

Probing Reaction Dynamics of Transition-Metal Complexes *in Solution* via Time-Resolved X-ray Spectroscopy

Nils Huse¹, Munira Khalil², Tae Kyu Kim³, Amanda L. Smeigh⁵, Lindsey Jamula⁵, James K. McCusker⁵, and Robert W. Schoenlein⁶

¹ Chemical Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

² Department of Chemistry, University of Washington, Seattle, WA 98195, USA

³ Department of Chemistry, Pusan National University, Busan 609-735, Korea

⁵ Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA

⁶ Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

nhuse@lbl.gov, rwschoenlein@lbl.gov

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Abstract. We report measurements of the photoinduced Fe^{II} spin crossover reaction dynamics *in solution* via time-resolved x-ray absorption spectroscopy. EXAFS measurements reveal that the iron–nitrogen bond lengthens by 0.21 ± 0.03 Å in the high-spin transient excited state relative to the ground state. XANES measurements at the Fe L-edge show directly the influence of the structural change on the ligand-field splitting of the Fe^{II} 3d orbitals associated with the spin transition.

1. Introduction

A major goal in chemistry is to quantitatively probe chemical bonding dynamics at the molecular level. That is: to follow nuclear motions and valence-charge distributions in real time, to observe the formation and dissolution of chemical bonds, and to understand their cooperative relationship with atomic rearrangement and the formation of new molecular structures. The emerging technique of ultrafast x-ray spectroscopy [1,2] provides important new insight to molecular dynamics because x-ray transitions are element specific, symmetry and spin state selective, and effective for probing lighter elements (C, N, O etc.). Extended x-ray absorption fine structure (EXAFS) delivers quantitative structural information with sub-Å accuracy; the x-ray near-edge spectral region (XANES) provides a quantitative fingerprint of the local chemical bonding geometry (orbital hybridization etc.) in the vicinity of the atom(s) of interest. This is particularly powerful for understanding molecular dynamics in solution, where much important chemistry occurs, and where the solvent environment substantially influences reaction dynamics (often precluding quantitative interpretation of transient absorption spectra in the visible regime).

Solvated transition-metal complexes are of fundamental interest due to the strong interaction between electronic and molecular structure. In particular, the octahedral ligands in Fe^{II} complexes effectively couple optical charge-transfer excitations to subtle changes of the molecular structure, leading to rapid spin-state interconversion [3]. The ultrafast spin crossover phenomenon (interconversion between low- and high-spin states) in an Fe^{II} complex serves as a prototypical reaction for understanding electron transfer processes in chemistry and biology, and light-induced excited spin-state trapping (LIESST) in Fe^{II} molecular crystals is of technological interest.

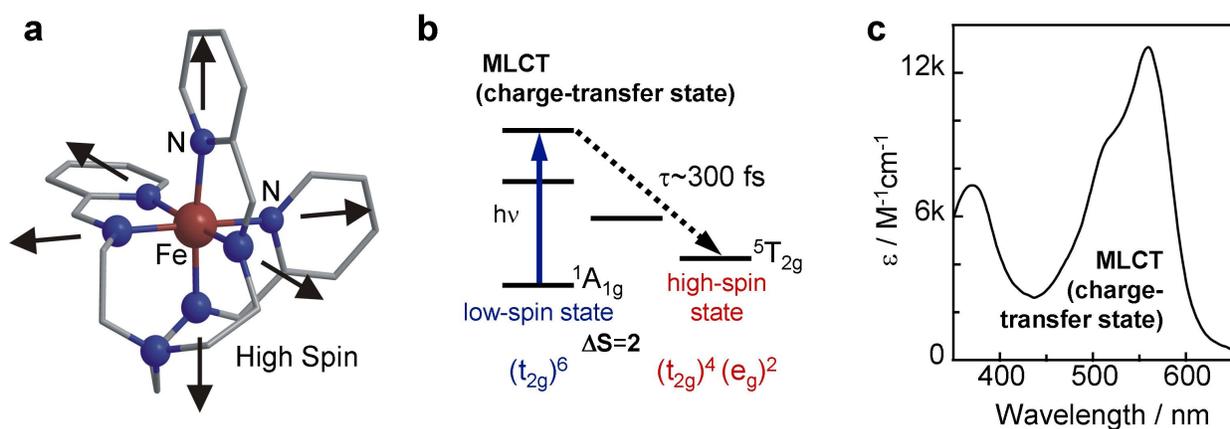


Fig. 1 (a) Schematic of $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$, arrows indicate the metal-ligand bond change associated with the spin transition. (b) Simplified energy levels of intersystem crossing after optical excitation to the charge-transfer state. (c) Absorption spectrum of the charge transfer band centered at 560 nm.

