

## 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:**

How synchrotron radiation can contribute to solve the energy problem: A combined X-ray absorption/X-ray emission study of light-driven water reduction

**Experiment number:**

MA-1774

**Beamline:**

ID26

**Date of experiment:**

from: 22/02/2013 to: 26/02/2013

**Date of report:**

28/02/2013

**Shifts:**

12

**Local contact(s):**

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*Received at ESRF:*

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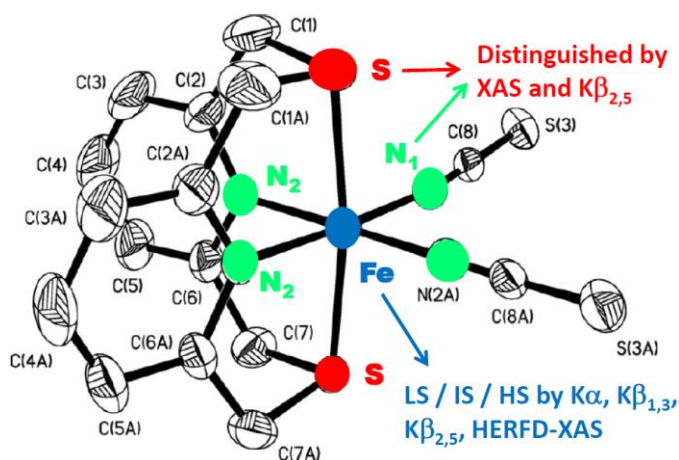
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**Report:**

Spin-crossover (SCO) is a representative example of molecular bistability, in which the high-spin (HS) and low-spin (LS) states are interconvertible by physical perturbation such as temperature.<sup>1</sup> Since the first discovery of the SCO phenomenon it has attracted much attention from chemists, biochemists, and physicists, because it offers an understanding of ligand field theory. But despite the tremendous insights that have been gained over the past decades into the underlying electronic principles responsible for the occurrence and the specific behavior of spin transition processes, the study of spin crossover complexes is still a highly attractive

research field due to their potential application in developing electronic devices.<sup>2</sup>

Especially the molecular mechanisms leading to specific spin cross-over behaviour are still not well-understood, since structural (XRD, XAS) and spin-state changes (SQUID, Mößbauer) are measured in two separate of experiments. In a very recent experiment we applied for X-ray emission based methods to study SCO complexes according to scheme 1. We could successfully use HERFD-XAS (high energy resolution fluorescence detected-XAS) and  $K\beta_{1,3}$ -XES (X-ray emission spectroscopy) to access the total spin by  $K\beta_{1,3}$ -XES and HERFD-XANES AND the local structure (by  $K\beta$ -detected XAS) of iron based spin cross-over compounds in ONE experiment (quasi)



*Scheme 1: Example of the mono-nuclear SCO complex containing N and S as coordinating atoms in axial and equatorial position.*

simultaneously. The results from analyzing the temperature dependent  $K\beta_{1,3}$ -XES and HERFD-XANES measurements are shown in figure 1. The  $K\beta_{1,3}$ -XES spectra were analyzed according to the so-called IAD-method. In this method proposed by Vanko et al.,<sup>3</sup> in brief, the difference between the spectrum of a pure spin

state and unknown spin states are formed and integrated, which gives the IAD value that is proportional to either the high or low spin fraction. An example for the spectra obtained with this method is given in figure 1 bottom left. In Figure 1 to right, the results of this analysis are shown. It is obvious that the spin states do not exactly follow the magnetization curve. Moreover there is a pronounced effect at around 190 K that can not be easily explained. The according EXAFS spectra shown in figure 1 bottom right were supposed to give a structural insight in this case. However due to a rather high noise level, it is not possible to distinguish for example the different Fe-N distances present in the complex in dependence of the spin state. Also, the sulfur backscatterers and their distance can only be determined with rather low precision. Valence to core X-ray emission could give further insights in this case, since Fe-N pairs of different distances will give separated signals in the  $v2c$  spectra, this same is true for the Fe-S pairs. Therefore in the continuation of this project,  $v2c$  measurements are planned. Moreover, the presented studies here will be extended to multinuclear sSCO compounds. In these complexes, the low-temperature ground state is composed of a mixed hs-ls state, which allows to establish spin selective XAS spectroscopy.

It has to be mentioned here, that during the first experiments, all samples showed highly sufficient stability against radiation damages, and with the cryostat at ID26 a very good temperature resolution could be achieved ( $\pm 0.1$  °C).

