

European XFEL Seminar

Wednesday, 7 December 2016, 14:30

Campus Schenefeld, Main building (XHQ), Room E1.173

Tadesse Abebaw Assefa

European XFEL

"Tracking chemical reactions with ultrafast x-ray spectroscopic techniques"

Chemical reactions in transition metal complexes can be triggered with light, which results in structural and electronic changes. These changes can be visualised by measuring the geometric and electronic structure of a complex in real-time during a chemical reaction pathway. Time-resolved (TR) X-ray Absorption and Emission Spectroscopy (XAS and XES) delivers information about the geometric (via XANES and EXAFS) and electronic (via XES) transient changes when used in synchronisation with an ultrafast laser in a pump-probe scheme. Element specificity and sensitivity to the local structure of X-ray spectroscopic tools around the absorbing atom allows us to look at the photoexcited changes of transition metal complexes.

We studied aqueous ferrocyanide ($[\text{Fe}(\text{CN})_6]^{4-}$) following photoexcitation with UV laser light which results in two photoproducts namely $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ [1]. Picosecond-resolved XANES measurements after 266 nm excitation show both photoproducts and the ratio of extracted excited state fractions is consistent with quantum yield measurements reported by Shirom et al. [1, 2]. TR XES was used to look at the spin state and ligand environment changes with the core-to-core ($K\beta_{1,3}$) and valence-to-core (vtc) (or $K\beta_{2,5}$) emission lines of the central Fe atom. Furthermore, we investigated the ultrafast ligand dissociation of aqueous ferrocyanide ions upon irradiation of 355 nm laser light. Based on a comparison of the simulated pre-edge peaks of $1s \rightarrow 3d$ transition and the experimental data, we concluded that the reaction pathway commences via ligand detachment followed by the formation of the long-lived photoaquated complex. TR XES reveals the spin state of the intermediate complex. Combining these findings we interpret that the aquation process happens from a non-singlet potential energy surface and takes about 13 ps.

Also, we characterised the molecular structure of photoexcited $[\text{Fe}(\text{terpy})_2]^{2+}$ molecule via TR EXAFS. The data analysis in energy space used two structural model expansions which are the representations of DFT predicted 5E and 5B2 quintet high spin states. After statistical evaluation of the two structural models, the 5E high spin state structure is in better agreement with experimental data. The transient EXAFS fitting implemented here can be used to characterise molecular structures of other spin crossover complexes.

[1] M. Shirom, "Excited State Chemistry of the Ferrocyanide Ion in Aqueous Solution. I. Formation of the Hydrated Electron," J. Chem. Phys., vol. 55, no. 7, p. 3372, 1971.

[2] M. Shirom and G. Stein, "Excited State Chemistry of the Ferrocyanide Ion in Aqueous Solution . II . Photoaquation," J. Am. Chem. Soc., vol. 55, no. 7, pp. 3379–3382, 1971.

Host: Christian Bressler

