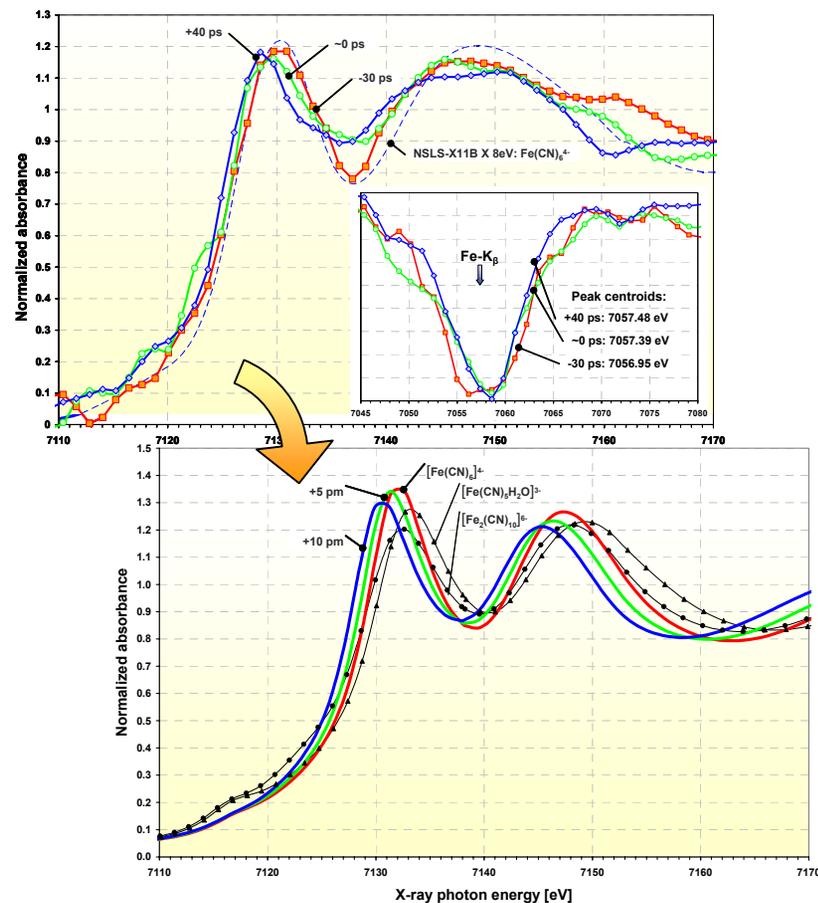


Observing atomic motions during chemical reactions

Christoph Rose-Petruck, Brown University

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Ultrafast atomic motions are the essence of every chemical process and detailed knowledge about their nature is of fundamental importance. Ultrafast X-ray Absorption Fine Structure (XAFS) spectroscopy permits the measurements of bond distances as a function of time after photo-excitation of a molecular system. Here we report on the first laser pump – picosecond x-ray probe measurements of solvated transition metal complexes carried out with a table-top ultrafast laser driven plasma x-ray source. The XAFS spectra of $\text{Fe}(\text{CN})_6^{4-}$ solvated in water have been measured tens of picoseconds after photoexcitation with ultrashort UV laser pulses. The spectra after photoexcitation exhibit an iron K-edge shift indicating the increase of the iron-ligand distances (see upper Figure). This observation is not caused by an accidental shift of the entire absorption spectrum as proven by the spectral stability of the iron K_β line. (see the inset of upper Figure) The observation can be explained through an increase of the Fe-C bond lengths. Photoexcitation is likely to instantaneously increase the average metal-ligand bond length *en route* to ligand substitution. Theoretical XANES spectra reproduced in the lower Figure, demonstrate the effect of bond-lengths increase. An elongation on the order of 5 to 10 pm causes a shift comparable to the one observed in our measurements. Additionally, the spectra of two possible products are shown.



"Ultrafast table-top laser pump - x-ray probe measurement of solvated $\text{Fe}(\text{CN})_6^{4-}$," T. Lee, F. Benesch, Y. Jiang and C. Rose-Petruck, *J. Chem. Phys.* **Subm.** (2004).