



## 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.

	<b>Experiment title: Determination of the structure of uranium(IV) chloro-complexes highly coordinated in room temperature ionic liquids by EXAFS and XANES measurements</b>	<b>Experiment number:</b> 20-01-643
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 11/09/2005 to: 13/09/2005	<b>Date of report:</b>
<b>Shifts:6</b>	<b>Local contact(s):</b> Ch Hennig	<i>Received at ESRF:</i>

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

Claire Le Naour\*, Didier Trubert\*, Celine Cannes,

CNRS/IN2P3/UPS Institut de Physique Nucléaire 91406 Orsay Cedex, France

Serguei Nikitenko\*, Mikhail Grigor iev

Physical chemistry Institute, Moscow, (Russia)

Christoph Hennig\*

ESRF, ROBL - Forschungszentrum Rossendorf 38000 Grenoble, France

Philippe Moisy

CEA/Valrhô, DEN/DRCP/SCPS, 30207 Bagnols sur Ceze Cedex, France

### Report:

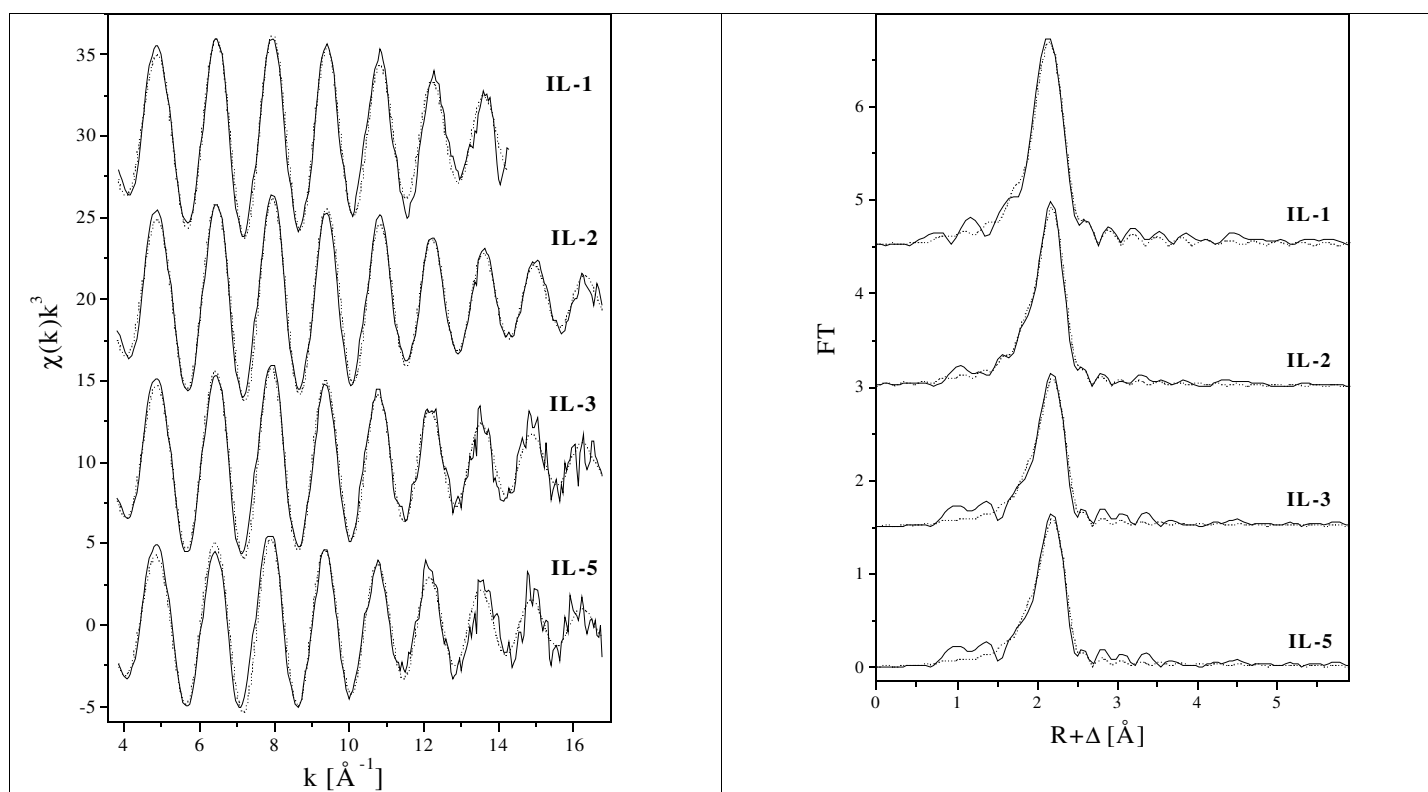
The ionic liquid chosen was: 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide (there after called [Bumim][Tf<sub>2</sub>N]). Uranium(IV) hexa-chloro-complexes are introduced under [Bumim]<sub>2</sub>[UCl<sub>6</sub>] form. Addition of Chloride is achieved by [Bumim][Cl].