The $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ complex (Fig. 1a) has an octahedral ligand geometry around a central Fe atom. Hybridization with the nearest ligand N-2p orbitals lifts the degeneracy of the Fe-3d orbitals to form t_{2g} and e_g (Fig. 1b). The associated Fe-N charge-transfer transition shown in Fig. 1c has a maximum absorption at 560 nm. Optical spectroscopy has extracted a 300 fs time constant [4], and this has been interpreted as a signature of intersystem crossing to a high-spin state with a change in spin of $\Delta S=2$.

Here we report time-resolved Fe K- and L-edge x-ray absorption spectroscopy (XAS) of the ultrafast photo-induced intersystem crossing occurring in the solvated transition-metal complex $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ and the chemically stabilized high-spin analogue $[\text{Fe}(\text{tren}(6\text{-Me-py})_3)]^{2+}$. Particular interest in the Fe^{II} complex stems from the rapid spin transition ($\Delta S=2$) that is thought to result from changes in the ligand-field splitting of the Fe-3d orbitals, and associated changes in Fe-3d/N-2p hybridization. These changes are mediated by a dilation of the octahedrally-coordinated Fe-N bonds, and optically triggered by the initial metal-to-ligand charge transfer excitation. Time-resolved spectroscopy of the extended x-ray absorption fine structure at the Fe K-edge directly measures the Fe-N bond distance while spectroscopy of the Fe L-edges directly probes the evolution of the ligand-field split 3d orbitals via selective transitions from the spin-orbit-split Fe-2p_{1/2}/2p_{3/2} levels.

2. K-edge Spectroscopy

Time-resolved EXAFS measurements at the Fe K-edge directly probe the dynamic relationship between the molecular structure and the ultrafast spin cross-over transition in the low-spin complex, $[\text{Fe}(\text{tren}(\text{py})_3)](\text{PF}_6)_2$, dissolved in acetonitrile. Time-resolved x-ray absorption spectra of this complex are collected using tunable 70 ps x-ray pulses after excitation with a 100 fs optical pulse. The results are compared with model calculations and the static x-ray absorption spectrum of a chemically-stabilized high-spin analogue. Transient pump-probe experiments observe that the structural and electronic changes following excitation are complete within 70 ps and the Fe-N bond length is increased by 0.21 Å in the photo-excited high-spin state. Details of the experiment have been described previously [5].

For reference, Fig. 2a displays static spectra of the low-spin complex and the chemically-stabilized high-spin analogue. Analysis of the static EXAFS spectra indicates an average Fe-N bond length that is ~0.23 Å longer in the high-spin analogue than in the low-spin complex. This significant bond elongation reflects the difference in electronic configuration between the low-spin and high-spin compounds and accounts for all features observed in the XANES region. Figure 2b shows the *transient difference* XAS spectrum of $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ (photo-excited high-spin state compared to the low-spin ground state) above the Fe K-edge, 330 ps after laser excitation. For comparison, the difference of the steady-state spectra of Fig. 2a is plotted below the transient data (scaled by a factor of 0.1 to account for 10% laser photolysis).

