

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:

CH-3532

Beamline:

ID26

Date of experiment:

from: 20/06/2012 to: 26/06/2012

Date of report:

28/02/2013

Shifts:

18

Local contact(s):

Dr. Kristina Kvashnina

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

*Matthias Bauer, FB Chemie, TU Kaiserslautern, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern

*Roland Schoch, FB Chemie, TU Kaiserslautern, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern

Report:

The photocatalytic water splitting by iron carbonyl catalysts using an iridium photosensitizer has been studied by higher energy resolution XANES (HERFD-XANES), $K\beta_{1,3}$ - and $K\beta_{2,5}$ -X-ray emission spectroscopy in order to gain insights into the the electronic structure formed in course of the reaction. A picture of the experiment utilizing an artificial sun that illuminates the reaction mixture in a separate reaction vessel is shown in figure 1. The reaction mixture containing the long-lived iron species is then pumped by a pulse-free gear-wheel pump through the reaction cell, where the spectra are recorded.

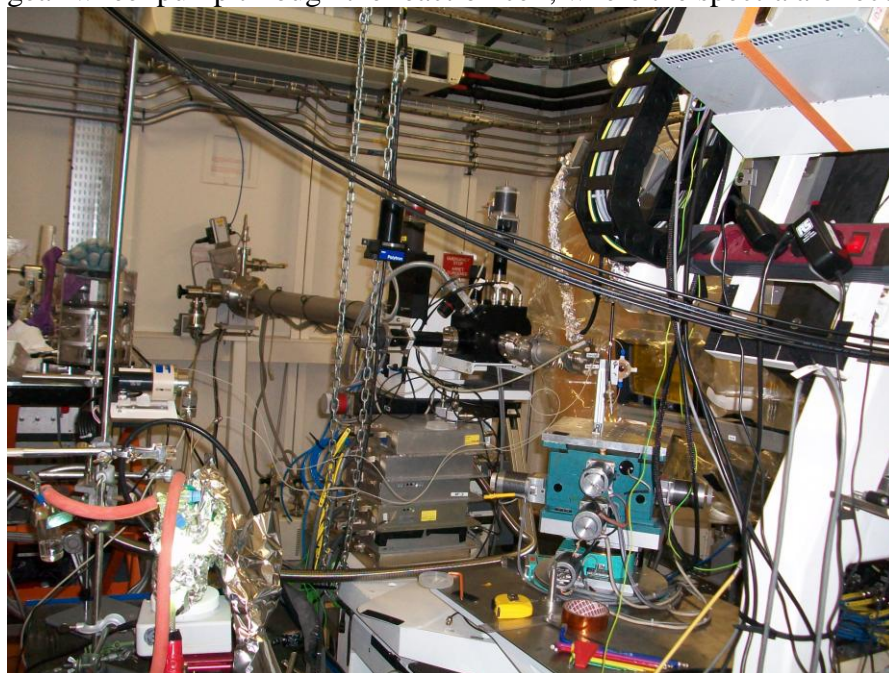


Figure 1: Picture of the experimental set-up at beamline ID26. The illuminated reaction vessel is visible in the lower left corner, the measurement cell on the green tower.

$\text{Fe}_3(\text{CO})_{12}$ was used as precatalyst, it was studied in pure THF (1), in the reaction mixture consisting of THF/water/triethylamine (2), with an activating phosphine ligand PR_3 (3) and under reaction conditions. Since an intermediate of the form $[\text{HFe}_3\text{CO}_{11}]^-$ is suspected to be formed during the reaction, it was synthesized and also measured in THF (4) and the reaction mixture after illumination (5). The corresponding HERFD-XANES and $\text{K}\beta_{2,5}$ -XES spectra are shown in figure 2.

