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Experiment Report Form

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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.

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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 logo]	**Experiment title:** Hydrogen ligands made visible with hard X-rays: HERFD-XANES and Valence emission spectroscopy on catalytic hydride complexes	**Experiment number**: CH-4958
Beamline: ID26	**Date of experiment**: from: 16 November 2016 to: 22 November 2016	**Date of report**:
Shifts: 18	**Local contact(s)**: Baran Rafal	*Received at ESRF:*

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Report:
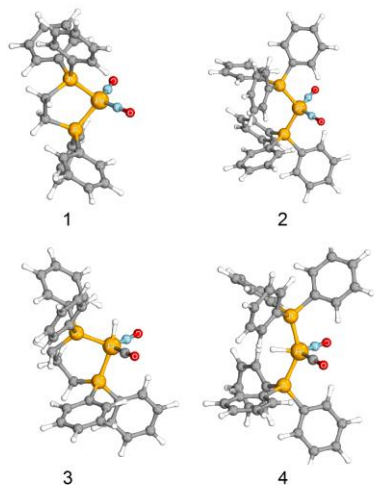
Scheme 1: Used model complexes.

Over the last years several authors showed, that VtC-XES is able to probe the nature of ligand bonds and allows to distinguish different kinds of ligands.[1-5] In case of hydrogenases it has been shown that hydride ligands contribute to significant changes in the VtC-XES spectra.[6-8] In order to put the mentioned preliminary hints about the influence of hydrogen ligands on a solid foundation and to establish the methodical combination of VtC-XES and HERFD-XANES for the investigation of metal-bound hydrides in catalytic processes, we chose the iron-catalyzed hydrosilylation reaction as important example. The two hydride complexes [Fe(CO)(dppp)H(NO)] (3) and [Fe(CO)H(NO)(PPh$_3$)$_2$] (4) are effective catalysts for hydrogen formation via dehydrogenative silylation of alcohols.[9]

Scheme 1 shows the optimized structures of the compounds investigated. The catalytically active species (3) and (4) and the non-hydride refrences [Fe(dppe)(NO)$_2$] (1) and [Fe(NO)$_2$(PPh$_3$)$_2$] (2).

In order to investigate the impact of iron-hydride antibonding states on the overall LUMO levels, HERFD-XANES spectra were recorded. The first pre-edge peak maximum A possesses the same energy for 1 and 2 (fig. 1). Compared to this, the overall intensity of A decreases in 3 and 4, while the intensity at the high-energy sides increases (compared to 1 and 2). Obviously feature A doesn´t show a true shift in 3 and 4, more it is superimposed by an additional transition (fig. 2). In the calculated spectra , the shift of A in both hydrides (3, 4) is indicated through excited state 3 (fig. 2), which is significantly shifted to higher energies (compared to 1 and 2). This state is described as a combination of different orbital pairs. Nevertheless in both hydride compounds (3, 4) the main components are transitions to acceptor orbitals which reflect the antibonding combination of Fe 3d and the H 1s orbital.
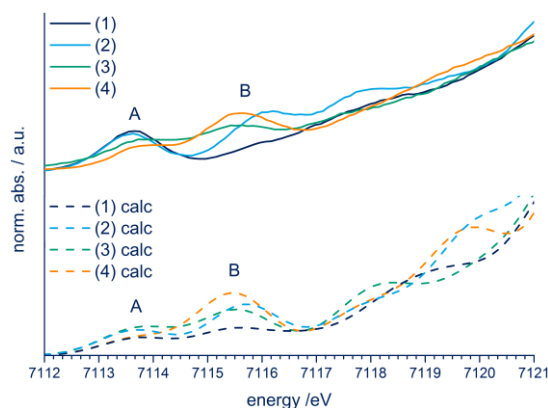