Three liquid samples containing 20mM Uranium in [Bumim][Tf<sub>2</sub>N] and two solid samples used as reference compound were analysed.

<b>IL_0 1</b>	UCl <sub>6</sub> (Bumim) <sub>2</sub> (pellet in boron nitride )
<b>IL_0 2</b>	UCl <sub>6</sub> (Cs) <sub>2</sub> (pellet in boron nitride)
<b>IL_0 3</b>	UCl <sub>6</sub> (Bumim) <sub>2</sub> in BumimTf <sub>2</sub> N
<b>IL_0 4</b>	UCl <sub>6</sub> (Bumim) <sub>2</sub> in BumimTf <sub>2</sub> N + 0.05M Bumim Cl
<b>IL-05</b>	UCl <sub>6</sub> (Bumim) <sub>2</sub> in BumimTf <sub>2</sub> N + 1M Bumim Cl

Uranium L<sub>III</sub>-edge EXAFS spectra were collected at the Rossendorf Beamline[1] at the ESRF (6.0 GeV, 200 mA). The measurements were carried out in transmission mode using argon-filled ionization chambers at ambient temperature and pressure. The measurements were performed using a double crystal Si (111) monochromator. Data were collected in equidistant *k*-steps of 0.05 Å<sup>-1</sup> across the EXAFS region. 6 to 10 scans were recorded for each sample and then averaged. A Y metal foil (first inflection point at 17038 eV) was used for energy calibration. The U L<sub>III</sub> threshold energy, *E*<sub>*k*=0</sub>, was defined as 17185 eV. EXAFS data were extracted from the raw absorption spectra by standard methods including a spline approximation for the atomic background using the program EXAFSPAK [2]. Theoretical phase and amplitude functions were calculated with FEFF 8.2 [3]. The scattering path and amplitude functions were calculated using the crystal structure of UCl<sub>6</sub>(bumim)<sub>2</sub> described here. The

amplitude reduction factor,  $S_0^2$ , was defined as 1.0 in the FEFF calculation and fixed to that value in the data fits.



**Figure 1.** U L<sub>III</sub>-edge  $k^3$  weighted EXAFS data, experimental data (line) and theoretical curve fit (dots) and Fourier transforms, experimental data (line) and theoretical curve fit (dots).

sample	$\Delta k$ [Å <sup>-1</sup> ]	$N$	$R$ [Å]	$\sigma^2$ [Å <sup>2</sup> ]	$\Delta E$ [eV]	fit error
IL-1	3.8-14.3	6.5	2.619(2)	0.0045	-1.1	0.35
IL-2	3.8-16.8	6.1	2.620(1)	0.0040	-1.2	0.17
IL-3	3.8-16.8	6.1	2.632(2)	0.0044	-0.3	0.28
IL-5	3.8-16.8	5.6	2.634(2)	0.0044	-0.9	0.46

**Table 1.** Structure parameters obtained from EXAFS shell fit. Errors in distances  $R$  are  $\pm 0.01$  Å standard deviations for  $R$  as estimated by EXAFSPAK are given in brackets, errors in coordination numbers  $N$  are  $\pm 15$  %,  $\sigma$  - Debye-Waller factor.

The bond distances are perfectly identical in all samples, the deviation in coordination numbers are in the typical range of 10-15%. U-Cl distances of both liquids are slightly longer than that of the solids, but the effect is in the error limit and therefore not significant.

Determination of the bond length of UCl<sub>6</sub> were achieved for the first time in ionic liquid. However no evidence of highly coordinated complex (UCl<sub>7</sub> or UCl<sub>8</sub>) in concentrated chloride media was demonstrated in the analyzed samples. This could be related to a low concentration of these species in the samples, far out of the range that could be investigated with EXAFS measurements.

Results will be submitted for publication in a near future.

- 1) Matz, W.; Schell, N.; Bernhard, G.; Prokert, F.; Reich, T.; Claußner, J.; Oehme, W.; Schlenk, R.; Dienel, S.; Funke, H.; Eichhorn, F.; Betzl, M.; Pröhl, D.; Strauch, U.; Hüttig, G.; Krug, H.; Neumann, W.; Brendler, V.; Reichel, P.; Denecke, M.A.; Nitsche, H. *J. Synchrotron Rad.* **1999**, *6*, 1076-1085.
- 2) George, G. N.; Pickering, I. J. *EXAFSPAK, a suite of computer programs for analysis of X-ray absorption spectra*; Stanford Synchrotron Radiation Laboratory, Stanford, 2000.
- 3) Ankudinov, A.L.; Ravel, B.; Rehr, J.J.; Conradson, S.D. *Phys. Rev.* **1998**, *B58*, 7565-7576.