



	<b>Experiment title:</b> Towards implementing the picosecond-resolved X-ray emission spectroscopy as a complementary technique to time-resolved X-ray scattering	<b>Experiment number:</b> MI1181
<b>Beamline:</b> ID 09	<b>Date of experiment:</b> from: 23/05/2014 to: 27/05/2014	<b>Date of report:</b> 05/09/2014
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dmitry Khakhulin	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Dr. György Vankó*, Dr. Zoltán Németh*, Dorottya Szemes*, Mátyás Pápai, Emese Rozsályi (MTA Wigner Research Centre for Physics, Budapest, Hungary) Dr. Wojciech Gawelda*, Alex Britz*, Tadesse Assefa* (European XFEL, Hamburg) Dr. Kristoffer Haldrup*, Elisa Biasin* (DTU Copenhagen, Denmark)		

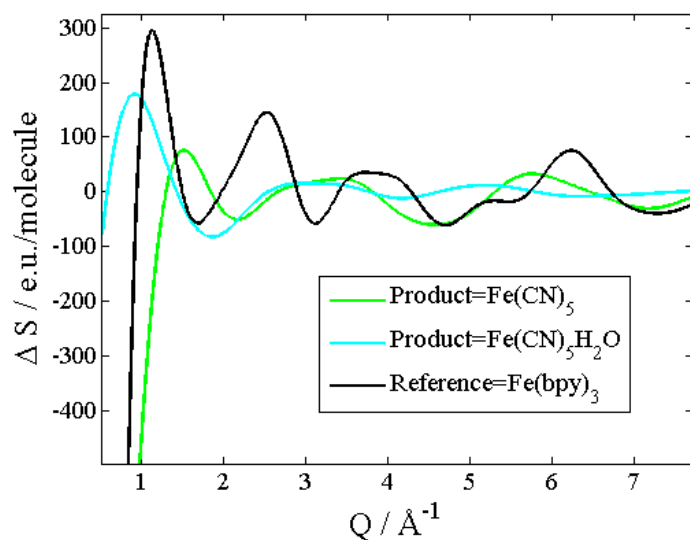
## Report:

*This is a preliminary report on the MI-1181 experiment so that it provides background for our new beamtime application.*

We have performed preliminary time resolved studies on 250 mM aqueous solution of  $[\text{Fe}(\text{CN})_6]^{4-}$  using X-ray Diffuse Scattering (XDS, i.e., liquid-phase WAXS) simultaneously with X-ray Emission Spectroscopy (XES) at ID09 at 266 nm and 355 nm laser excitation. The XDS showed transients at both wavelengths, and provided results of *publishable quality*, as it will be partly described below. Furthermore, the valence-to-core (vtc) XES spectra we will *include in a review paper* that describes opportunities of time-resolved studies with vtc-XES. Based on this experiment we can design better the next experiments, and pave the way to using XES as a standard tool at ID09.

