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Using picosecond x-ray absorption spectroscopy to probe the structural dynamics of a photo-induced spin cross-over transition in solution

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The ultrafast photo-induced transition from the low spin 1A_1 to the high spin 5T_2 state in Fe^{II} complexes serves as a prototype for understanding complex electron transfer reactions in chemistry and biology. The ultimate goal of these experiments is to provide a truly local picture of ultrafast dynamics accompanying fundamental electron transfer reactions in solution. We perform visible pump and x-ray probe spectroscopy on Fe K-edge of $Fe[tren(py)_3](PF_6)_2$ in acetonitrile solution with 100 ps time resolution. The charge transfer process is initiated by the 400 nm pump light and the structural dynamics accompanying the reaction are probed using the x-ray pulses from the Advanced Light Source. Static x-ray absorption measurements at the Fe K-edge on the low-spin parent compound and a high-spin analogue ($Fe[tren(6-Me-py)_3](PF_6)_2$) reveal distinct spectroscopic signatures of the $S=0$ and the $S=2$ states in the XANES and EXAFS regions. The pump-probe results show that the intersystem crossing is complete within the ~ 100 ps time resolution of our experiment. Comparison of the transient pump-probe signal with the static absorption spectra reveals a significant red shift in the edge position and an increase in the Fe-N bond lengths by 0.25 Å. Our results represent initial efforts at characterizing the electronic and molecular structure of photo-excited chemical species in solution via x-ray absorption spectroscopy on a 100 ps timescale. This experiment paves the way for future femtosecond x-ray absorption studies of solution phase chemistry at the Advanced Light Source.