



	Experiment title: Structure and reactivity of non-heme high valent iron peroxo complexes.	Experiment number: CH 4741
Beamline:	Date of experiment: from: 13/07/2016 to: 19/07/2016	Date of report: 28/02/2017
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Report:

Oxidation catalyzed by non-heme iron complexes is one of the most promising approaches to achieve selective non-activated C-H bond hydroxylation. In this framework the main goal of our project was to investigate the time evolution of two reactions between $[\text{Fe}^{\text{II}}(\text{TPA})(\text{CH}_3\text{CN})_2]^{2+}$ and the two oxidants H_2O_2 and $\text{CH}_3\text{COO}_2\text{H}$.

We modified the stopped flow cell available at the ID24 beam line and we mounted a glass capillary to have the correct thickness of the sample holder to collect transmission spectra at the Fe K-edge. Moreover, we collected UV spectra at the same time to better characterize the intermediate species.

In the former reaction the transformation of a Fe^{II} species into two subsequent Fe^{III} species was monitored, while in the latter a more complex $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}\text{-Fe}^{\text{IV}}\text{-Fe}^{\text{III}}$ sequence was demonstrated to occur in accordance with indirect observations previously reported. The observed structural modifications occurring around the iron center were correlated with the reaction mechanisms (see Figures 1 and 2). This experiment demonstrates that bimolecular reactions in solution occurring in the ms time scale can be profitably followed using a combined EDXAS-UV/Vis spectroscopic analysis. It is possible to directly monitor the oxidation state evolution of an absorbing metal that is oxidized/reduced during the reaction. At the same time the simultaneous collection of the XANES and UV/Vis spectra allows one to follow the structural modification occurring in the reaction time-course with a ms time resolution.