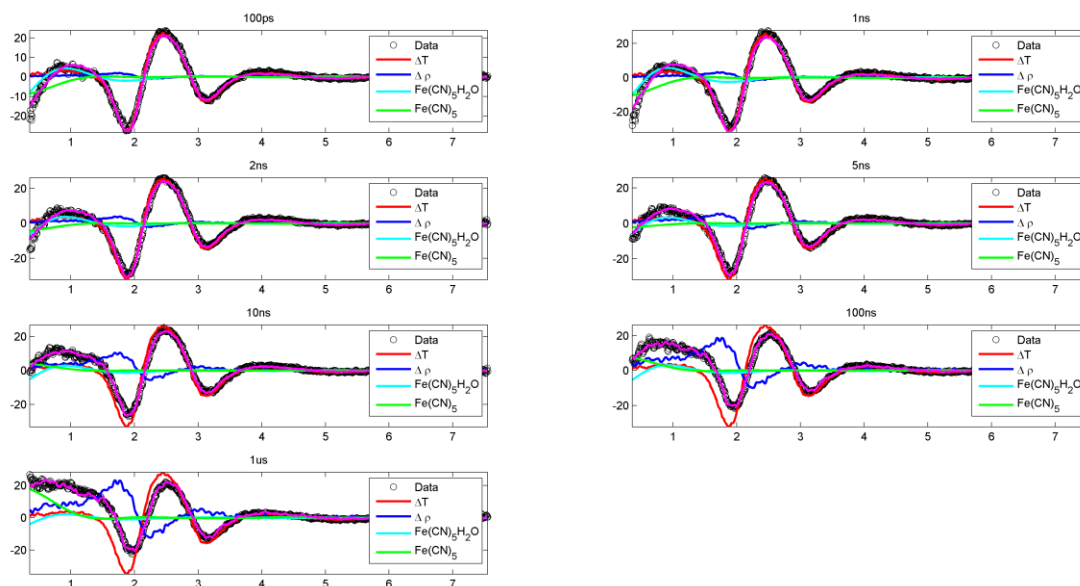
The time-resolved XES experiment is a new development on the beamline, which the present users have been developing at other facilities over the past few years. The availability of a tunable ultrafast laser, the pink X-ray beam combined with a kHz X-ray chopper provides a great opportunity for TR-XES on ID09; this work is among the first one which tried to exploit this and establish TR-XES as a standard tool at this beamline. The diagram lines of iron does not present a great challenge to measure, and we had K $\beta$  spectra for this system from APS 7-ID, therefore, we decided to focus on the valence-to-1s-core transition, which delivers the chemically most sensitive spectra. Furthermore, as at 266 nm primarily a photoionisation takes place, we decided to focus on the 355 nm excitation, where the transitions are not fully understood. At this wavelength the main process is the so-called photoaquation, and it is argued that the Fe–CN bond braking and the Fe–OH<sub>2</sub> bond formation occur simultaneously, producing an aquated  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$  complex. This is in contrast with our recent ps-resolved MHz XAS study at the APS which hinted the rapid formation of a pentacyanide  $[\text{Fe}(\text{CN})_5]^{3-}$ . Moreover, our *ab initio* calculations also confirm the stability of the  $[\text{Fe}(\text{CN})_5]^{3-}$  species, supporting it as a good candidate for this transient. The following figure shows the simulated difference XDS for each of

the two photoproducts, and the transient in  $[\text{Fe}(\text{bpy})_3]^{2+}$  as a reference:



Note that all of these are for the DFT structures *in vacuo*, meaning that no effects of solvation cage changes etc. are included. Also, as expected, the dissociation reaction has a very pronounced fingerprint at low  $Q$ .

The following figure shows the difference signals and fits for one good experimental data set:

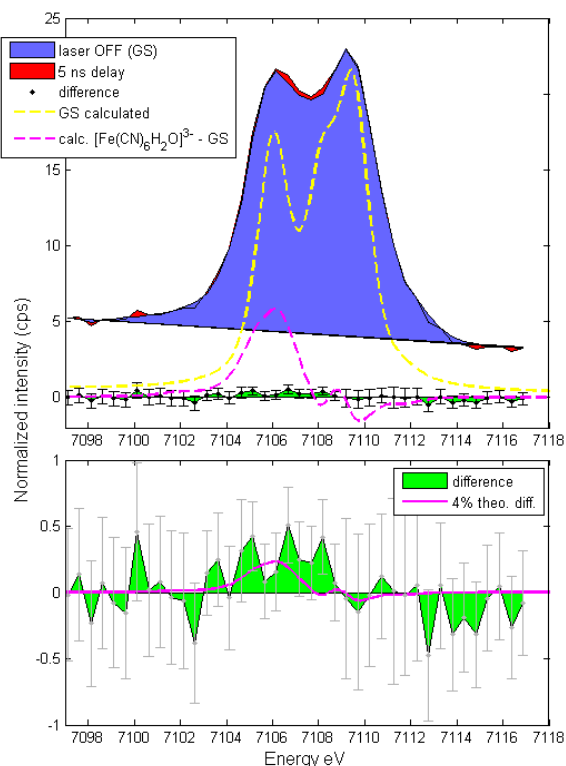


The data set has been subjected to a preliminary analysis by assuming that the observed difference signals could at all time be modelled by a linear combination of 4 contributions: the two solvent differentials (pink-beam version) plus the two DFT-derived difference signals shown above.

