

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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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.



	Experiment title: XES studies of aqueous solutions of Fe ²⁺ -based atomic and molecular species	Experiment number: CH-3332
Beamline: ID26	Date of experiment: from: 29.03.2011 to: 05.04.2011	Date of report: 31.08.2011
Shifts: 21	Local contact(s): Dr. Pieter Glatzel	<i>Received at ESRF:</i>

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Report:

We successfully recorded energy-dispersive X-ray absorption near edge structures (XANES), non-resonant X-ray emission spectra (NXES) and resonant inelastic X-ray scattering (RIXS) planes of various iron –based atomic and molecular species dissolved in a range of different solvents.

Specifically, we measured and compared spectra of hexacyanoferrate(II / III) ions dissolved in water and ethylene glycol, tris(2,2'-bipyridine)iron(II) chloride in water and acetonitrile, iron(II / III) chlorides in water, heavy water and ethanol, hemin in water and myoglobin cyanide (MbCN) in water.

The most distinct solvent effects were expected in the case of dissolved iron chlorides where water molecules directly coordinate to the iron. This was confirmed by the measurements though the analysis of the iron chloride data will be challenging due to the high sensitivity of the spectra to sample preparation and measurement conditions. XANES of solvated hexacyanoferrate(II / III) ions revealed distinct solvent effects as well (figure 1). We could resolve changes of pre-edge / edge transitions and observe features which are present in one solvent but absent in the other. On the other side solvent effects are less pronounced in XANES of tris(2,2'-bipyridine)iron(II) chloride (figure 2).

Figures 3 – 6 demonstrate the chemical sensitivity of the measured $K\alpha_{1,2}$ / $K\beta_{1,3}$ / $K\beta'$ and $K\beta_{2,5}$ / $K\beta''$ lines. However, the character of the valence orbitals changes the most between different chemical environments and consequently pronounced solvent effects were mainly found in the shapes of $K\beta_{2,5}$ / $K\beta''$ satellite lines (valence-to-core transitions) of iron chlorides and hexacyanoferrate(II / III) ions but not in the lineshapes of solvated tris(2,2'-bipyridine)iron(II) chloride.

The recorded 1s2p-RIXS plane data (e.g. figures 7, 9, 11) clearly resolves the pre-edge structures of the measured compounds and will thus allow for a quantitative analysis. Integrating in the incident energy yields spectra which can be directly compared to L-edge XAS (figure 13). Figures 8, 10 and 12 illustrate the visibility of solvent effects in the RIXS plane differences of solvated hexacyanoferrate(II / III) ions and tris(2,2'-bipyridine)iron(II) chloride.

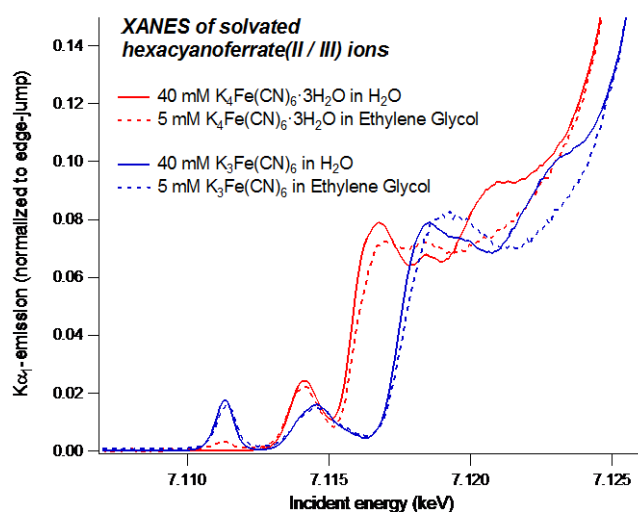


Figure 1: XANES of hexacyanoferrate(II / III) ions in solution (detected on $K\alpha_1$ – line). Solvent dependency.

