

Tracking light-induced ultrafast transformations of transition metal complexes with hard X-ray spectroscopy

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Femtosecond X-ray hard tools offer direct element specific access to the changes in the charge, spin state and nuclear degrees of freedom in the elementary processes of a chemical reaction, photophysical transformation, or biological function. We report on the implementation of hard X-ray spectroscopies in time-resolved experiments, which allows us to simultaneously address both the electronic and structural dynamics, greatly enhancing the information obtained from a single experiment. These photon-in/photon-out techniques combine chemical sensitivity and element selectivity with high penetration, which make it ideal to study transformations in the condensed phase.

The implementation of time-resolved X-ray emission started as a challenging experiment with a kHz laser at a synchrotron,^[1] but soon reached high performance after the availability of MHz lasers at X-ray beamlines,^[2,3] and it has been already exploited at X-ray free electron lasers to study the spin state dynamics of Fe- and Co-bearing complexes.^[4,5] Also, resonant X-ray emission appeared at the same time.^[3,4] The experimental opportunities and the performance of XES and RXES can be appreciated from a recent study describing the detailed X-ray characterisation of the excited quintet state of the $[\text{Fe}(\text{terpy})_2]^{2+}$ complex.^[6] A single, but important element missing from this toolset was valence-to-core (vtc) X-ray emission, where the core hole created in the ionisation process is filled by a valence electron. This process has a low cross section; however, it offers the highest chemical sensitivity. In the final state of this process there is a hole in the valence orbital/band, so it is identical to the final state of the photoemission process. Despite differences in the selection rules and the transition matrix elements, it still offers information similar to photoelectron spectroscopy. Moreover, the single-particle model is rather successful in describing the transition. Therefore, the spectra can be predicted knowing the occupied density of states, so quantum chemistry computations can provide a reliable description.

We have recently managed to complete the toolbox of ultrafast hard X-ray probes with this missing technique. We have first examined the feasibility of vtc-XES studies at the 7-ID beamline of the APS using a Johann spectrometer, on the aqueous solution of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, which was excited at 266 nm, where the dominant process is photooxidation.^[7] The study shows an excellent agreement between theory and experiment, and the variation of the

spectral intensities measured 100 ps after the excitation experiment at chosen energies followed the expectations for the oxidation of the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ complex, as it is seen in Fig. 1.

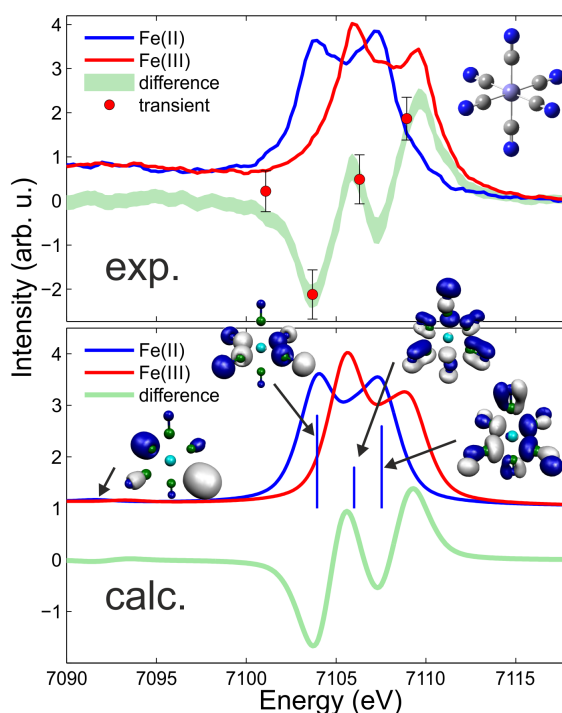


Figure 1. Static vtc-XES emission spectra of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ (blue) and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ (red) measured in aqueous solution, and their difference (green) are shown in the top panel, together with the red data points representic the intensity difference between laser-on and laser-off measurements 100 ps after 266 nm excitation of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. DFT-calculated spectra and their difference are shown in the bottom panel using the same colour code; with molecular orbitals related to the transitions for the Fe^{II} case.

Very recently, we have set up a von Hámos spectrometer with 16 analyzer crystals to measure the full 1s XES, including vtc-XES from the photoexcited $[\text{Fe}(\text{terpy})_2]^{2+}$ complex at the same beamline.^[8] The resulting spectra, displayed in Fig. 2, beside being unique in showing the full XES recorded at the same time, also represents the first proper time-resolved vtc-XES. The vtc-XES of the transient quintet state is found to be reduced in intensity and shifted slightly to higher energy. DFT calculations capture the experimental spectral changes well. The intensity reduction is understood to be a result of the expansion of the Fe–ligand bonds; photoexcitation leads to population of antibonding orbitals which causes elongation of the Fe–ligand bonds, loss of Fe–ligand orbital overlap, and therefore reduction of the Fe p MO character that contributes to the vtc emission lines. The energy shift is also expected from the bond elongation; the blue shift indicates a destabilization of the probed MOs, a result of the diminished orbital overlap. The study demonstrates that new experimental opportunities with X-ray sources providing higher flux, such as pink beam capability at synchrotrons and upcoming high-repetition-rate XFELs, promise to enable more detailed experimental observations at directly monitoring photoinduced changes in the valence orbitals, with penetration power and elemental specificity.

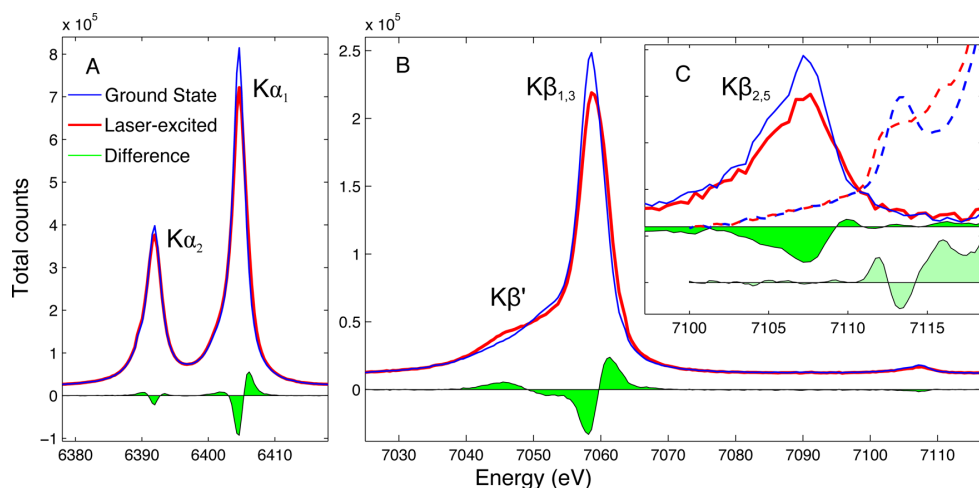


Figure 2. Full 1s XES of $[\text{Fe}(\text{terpy})_2]^{2+}$; blue (thin) lines denote spectra of the ground state, red (thick) lines denote data measured 100 ps after laser excitation, and the green filled areas show the spectral variation. (A) The $K\alpha$ region. (B) The main $K\beta$ and vtc-XES regions. (C) The inset shows the contributions from the region of the frontier orbitals: the $K\beta_{2,5}$ region of vtc-XES maps the highest occupied MOs, while the 1s X-ray absorption pre-edge (dashed lines) projects the lowest unoccupied MOs.

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