

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:**

Sustainable chemistry at the synchrotron: Water oxidation

Experiment number:

CH-4078

Beamline: BM23	Date of experiment: from: 12.6.14 to: 17.6.14	Date of report: 14.12.14
Shifts: 15	Local contact(s): Suresh Gatla	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

*Roland Schoch, *Prof. Dr. Matthias Bauer, Universität Paderborn, 33098 Paderborn, Germany

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Report:

Utilization of sunlight in energy applications requires light harvesting, energy conversion, and storage. One effective way to store energy is to convert it into chemical energy by fuel forming reactions, such as water splitting into hydrogen and oxygen ($2\text{H}_2\text{O} + 4h\nu \rightarrow \text{O}_2 + 2\text{H}_2$).

Study of homogeneous catalysts offers promise in providing valuable insights about the mechanism of the water oxidation reaction part. Ruthenium-based molecular water oxidation catalysts have been known since the early 1980s. With the present report we will summarize our investigations into the water oxidation mechanism with a new class of dinuclear Ru complexes by means of X-ray absorption spectroscopy. The chemical nature of these complexes can not be revealed at the present stage, since the results are not published yet.

In figure 1, the XANES spectra of dimeric complexes with different oxidation state combinations are shown (top right), together with the enlarged area around an edge jump of 0.5 (top left). The energy value at a jump of 0.5 was used to determine the edge position that is correlated to the nominal oxidation state in the samples (bottom). The spectra of the sample SN164 with an average oxidation state of +II was then aligned to the Ru(II) spectra given by Llobet.^[1] A clear correlation of the edge position with the oxidation state combination is found, which can be expressed as $f(E)=[22123.89 + 0.427x]\text{eV}$, where x denotes the sum of both oxidation states in the dinuclear complexes. In other words, the edge position shifts by a value of 0.427 eV per oxidation state unit change at one of the centers. Such an increment results in an effective (average) oxidation state change by 0.5 in dinuclear complexes, and for an overall oxidation state change of +I a shift by 0.854 eV is detected. This value is in very good agreement with^[1] where a shift of 0.9 eV was found for a change from Ru(II) to Ru(III).

These results were also backed by a thorough EXAFS analysis, that cannot be presented in frame of this report until the final publication has been accepted for publication. The obtained results provide important information on the mechanism of water oxidation in this new class of water oxidation catalysts.

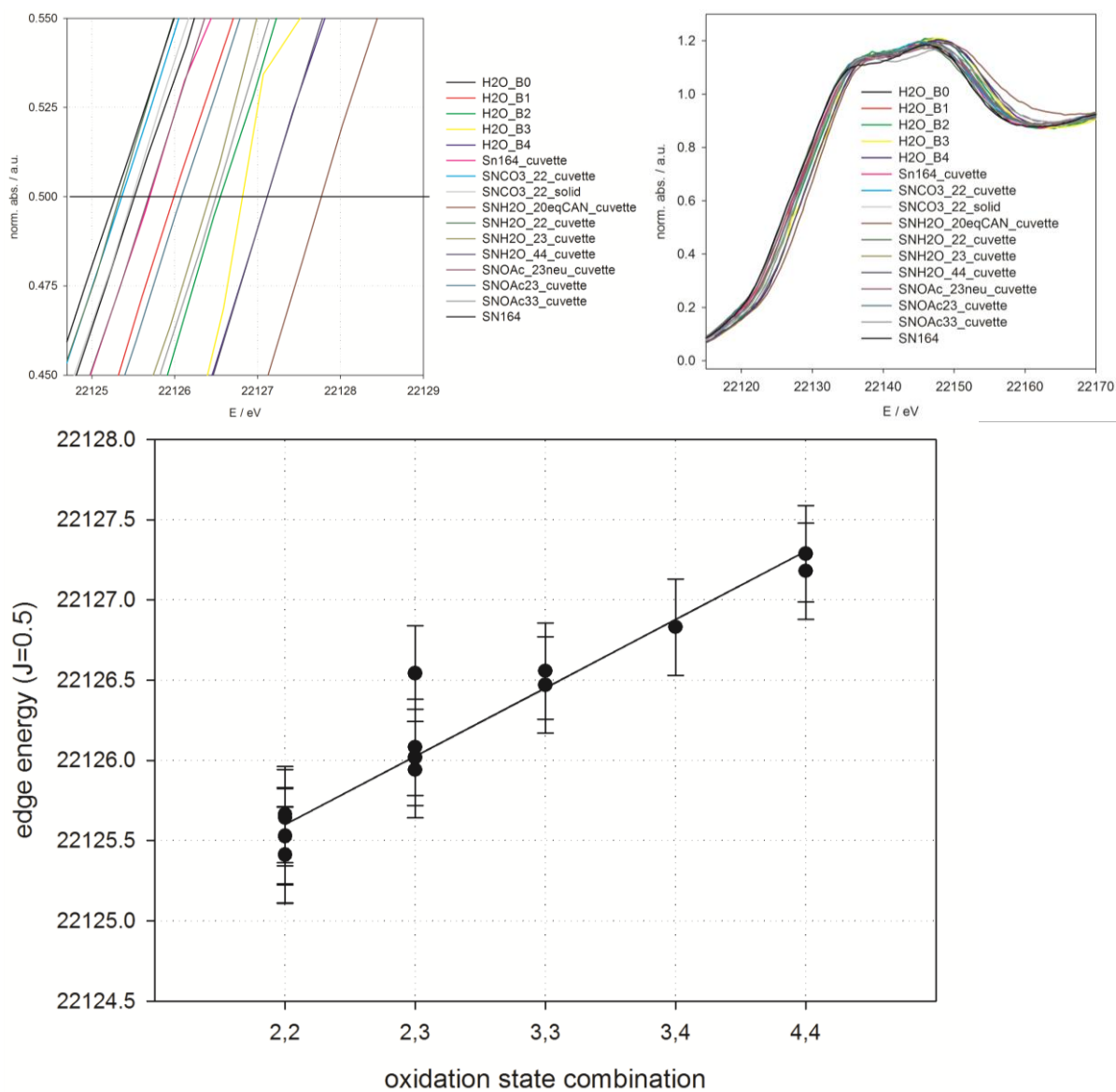


Figure 1: XANES spectra (top right) and enlarged area around a normalized absorption of 0.5 (top left). The edge energy is correlated with the nominal oxidation states (bottom).

- [1] L. Vigara, M. Z. Ertem, N. Planas, F. Bozoglian, N. Leidel, H. Dau, M. Haumann, L. Gagliardi, C. J. Cramer, A. Llobet, *Chemical Science* **2012**, 3, 2576-2586.