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 of Molybdenum and Vanadium Nitrogenases	**Experiment number:** CH-3556
Beamline: ID26	**Date of experiment:** from: 16.05.2012 to: 22.05.2012	**Date of report:** 01.09.2012 *Received at ESRF:*
Shifts: 18	**Local contact(s):** Pieter Glatzel	

Names and affiliations of applicants (* indicates experimentalists):

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Report:

We successfully measured molybdenum K-α detected XANES (*aka.* HERFD, high energy resolution fluorescence detection) spectra of the iron-molybdenum nitrogenase (N2ase) and nine different Mo model complexes in order to precisely determine the oxidation state assignment of the Mo atom in N2ase. Detailed pre-edge transitions usually obscured by traditional total fluorescence detection were also observed.

Figure 1 (a) shows the result of the Mo K-α HERFD XANES spectrum of N2ase compared with preliminary FEFF9.0 simulations. Despite the rather simplistic model used to describe the atomic potentials, the features in the pre-edge and edge regions (around 20 keV) are reasonably reproduced. More detailed calculations using the ORCA package [1] are currently under way. Those calculations should provide a better description of the electronic transitions giving rise to the features in the pre-edge and edge region of the spectrum.

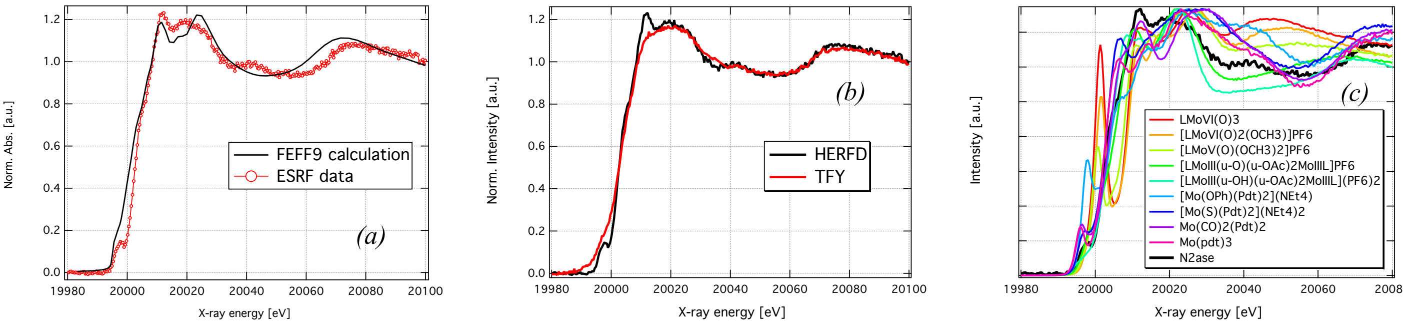

Figure 1 – Molybdenum K-edge XANES spectrum of the iron-molybdenum nitrogenase and the several model compounds. Data collected using HERFD overlaid with a FEFF9.0 calculation (a). Comparison between the TFY and HERFD data of N2ase (b). HERFD spectra of the measured model compounds of Mo with different oxidation states (c).

Fig. 1 (b) shows a comparison of the Mo K-edge XANES spectrum of N2ase collected using total fluorescence yield (TFY) and HERFD. Here, one can clearly observe the advantages of using HERFD. While the fine structure in the pre-edge and edge regions of the TFY spectrum are not well-resolved due to core hole lifetime broadening (~4.52 eV for the K-edge [2]), the HERFD spectra show much greater detail. The better resolved HERFD spectra should greatly assist in theoretical correlations to determine the electronic structure and oxidation stte of the Mo site in nitrogenase.

A total of nine Mo-based compounds were measured in order to serve as models for the Mo K-edge data of N2ase. The models vary in the formal oxidation state of the Mo (Mo^{VI}, Mo^{V}, Mo^{IV} and Mo^{III}), the total charge attributed to the molecule and the environment around the molydbedum atom. These data will serve as a basis to callibrate a TDDFT protocol in order to extract quantitative information from the pre-edge features presented in the N2ase Mo K-edge data. Complementary multiple-scattering calculations using FEFF9.0 [3] and FDMNES [4] are currently being carried out.