Figure 1: Comparison of experimental (solid) and theoretical TD-DFT Fe K-edge spectra (dashed) (1 – 4). Theoretical spectra were shifted by 151.3 eV and
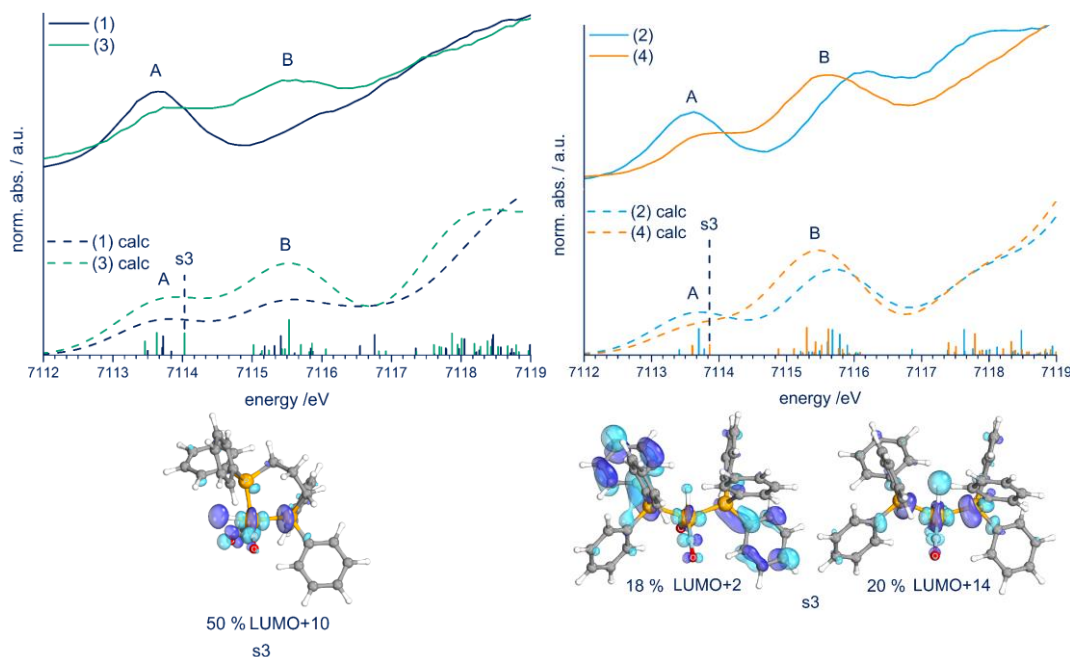
In order to investigate the influence of Fe-H bonding states on the HOMO levels, VtC spectra of 1 – 4 were collected (fig. 3). In the area of C significant intensity changes can be observed on hydride coordination (3, 4). However, there are significant differences between both hydrides (3, 4) in the area of C, which may arise from their varying coordination geometry. In 3 a rise in intensity at the low-energy side of D

Figure 2: Comparison of experimental (solid) and theoretical TD-DFT Fe K-edge spectra (dashed) (left: 1 and 3,

is observed (compared to 1, 2 and 4). While in 4 a rise in intensity at the high-energy side of B is observed (compared to 3). The increased intensity in the area of feature C (3 and 4), respectively the broadening of feature D in 3 to the low-energy side in the calculated VtC emission spectra, can be attributed to donor orbitals with significant hydride density (fig. 4). In 3 the donor orbital describes the bonding interaction of the Fe $3d_{z^2}$ (Fig. 4, 3a) with the H 1s. This explains the broadening and shift of feature D to the low-energy side. For geometric reasons, 4 exhibits a more complicated interaction of the in-plane located hydride ligand, an additional interaction with both P atoms. *4b* describes the interaction of the H 1s and Fe 3d (fig. 4), which illustrates the intensity rise in the area of C. *4a* describes the interaction of the H
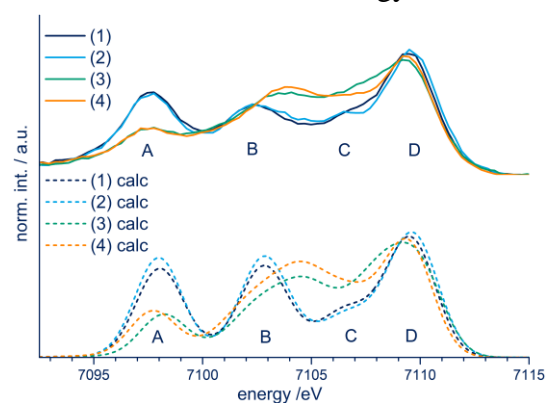

Figure 3: Comparison of experimental (solid) and theoretical DFT Fe VtC spectra (dashed).

1s with P 3p orbitals of both phosphine ligands (fig. 4). This clearly explains the increased intensity and shift of B to the high-energy side of 4 compared to 3.

