



ROBL-CRG

**Experiment title:**

Structural investigations of uranium(VI) at different fluoride concentrations using EXAFS. A comparison between experiment and theory.

**Experiment number:**

20\_01\_017

**Beamline:**

BM 20

**Date of experiment:**

on: 25/03/2000

**Date of report:**

21/03/2001

**Shifts:**

3

**Local contact(s):**

Dr. Reich, Tobias

*Received at ROBL:*

27/03/2001

**Names and affiliations of applicants (\* indicates experimentalists):**Henry Moll<sup>\*a</sup>, Zoltán Szabó<sup>b</sup>, Tobias Reich<sup>\*a</sup>, Christoph Hennig<sup>\*a</sup>, Harald Funke<sup>a\*</sup>, Margret Rutsch<sup>a\*</sup>, Andre Roßberg<sup>a\*</sup>, Samer Amayri<sup>a\*</sup> and Ingmar Grenthe<sup>b</sup><sup>a</sup>Institute of Radiochemistry, Forschungszentrum Rossendorf e.V., P.O. Box 510119, D-01314 Dresden, Germany<sup>b</sup>Inorganic Chemistry, Department of Chemistry, Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden**Report:**

*Experimental.* Appropriate aliquots of the U(VI) stock solutions were taken to obtain the 0.05 M test solutions B, C and D. Their fluoride concentrations, 0.21, 0.45 and 3.00 M, respectively, were adjusted by adding NaF (solutions B and C) or tetramethyl-ammonium fluoride (solution D). The  $-\log[\text{H}^+]$  of the test solutions was adjusted using NaOH and/or  $\text{HClO}_4$ . EXAFS data were recorded at the Rossendorf Beamline (ROBL) at the ESRF in Grenoble. For energy calibration of the sample spectra, the spectrum from a Zr foil was recorded simultaneously. The ionization energy of the U  $L_{\text{III}}$  electron,  $E_0$ , was arbitrarily defined as 17 185 eV. The data were treated using the EXAFSPAK software developed by George and Pickering (1995) at SSRL. Theoretical backscattering phase and amplitude functions used in data analysis were calculated for the model complex  $\text{UO}_2\text{F}_4(\text{H}_2\text{O})^{2-}$  and  $\text{UO}_2\text{F}_5^{3-}$  using the FEFF7 program. The MS path O-U-O (4 legged path) of the linear  $\text{UO}_2^{2+}$  unit was included in the model fitting.

*Results and discussion.* The EXAFS oscillations of U(VI) at different fluoride concentrations are similar (see Fig. 1). The uranyl sample in the acidic pH region shows a different pattern of the EXAFS oscillation [1]. The differences are more transparent in the FTs. There are two trends observable in the EXAFS data shown in Fig. 1. The first one is a pronounced lengthening of the uranium -"yl" oxygen distance and the second is a shortening of the U-( $\text{O}_{\text{eq}}$ ,F) distance in fluoride containing test solutions, compared to the U(VI) aqua cation. Similar trends were found in alkaline uranyl systems [1-3] as well as in U(VI) oxide precipitates prepared at pH values above 7 [4]. The first co-ordination sphere, presumably fluoride, is stronger bonded to the uranyl center as the water ligands in the aqua ion shown by the distance of 2.26 Å.

