

Exploring the Sensitivity of HERFD-XANES and VtC-XES to Probe Hydride Interactions and Spin States in Transition Metal Complexes

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Introduction: Transition metal hydrides gain increasingly importance in chemistry and biology as active compounds or intermediates for many chemical transformations, hydrogen storage or in renewable energy applications like water reduction. In order to understand the working principle of applied catalysts, enzymes and materials in these subjects, determination of the electronic and geometric structure is indispensable. However, there are many cases where hydrides are not accessible by standard spectroscopic or scattering methods. For such cases, new methods are required to obtain electronic and geometric parameters. High-energy resolution fluorescence detected XANES (HERFD-XANES) and valence-to-core X-ray emission spectroscopy (VtC-XES) at metal K-edges are able to substitute conventional methods without being subject to any experimental restrictions.^[1-3]

Methods: HERFD-XANES and VtC-XES measurements were carried out at beamline ID26 of the ESRF (Grenoble, France). All measurements were realized at 50 K using a He cryostat under vacuum conditions. Measurements were conducted with a Johann-type X-ray emission spectrometer in the horizontal plane, where the sample, five crystal analyzers (Ge <620>) and photon detector (avalanche photodiode) were arranged in a vertical Rowland geometry (with $R = 1$ m). The incident energy was selected using the <311> reflection from a Si DCM.

Results: Terminal hydride-, bridged poly-hydride iron complexes and their non-hydride analogues are investigated with a combination of VtC-XES and HERFD-XANES. In order to fully understand the experiments and to obtain precise information about molecular levels being involved in the spectral signals, (TD)DFT calculations are applied.

In the pre-edge region a significant intensity increase or an additional feature around 7104 eV is observed in relation to their non-hydride analogues. It will be shown, that observed spectral discrepancies are caused by antibonding Fe-hydride interactions.

Complementary, VtC-XES spectra exhibit a significant intensity increase in all investigated hydrides around 7107 eV, while only one hydride features an additional increase around 7105 eV. The increase around 7107 eV will be shown to originate from bonding Fe-hydride interactions, while the increase around 7105 eV is reduced to hydride-phosphine interactions.^[4]

The sensitivity of both methods to the spin state and Fe-hydride distance will be demonstrated by theoretical spectroscopy.

Conclusion: HERFD-XANES and VtC-XES in combination with (TD)DFT are able to effectively probe Fe-hydride and ligand-hydride interactions. Distinct hydride induced spectral changes in the VtC-XES and HERFD-XANES regions are observed and allocated to bonding- or antibonding Fe-hydride interactions. The sensitivity of both methods to discriminate spin states of Fe ions is illustrated by theoretical spectroscopy and the application of hard X-ray spectroscopy to investigate Fe hydrides *in situ* is explored and discussed.

References: [1] Bauer, M., *Phys. Chem. Chem. Phys.* **2014**, *16* (27), 13827-13837. [2] Hugenbruch, S. *et al.*, *Phys. Chem. Chem. Phys.* **2016**, *18* (16), 10688-10699. [3] Chernev, P. *et al.*, *Inorg. Chem.* **2014**, *53* (22), 12164-12177. [4] Burkhardt, L. *et al.*, *Inorg. Chem.* **2017** *56* (21), 13300-13310.