

# Femtosecond Soft X-ray Spectroscopy of Solvated Transition-Metal Complexes: Deciphering the Interplay of Electronic and Structural Dynamics

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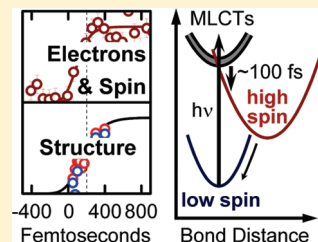
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**S** Supporting Information

**ABSTRACT:** We present the first implementation of femtosecond soft X-ray spectroscopy as an ultrafast direct probe of the excited-state valence orbitals in solution-phase molecules. This method is applied to photoinduced spin crossover of  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ , where the ultrafast spin-state conversion of the metal ion, initiated by metal-to-ligand charge-transfer excitation, is directly measured using the intrinsic spin-state selectivity of the soft X-ray L-edge transitions. Our results provide important experimental data concerning the mechanism of ultrafast spin-state conversion and subsequent electronic and structural dynamics, highlighting the potential of this technique to study ultrafast phenomena in the solution phase.



**SECTION:** Electron Transport, Optical and Electronic Devices, Hard Matter

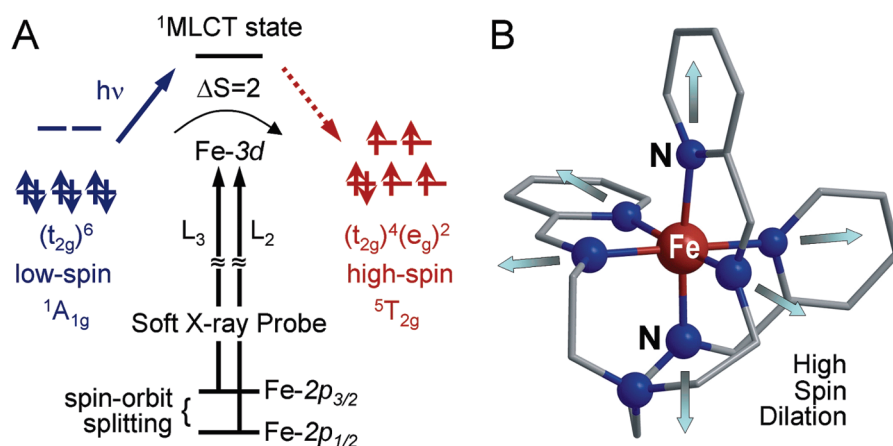
Transition-metal-based spin crossover complexes are a fascinating class of compounds due to their ability to change the spin-state in response to external perturbations such as temperature, pressure, and light.<sup>1</sup> The dramatic differences in the structural, optical, and magnetic properties between the low- and high-spin forms of such systems has generated interest in their potential application in a variety of molecule-based devices. In this context, it is crucial to understand the interplay of structure and valence charge distributions. Ultrafast optical spectroscopy methods have been successfully used in the past to elucidate details associated with photoinduced spin-state conversion;<sup>2–6</sup> however, the link between these observables and changes in molecular structure and electronic configuration can often be difficult to establish. Transient core-level spectroscopy and X-ray diffraction provide an attractive route to study the interplay of molecular structure and valence electronic configuration of metal centers in such systems while in the excited state.<sup>7–11,26</sup> For example, transient X-ray absorption spectroscopy (XAS) at the Fe K-edge of low-spin Fe(II) complexes has provided detailed information on structural changes (e.g.,  $\sim 0.2$  Å elongation of the Fe—N bonds) subsequent to excitation of metal-to-ligand charge-transfer transitions.<sup>8–11,26</sup>

While much insight has been obtained from structural probes, transient K-edge absorption spectroscopy of the important first-row transition metals delivers limited information about changes in electronic configuration because of the broad and relatively weak spectral features arising from formally dipole-forbidden transitions ( $1s \rightarrow 3d$ ).<sup>10</sup> In contrast, transient L-edge absorption spectroscopy in the soft X-ray range exploits Laporte allowed