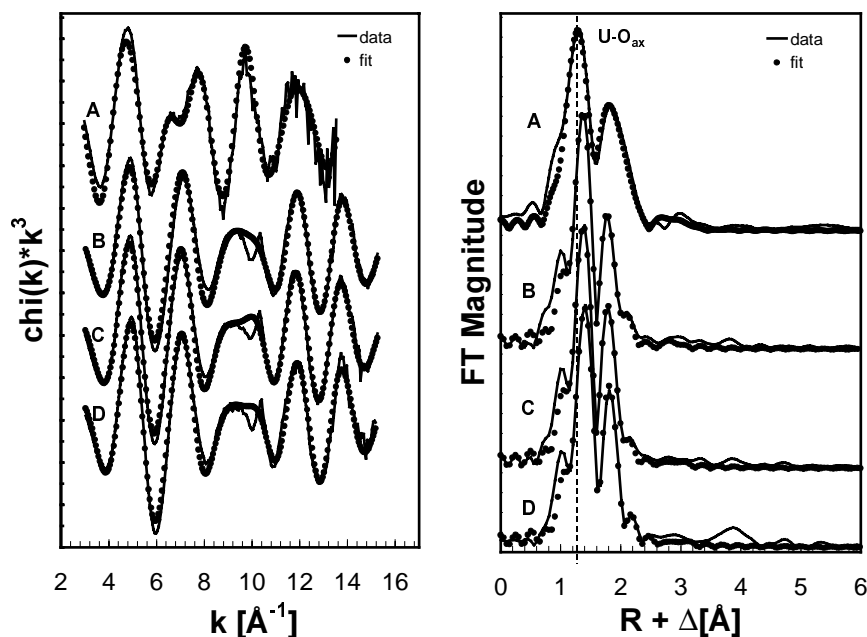


Fig. 1: U L<sub>III</sub> -edge  $k^3$ -weighted EXAFS data and corresponding FT's measured for (A) 0.05 M  $\text{UO}_2^{2+}$  in 0.1 M  $\text{HClO}_4$ , (B) 0.052 M  $\text{UO}_2^{2+}$  + 0.21 M  $\text{F}^-$  (pH=5.0), (C) 0.052 M  $\text{UO}_2^{2+}$  + 0.45 M  $\text{F}^-$  (pH=5.3), and (D) containing  $\text{UO}_2\text{F}_5^{3-}$ . The solid line is the experimental data, and the dashed line represents the best theoretical fit of the data.

A main result of the EXAFS data evaluation was the improvement of the fit by including a third shell, in contrast to the tetrahydroxo uranyl complex at high pH [3]. It is very likely that the third shell represents coordinated water at a distance of 2.50 Å. The two equatorial shells interfere another and the fact that oxygen is a light backscatterer makes it difficult to estimate a precise value of the number of coordinated water. On the other hand the calculations showed that the number of ligands in the second shell can be determined within an error range of  $\pm 0.5$ . We used chemical information for the final refinement of the data. The speciation within the system is perfectly known from the literature [5]. And we used this chemical information and fixed the coordination numbers to the theoretical values. A further argument for fluoride as the second shell might be that similar U-F bond distances are reported for the solid-state structure of  $\text{Na}_4[(\text{UO}_2)_2(\text{OCH}_2\text{COO})_2\text{F}_4] \cdot 6\text{H}_2\text{O}$  [6]. With increasing fluoride within the second coordination sphere of uranium, an increasing coordination number for fluoride was determined. The FT magnitude of sample D shows a peak at around 4.1 Å. This feature could result from MS pathways like U-O-F. But fit calculations including such contributions failed. Another explanation would be an U-U interaction. This is on the other hand not very likely because bridging fluoride is only known in solid state structures, not in solution. Furthermore, one would also expect that the bond distance U-F in the bridge to be substantially longer than in the non-bridged bonded fluorides. No such evidence is seen. The changes in distance of the second shell are within the error limit of this method.

#### References

- [1] Wahlgren, U., et al., *J. Phys. Chem. A* **103**, 8257-8264 (1999).
- [2] Clark, D.L., et al., *Inorg. Chem.* **38**, 1456-1466 (1999).
- [3] Moll, H., et al., *Radiochim. Acta* **88**, 411 (2000).
- [4] Allen, P.G., et al., *Radiochim. Acta* **75**, (1996) 47-53.
- [5] Grenthe, I., et al., in: Wanner, H. and Forrest, I. (eds.): *Chemical Thermodynamics of Uranium*, NEA OECD, Issy-les-Moulineaux, France (1992).
- [6] Farkas, I., et al., *Acta Chim. Scand.* **53**, 1009-1012 (1999).