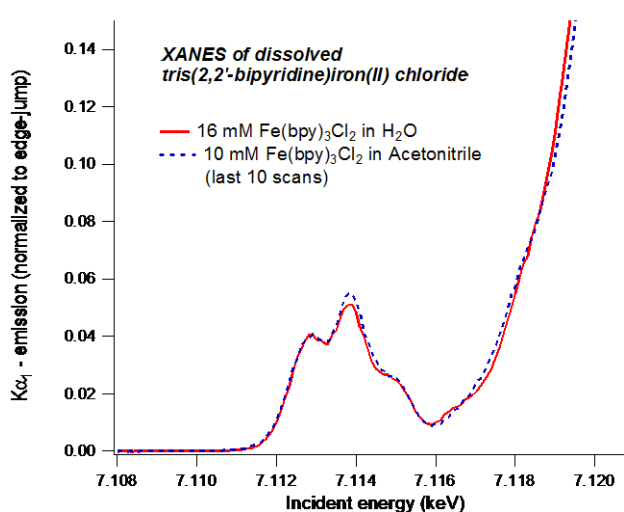


Figure 2: XANES of tris(2,2'-bipyridine)iron(II) chloride in solution (detected on $K\alpha_1$ – line). Solvent dependency.

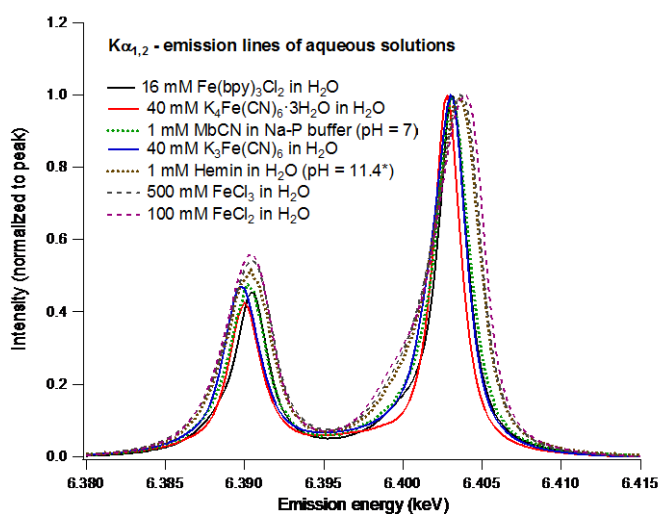


Figure 3: $K\alpha_{1,2}$ -emission lines of aqueous solutions.

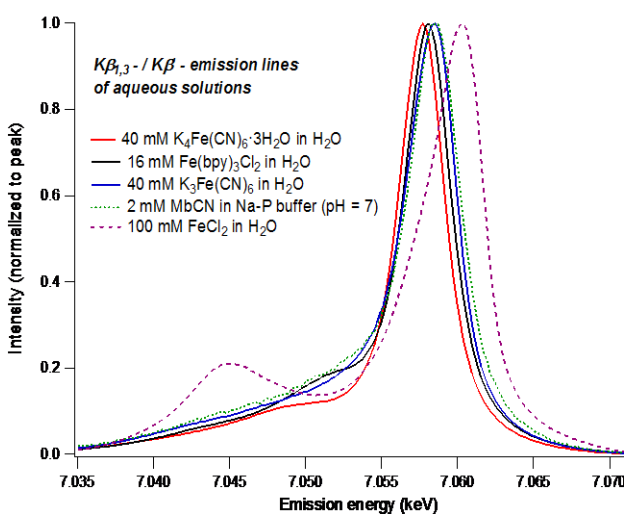


Figure 4: $K\beta_{1,3}$ - / $K\beta'$ – emission lines of aqueous solutions.

