EUROPEAN SYNCHROTRON RADIATION FACILITY

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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 via the User Portal:

https://wwws.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.

ESRF	**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: BM23	**Date of experiment**: from: 18/07/2012 to: 24/07/2012 05/09/2012 08/09/2012	**Date of report**: 28/02/2013
Shifts: 18	**Local contact(s)**: Olivier Mathon	*Received at ESRF:*

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Report:

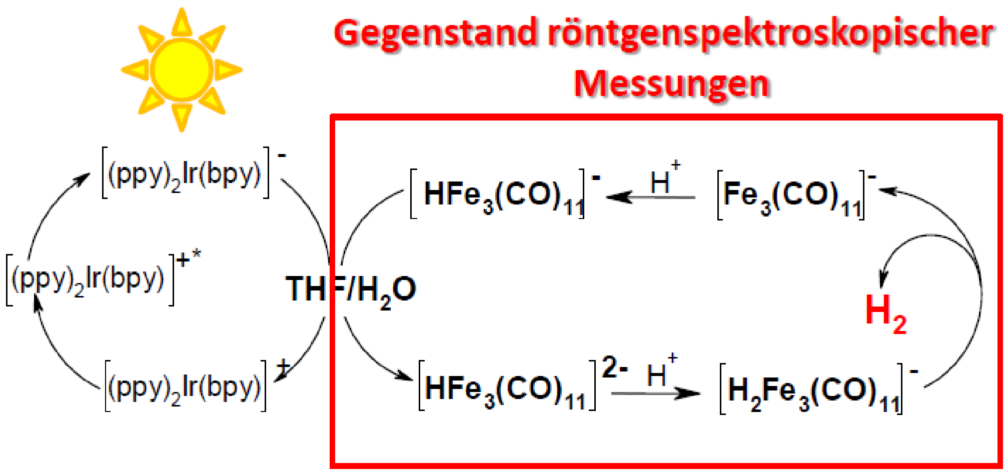

Fig. 1: Proposed mechanism for photocatalytic water readuction. The iron part is subject of this present report.

The need for clean and abundant fuels will be one of the greatest challenges to mankind in the near future, as the peak oil discussion has settled, stating that the peak of oil production will be reached within the next 10-20 years. Fuel cells are one of the most promising alternatives, since their working principle is mostly understood and recent activities focus on increasing their efficiency. However, the production of “fuels” for fuels cells, i.e. hydrogen H_2 and oxygen O_2 in the simplest case, remains one bottleneck that prevents fuel cells to be already considered a serious alternative to fossil fuels. Solar light driven water splitting reactions are a very promising approach to overcome this limitation, since “*The ultimate solution to satisfy the world’s energy demand is the cleavage of water into its atomic building blocks, hydrogen and oxygen*“.[1] Empiric studies identified iron-carbonyls as catalysts of rather high activity for light-driven water reduction (i.e. H_2

production), as revealed by increasing numbers of high-impact publications.[2] Although the results are very promising, the activity of the catalysts does not yet allow a real industrial application.[2] It is known that phosphine based ligands (“PR” in the following) increase the catalytic activity, but the mechanism induced by these phosphine ligands remains unclear. Therefore directed improvements are hindered by the lack of knowledge about the mechanistic details in the iron cycle. A proposed general mechanism is given in figure 1 with $Fe(CO)_5$ as pre-catalyst. Despite EPR and IR/Raman studies, which gave first hints, no direct image of the species formed in course of the reaction is accessible yet.[3] The aggregation degree of the iron core of the formed cluster in dependence of the used precatalyst is still a matter of debate and the number of remaining CO ligands and coordinating phosphine molecules are unknown.

We therefore carried out XAS measurement to study the iron cycle of light-driven water reduction *in-situ/in operando* (part of the measurements were carried out at ANKA, Karlsruhe as well). Although the data analysis is still in progress, preliminary results can be presented here. The studied catalyst was $Fe_3(CO)_{12}$ in the reaction solution consisting of a 4/1/1 mixture THF/triethylamin/H_2O. The phosphine ligand used was $P(PhCF_3)_3$, it was used in different stoichiometric ratios together with an Iridium photoactive system. The results from fitting the EXAFS results are given in the following table.

