EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** X-ray spectroscopic studies to elucidate the charge on the Iron Molybdenum Cofactor in Nitrogenase	**Experiment number**: CH - 4046
Beamline:	**Date of experiment**: from: 02.07.2014 to: 08.07.2014	**Date of report**:
Shifts: 18	**Local contact(s)**: Pieter Glatzel	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Serena DeBeer – Max-Planck-Institut für chemische Energiekonversion
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Report:

The iron-moleybdenum cofactor of nitrogenase utilizes an unusual MoFe7S9C cluster to enable the conversion of atmospheric dinitrogen to bioavailable ammonia. In 2011, we utilized valence-to-core (VtC) X-ray emission spectroscopy (XES) to reveal to presence of a central carbon in this cluster.[1] More recently, under ESRF proposals CH3556 and CH3756, we have developed the information content of Mo high-energy resolution fluorescnce detected XAS (HERFD XAS)[2] and applied this to provide the first experimental evidence for an unusual spin-coupled Mo(III) in the FeMo cofactor.[3] This represents the first example of Mo(III) in biology and has interesting parallel with the known catalysts for homogeneous N2 reduction at Mo.

In the present proposal, we shought to determine the total charge on FeMoco and a related small molecule MoFe3 cubane cluster, which had also been used as a reference in our Mo HERFD studies. During this beam time, we obtained RIXS planes on both the MoFe3 cubane and the MoFe protein. These plots are shown below.

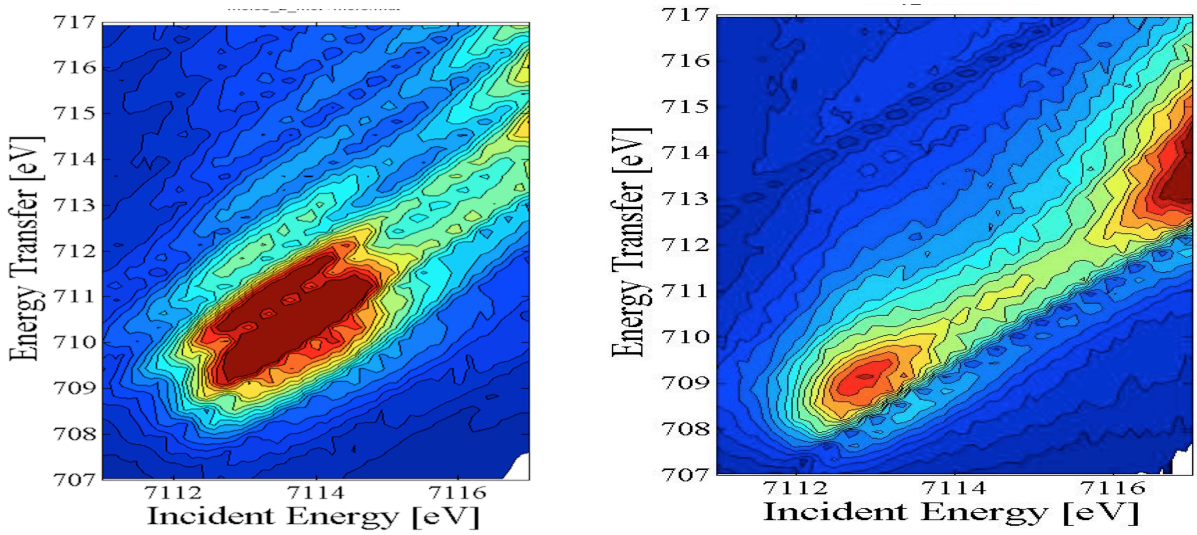

Figure 1. RIXS planes of MoFe3 cubane and MoFe protein of nitrogenase.

These data indicate a larger component of reduced iron in the protein than in the model. This can in part be attributed to the presence of the P-Clusters within the MoFe protein, which is an all ferrous cluster. Ideally, we would like to obtain data on the isolated FeMoco in order to isolate the signal of this cluster. Unfortunately, our collaborators have not been able to produce large enough quantities of isolated cofactor needed for the RIXS experiments. We hope that this will be possible in an upcoming beam time scycle.

To further complement our RIXS data on the MoFe3 cubane and the MoFe protein, we also obtained Fe HERFD data on a series of FeS model complexes of known oxidation state. A representative example of these data are shown in Figure 2 below. These data again suggest that MoFe protein is composed largely ferrous iron. Analysis of these data and the correlation to calculations are currently underway.

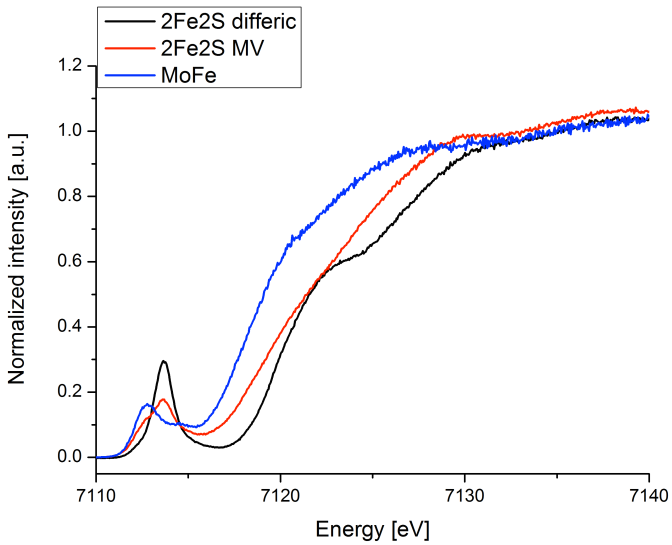

Figure 2. Fe HERFD XAS data for a series of Fe dimers compared to MoFe protein.

References:

1. Lancaster KM, Roemelt M, Ettenhuber P, Hu Y, Ribbe MW, Neese F, Bergmann U, DeBeer S (2011) Science 334:974-977

2. Lima, F.A., Bjornsson, R., Weyhermüller, T., Chandrasekaran, P. Glatzel, P., Neese, F., DeBeer, S. *Phys. Chem. Chem. Phys.,***2013,** *15,* 20911.

3. Bjornsson R, Lima FA, Spatzal T, Weyhermueller T, Glatzel P, Einsle O, Neese F, DeBeer S (2014) Chemical Science 5:3096-3103