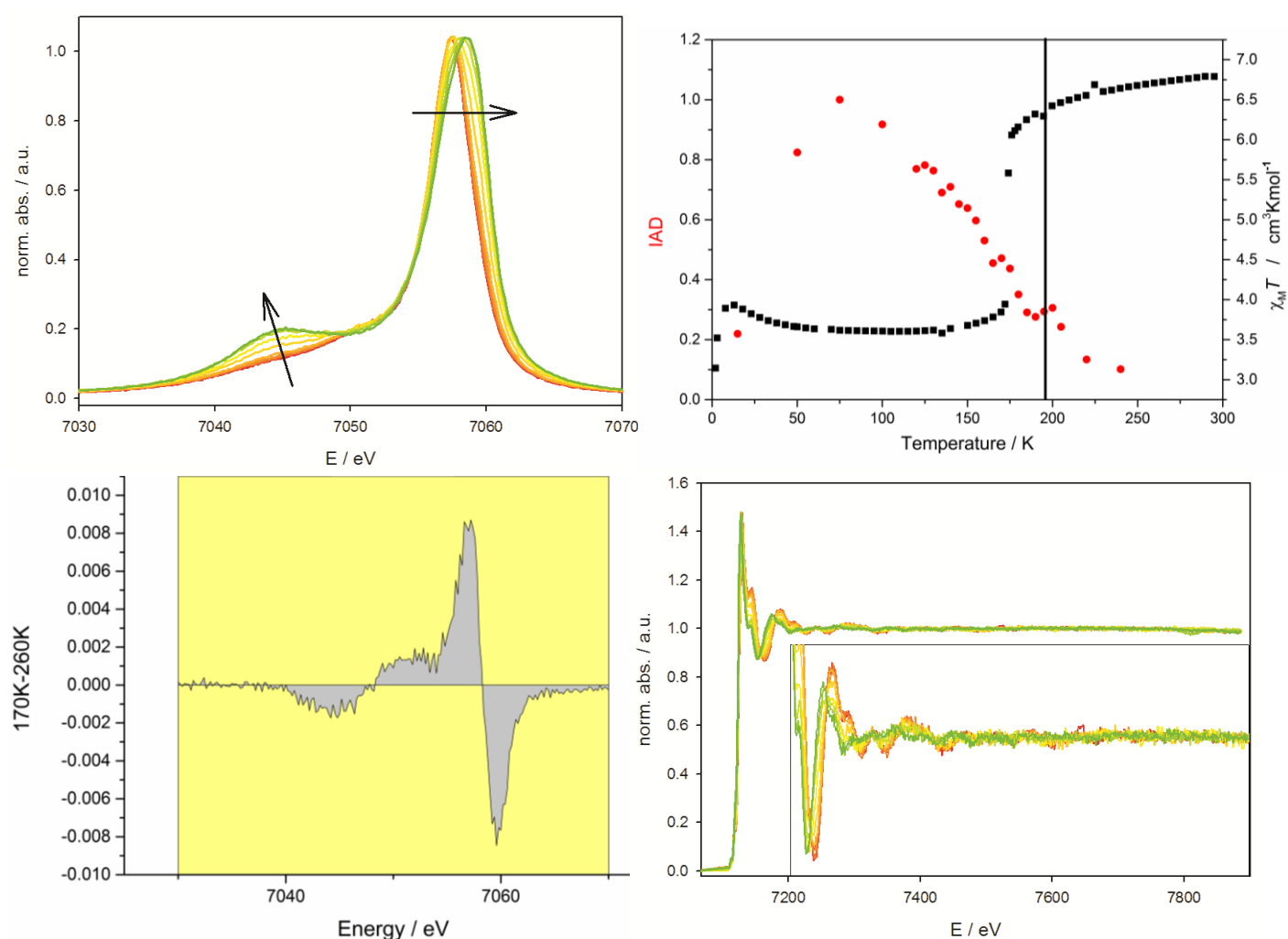


Figure 2: Magnetization curve (top left) and temperature-dependent  $K\beta_{1,3}$ -XES (top right), HERFD-XANES (bottom left) and EXAFS (bottom right) measurements carried out on  $[\text{Fe}(\text{L-N}_4\text{Me}_2)(\text{NCS})_2]$  at ID26.

- [1] P. Gülich, H.A. Goodwin, *Top. Curr. Chem.* 2004, **233**, 1. [2] J.-F. Letard, P. Guionneau, L. Goux-Capes, *Top. Curr. Chem.* 2004, **235**, 221. [3] H.-J. Krüger, *Coord. Chem. Rev.* **2009**, 253, 2450. [4] G. Vanko, F. de Groot et al., *J. Phys. Chem. B* 2006, **110**, 11647. [4] V. Briois et al., *Inorg. Chem.* 2001, **40**, 912.

