

Ultrafast X-Ray Studies of $\text{Fe}[\text{tren}(\text{py})_3]^{2+}$ at the Advanced Light Source

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The emergence of ultrafast x-ray spectroscopy as a viable technique at the Advanced Light Source (ALS) [1] allows for the observation of atomic re-arrangement in condensed-matter and chemical systems on the limiting time-scales of atomic motion. An intriguing initial experiment is the time-resolved study of Fe(II) complexes, a family of transition metal complexes including heme molecules and photo-sensitizers[2], which exhibit strongly coupled electronic, magnetic and structural dynamics upon impulsive photo-excitation [3,4]. Specifically, with the time-resolved study of the photo-sensitizer, $\text{Fe}[\text{tren}(\text{py})_3]^{2+}$, pictured in Figure 1, it is hoped that the roles of the various degrees of freedom in the excited state evolution of these systems can be elucidated.

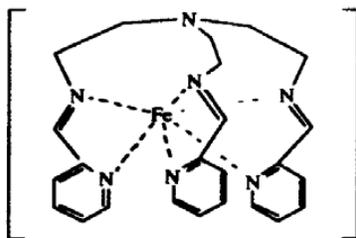


Figure 1: $\text{Fe}[\text{tren}(\text{py})_3]^{2+}$

$\text{Fe}[\text{tren}(\text{py})_3]^{2+}$ has a singlet ground state. Upon photo-excitation, the molecule is excited to a metal-to-ligand charge transfer state. Optical measurements, plotted in Figure 2, have determined the transient, high-spin ($\Delta S=2$) state forms within 500 femtoseconds. Concomitant with this highly spin-forbidden transition is a structural dilation of the iron-nitrogen bond lengths by roughly 10%.

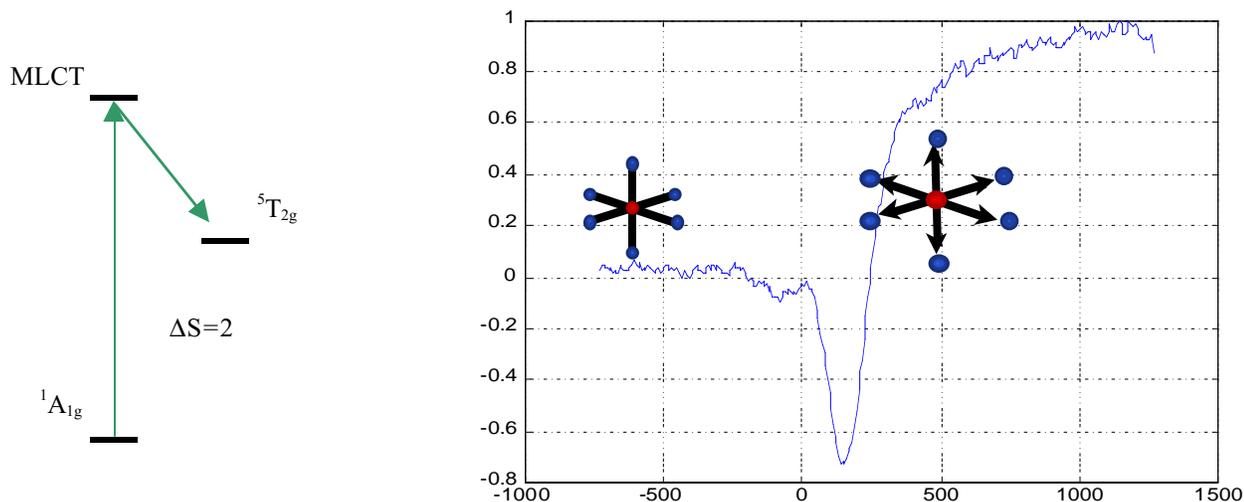


Figure 2: Relevant electronic transitions and structural changes in $\text{Fe}[\text{tren}(\text{py})_3]^{2+}$ upon photo-excitation. In the time-resolved optical trace, a strong excited state absorption appears soon after photo-excitation, followed by a bleach, indicating the formation of the high-spin (bond-distended) state in $\sim 500\text{fs}$.

Two possible scenarios can account for this behavior. The first being a direct structural distortion generated by photo-excitation gives rise to the transient, high-spin ground state. High-spin analogs of $\text{Fe}[\text{tren}(\text{py})_3]^{2+}$ created by distention of three of the six iron-nitrogen bonds have been synthesized by the McCusker group, and lend credence to this scenario. The second possibility is that electronic dynamics in the intermediate metal-to-ligand charge transfer state give rise to a high-spin transient state (persistent during the strong excited state absorption), which requires bond dilation for stability. The bond dilation then confers energetic preference to a transient high-spin state when the electron relaxes from the charge-transfer state, forming the long-lived high-spin state.

The ultimate resolution of this issue relies on experiment. Current efforts at beamline 5.3.1 are focused on observing shifts in the iron L-edge, a signature of formation of the high-spin state [3], on the ultrafast time scale. Ultimately, work will proceed to measure time-resolved EXAFS above the L- and K-edge to unravel the specific nature of the ligand cage distortion about the central iron atom. Together with time-resolved optical dichroism measurements and time-resolved absorption measurements, x-ray measurements on the ultrafast time-scale will provide complete information regarding the roles the electronic, magnetic and structural degrees of the freedom play in the light-induced spin-crossover transition of Fe(II) complexes.

REFERENCES

- [1] R.W. Schoenlein, et. al., *Science* **287**, 2237 (2000).
- [2] P. Gutlich, et. al., *Chem. Soc. Rev.* **29**, 419 (2000).
- [3] J.-J. Lee, et. al., *J. Am. Chem. Soc.* **122**, 5742 (2000).
- [4] J.E. Monat and J.K. McCusker, *J. Am. Chem. Soc.* **122**, 4092 (2000).

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