

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: Employing VtC RXES to understand methane oxidation in Nature	Experiment number: CH4748
Beamline: ID26	Date of experiment: from: 01.07.2016 to: 04.07.2016	Date of report: 22.08.2016
Shifts: 9	Local contact(s): Blanka Detlefs	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *George Cutsail, Max Planck Institute for Chemical Energy Conversion Serena DeBeer, Max Planck Institute for Chemical Energy Conversion *Rebeca Gomez Castillo, Max Planck Institute for Chemical Energy Conversion *Stefan Hugenbruch, Max Planck Institute for Chemical Energy Conversion		

Report:

During the current scheduling period, our research group was awarded time for three different proposals:

March 2016 (20 Shifts/18 requested): CH- 4749, “Probing the Activation of Dioxygen by Iron K-beta XES”

July 2016 (18 Shifts requested/9 Shifts awarded): CH-4748, “Employing VtC RXES to understand methane oxidation in Nature”

July 2016 (9 shifts): CH-4750, “Characterization of Intermediates in Biological Methane to Methanol Conversion”

As all three awarded beamtimes relate, we employed the earlier March beamtime to complete primary feasibility studies of our proposed experiments (some portions of the projects were completed in March). This allowed for better beamtime and resource management for two consecutive 9-shift beamtimes awarded in July. This report highlights one-half of the July beamtime (CH-4748)

July 2016 Results: *EXAFS*

During the previous beamtime (March 2016), we were able to complete $K\alpha$ HERFD XAS and Valence-to-Core XES studies of several biomimetic complexes of various diiron ‘oxo’ core confirmations and oxidation states, (**Schemes 1 and 2**). Preliminary analysis of these spectra has yielded insight into the mechanisms of pre-edge intensity trends of diiron oxo cores and has been reported previously (see report for CH-4749). To further structurally characterize these complexes, EXAFS was collected (complexes **1-3**) during this beamtime, and will be utilized to confirm the oxygen core confirmations, along with resonance Raman vibrational spectroscopy.

Without any rebinning of the EXAFS data, or smoothing, the $\mu(E)$ spectra are of good quality up to k of approximately 11. The R-space spectra (FT from $k = 2 - 11$), **Figure 2**, reveals significant core confirmation changes between **5, 6 and 7**. The Fe-Fe vector has been primarily modeled at approximately 3.5 Å in complexes **5 and 6**, consistent with a Fe- μ -O-Fe core. The Fe-Fe scattering shell is observed at lower R in complex **7**, modeled at Fe-Fe = 3.0 Å. This is consistent with the formation of a Fe-(μ -O)₂-Fe core.

The study of complexes **1** – **4** was restricted to $K\alpha$ HERFD XAS only. Quantum mechanical chemistry computations previously predicted differing pre-edge XAS spectra for closed and open cores ([**1**, **2**] vs. [**3**, **4**]). Our collaborators were unable to provide each of the complexes at high enough purity to complete the proposed VtC RXES study in the allotted time. Because each sample contained a maximum of 50% of the desired product, the other diiron species must be studied and subtracted from the sample spectra to yield ‘deconvoluted’ spectrum. As many as four components make up the sample spectrum: the desired product, precursor material, diiron(III) decay species, and a diiron(III) contaminant. For each sample, the sample product was studied along with its unreacted precursor material, decay product, and the suspected diiron(III) contaminant. The quantity of each diiron species was determined by Mössbauer spectroscopy prior to X-ray studies, allowing for quantitative subtraction of each undesired component.

Figure 2, top, exhibits a *raw* sample set of four $K\alpha$ -HERFD XAS spectra that was collected for a single complex. Because of the increased number of samples to be studied, the experiment was restricted to XAS only. During this beamtime, a reliable, complete set of data for these samples was collected along with secondary characterization (i.e. Mössbauer and UV/vis spectroscopy).