( $2p \rightarrow 3d$ ) transitions that directly probe electronic changes associated with valence orbitals (Figure 1A) that dominate the chemistry in these systems. We recently demonstrated the first transient soft X-ray spectroscopy<sup>12,13</sup> of solvated molecules, which provided a detailed picture of the changes in valence electron distributions in the 3d manifold of a low-spin iron(II) complex subsequent to charge-transfer excitation. This type of spectroscopy provides crucial information on photoinduced changes in bonding and electronic configuration<sup>13</sup> not accessible by other methods.<sup>14</sup> Our previous picosecond study only allowed characterization of the initial- and final-state valence charge distributions due to the subpicosecond time scale of charge transfer to high-spin relaxation.<sup>2,5</sup> Extending L-edge spectroscopy of first-row transition metals to femtosecond time resolution holds great potential for examining changes in valence charge density during the course of photoinduced chemical transformations, but it has never been demonstrated for solution-phase systems due, in part, to the difficulties associated with the application of soft X-ray spectroscopy to liquid samples.<sup>15,16,27</sup> Herein, we report the first example of such a measurement. Specifically, photoinduced low-spin to high-spin conversion of a six-coordinate Fe(II) compound has been studied with femtosecond soft X-rays at the Fe L<sub>3</sub>-edge, providing a direct measure of changes in the valence orbital configuration concomitant with photoinduced spin crossover.

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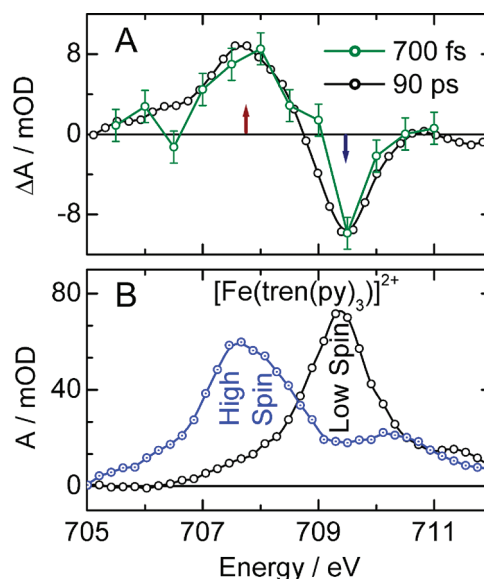


**Figure 1.** (A) Qualitative orbital diagram for an octahedral Fe(II) complex, illustrating how the photoinitiated spin crossover is probed via metal 2p  $\rightarrow$  3d dipole transitions. (B) Schematic drawing of the molecular structure of  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ . Photoinduced metal-to-ligand charge transfer results in ultrafast structural changes that have been previously characterized by picosecond time-resolved EXAFS measurements.<sup>8</sup>

$[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  (where  $\text{tren}(\text{py})_3 = \text{tris}(2\text{-pyridylmethylimino-ethyl)amine}$ ) (Figure 1B) represents a prototypical iron-based spin crossover with a low-spin ( $^1A_{1g}$ ) ground state that undergoes ultrafast spin-state conversion to a high-spin ( $^5T_{2g}$ ) state upon excitation into a singlet metal-to-ligand charge-transfer state ( $^1\text{MLCT}$ ,  $\lambda_{\text{max}} = 560 \text{ nm}$ ). The photoinduced excited-state dynamics of this compound have been studied by a range of experimental techniques including femtosecond electronic absorption spectroscopy and stimulated Raman scattering<sup>2,5</sup> as well as picosecond EXAFS spectroscopy.<sup>8</sup> The confluence of the femtosecond laser experiments indicate that the final state is formed on subpicosecond time scales after the initial MLCT absorption; femtosecond soft X-ray spectroscopy is therefore uniquely positioned to examine this process.

Measurements were carried out at the ultrafast X-ray facility of the Advanced Light Source. Briefly, a 100 mM acetonitrile solution of  $[\text{Fe}(\text{tren}(\text{py})_3)](\text{PF}_6)_2$  in a 2  $\mu\text{m}$  thick silicon nitride cell was excited by a 560 nm laser pulse (70 fs duration, 3  $\text{mJ}/\text{cm}^2$  incident flux, 0.5 kHz repetition rate). Transmission changes were probed by tunable soft X-ray pulses ( $\sim 10$  photons/pulse/0.1% bandwidth, 200 fs duration) from a slicing source<sup>17</sup> at a repetition rate of 1 kHz. Differential absorption changes at the Fe  $L_3$ -edge were recorded by creating interleaved data from the laser-excited and ground-state sample. A schematic of the experimental apparatus can be found in Figure S1 of the Supporting Information.