Sample	**Abs-Bs**	**N(Bs)**	**R(Abs-Bs)**
0.01 M $Fe_3(CO)_{12}$ in solution (1)	Fe-C Fe-Fe Fe-O/CO_{MS}	4.7 ± 0.5 2.0 ± 0.2 12.0 ± 1.2	1.80 ± 0.02 2.51 ± 0.03 2.99 ± 0.03
0.01 M $Fe_3(CO)_{12}$ in solution + Ir-PS after 5 h irradiation (2)	Fe-C Fe-Fe Fe-O/CO_{MS}	4.4 ± 0.4 1.7 ± 0.2 11.6 ± 1.2	1.79 ± 0.02 2.57 ± 0.03 2.97 ± 0.03
0.025 M $Fe_3(CO)_{12}$ in solution + 1 eq. $P(PhCF_3)_3$ (3)	Fe-C Fe-P Fe-Fe Fe-O/CO_{MS}	4.8 ± 0.5 0.3 ± 0.1 0.1 ± 0.1 14.0 ± 1.4	1.76 ± 0.02 2.18 ± 0.02 2.47 ± 0.03 2.98 ± 0.03
0.025 M $Fe_3(CO)_{12}$ in solution + 1 eq. $P(PhCF_3)_3$ + Ir-PS after 9 h irradiation (4)	Fe-C Fe-P Fe-Fe Fe-O/CO_{MS}	3.5 ± 0.4 0.8 ± 0.1 1.6 ± 0.2 9.1 ± 1.2	1.79 ± 0.02 2.13 ± 0.02 2.42 ± 0.03 2.94 ± 0.03
0.025 M $Fe_3(CO)_{12}$ in solution + 3 eq. $P(PhCF_3)_3$ (5)	Fe-C Fe-P Fe-Fe Fe-O/CO_{MS}	5.3 ± 0.5 1.2 ± 0.1 1.5 ± 0.2 14 ± 1.4	1.75 ± 0.02 2.17 ± 0.02 2.34 ± 0.03 2.99 ± 0.03

It can be seen, that the structure of $Fe_3(CO)_{12}$ is preserve in solution, while under irradiation, a CO ligand is abstracted, as can be seen from the reduced Fe-C coordination number. When the phosphine ligand is added, its coordination can be detected by XAS. However, the trimeric nature of the iron species is destroyed, and only monomers are left. This changes again under reaction conditions, when the Ir photosystem is added and light is switched on. In this case, a significant Fe-Fe contribution appears again, which has to be understood

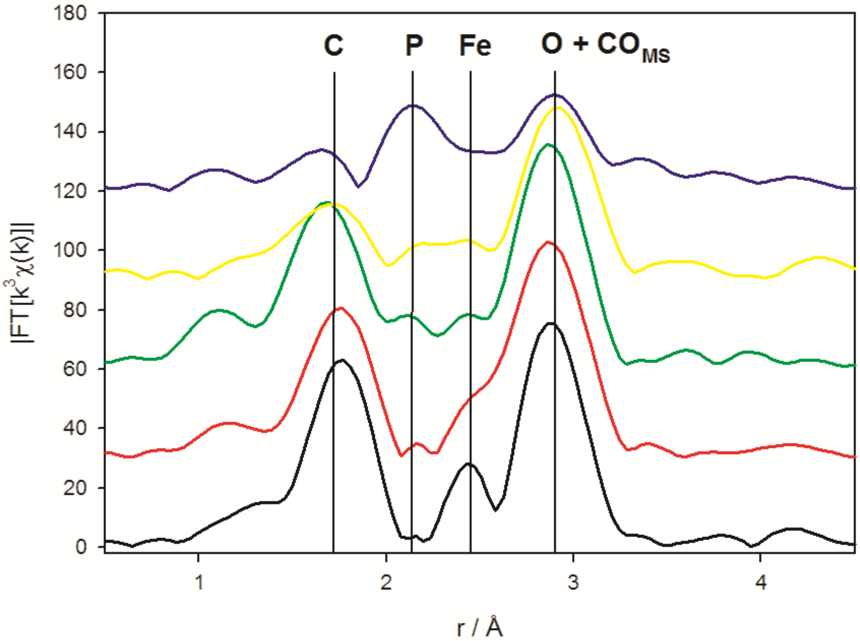

Fig. 2: Fourier transformed EXAFS spectra of the samples described in the table. (1) black, (2) red, (3) green, (4) yellow, (5) blue.

by further analysis. The according spectra are given in figure 2, a detailed analysis will be published as full paper.

[1] M. Beller, *ChemSusChem 2008*, **1**, 463.
[2] R. Ludwig, M. Beller et al., *Science*, accepted.
[3] A. Brückner, R. Ludwig, M. Beller et al., *Chem. Eur. J. 2011*, **17**, 6425.