



	Experiment title: Coordination sphere of the uranyl ion in solutions of perchloric and triflic acid	Experiment number: CH-618
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Report :

Highly acidic uranium(VI) solutions play an important role in the spent nuclear fuel cycle. In this context, the interaction of uranyl ions (UO_2^{2+}) with perchloric (HClO_4) and triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) have previously been studied [1] with laser fluorescence spectroscopy. The fluorescence life times of uranium were found to generally increase with acidity. The effect is related to the number of H_3O^+ ions, but it remains largely unexplained on a molecular level. The aim of the present investigations is to determine the coordination sphere of uranyl ions in solutions of up to 12 M perchloric and 10 M triflic acid by extended X-ray absorption fine structure spectroscopy (EXAFS).

Uranium L_{III} -edge EXAFS spectra were measured in transmission mode at the Rossendorf beam line (ROBL) of the ESRF using a Si(111) double-crystal monochromator. The EXAFS spectra were analyzed according to standard procedures using the program EXAFSPAK and theoretical scattering phases and amplitudes calculated with the scattering code FEFF [2].

For the perchlorate solutions, uranium is found to be coordinated with two axial oxygen atoms (O_{ax} , at a distance $R=1.76 \text{ \AA}$) and a single shell of 4.8 ± 0.3 equatorial oxygen atoms (O_{eq} , at $R=2.41 \text{ \AA}$). No chlorine scattering contribution is observed at room temperature

EXAFS measurements up to the highest perchlorate concentrations of 12 M. We conclude that UO_2^{2+} is coordinated with five water molecules and that the electrostatic interaction with the ClO_4^- ions takes place over longer distances. This is consistent with an EXAFS measurement of solid $\text{UO}_2(\text{ClO}_4)_2$, where chlorine scattering could neither be observed. Crystal structure data of this compound [3] show that the perchlorate tetrahedra are separated from uranium at U–Cl distances of 5.40 – 6.17 Å.

For uranium in triflic acid, the raw k^3 -weighted EXAFS data and the corresponding Fourier transform are shown for a 10 M triflic acid solution in Fig. 1. In the FT spectra, single-scattering peaks of U–O_{ax} and U–O_{eq} are clearly visible at $R+\Delta \approx 1.2$ Å and 1.8 Å, respectively. In addition, a third peak is visible at $R+\Delta \approx 3.0$ Å. The respective distances derived from the fits are U–O_{ax} = 1.75 Å, U–O_{eq} = 2.42 Å, and U–S = 3.61 Å. The coordination numbers increase from $N_S \approx 1.0$ (at 5 M perchlorate concentration) up to $N_S \approx 2.6$ (at 10 M perchlorate concentration). This result points at the presence of multiple uranium triflate complexes in the solution.

From the measured U–S bond length one may conclude on the type of complexation (mono- or bidentate): The average U–S radial distance of 3.61 Å is independent of the N_S value. It is somewhat below the crystal structure value (3.67 – 3.68 Å) which results from a monodentate bond. Assuming a bidentate complex, on the other hand, with the measured U–S distance of 3.61 Å, and with bond lengths and angles of the $\text{CF}_3\text{SO}_3\text{H}$ molecule ($\text{S–O} = 1.40 - 1.44$ Å and $\angle(\text{O–S–O}) = 111 - 119^\circ$), the calculated U–O_{eq} distance should be about 3.3 Å rather than the 2.42 Å found here. Results for uranium(III,IV) triflate complexes and other complexes [4] have also shown that the shorter U–O_{eq} distance is characteristic of a monodentate configuration. Therefore, these results point at the presence of multiple uranyl triflate species with monodentate complexation in highly concentrated triflic acid solutions (≥ 8 M).

In addition, at these high concentrations a change of the uranyl coordination sphere is found: uranium is coordinated with only four O_{eq} (10 M $\text{CF}_3\text{SO}_3\text{H}$) whereas it is coordinated with five O_{eq} at lower concentrations. This change in the coordination sphere is observed at a concentration where a drastic increase of the fluorescence life time of photoexcited uranyl ions has previously been found (from 5 μs at 8 M $\text{CF}_3\text{SO}_3\text{H}$ to 30 μs at 10 M $\text{CF}_3\text{SO}_3\text{H}$ [1]). The lifetime increase is consistent with the EXAFS result which shows that water molecules are replaced in the uranyl coordination sphere by triflic acid molecules: Compared to water, triflic acid has a smaller number of O–H bonds which are good quenchers of the uranyl excitation energy due to their large vibrational energy. With an increasing number of triflate

molecules the quenching becomes less effective, the decay rate of the excited uranyl unit decreases and, in turn, the measured lifetimes increase. In conclusion, the combination of EXAFS measurements and laser-induced fluorescence studies [1] allows to determine the quenching effects of photoexcited uranyl ions in triflic acid on a molecular level.

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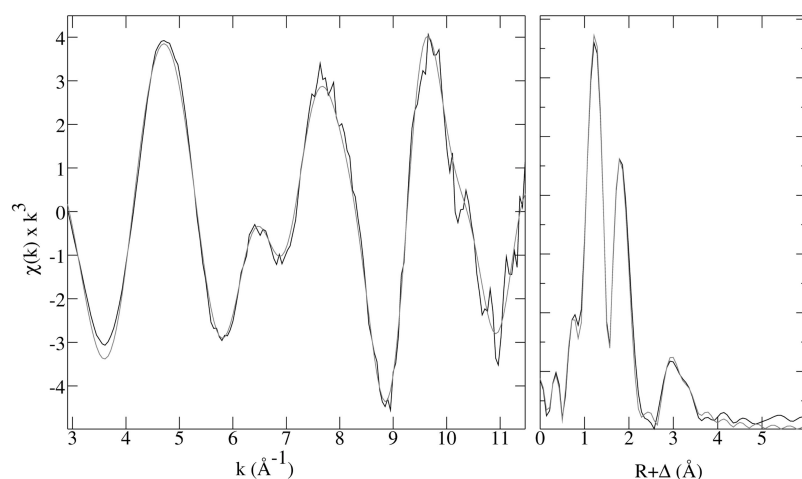


Fig. 1: k^3 -weighted uranium L_{III} -edge EXAFS spectrum (left) and its Fourier transform (right) of a 10^{-2} M U(VI) solution in 10 M triflic acid. Solid line: Data
Dashed line: Fit