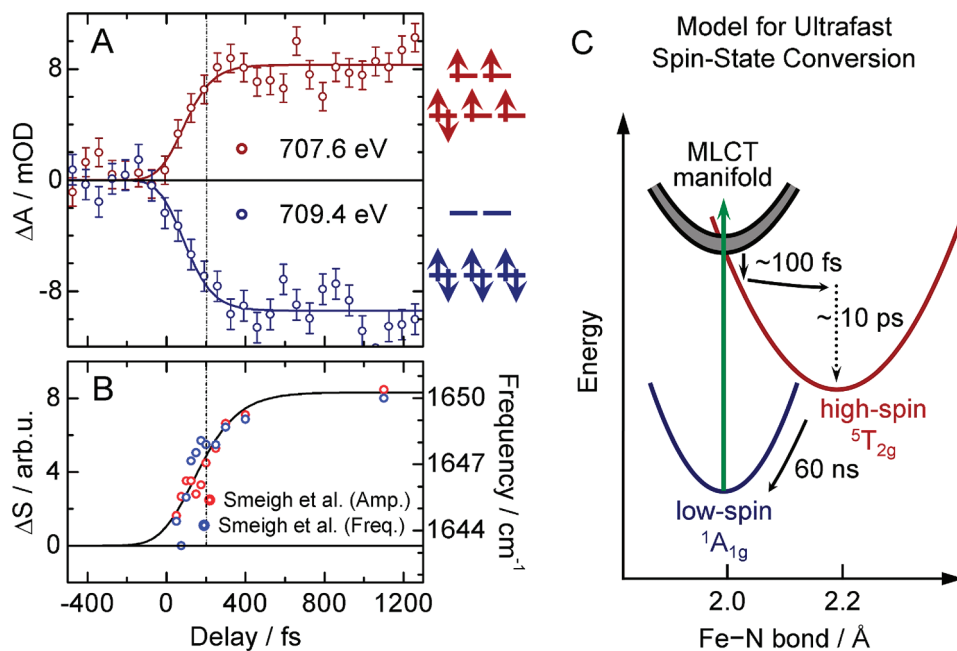
Figure 2A shows a comparison of the differential X-ray absorption spectrum from our picosecond study with our new results recorded with almost 3 orders of magnitude higher temporal resolution. Both differential spectra reveal a shift in the absorption spectrum to lower energies in addition to changes in the overall line shape and an increase in absorption integrated across the  $L_3$ -edge. More significantly, the strong similarity of the differential absorption spectra at time delays of 700 fs and 90 ps demonstrates the existence of a new core-level transition associated with the excited state formed subsequent to charge-transfer excitation of the chromophore. The  $L_3$ -edge of the  $^1A_{1g}$  state and transient  $^5T_{2g}$  state reconstructed from the picosecond differential X-ray absorption spectrum is plotted in Figure 2B. For an understanding of these spectra we briefly summarize our previous work<sup>13</sup> which concluded from comparison of the  $L_2$  and  $L_3$  absorption line shapes with model systems and multiplet calculations that in the low-spin  $^1A_{1g}$  ground state,



**Figure 2.** (A) Time-resolved differential X-ray absorption spectra of  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  in  $\text{CH}_3\text{CN}$  solution at the Fe  $L_3$ -edge. The red and blue arrows indicate spectral positions at which the time-dependent data shown in Figure 3A were acquired. (B)  $L_3$ -edge spectra of  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  in  $\text{CH}_3\text{CN}$  in the low-spin ground state (black) and the transient high-spin excited state (blue) at  $\Delta t = 90 \text{ ps}$ .

strong  $\pi$ -back-bonding results in delocalization of the Fe  $3d(t_{2g})$  electron into the  $\pi^*$ -orbitals of the  $\text{tren}(\text{py})_3$  ligands. The high-spin  $^5T_2$  excited state is characterized by suppressed  $\pi$ -back-bonding and attenuated  $\sigma$ -donation from the  $\text{tren}(\text{py})_3$  ligand relative to the low-spin ground state. Both effects lead to more localized N 2p and Fe 3d orbitals while keeping the integrated occupancy of the metal-based  $e_g$  and  $t_{2g}$  orbitals roughly constant, that is, the overall Fe 3d charge density is unchanged while the character of the metal–ligand bonding becomes more ionic in nature.<sup>13</sup>

Complementary to the spectral domain, femtosecond absorption changes as a function of time delay have been recorded (Figure 3A). Transients at the maxima of the bleach and absorptive features are both characterized by a steep rise followed by a plateau which extends well beyond 1 ps; no further absorption changes on time scales between a few picoseconds and several nanoseconds



