

## Tracking Ligand Exchange in Solvated Iron Complexes by Ultrafast X-ray Scattering and Emission Spectroscopy

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One of the most important types of photochemical reactivity concerns the ligand exchange processes. In addition to internal structural and solvation shell changes during the reaction, the substitution of a cleaved ligand group by a solvent molecule leads to an ultrafast and dramatic rearrangement of molecular orbitals driven by the symmetry changes. Combining structurally and electronically sensitive probes, namely pump-probe X-ray solution scattering (XSS) and X-ray emission spectroscopy (XES), into the same experiment, we have studied laser induced ligand exchange reactions in two iron complexes in aqueous and acetonitrile solutions on a sub-picosecond timescale at the Japanese XFEL SACLA. Simultaneous acquisition of the XES and XSS signals enables to record subsequent fundamental steps of the ligand exchange processes by tracking the local electronic and global structural degrees of freedom in the solute and the solvation shell, thus mapping both intra- and intermolecular transient interactions on the intrinsic (sub)picosecond timescale.

The first investigated complex, aqueous hexacyanoferrate(II) ( $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ), is a model system for the photoaquation reaction where one  $\text{CN}^-$  ligand can be detached upon the UV excitation at e.g. 355 nm and quickly replaced by an  $\text{H}_2\text{O}$  molecule [1]. Our picosecond XSS data from SACLA XFEL are analyzed within a global kinetic model taking into account the reaction rate equations and the heat exchange with the surrounding solvent [2]. Calculation of the solute-related contribution to the difference scattering is done using DFT and classical molecular dynamics simulations for all reacting species. The resulting best

model reveals formation of a penta-coordinated intermediate complex, which partially geminately recombines with the  $\text{CN}^-$  fragment within a few picoseconds or otherwise binds with a nearby water molecule to form the aquated specie after tens of picoseconds (Figure 1). The simultaneous Fe  $K_\beta$  XES measurement provides the corresponding fingerprint of the transient spin state changes [3] associated with the formation of the triplet penta-coordinated complex followed by creation of the aquated specie with singlet multiplicity.

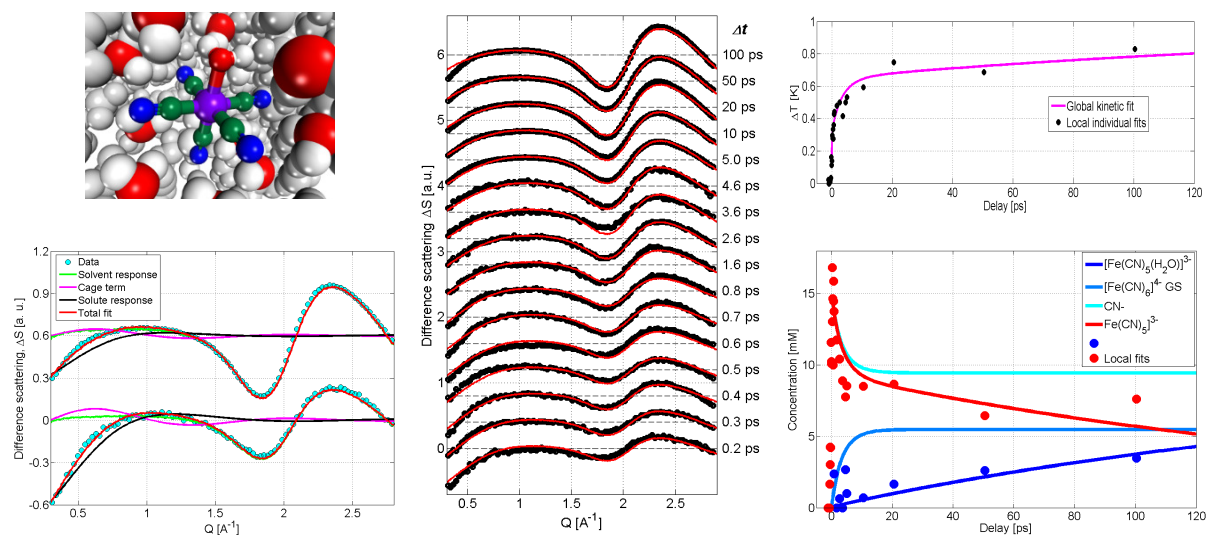


Figure 1. Left: Snapshot of the classical MD simulation for the aquated  $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$  complex (top) and representation of the local linear combination fit of the difference XSS signals (bottom). Middle: The global fit curves (red lines) of the difference XSS data (dots) for the set of measured pump-probe delays. Right: Transient concentration kinetics (bottom) and the solute temperature changes (top) as extracted from the local (dots) and the global (lines) fitting procedures.

In the second compound,  $\text{trans}-[(\text{cyclam})\text{Fe}^{\text{III}}(\text{N}_3)_2]^+$  in a  $\text{CH}_3\text{CN}$  solution, 355 nm excitation leads to a cleavage of one of the  $\text{N}_3$  azide ligands as the primary reaction pathway [4]. The vacant coordination site is then occupied by a  $\text{CH}_3\text{CN}$  molecule from the surrounding solvent. Measuring the transient line-shape changes and kinetic traces of the Iron  $K_\beta$  emission we are able to assign the multiplicity of the intermediate complex  $\text{trans}-[(\text{cyclam})\text{Fe}^{\text{II}}(\text{N}_3)]^+$  as quartet and reveal the timescale of the ligation process to be on the order of 40 ps. At the same time the transient XSS results confirm the existence of an intermediate photoproduct and additionally provide the information on the excess energy release into the solvent bath within 13 ps suggesting initial formation and relaxation of the “vibrationally hot” intermediate in the quartet state.

The approach of combining simultaneous structural and electronic observables provides great advantages for investigations of ultrafast reaction dynamics in solution chemistry allowing to accurately monitor both the solvation changes and the solute transformations [5]. Such approach will be applied in upcoming experiments at the European XFEL for studies of photochemical processes by the suite of complementary X-ray tools.

## References:

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