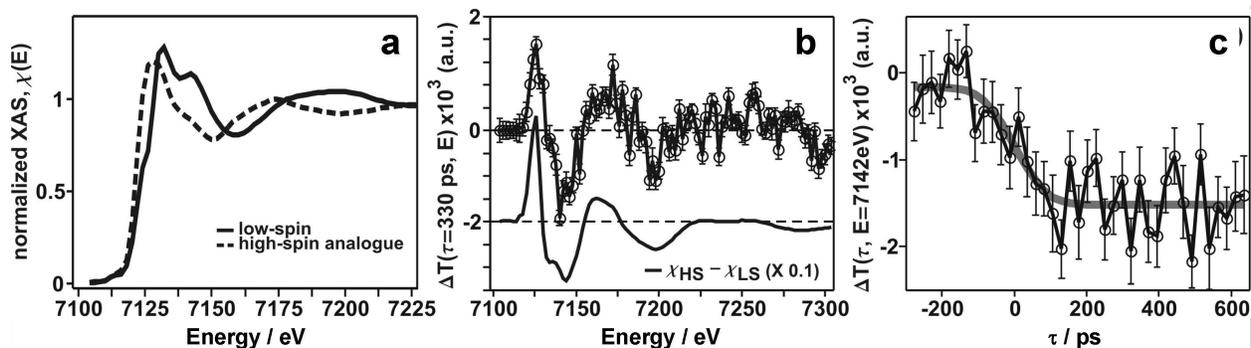


Fig. 2 (a) XANES spectra at the Fe K-edge of the low-spin complex $[\text{Fe}(\text{tren}(\text{py})_3)](\text{PF}_6)_2$ and the high-spin analogue $[\text{Fe}(\text{tren}(6\text{-Me-py})_3)](\text{PF}_6)_2$, both dissolved in acetonitrile. (b) Transient difference XAS spectrum at $\tau = 330$ ps ($\text{HS}_{\text{photo-excited}} - \text{LS}_{\text{ground state}}$). The difference between steady-state XAS spectra of the high-spin and low-spin compounds is plotted below. (c) Pump-probe x-ray absorption signal at 7142 eV. $\Delta T = I(\tau) - I_{\text{ref}}$, where $I(\tau)$ and I_{ref} refer to the XAS signals with and without the laser pulse, respectively.

Figure 2c shows the time-evolution of the spectral feature at 7142 eV as a function of the delay between the optical pump and x-ray probe pulses. The results show a decrease in the amplitude of the spectral feature at 7142 eV following photo excitation of the low-spin compound. The temporal evolution of the difference x-ray signal is fitted by a Gaussian error function (thick solid curve) which corresponds to the 70 ps x-ray pulse. It indicates that the structural evolution following photoexcitation of the low-spin compound is complete within the time resolution of our experiment. A fit of the k space differential XAS spectrum obtained at $\tau = 330$ ps to determine the structure of the transient high-spin state shows good agreement, demonstrating that the excited high-spin state of $[\text{Fe}(\text{tren}(\text{py})_3)](\text{PF}_6)_2$ is characterized by a lengthening of the Fe–N bond by 0.21 Å, an interpretation supported by subsequent experiments [6].

3. L-edge Spectroscopy

The ultrafast intersystem crossing and the structural changes point to an intricate interplay of electronic, atomic, and magnetic structure. For further insight, we apply time-resolved soft x-ray spectroscopy at the Fe L_3 -edge, using Beamline 6.0.2 at the ALS. Critical to such liquid-phase studies has been the development of a sample cell (Fig. 3, left) in which a liquid film is held between two 100 nm-thick silicon nitride membranes while the interior cell pressure is balanced against the pressure of the sample chamber, thereby controlling the liquid film thickness with sub-200 nm accuracy [7]. A third silicon-nitride membrane isolates the low-pressure sample chamber from the ultrahigh vacuum of the femtosecond soft x-ray beamline at the ALS. $[\text{Fe}(\text{tren}(\text{py})_3)](\text{PF}_6)_2$ is dissolved in acetonitrile at 100 mM concentration, and excited with ultrashort 560 nm pulses at 1 kHz. Transient absorption changes at the Fe L_2 - and L_3 -edges are probed with tunable 70 ps synchrotron pulses at 2 kHz as a function of x-ray probe energy and time delay between excitation and probe pulses. From the spectral measurements of the ground- and the photo-excited state, transient XAS spectra of the high-spin state at the Fe L_2 - and L_3 -edges are reconstructed.