**Figure 3.** (A)  $L_3$ -edge absorption changes of  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  in  $\text{CH}_3\text{CN}$  solution as a function of pump–probe delay (open circles) at the two spectral positions indicated in Figure 2A. The solid lines correspond to a fit of the data to a model which includes a time constant for the formation of the  $^5T_{2g}$  state and a 60 ns lifetime for the  $^5T_{2g}$  state.<sup>2</sup> See the Supporting Information for a more detailed discussion of the kinetic model. (B) Transients acquired from femtosecond stimulated Raman scattering<sup>5</sup> (FSRS) of the C—N stretching mode of  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  in  $\text{CH}_3\text{CN}$  solution; the red and blue circles correspond to changes in the amplitude and frequency of the FSRS signal, respectively. The data were fit with the kinetic model used in panel A. (C) Schematic representation of the excited-state evolution of  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  following charge-transfer excitation based on all of the available data on this compound. The  $\sim 10$  ps component corresponds to vibrational cooling in the high-spin state as determined by time-resolved electronic absorption and resonance Raman measurements.<sup>2,5</sup>

were observed, implying that the differential spectra in Figure 2A and hence the changes in spin-state and electronic configuration reported previously<sup>13</sup> occur within 300 fs. Fitting these transients to a three-level rate equation model convolved with the instrumental response function of 200 fs (fwhm) yields a time constant of  $85 \pm 75$  fs for the formation time of the high-spin  $^5T_{2g}$  state. This constitutes a unique, direct measurement of photoinduced spin-state conversion in a solvated compound on femtosecond time scales, owing to the intrinsic spin-state selectivity of the  $2p \rightarrow 3d$  transitions. Specifically, the spin–orbit splitting of the Fe 2p orbitals renders the number of allowed dipole transitions (and hence the spectral weight) of the  $L_2$ -edge ( $2p_{1/2} \rightarrow 3d$ ) and the  $L_3$ -edge ( $2p_{3/2} \rightarrow 3d$ ) dependent on the orbital occupancy of the 3d manifold. This in turn defines the configuration from which the electronic term states of the compound derive and, ultimately, the spin-state of the molecule.<sup>18</sup>

Our detailed findings on the ultrafast changes in the metal-centered valence electron distribution can be compared with all of the other ultrafast spectroscopic data that have been acquired on this compound. Transient absorption spectroscopy in the visible and ultraviolet wavelength range have established a time constant of  $80 \pm 20$  fs for the depopulation of the MLCT manifold<sup>2</sup> and the presence of two low-spin/high-spin isosbestic points identical to those determined from steady-state spectroscopy.<sup>5</sup> The latter measurements placed an upper limit on the time scale for  $^5T_{2g}$  formation of  $<250$  fs, consistent with the data in Figure 3A. The similar time constants for depopulation of the MLCT manifold and population of the  $^5T_{2g}$  state as measured by femtosecond L-edge spectroscopy (Figure 3A) hint at a direct relaxation from the MLCT manifold to the  $^5T_{2g}$  state, as already suggested recently for a similar compound,<sup>19</sup> although involvement

of other excited states in the relaxation process cannot be excluded based on the data in Figure 3A due, in part, to the time resolution of the soft X-ray experiment.<sup>20</sup>

Femtosecond stimulated Raman spectroscopy (FSRS) has been used to probe vibrational changes associated with the photoinduced spin-state conversion in  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  in solution.<sup>5</sup> This experiment probed structural dynamics upon photoinduced spin crossover by measuring changes in frequency and amplitude of the C—N(imine) stretching mode, establishing a formation time of  $<200$  fs for the ligand cage dilation associated with the high-spin form.<sup>5</sup> Figure 3B shows a plot of both Raman signatures along with fits to our kinetic model, yielding a formation time of  $150 \pm 60$  fs. It can be seen that all of the data sets can be described with a common model, except for slight differences in the formation time of spectral features associated with the high-spin state (vide infra). In this context, it is important to note that the three types of femtosecond data that we have been discussing—visible absorption, Raman, and soft X-ray absorption—probe different aspects of the electronic and geometric properties of the molecule. We therefore view the remarkable consistency across all of these measurements as strong support for the overall kinetic scheme describing the excited-state dynamics of this compound (Figure 3C).

Studies of other metal polypyridyl complexes in solution using ultraviolet/visible absorption and fluorescence up-conversion spectroscopy have established very similar time constants for the depopulation of the respective MLCT manifold.<sup>3,6</sup> The structural changes in these systems were probed with femtosecond infrared<sup>4</sup> and iron K-edge XANES<sup>9</sup> spectroscopy, with the latter resembling precisely the kinetics of  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  that

underlie the femtosecond Raman data in Figure 3B (see Figure S2 in the Supporting Information). While the ligand cage expansion results in an increase in the polarizability of the compound (and therefore the Raman scattering cross section),<sup>5</sup> it also changes the spectral interference in the multiscattering region of the iron K-edge XANES spectrum.<sup>9</sup> Both techniques are therefore sensitive to atomic structure, albeit in different ways. With regard to core-level transitions, we note that the femtosecond XANES study with hard X-rays<sup>9</sup> is complementary to our femtosecond L-edge study with soft X-rays,<sup>13</sup> with the former probing changes in atomic structure and the latter probing changes in valence charge density.