A detailed investigation of a series of different low-valent iron complexes (1, 2) and their hydride analogues (3, 4) has been carried out using VtC-XES and HERFD-XANES. The sensibility of both methods to the M-H interaction has been shown. VtC-XES and
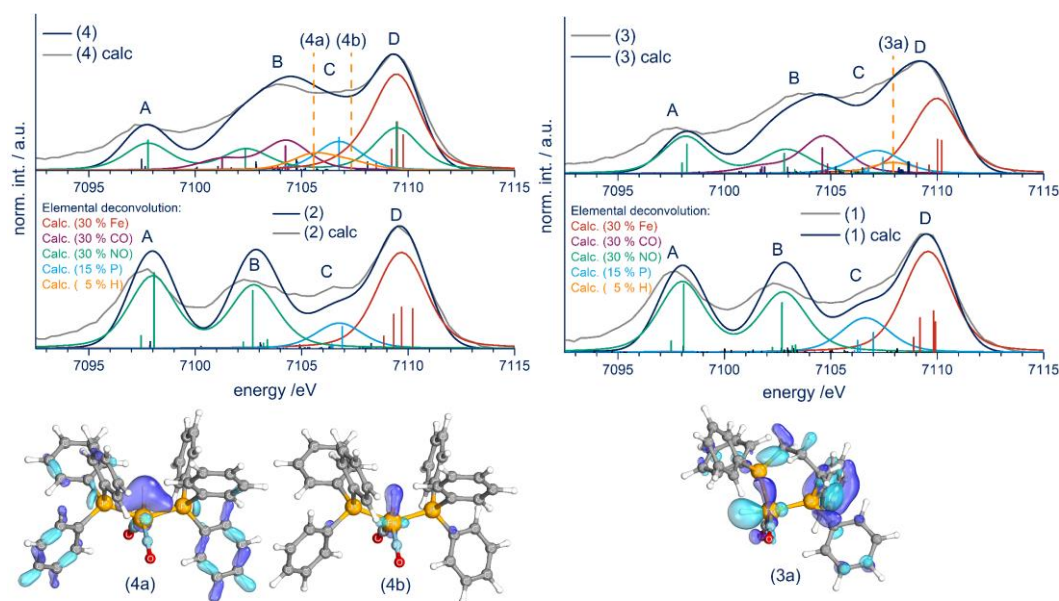

Figure 4: Comparison of 2 (top) and 4 (bottom) (left), respectively 1 (top) and 3 (bottom) (right), experimental (grey) and theoretical DFT Fe VtC spctra (blue).

HERFD-XANES in combination with DFT (XES) respectivley TD-DFT (XANES) calculations are promising tools to study hydride species in catalysis.

[1] Chandrasekaran, P.; Chiang, K. P.; Nordlund, D.; Bergmann, U.; Holland, P. L.; DeBeer, S.; *Inorg. Chem.* 2013, **52** (11), 6286–6298. [2] Lancaster, K. M.; Roemelt, M.; Ettenhuber, P.; Hu, Y.; Ribbe, M. W.; Neese, F.; Bergmann, U.; DeBeer, S.; *Science* 2011, **334** (6058), 974–977. [3] Martin-Diaconescu, V.; Chacon, K. N.; Delgado-Jaime, M. U.; Sokaras, D.; Weng, T.-C.; DeBeer, S.; Blackburn, N. J.; *Inorg. Chem.* 2016, **55** (7), 3431–3439.[4] Pollock, C. J.; DeBeer, S.; *J. Am. Chem. Soc.* 2011, **133** (14), 5594–5601. [5] Pollock, C. J.; Lancaster, K. M.; Finkelstein, K. D.; DeBeer, S.; *Inorg. Chem.* 2014, **53** (19), 10378–10385. [6] Chernev, P.; Lambertz, C.; Brunje, A.; Leidel, N.; Sigfridsson, K. G. V.; Kositzki, R.; Hsieh, C.-H.; Yao, S.; Schiwon, R.; Driess, M.; Limberg, C.; Happe, T.; Haumann, M.; *Inorg. Chem.* 2014, **53** (22), 12164–12177. [7] Leidel, N.; Hsieh, C.-H.; Chernev, P.; Sigfridsson, K. G. V.; Darensbourg, M. Y.; Haumann, M.; *Dalton Trans.* 2013, **42** (21), 7539–7554. [8] Hugenbruch, S.; Shafaat, H. S.; Kramer, T.; Delgado-Jaime, M. U.; Weber, K.; Neese, F.; Lubitz, W.; DeBeer, S.; *Phys. Chem. Chem. Phys.* 2016, **18** (16), 10688–10699. [9] Rommel, S.; Hettmanczyk, L.; Klein, J. E. M. N.; Plietker, B.; *Chem. Asian J.* 2014, **9** (8), 2140–2147.