

Experiment Report Form



Experiment title: Dynamics of the successive spin switching and redox state variations in photomagnetic square metal complexes with Fe and Co centers

Experiment number:
CH-4298

Beamline:	Date of experiment: from: 22.01.2015 to: 27.01.2015	Date of report: 04.03.2015
Shifts: 15	Local contact(s): Michael Wulff	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dmitry Khakhulin*, Alexander Britz* (European XFEL, Hamburg) Sophie Canton*, Darina Storozhuk*, Simone Techert (MPI für Biophysikalische Chemie, Göttingen)		

Report: *This is a preliminary report on the CH-4298 experiment to support our future applications.*

We performed preliminary characterization of several samples using the ID09B setup (**Fig.1**) for combined time-resolved liquid wide-angle x-ray scattering (WAXS) and x-ray emission spectroscopy (XES). Due to technical problems with the storage ring (beam dumps and RF clock instabilities) the experimental program was adjusted to concentrate primarily on the static measurements. Only about 9 shifts were effectively used for alignment and data collection. Nevertheless some important reference measurements were possible for the samples of interest that are essential for the future data analysis as we proceed through the project.

The proposed experiment aimed at measuring combined time-resolved WAXS and XES for a family of interesting, so called, Fe₄-grid samples with four iron (or also cobalt) centres having the same of mixed spin and oxidation state. The cyano-bridged metal centers are surrounded with polypyridyl ligands. Upon laser illumination one of the iron centers is expected to change the spin state and the transient charge transfer along with the structural coupling to the neighbouring centers in the molecule were under investigation. The purely structural tool, namely WAXS, is sensitive to the global molecular structure and the solvation whereas the spin and oxidation state of the Fe can be selectively monitored by the spectroscopic technique, i.e. XES. Having these two measurements combined at

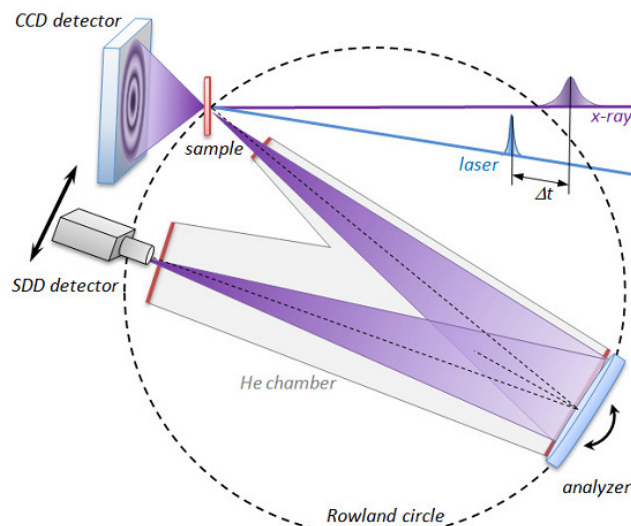


Fig.1 Experimental setup for combined WAXS and XES

the same experimental conditions facilitates the data interpretation and brings new insight to the photo-induced dynamics in such spin-crossover systems.

An important part in the transient XES measurements of the metal spin and oxidation state is to collect proper reference spectra to be able to assign the above properties to the transient species. At first we aligned the XES spectrometer using a Si(531) crystal analyser to measure the iron K β lines for the Fe₄ grid samples in solid state. The results are shown as difference spectra for each of the three studied grid samples and the LS reference ([Fe^{II}(phen)₃]²⁺) as compared to the HS-LS differential reference (HS reference is ([Fe^{II}(phen)₂(NCS)₂]²⁺)) (**Fig.2**). Using the scaling by “integral of absolute difference” method we found an average spin and respective states of iron centers for various complexes. For example for the [Fe₄L₁](1⁴⁺) system we got the S=1, which matches the assumption of the Fe^{II}₂:Fe^{II}₂ to be divided as 2HS:2LS ((2+2+0+0)/4=1). Similar, for the [Fe₄L₄](1⁶⁺), where the iron is in mixed valence states of 2+ and 3+, i.e. Fe^{II}₂:Fe^{III}₂, the obtained spin of S=1.3 roughly gives the ratio 2HS:2LS ((2+2+0.5+0.5)/4=1.25, noting that the LS of Fe^{III} corresponds to S=0.5). And finally for the Fe^{II}₂:Fe^{II}₂ complex namely [Fe₄L₂](1⁴⁺) we obtain S=1.5 corresponding to the 3HS:1LS ratio ((2+2+2+0)/4=1.5).

