordination becomes important at higher ones. The analogue solid compound shows only one U-S distance at  $3.67 \pm 0.02 \text{ \AA}$ , suggesting a rearrangement of the bonds with predominance of a monodentate linkage between U(IV) and sulfate [2].



**FIGURE 1.** U  $L_{3}$ -edge  $k^3$  weighted EXAFS data (left), and the corresponding Fourier transforms (right) of U(IV) sulfato species with 0.05 M  $[\text{UO}_2^{2+}]$  and 0.4 M  $[\text{SO}_4^{2-}]$ .



**FIGURE 2.** Structure of  $\text{U}(\text{SO}_4)_{\text{bid}}(\text{H}_2\text{O})_7^{2+}$  and  $\text{U}(\text{SO}_4)_{\text{mon}}(\text{H}_2\text{O})_8^{2+}$  complexes.

- [1] Hennig, C., Tutschku, J., Rossberg, A., Bernhard, G., Scheinost, A.C. Comparative EXAFS investigation of uranium(VI) and -(IV) aquo chloro complexes in solution using a newly developed spectroelectrochemical cell. *Inorganic Chemistry* **44** (2005) 6655
- [2] Hennig, C., Schmeide, K., Brendler, V., Moll, H., Tsushima, S., Scheinost, A.C. EXAFS investigation of U(VI), U(IV) and Th(IV) sulfato complexes in aqueous solution. *Inorganic Chemistry*, submitted
- [3] Hennig, C. Evidence for double-electron excitations in the  $L_3$ -edge x-ray absorption spectra of actinides. *Physical Review B* **44** (2007) 035120