In addition, we measured iron resonant XANES (K-β detection) of N2ase, as shown in figure 2 (b). These data correspond to 'cuts' at specific energies on a RIXS plane. However, as discussed by Glatzel *et al.* [5] these cuts can be very hard to interpret, mainly due to lifetime broadening effects interfering with the resonant states. In collboration with F. Neese's group in the Max-Planck-Institut für Chemische Energiekonversion, we are currently developing theortical methodology to interpret these spectra. These data should aid in a more detailed assignment of both the geometric and electronic environment of the iron atoms in the FeMoco cofactor of N2ase.

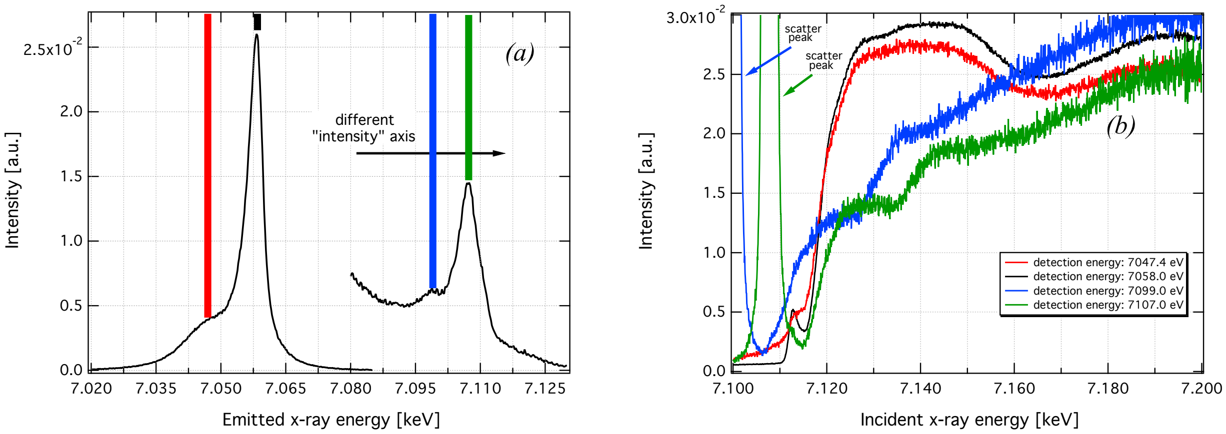

Figure 2 – (a) Iron K-β XES spectrum of iron-molybdenum nitrogenase. (b) XANES K-β detected XANES spectra of the iron-molybdenum N2ase collected at different emission energies. The colored bars in (a) indicate the energies at wich the XANES measurements were done.

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1. Neese, F. The ORCA program system. *Wiley Interdisciplinary Reviews: Computational Molecular Science* 1–6 (2011).
2. Krause, M. O. & Oliver, J. H. Natural widths of atomic K and L levels, K-α X-ray lines and several KLL Auger lines. *Journal of Physical and Chemical Reference Data* **8**, 329–338 (1979).
3. Rehr, J., Kas, J., Vila, F., Prange, M. & Jorissen, K. Parameter-free calculations of X-ray spectra with FEFF9. *Phys. Chem. Chem. Phys.* **12**, 5503–5513 (2010).
4. Joly, Y. *et al.* Self-consistency, spin-orbit and other advances in the FDMNES code to simulate XANES and RXD experiments. *Journal of Physics: Conference Series* **190**, 012007 (2009).
5. Glatzel, P., Sikora, M. & Fernandez-Garcia, M. Resonant X-ray spectroscopy to study K absorption pre-edges in 3d transition metal compounds. *Eur. Phys. J. Special Topics* **169**, 207–214 (2009).