A few notes:

- The fit is rather good for all time delays
- There is a pronounced low- $Q$  dip, that decays in  $\sim 5$  ns and
- This dip is rather well caught by the inclusion of the  $[\text{Fe}(\text{CN})_5]^{3-}$  signal
- The  $[\text{Fe}(\text{CN})_5]^{3-}$  disappears in the first couple of nanoseconds

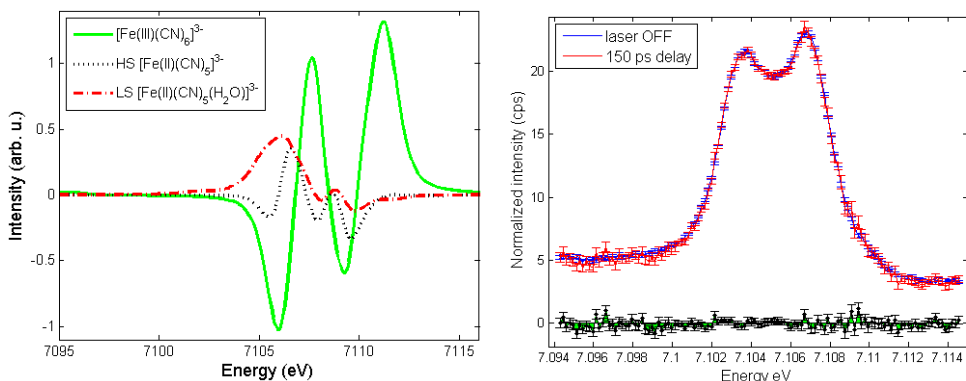
- Excited state fraction is estimated to be  $\sim 4\%$ , with less than a quarter of this being  $[\text{Fe}(\text{CN})_5]^{3-}$
- Quite intense heating is observed, 1.5 degrees or so, but this is readily understood from the large concentration of solutes
- The low-Q region at long time scales shows some unexpected features, which needs further analysis



**Figure 3** (top) The blue area corresponds to the ground state spectrum, while the red one was taken with 5 ns delay after the laser pulse. The yellow dashed line shows the calculation for the  $[\text{Fe}(\text{CN})_6]$  vtc-spectrum, and the magenta one shows the difference of the photoaquated and the ground state. (bottom) The difference, depicting the transient as well as the expected theoretical difference signal with 4% excitation yield.

We have also performed the very count-rate hungry vtc-XES measurements. At 5 ns delay, where the formation of the  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]$  complex is expected, the first set of scans have indeed seemed to reflect the photoaquated species. However, a later analysis and cleaning of the data from artefacts showed only a small difference with delay, as it is seen in Figure 3. However, if we compare it with the 4% excitation yield that was determined from the XDS analysis, the scaled difference compares well with the simulation. The statistics did not improve, as we collected spectra at several delay values (as an example, a pump-probe spectrum at 150 ps is shown in Fig. 4) and also made an attempt to perform delay scans, but as we know with hindsight, this excitation yield was not sufficient to get good enough statistics to reach a sufficient S/N for all these. After our other experiences at other facilities, and observing transients in the XDS signal, we were surprised to find such a small excitation yield.

The lesson learnt is that a quick look at the scattering patterns, while it is optimal for verifying the spatial and temporal overlap, it is insufficient to determine the excitation yield during the experiment without analysis. Therefore, we should always utilise some intensity monitors for the excitation yield; the diagram emission lines can serve well for this purpose.



**Figure 4** (left) Theoretical transients expected for  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ , and  $[\text{Fe}(\text{CN})_5]^{3-}$ . (right) Ground state spectrum (blue), and excited one taken at 150 ps delay after the laser pulse.

Finally, several problems occurred during the beamtime, which we list up briefly:

- chopper quickly overheated (had to wait 2h each time to cool down)
- high speed shutter was overheated
- microscope computer crashed
- beam current dropped to 50% for a while
- graphics card in EWALD control computer crashed
- sample pump head became unstable