A recent theoretical study by de Graaf and Sousa<sup>21</sup> on  $[\text{Fe}(\text{bpy})_3]^{2+}$  (where bpy = bipyridine) concludes that the <sup>1</sup>MLCT and <sup>3</sup>MLCT states substantially mix upon photoexcitation, leading to ultrafast initial spin-state conversion in this spin crossover compound while in the charge-transfer manifold.<sup>3</sup> Moreover, the theoretical calculations predict that the MLCT states' equilibrium position along the Fe—N bond coordinate is close to that of the low-spin ground state and that the metal-centered <sup>5</sup>T<sub>2g</sub> quintet state crosses the MLCT band near this equilibrium geometry. The resulting model as depicted in Figure 3C is along the lines of a previously proposed mechanism for ultrafast spin crossover in this class of systems.<sup>19</sup> Initial formation of the MLCT state(s) occurs without substantial ligand cage dilation, followed by depopulation of the charge-transfer manifold to ligand field state(s) with a time constant of  $\leq 100$  fs.<sup>2</sup> The evolution to the <sup>5</sup>T<sub>2g</sub> state proceeds with a similar time constant and triggers ultrafast structural dynamics along the Fe—N bond coordinate. Subsequent slower structural rearrangements occur on the time scale of  $\sim 10$  ps as the compound relaxes further toward the equilibrium structure within the <sup>5</sup>T<sub>2g</sub> state.<sup>2,5</sup> This model explains why the electronic/spin-state conversion probed by the L-edge transients in Figure 3A could display a shorter time constant than the structural dynamics associated with ligand cage dilation, probed via the FSRS measurements in Figure 3B; the system assumes high-spin <sup>5</sup>T<sub>2g</sub> character before structural relaxation sets in.

The current model of photoinitiated spin crossover with initial population of the MLCT manifold and subsequent formation of the high-spin state would be best tested by ultrafast L-edge spectroscopy with even higher temporal resolution. In principle, free-electron lasers (FELs) provide X-ray pulses of sufficiently short duration to allow for such measurements. The current timing systems limit the effective resolution of averaged transients to  $\geq 200$  fs, which is comparable to the time resolution of our experiment. However, single-shot experiments could not only exploit the short and intense X-ray pulses provided by X-ray FELs but would serve as a temporal cross-correlation between laser and X-ray pulses. We note that solvation dynamics on a subpicosecond time scale should influence the dynamics that underlie the transients in Figure 3A. This is particularly true while the system is in the charge-transfer manifold, where fluctuating electric forces are more effective in perturbing the excited valence charge distribution that is delocalized across the exposed ligand structure.<sup>22</sup> We expect the solvent influence on the ligand field states to be much weaker because they are metal-localized and thus sterically and dielectrically shielded by the ligand framework.<sup>23</sup> A static X-ray absorption spectroscopic study<sup>24</sup> in fluorescence yield mode has attributed unusual ground-state L-edge line shapes of aqueous  $[\text{Fe}(\text{bpy})_3]^{2+}$  to orbital interactions between the iron site and unoccupied oxygen orbitals

(however, fluorescence yield XAS signals may be obscured by substantial contributions from solvent absorption and emission as well as diffuse scattering). A systematic solvent study with  $< 50$  fs time resolution could aid in clarifying the role of the solvent in these excited-state dynamics.

In summary, the work presented herein constitutes the first ultrafast soft X-ray study of a molecule in solution and provides important experimental evidence on the mechanism of photo-induced spin-state conversion. More generally, these results underscore the power of ultrafast soft X-ray absorption spectroscopy for the study of electron and related spin dynamics of solution-phase systems with femtosecond time resolution. We believe that this method opens up a range of future opportunities to investigate ultrafast chemical reactions in molecules as well as functional nanoscopic systems under ambient conditions, providing unprecedented information on spin-states and valence electron distributions not accessible with visible spectroscopy or diffractive techniques. Finally, the prevalence of first-row transition-metal centers in many biological systems<sup>25</sup> and their important role in catalysis underscores the importance of this method for many other research areas to interrogate the evolution of electronic valence charge distribution.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Schematic of the femtosecond X-ray experiment. Compilation of transients acquired from ultrafast structural probes. Four-level rate equation model and initial condition. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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