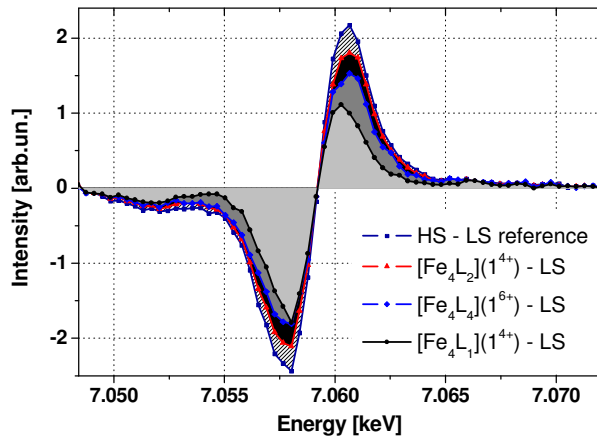


Fig.2 Static differences Fe K β for the different Fe₄-grid samples. The individual difference is compared against the HS-LS difference to obtain the average spin of iron.

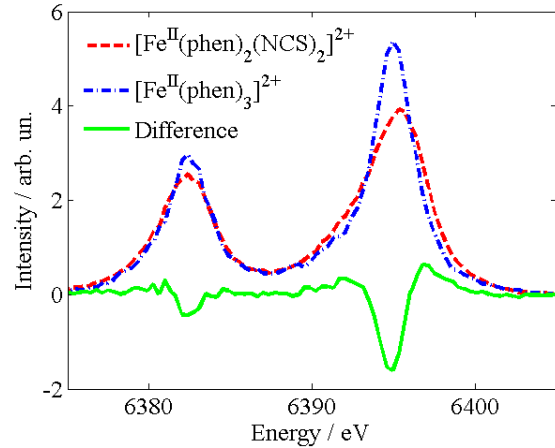


Fig.3 Typical Fe K $\alpha_{1,2}$ lineshapes for a HS ([Fe^{II}(phen)₂(NCS)₂]²⁺) and a LS ([Fe^{II}(phen)₃]²⁺) reference samples.

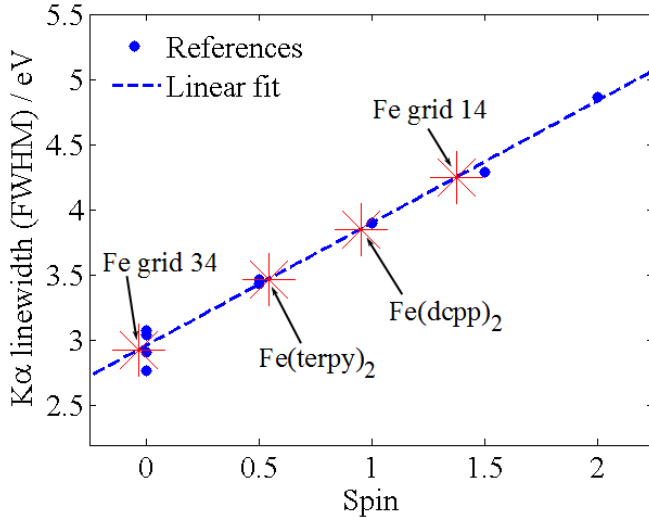


Fig.4 Fe K α_1 linewidths plot for a set of reference samples (see text) and two laser excited samples.