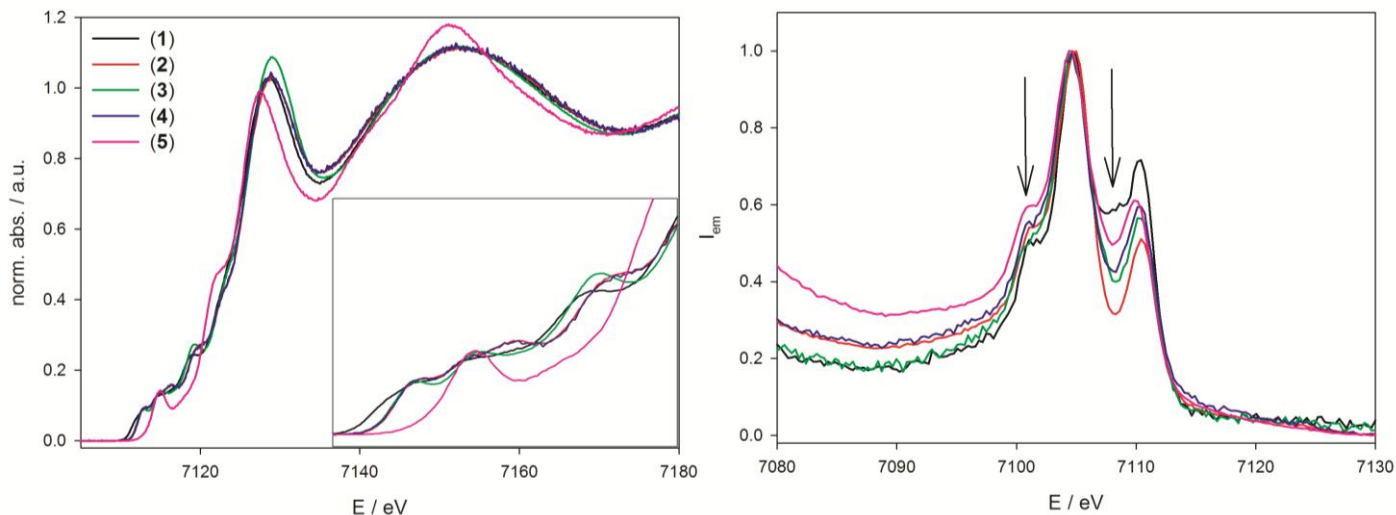


Figure 2: HERFD-XANES (left) and $\text{K}\beta_{2,5}$ -XES spectra (right) of reference systems.

The LUMO (Lowest unoccupied molecular orbitals) structure of $\text{Fe}_3(\text{CO})_{12}$ (1) is slightly altered in the reaction mixture (2), since the prepeak structure, which reflects transitions to the LUMOs changes. This changes proceed with the addition of the phosphine ligand (3). Although the spectrum of the possible intermediate $[\text{HFe}_3\text{CO}_{11}]^-$ in THF (4) is very similar to that of $\text{Fe}_3(\text{CO})_{12}$ in the reaction mixture (2), it changes drastically in the reaction mixture under illumination (5). This gives a hint that $[\text{HFe}_3\text{CO}_{11}]^-$ is in fact the reaction product of $\text{Fe}_3(\text{CO})_{12}$ in the reaction mixture. Additionally, the $\text{K}\beta_{2,5}$ -XES show also changes, however, these are not so obvious as in the HERFD-XANES spectra. The regions where the most obvious changes occur are highlighted with arrows in figure 2.

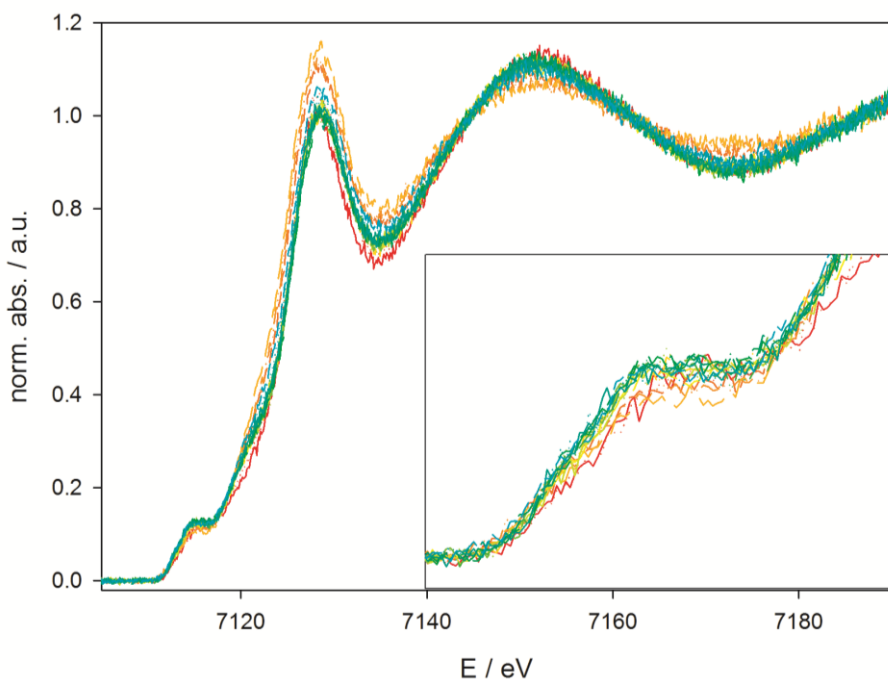


Figure 3: Operando HERFD-XANES spectra during the $\text{Fe}_3(\text{CO})_{12}$ catalyzed water reduction reaction.

What is most interesting are the energy shift between the spectra, although they are not very large. These will give the chance to achieve information on the formal oxidation state of the formed complexes, which are of urgent interest. All these reference measurements as well as a similar set for $[\text{Fe}(\text{CO})_3\text{NO}]^-$ as precatalyst are currently analyzed by TD-DFT calculations. Since the measurements were carried out in June 2012, these calculations could not be finished yet. However, the results are promising, and currently two publications are in preparation using the results of this beamtime. In addition to the reference measurements, which are also

used to “calibrate” theoretical approaches, *in-operando* studies in course of the reaction were carried out. These are summarized in figure 3 for the reaction catalyzed by $\text{Fe}_3(\text{CO})_{12}$ for the first hour of the reaction. As can be seen, only small changes occur during that time, indicating the catalytic resting state is formed rather fast. Nonetheless, the prepeak decrease and white line increase are currently analyzed to draw more detailed conclusion.