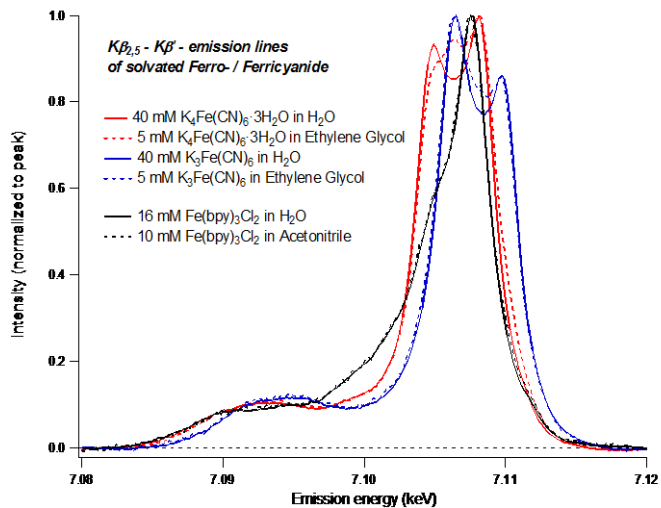


Figure 5: $K\beta_{2,5}$ - / $K\beta'$ - emission lines of aqueous solutions. Clearly visible solvent effects.

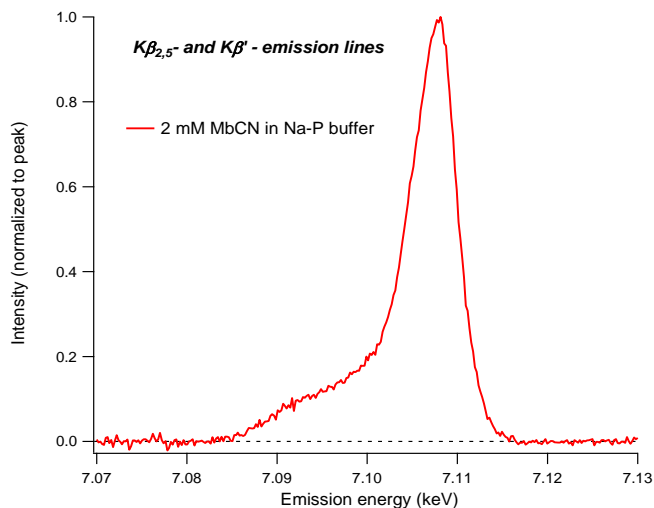


Figure 6: $K\beta_{2,5}$ - / $K\beta'$ - emission lines of aqueous Myoglobin cyanide.

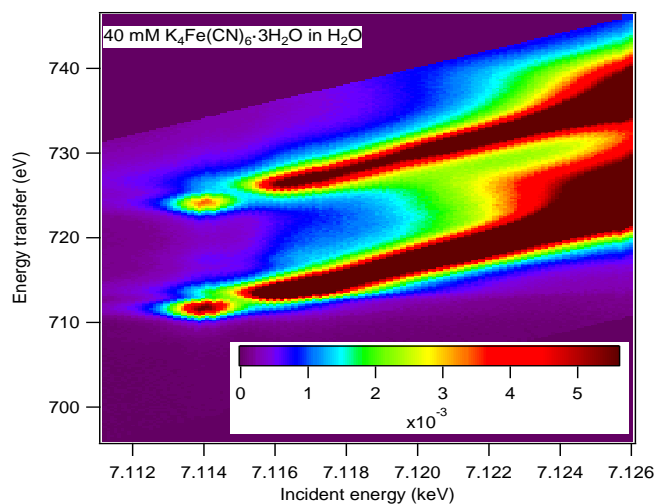


Figure 7: $1s2p$ -RIXS plane of aqueous hexacyanoferrate(II) ions.

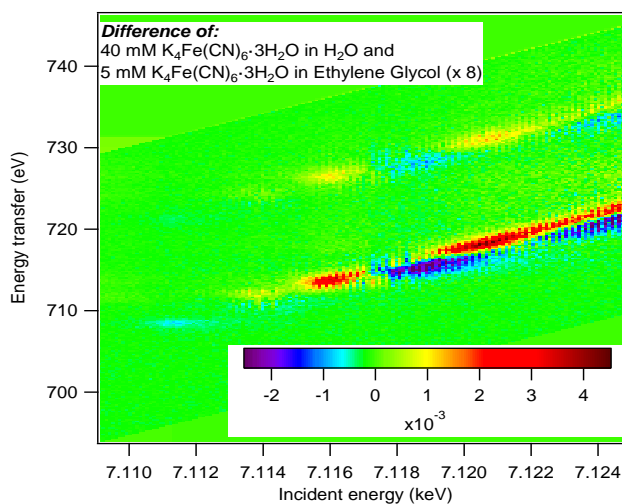


Figure 8: $1s2p$ -RIXS plane difference of hexacyanoferrate(II) ions dissolved in H_2O and Ethylene Glycol.