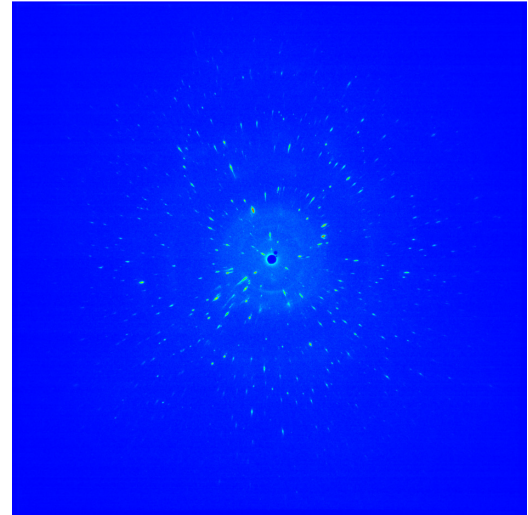


Fig.5 Laue diffraction pattern of the [Fe₄L₂](1⁴⁺) crystalline sample using a pink beam.

S=0	S=1/2	S=1	S=3/2	S=2
[Fe ^{II} (CN) ₆] ₄ ; [Fe ^{II} (phen) ₃](PF) ₆ ; [Fe ^{II} (dcpp) ₂](PF) ₆	[Fe ^{III} (CN) ₆] ₃	[Fe ^{II} (PC)] ²⁺	[Fe ^{III} (PC)] ⁺	[Fe ^{II} (phen) ₂ (NCS) ₂] ²⁺

Tab. 1 The list of reference samples for different Fe spin states.

After the problems with the storage ring and reduced current we switched to the characterisation using the Fe $K\alpha_1$ line (**Fig.3**) (Ge (220) analyser) since it requires less incoming flux and tried to make a systematic study of the linewidth vs spin dependence. We used some reference samples (**Tab. 1**) with known spin state and made a linear fit (**Fig.4**). Using this fit one can assign the spin state to an unknown sample by measuring the $K\alpha_1$ linewidth. For instance we could determine $S=0$ for the $[\text{Fe}_4\text{L}_2](3^{4+})$ compound, i.e. 4LS and $S=1.45$ for the previous $[\text{Fe}_4\text{L}_2](1^{4+})$ complex.

We also tried to do a time-resolved photo-excited measurement on the known $[\text{Fe}(\text{terpy})_2]^{2+}$ sample in water solution and got $S=0.5$ (also **Fig.4**), but since it has a quintet excited state ($S=2$) the excitation fraction is estimated to be about 25%. Similar measurement was done on photoexcited $[\text{Fe}(\text{dcpp})_2]^{2+}$ sample in acetonitrile resulting in average spin $S=1$, however since the excited state multiplicity is not known precisely there are three possibilities: 50% excitation fraction of a quintet state ($S=2$), 100% excitation fraction of a triplet state ($S=1$) or a mixture of both. More investigations required.

Overall we gained a lot of experience and confidence with reference measurements of the XES spectra and collected a library of important reference lineshapes which will be used in the analysis.

We tried to measure the time-resolved WAXS on the two abovementioned solutions however the signal was extremely low and noisy which afterwards was attributed to timing and pointing instabilities in the storage ring.

Finally for one of the Fe_4 grid samples ($[\text{Fe}_4\text{L}_2](1^{4+})$) we collected a pink beam laue diffraction pattern since the sample was in a form of nice small crystals. The respective pattern is shown in **Fig.5** and may motivate a similar combined XES + Laue diffraction experiment on light induced spin-crossover in this crystalline solid sample.

Following technical issues were encountered during the beamtime:

- After the full alignment of the setup beam was dumped for several hours. Since the problem was with the RF clock and the electron beam feedback the x-ray beam and the timing had to be realigned after the beam came back. The procedure was repeated 2-3 time because the beam was repeatedly lost then again.
- When the beam was back (half the nominal current) and alignment redone the first data WAXS collection was launched. However since the SPEC session recently migrated to another PC no on-the-fly image correction was possible, which is required by the data reduction software. The SPEC was then recovered on one of the older PCs thanks to the effort of the beamline staff and the ESRF computing support.
- The first WAXS measurement resulted in unexpectedly low difference signal. We noticed that the timing jitter of the high speed chopper was a lot higher than usual (~ 200 ns compared to 2-5 ns). After communication to the machine room we realized the jitter is due to degraded RF clock signal so it was decided to collect as much static data as possible.