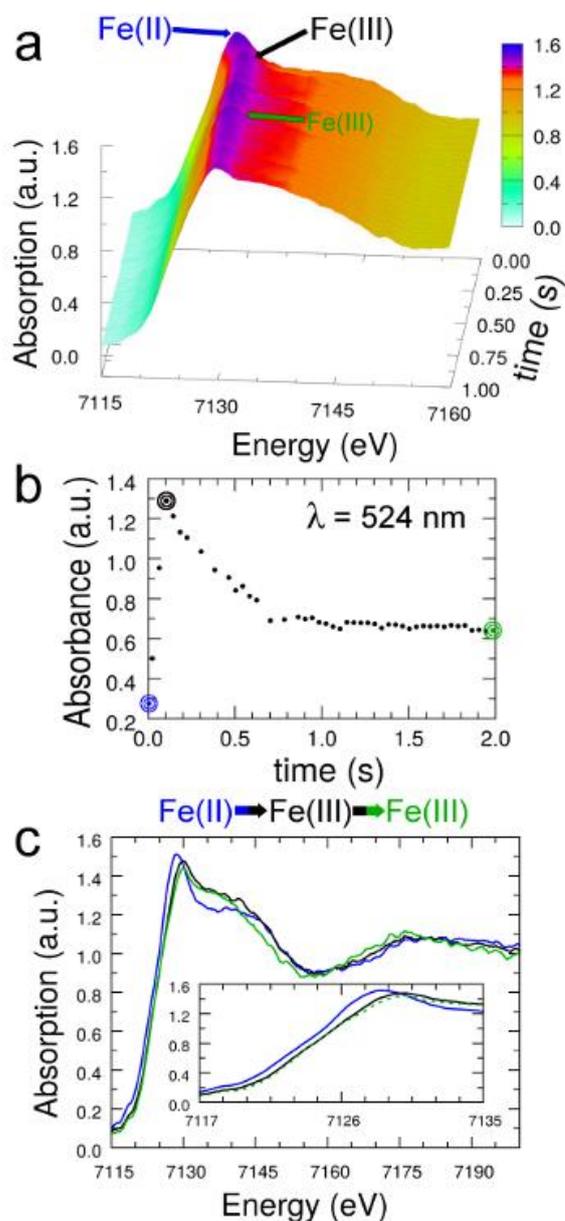


Figure 1 | Following the reaction between $[\text{Fe}^{\text{II}}(\text{TPA})(\text{CH}_3\text{CN})_2]^{2+}$ and H_2O_2 by simultaneous time resolved EDXAS and UV/Vis spectroscopies with a time resolution of 40 ms. a) Time evolution of the Fe K-edge EDXAS spectra of $[\text{Fe}^{\text{II}}(\text{TPA})(\text{CH}_3\text{CN})_2]^{2+}$ (35 mM) after addition of H_2O_2 (70 mM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 99.8:0.2 (v/v) at 25 °C. b) Time evolution of the absorbance at $\lambda = 524 \text{ nm}$ of the same reaction mixture of Fig. 1a. EDXAS and UV/Vis spectra have been recorded simultaneously in the stopped-flow cell. c) Selected EDXAS spectra of Fig. 1a recorded at 0 ms (blue), 104 ms (black) and 1984 ms (green). A magnification of Fe K-edge region is shown in the inset.

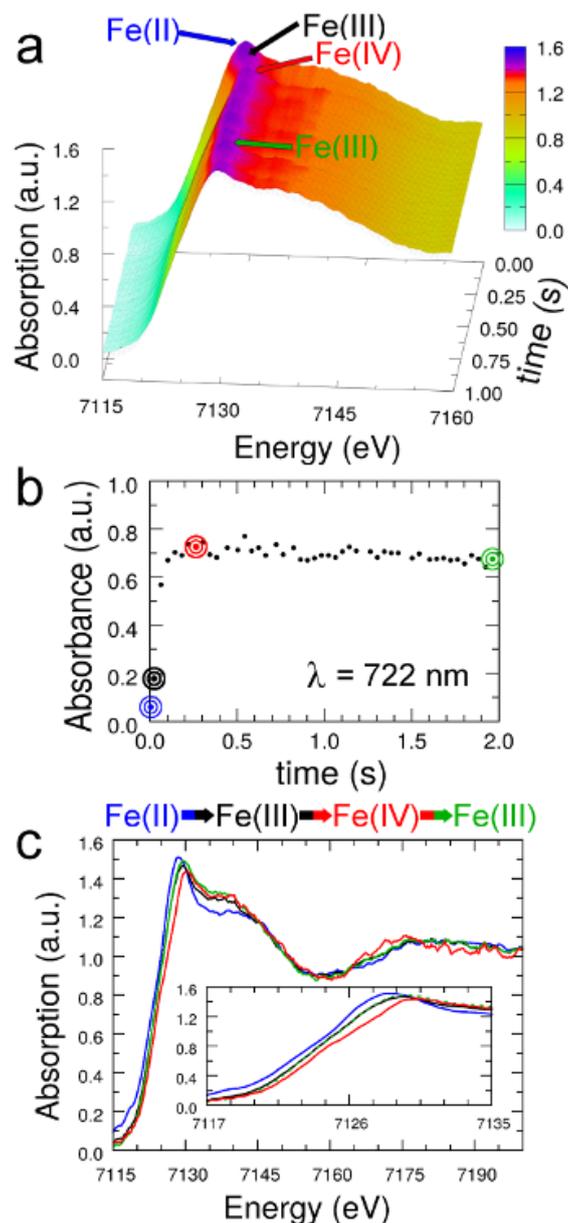


Figure 2 | Following the reaction between $[\text{Fe}^{\text{II}}(\text{TPA})(\text{CH}_3\text{CN})_2]^{2+}$ and $\text{CH}_3\text{COO}_2\text{H}$ by simultaneous time resolved EDXAS and UV/Vis spectroscopies with a time resolution of 40 ms. a) Time evolution of the Fe K-edge EDXAS spectra of $[\text{Fe}^{\text{II}}(\text{TPA})(\text{CH}_3\text{CN})_2]^{2+}$ (35 mM) after addition of $\text{CH}_3\text{COO}_2\text{H}$ (35 mM) in $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$ 99.6:0.4 (v/v) at 25 °C. b) Time evolution of the absorbance at λ 722 nm of the same reaction mixture of Fig. 2a. EDXAS and UV/Vis spectra have been recorded simultaneously in the stopped-flow cell. c, Selected EDXAS spectra of Fig. 2a recorded at 0 ms (blue), 24 ms (black), 264 ms (red) and 1964 ms (green). A magnification of Fe K-edge region is shown in the inset.