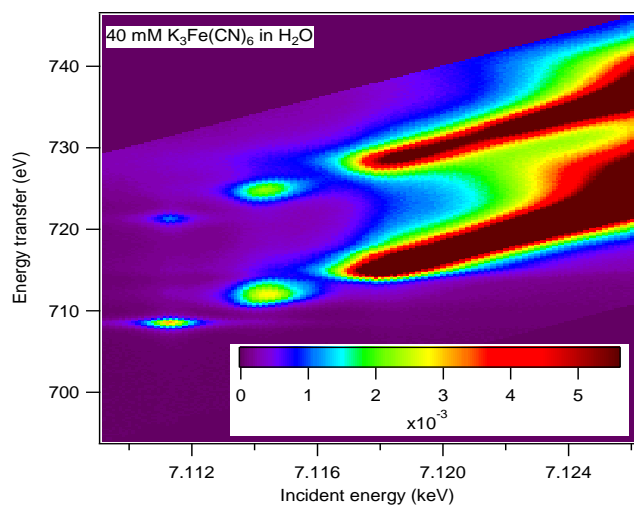


Figure 9: $1s2p$ -RIXS plane of aqueous hexacyanoferrate(III) ions.

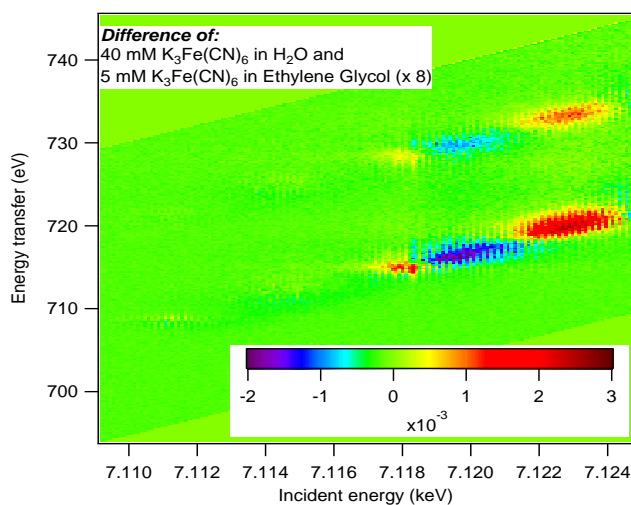


Figure 10: $1s2p$ -RIXS plane difference of hexacyanoferrate(III) ions dissolved in H_2O and Ethylene Glycol.