Figure 3 shows the absorption of the high and low-spin state after the photo-induced metal-to-ligand charge transfer. These are to our knowledge the first time-resolved solution-phase transmission spectra ever recorded in the soft x-ray region. The L_3 -edge of the high-spin state shows a pronounced red-shift by 1.6 eV with no discernable change in linewidth relative to the low-spin state. However, more complex absorption features on the blue side of the maximum are present. The L_2 -edge exhibits only a small red-shift by about 0.4 eV upon laser excitation but the absorption cross-section is diminished by nearly a factor of 2 (data not shown). The time delay scans in the inset show changes in sample absorption at specific probe photon energies, consistent with the spectral scans. While the absorption decreases at the spectral absorption maxima of the low-spin state after excitation, it increases around 707 eV where the absorption of the high-spin state is maximal. As for the K-edge measurements, the delay scans reflect the 70 ps width of the x-ray probe pulses and demonstrate that the Fe^{II} compound reaches its meta-stable

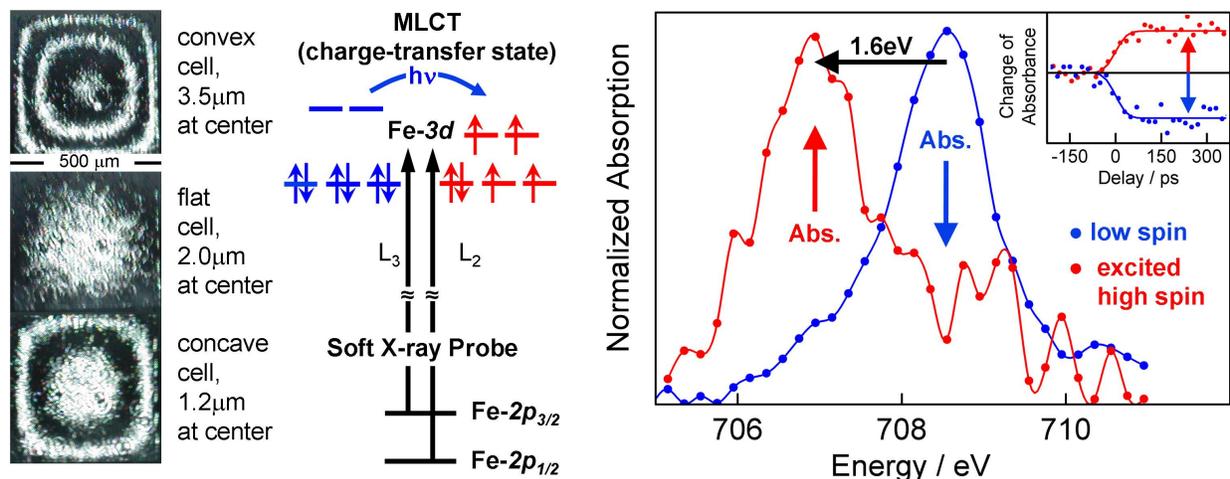


Fig. 3. Transmission interferograms of the sample cell that indicate liquid film thickness are shown on the left. In the center is a simplified level scheme of the soft x-ray probe transition. To the right, absorption spectra of the Fe L₃-edge for the low-spin ground state (blue) and excited high-spin state (red) at 5 ns delay. The inset shows time delay scans at the absorption maxima of the low and high-spin state.

high-spin state within the time resolution of the experiment. Transient XAS spectra at 5 ns delay demonstrate that the evolution of the high-spin electronic structure is complete within 70 ps

4. Conclusions

The photo-excited high-spin state of [Fe(tren(py)₃)](PF₆)₂ is characterized by a lengthening of the F–N bond by 0.21 Å occurring within 70 ps. Our time-resolved L-edge measurements in liquid phase exhibit a red-shift of the Fe^{II} L-edges by 1.6 eV due to a change in ligand-field splitting that is mediated by the changes in ligand-bonding. L-edge measurements are consistent with static x-ray measurements of a similar compound in crystalline phase (where the high-spin state is trapped at low temperature) [8], and offer an important opportunity to investigate the solvent influence on the ultrafast dynamics of the electronic and spin states. Our experimental results are in good agreement with theoretical calculations of the high- and low-spin electronic structure. In particular, the size of the red-shift of both L₃ and L₂-edges is reproduced. Crystal field multiplet calculations attribute our observations to changes in 3d occupancy.

Acknowledgement

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