EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*http://193.49.43.2:8080/smis/servlet/UserUtils?start*

***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

## Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

## Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| ESRF | **Experiment title:**<br>Structural investigations of uranyl in ionic liquids | **Experiment number**:<br>20-01-600 |
|---|---|---|
| **Beamline**:<br>BM 20 | **Date of experiment**:<br>from: 04/12/2002 to: 07/12/2002 | **Date of report**:<br>28/08/2003 |
| **Shifts: 6** | **Local contact(s)**:<br>Andreas Bauer, Christoph Hennig | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

Clotilde Gaillard*, Isabelle Billard*, Klaus Lützenkirchen

Institut de Recherches Subatomiques
Chimie Nucléaire
F-67037 STRASBOURG cedex 2

## Report:

The aim of the experiment is to characterize the solvation sphere of uranyl ($UO_2^{2+}$) in a limited series of room-temperature ionic liquids of the Bumin type (1-butyl-3-imidazolium), with the anions $(CF_3SO_2)_2N^-$ and $PF_6^-$. To this end, comparison with $UO_2^{2+}$ in aqueous solutions of the different anions is necessary, in order to get the structure of the complexes formed. Two types of samples were studied:

- Uranyl perchlorate in aqueous solution of $HClO_4$ (1), NaF (2), $HBF_4$ (3), $HN(CF_3SO_2)_2$ (4) and $HPF_6$ (5).
- Uranyl perchlorate dissolved in $BumimPF_6$ via the introduction of a chlorate salt (BumimCl) (6).

Samples were analysed in transmission mode at the uranium $L_{III}$ edge, fit results are given in Table 1. Uranyl ions do not complex with $(CF_3SO_2)_2N^-$ and the complexation with $PF_6^-$ is hardly achieved. Indeed, laser spectroscopy experiments indicates that less than 20 % of the uranyl-$PF_6^-$ complex should be present in solution for a 3,2 M concentration in $HPF_6$. Thus, it was impossible to determine the structure of this specie. The first coordination sphere of uranium in the $UO_2F^+$ and $UO_2BF_4^+$ complexes is equivalent, with U-F distance of 2.24 Å, which are consistent with those found by Vallet *et al.* [1] for uranyl/fluorine 1:4 and 1:5 complexes.

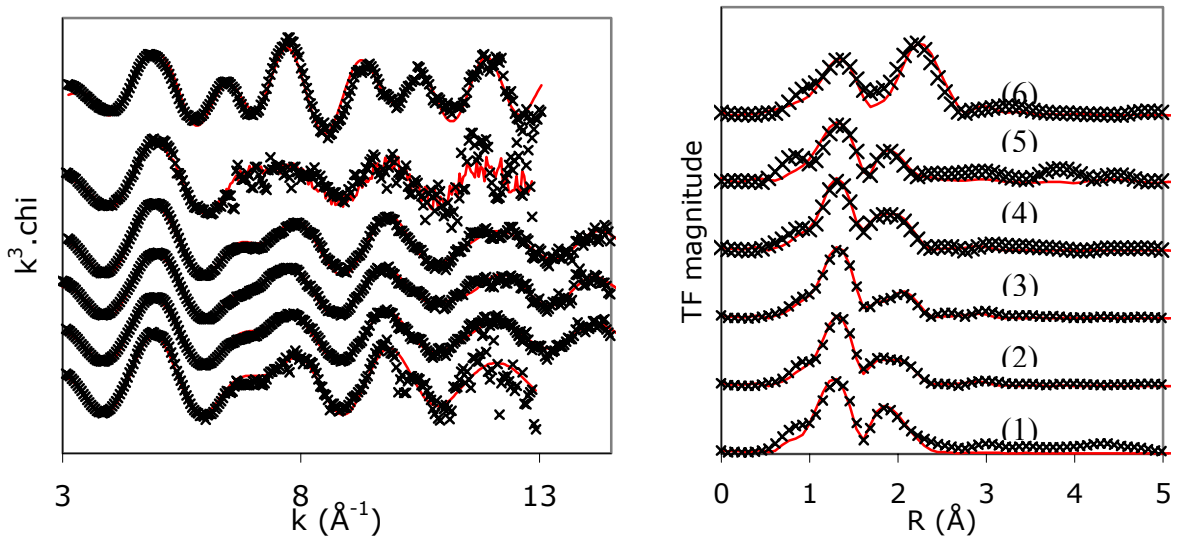


Figure 1: EXAFS spectra (left) and Fourier transform (right) of uranyl solutions

Table 1: EXAFS structural parameters

| | Sample | Shell | R (Å) | N | $\sigma^2$ (Å$^2$) |
|---|---|---|---|---|---|
| (1) | $UO_2^{2+}$ $10^{-2}$ M in $HClO_4$ 1 M | U-$O_{ax}$<br>U-$O_{eq}$ | 1.76<br>2.41 | 2*<br>5.5 | 0.0018<br>0.0081 |
| (2) | $UO_2^{2+}$ $10^{-2}$ M + NaF $1{,}8.10^{-2}$ M in $HClO_4$ 1 M | U-$O_{ax}$<br>U-$O_{eq}$<br>U-F | 1.77<br>2.42<br>2.24 | 2*<br>4.5<br>0.5 | 0.0030<br>0.0083<br>0.0049 |
| (3) | $UO_2^{2+}$ $10^{-2}$ M in $HBF_4$ 1 M | U-$O_{ax}$<br>U-$O_{eq}$<br>U-F | 1.76<br>2.44<br>2.24 | 2*<br>4.0<br>1.0 | 0.0030<br>0.0067<br>0.0050 |
| (4) | $UO_2^{2+}$ $10^{-2}$ M in $HN(CF_3SO_2)_2$ 3 M | U-$O_{ax}$<br>U-$O_{eq}$ | 1.76<br>2.41 | 2*<br>4.6 | 0.0026<br>0.0074 |
| (5) | $UO_2^{2+}$ $10^{-2}$ M in $HPF_6$ 3,2 M | U-$O_{ax}$<br>U-$O_{eq}$ | 1.78<br>2.39 | 2*<br>4.7 | 0.0035<br>0.0098 |
| (6) | $UO_2^{2+}$ $5.10^{-3}$ M in $BumimPF_6$ | U-$O_{ax}$<br>U-Cl | 1.79<br>2.70 | 2*<br>2.1 | 0.0040<br>0.0032 |

When uranyl is dissolved in the ionic liquid $BumimPF_6$, neither $PF_6^-$ nor $F^-$ (produced by dissociation of $PF_6$-) does complex with uranyl. Instead, we observe the formation of the neutral complex $UO_2Cl_2$. The Cl ions were brought in solution during the dissolution process. Contrary to what is known in water [2], the solvation sphere of uranyl in $BumimPF_6$ is constituted only by 2 atoms.

[1] V. Vallet *et al.*, Inorg. Chem., 2001, 40, 3516-3525.
[2] P.G. Allen *et al.*, Inorg. Chem., 1997, 36, 4676-4683.