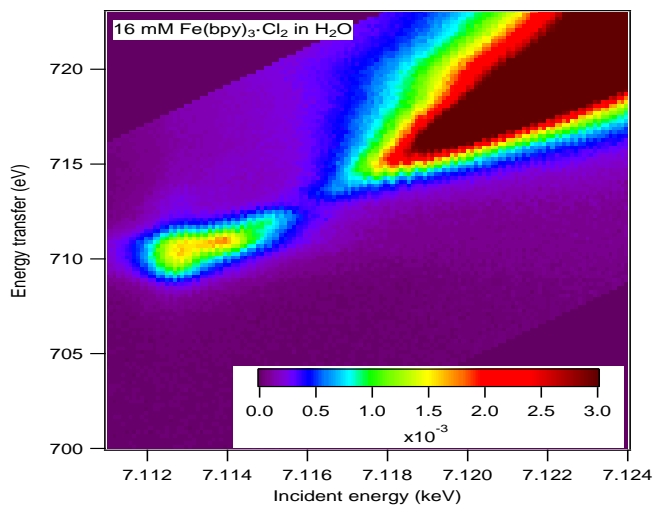


Figure 11: *1s2p-RIXS plane of aqueous Tris(2,2'-bipyridine)Iron(II) chloride*

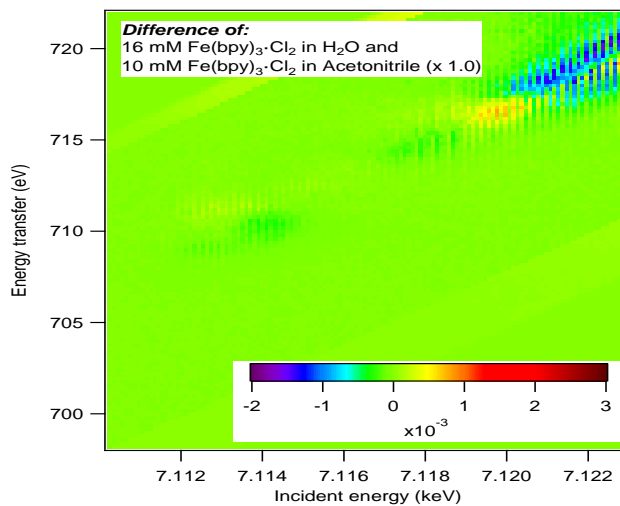


Figure 12: *1s2p-RIXS plane difference of tris(2,2'-bipyridine)Iron(II) chloride dissolved in H₂O and Acetonitrile*

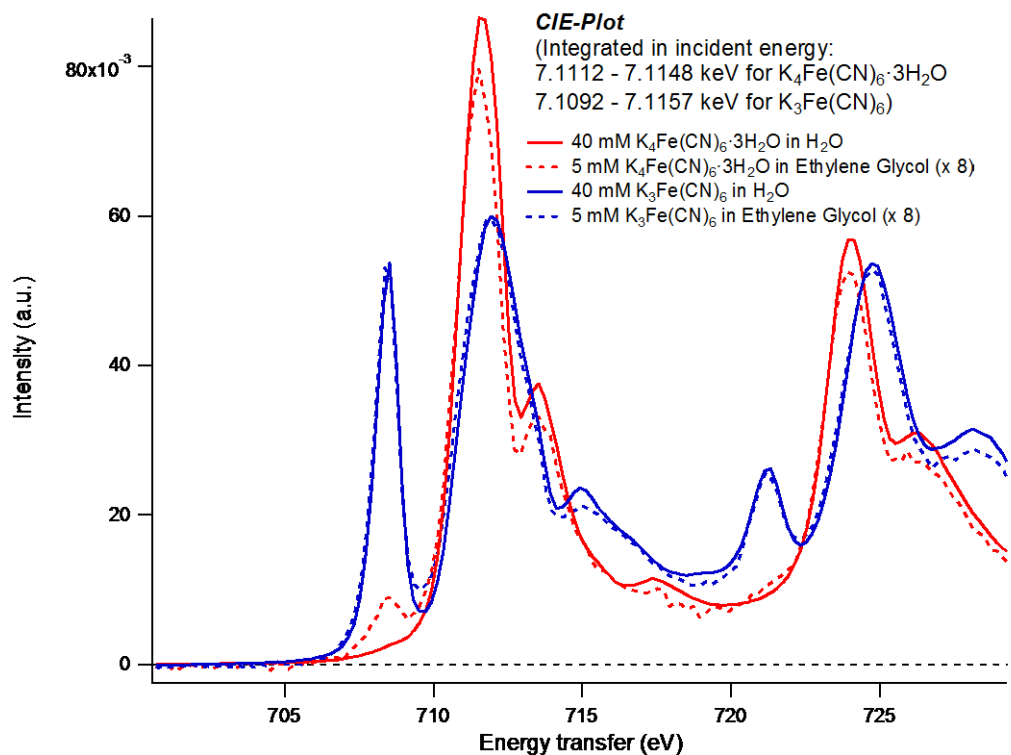


Figure 13: *Constant incident energy (CIE) graphs yield L-edge like spectra. Integration on the incident energy axis of the 1s2p-RIXS planes of solvated hexacyanoferrate(II / III) ions.*