ROBL-CRG	**Experiment title:** EXAFS Investigations of Uranyl Sulfate Complexes	**Experiment number**: 20_01_05
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Report:

Experimental

Samples were prepared by taking aliquots of an acidic $UO_2(ClO_4)_2$ stock solution to get a final uranyl concentration of 0.05M. The sulfate concentration in the acidic test solutions were adjusted using H_2SO_4 or Na_2SO_4. The solid, $UO_2SO_4{\cdot}2.5H_2O$, was prepared as described in /1/. The EXAFS spectra were recorded at the new Rossendorf Beamline (ROBL) at the ESRF in Grenoble. The transmission spectra were measured at room temperature using a cooled Si(111) double crystal monochromator of fixed-exit type (E= 5-35 keV). The higher harmonics were rejected by two Si and Pt coated mirrors. For energy calibration of the sample spectra, the spectrum from a Zr foil was recorded simultaneously. The ionization energy of the U L_{III} electron, E_0, was arbitrarily defined as 17 185 eV. The data were treated using the WinXAS software /2/. Theoretical backscattering phase and amplitude functions, $\delta(k)$ and $F(k)$, used in data analysis were calculated using the FEFF7 /3/ program.

Results

The isolated EXAFS oscillations and the corresponding Fourier transforms for samples A to D are shown in Fig. 1. The FT peaks below 1.5 Å (without phase-shift) are artifacts of the spline removal and are not associated with any coordination distance. The obtained structural parameters are given in Tab. 1.

There are no EXAFS results about uranyl sulfate complexes published yet. In all samples uranium is surrounded by two O_{ax} atoms at 1.77±0.01 Å. Approximately five O_{eq} atoms are coordinated to the linear uranyl group at 2.39-2.41 Å in the equatorial plane. The large Debye-Waller (DW) factor observed for the third shell in samples A-B indicates the difficulties to localize the S backscatterer, may be due to a broad distribution of U-S distances. In sample C, where $UO_2(SO_4)_2^{2-}$ is the dominant species, approximately two sulfur atoms were measured at 3.11 Å. Blatov et al. reported an U-S distance of 3.07 Å in the solid $UO_2SO_4{\cdot}2CH_3CON(CH_3)_2$, where SO_4^{2-} is bidentate coordinated to UO_2^{2+} /4/. If sulfate is bridging and monodentate bonded to uranyl, like in $UO_2SO_4{\cdot}2.5H_2O$, one expects a longer U-S distance. The EXAFS results confirm

this assumption. And a U-S distance of 3.63 Å was measured. The structural parameter determined for $UO_2SO_4 \cdot 2.5H_2O$ are consistent with XRD measurements /5/.
By considering both previous structure information and the EXAFS data, we conclude that SO_4^{2-} is bonded in a bidentate mode to the uranyl unit in solution. The results of these study provide necessary structural information to interpret ongoing reaction dynamic investigations in the binary uranyl sulfate system.

Tab. 1: EXAFS structural parameters for uranyl sulfate complexes in solution and in $UO_2SO_4 \cdot 2.5H_2O$.

Sample	Shell	R [Å]	N	σ^2 [Å^2]
A	U-O_{ax}	1.77	2f	0.0014
82% UO_2SO_4 (aq)	U-O_{eq}	2.41	4.0	0.0071
12% UO_2^{2+}	U-S	3.12f	1f	0.0105
B	U-O_{ax}	1.77	2f	0.0013
50% UO_2SO_4 (aq)	U-O_{eq}	2.40	4.3	0.0068
50% $UO_2(SO_4)_2^{2-}$	U-S	3.15	1f	0.0083
C	U-O_{ax}	1.78	2f	0.0013
12% UO_2SO_4 (aq)	U-O_{eq}	2.44	5.1	0.0110
88% $UO_2(SO_4)_2^{2-}$	U-S	3.11	2.4	0.0075
D	U-O_{ax}	1.77	2f	0.0016
$UO_2SO_4 \cdot 2.5H_2O$	U-O_{eq}	2.39	4.0	0.0048
	U-S	3.63	1.2	0.0021

f) parameter was held constant during the fit.

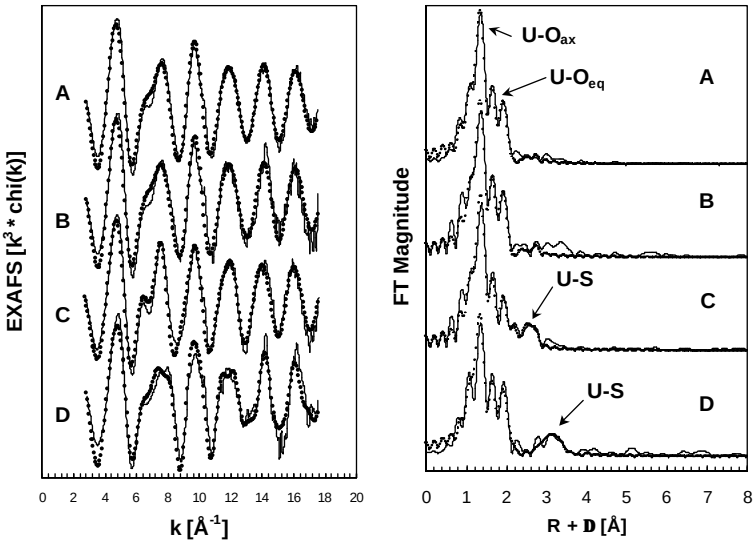

Fig. 1: Raw U L_{III} edge k^3-weighted EXAFS data for samples A-D and corresponding FT`s.

References
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