![ESRF logo]	**Experiment title:** Structure and reactivity of non-heme high valent iron peroxo complexes.	**Experiment number**: CH-4407
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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 the reaction between a series of non heme iron complexes such as $Fe(TPA)(OTf)_2$, $Fe(Me,MePyTACN)(OTf)_2$, $Fe(BPMCN)(OTf)_2$ and H_2O_2. Fe(III)-OOH species, which is the first formed intermediate in these reactions, usually accumulates in the reaction mixture being the following O-O bond scission rate determining. We intended to study the conversion of Fe(III)-OOH into the high valent iron intermediate, and eventually its decay. Time resolved XAS spectroscopy can be used to ascertain the Fe oxidation state throughout all reaction events in order to definitely disclose the nature of the intermediates.

We started with $Fe(TPA)(OTf)_2$ with the aim of studying the time evolution of the catalyst taking place when adding H_2O_2. 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 were working at -20 °C and we collected UV spectra at the same time to better characterize the intermediate species.

Unfortunately, during the experiment we realized that the stopped flow cell was not working properly as it was leaking and this did not allow us to carry out the time resolved experiment. After this experiment the beam line staff has sent the stopped flow cell out to be repaired and it will be ready by the end of this month.

Anyhow, we proved the feasibility of the experiment in the proposed experimental condition as we managed to collect XANES spectra of Fe(TPA)(OTf)$_2$ in 10 ms before mixing it with H$_2$O$_2$. As the reaction we want to study occurs in 100 ms we are confident that we will manage to characterize the nature of the intermediates that are formed. We managed to improve the quality of the spectra by collecting a spectrum of the cell windows that was then subtracted from the sample spectrum. The results are shown in Figure 1 where we show the raw Fe K-edge XANES spectrum of a 20 mM solution of Fe(TPA)(OTf)$_2$ in acetonitrile together with the absorption spectrum of the empty cell.
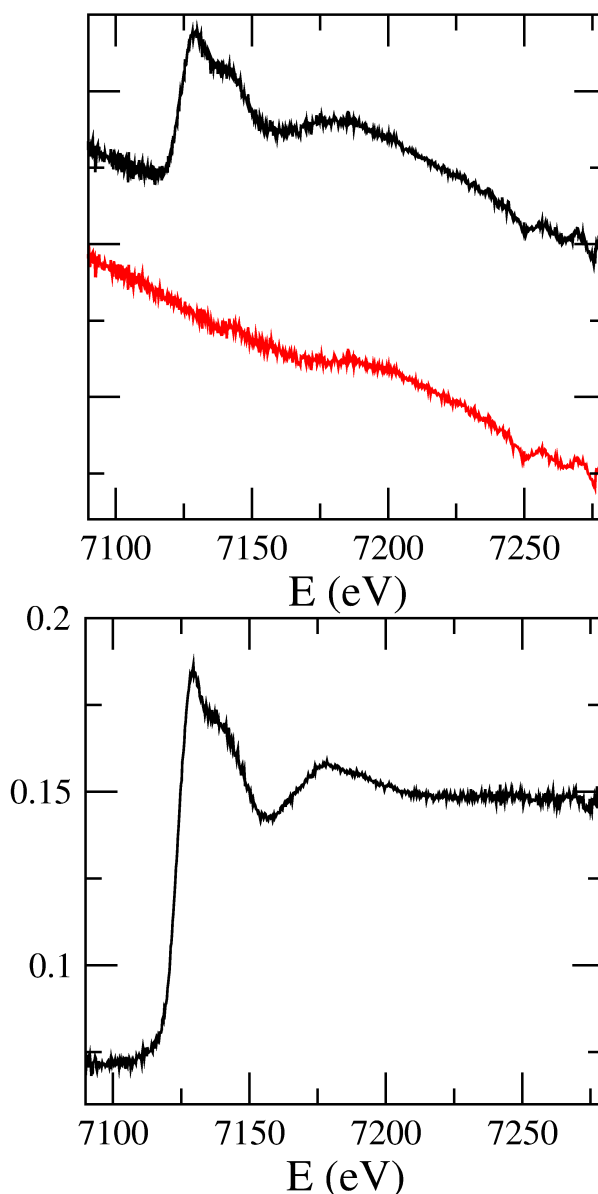
Figure 1. In the upper panel we show the raw XANES spectrum at the Fe K-edge of a 20 mM solution of Fe(TPA)(OTf)$_2$ in acetonitrile, collected in 10 ms (black line) together with the spectrum of the empty cell collected with the same statistics. In the lower panel we show the XANES spectrum obtained by subtracting the two spectra showed above.

The noise of both spectra is obviously due to the strong absorption of the windows that is also responsible for the distortion in the interval between 7150 and 7250 eV. In the lower panel of the figure we show the XANES spectrum obtained after subtraction, and the signal to noise ratio is very much improved. Moreover, the edge position is perfectly detected thus allowing us to determine variations of the oxidation state of Fe that is one of the key points

of this project. Also the XANES oscillations are not distorted anymore and they can be analysed on a quantitative ground.

We believe that the development of this experimental technique has the potential of a much wider application as a novel mechanistic tool to investigate metal-catalyzed redox reactions. Indeed, there is currently a lively debate on the nature of the actual oxidizing species in several oxidation catalysts (mostly on iron based ones), and from a broader perspective high oxidation states states of transition metals are receiving increasingly interest for their unexpected and promising reactivity. This technique would also provide a complementary tool to characterize the intermediates involved in catalytic systems where conventional spectroscopic methods (Mossbauer, EPR) cannot work (such as in manganese catalyzed oxidations, as Mn is EPR and Mossbauer silent).