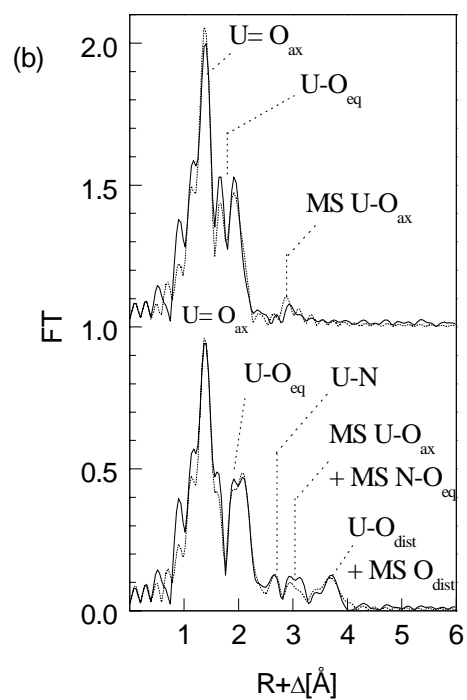
 ROBL-CRG	<b>Experiment title:</b> <b>EXAFS investigation of gradual chloride complexation to the uranyl cation in acetonitrile</b>	<b>Experiment number:</b>  <b>20-01-649</b>
	<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 26.11.2005 to: 29.11.2005
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. Christoph Hennig	<i>Received at ROBL:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  Dr. Rik Van Deun                      K.U.Leuven Dr. Linda Fluyt                         Chemistry Department Drs. Kelly Servaes                     Molecular Design and Synthesis Division Coordination Chemistry Group Celestijnenlaan 200F 3001 Heverlee Belgium		

## Report:

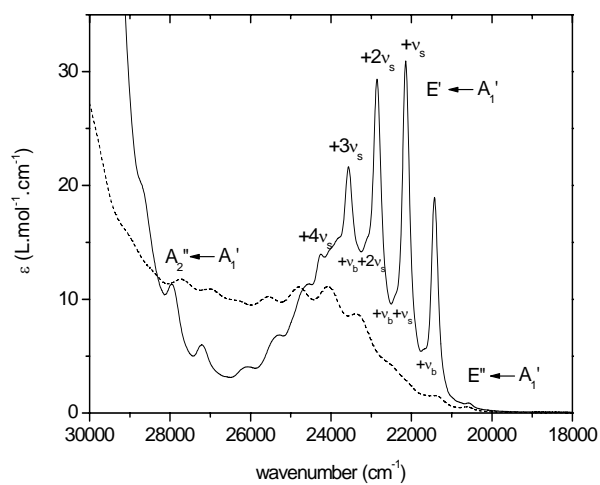
In the course of this experiment, several uranyl samples have been investigated, among which a concentration series of chloride-to-uranyl-complexes. These data are still being interpreted at the moment. Another complex that has been studied is the trinitrato-uranyl-complex. The analysis of the EXAFS-spectrum of this complex has been compared with the UV-vis results that had been obtained in our lab earlier and the total study will be submitted shortly to *Journal of the American Chemical Society*.

## Abstract:

*The complex formation of the uranyl ion  $UO_2^{2+}$  with nitrate ions has been studied by UV-Vis and  $U L_{III}$  EXAFS spectroscopy both in acetonitrile and in aqueous solution. The investigations point unambiguously to the existence of a  $[UO_2(NO_3)_3]^-$  species with  $D_{3h}$  coordination symmetry in acetonitrile. The distances in the U(VI) coordination sphere are  $U-O_{ax} = 1.77 \pm 0.01 \text{ \AA}$  and  $U-O_{eq} = 2.49 \pm 0.01 \text{ \AA}$ . The U-N distance of  $2.94 \pm 0.01 \text{ \AA}$  indicates a bidentate coordination of the  $NO_3^-$  group. A structural comparison is made between the uranyl trinitrato complex  $[UO_2(NO_3)_3]^-$  and the uranyl tricarbonato complex  $[UO_2(CO_3)_3]^{4-}$ . No evidence is found for the presence of uranyl nitrate complexes in aqueous solution under moderate conditions (50 mM  $UO_2(NO_3)_2 \cdot 6H_2O$ , pH 2.4). The UV-Vis spectrum as well as the EXAFS measurements resemble the corresponding spectra of the hydrated free uranyl ion. There are two  $O_{ax}$  atoms at  $1.77 \pm 0.01 \text{ \AA}$  and five  $O_{eq}$  atoms at  $2.41 \pm 0.01 \text{ \AA}$ . These values agree well with structural parameters obtained for the  $UO_2^{2+}$  aquo ion.*



**Figure 1:** Fourier transforms of the U  $L_{III}$ -edge  $k^3$ -weighted EXAFS data of uranyl nitrate in aqueous solution (top) and  $[UO_2(NO_3)_3]^-$  in acetonitrile (bottom); experimental data as line and theoretical curve fit as dots.



**Figure 2:** UV-Vis spectrum of  $UO_2(ClO_4)_2 \cdot xH_2O$  (dashed line) and  $[UO_2(NO_3)_3]^-$  (solid line) in acetonitrile at room temperature.