The processed data of complexes **2** and **3** serve as excellent models for the proposed ‘closed’ and ‘open’ cores of the diiron(IV) ‘Q’ intermediate of Soluble Methane Monooxygenase (sMMO). Comparing the pre-edge spectra of sMMO-Q (collected previously) to the newly collected, processed, spectra of **2** and **3**, insight into Q’s core confirmation is gained, **Figure 2**, bottom. The closed core, **2**, has significantly less pre-edge intensity than Q. The diiron(IV) open core model, **3**, better resembles Q, supporting the presence of an terminal oxo group, however, this result is at odds with recent transient resonance Raman measurements that proposed a closed core of high symmetry. The convergence of these high-quality spectra with the high-quality data obtained on the active intermediate of sMMO will allow us to determine its core active site geometry and structure. We are currently perusing computational studies of these models and the proposed active site of sMMO to further understand the spectroscopic results and the electronic structure of these diiron cores. As several different systems have been studied during this beamtime and the related beamtimes detailed above, we are in the midst of preparing *multiple* manuscripts for publication in high-impact peer-reviewed chemistry journals.

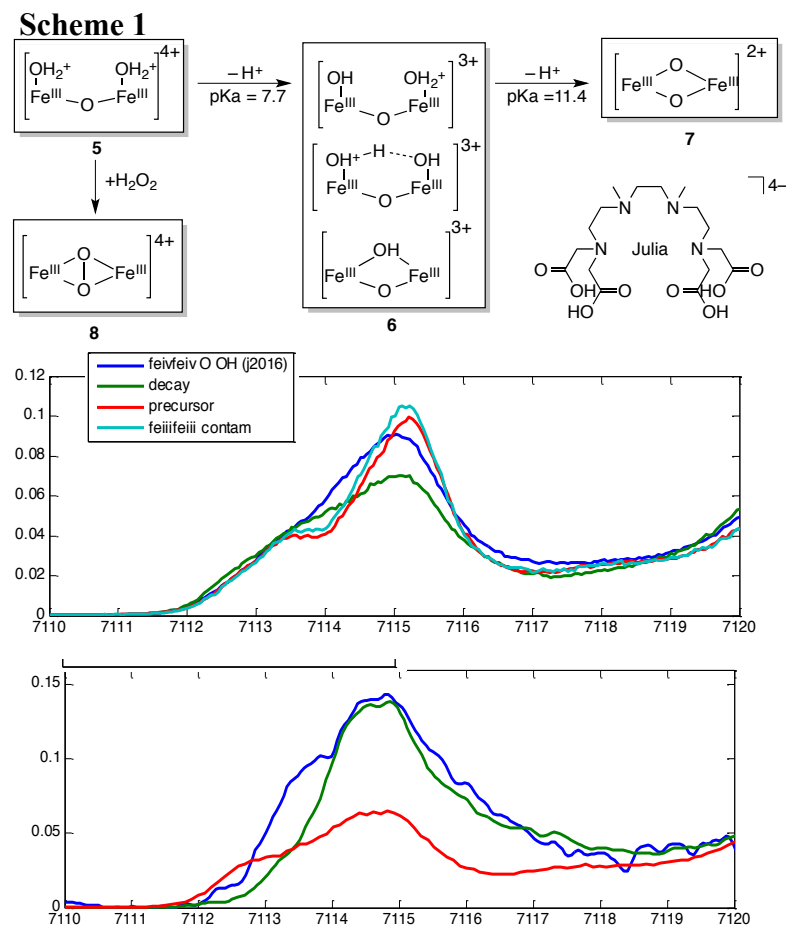


Figure 1. EXAFS of **5**, **6** and **7**. FT from $k = 2 - 11$. Vertical lines mark Fe-Fe scattering feature.

← **Figure 2.**
(top)
 $K\alpha$ HERFD pre-edge of **3** with isolated precursor, decay and diiron(III) contaminant.

(bottom)
Comparisons of **2** and **3** (post-subtraction) with sMMO-Q

