

Elucidating Charge Delocalization in the High-Spin State of aqueous Fe^{II} Spin-Crossover Compounds via Time-Resolved Spectroscopy in the X-ray Water Window

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Abstract. We report the first time-resolved spectroscopy of aqueous solution in the X-ray water window. Nitrogen K-edge spectra, combined with *ab initio* calculations, reveal distinct charge delocalization, shedding light on the origins of ultrafast spin crossover.

Ultrafast core-level spectroscopy is unique in its ability to probe transient states of matter with chemical specificity of single atom species by exciting core-level transitions from highly localized initial states. In principle, this allows for multiple ‘views’ of valence charge density depending on the probed atomic species. Recent *ab initio* calculations of core-level spectra have produced results in good agreement with time-resolved experimental data [1], providing new interpretations with details on the transient structure and valence charge density of a molecular system.

Previously, we have employed ultrafast X-ray spectroscopy to probe the valence charge density of first-row-transition-metal complexes in solution via metal 2p spectroscopy [2,3]. The latter directly probes the spin-state and valence charge density of the metal and its immediate chemical environment on ultrafast time-scales by dipole $2p \rightarrow 3d$ transitions. Here we report time-resolved nitrogen K-edge spectroscopy of the nearest-neighbor atoms of the metal center to provide a ‘ligand view’ of the valence charge density dynamics. These measurements in the water window are compared with *ab-initio* DFT calculations.

These transition-metal complexes are polypyridyl Fe^{II} compounds that exhibit ultrafast spin-transitions from a singlet low-spin (LS) ground state to a quintet high-spin (HS) state following light-induced metal-to-ligand charge-transfer (MLCT). Understanding the microscopic origins of this unusually fast spin crossover (SCO) has led to substantial research efforts over the past decades [4]. The emergence of ultrafast X-ray spectroscopy has provided new tools for studying structural, electronic, and spin-state changes with femtosecond time-resolution. Ligand cage dilation in SCO compounds has been reported from picosecond EXAFS and ultrafast XANES spectroscopy [5,6]. We have compared spectral changes of Fe-2p spectra by

analogy to other model systems and charge-transfer multiplet calculations, concluding that the total valence charge on the metal center in iron-based SCO compounds is not changed appreciably but substantially rearranged between π -symmetric and σ -symmetric orbitals with a spin-state change of $\Delta S=2$ [7]. Early time-resolved studies suggested a direct relaxation from the $^1\text{MLCT}$ state to the HS state and fluorescence upconversion measurements suggest an ultrafast intersystem crossing to the $^3\text{MLCT}$ state before the HS state is populated [8]. Despite the detailed information on structural and electronic dynamics, the microscopic origins of direct MLCT manifold \rightarrow HS state relaxation are not clear.

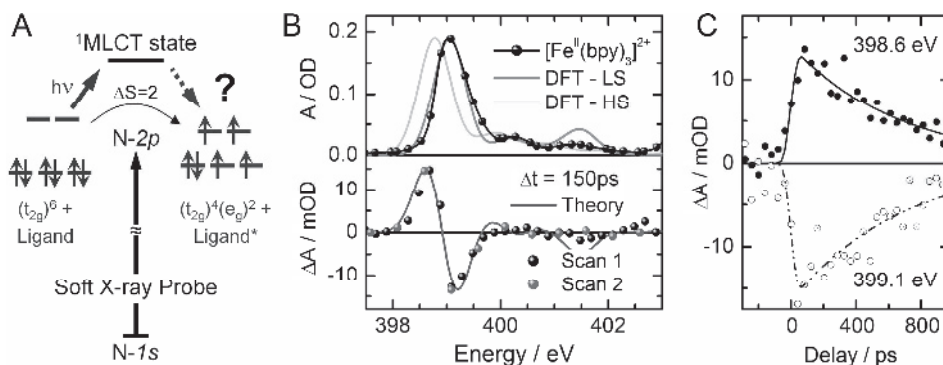


Fig. 1. A Probe scheme of time-resolved N K-edge spectroscopy. The metal-centered electronic configuration changes from low-spin to high-spin configuration, altering the metal-ligand interactions. B Static and transient spectra of $[\text{Fe}(\text{bpy})_3]^{2+}$. Ab initio data are plotted as solid lines. C Time delay scans at indicated probe energies.

Results from time-resolved nitrogen K-edge spectroscopy of the nearest-neighbor atoms of the metal center in aqueous $[\text{Fe}(\text{bpy})_3]^{2+}$ upon laser excitation are shown in Fig. 1B,C. In combination with *ab initio* DFT calculations, they elucidate the valence charge distribution of the HS state. The X-ray water window below the oxygen K-edge (~ 530 eV) provides sufficient solvent transmission. Transient x-ray absorption measurements were performed at the ultrafast x-ray facility of the Advanced Light Source. The $6 \mu\text{m}$ -thick liquid sample was held between 50-nm silicon nitride membranes and excited with 400 nm/70 fs pulses at 1 kHz. Differential absorption changes at the N K-edge were probed with a resolution of 0.4 eV at 2 kHz.

Fig. 1B displays the static (top) and transient spectrum (bottom) at the N K-edge. The main static absorption feature at 399 eV is the onset of the nitrogen $1s \rightarrow 2p$ transitions in the singlet ground state. The spectral changes after photo-induced LS \rightarrow HS interconversion become evident in the transient differential spectrum, exhibiting a bleaching signal at 399.1 eV and an induced absorption maximum 0.5 eV below in energy. The *ab initio* DFT calculations of the N-1s spectrum for the low-spin and high-spin are shown in Fig. 1B as blue and red lines, respectively. The ground-state spectrum is reproduced in all its features with remarkable resemblance to the experimental one. The difference of the calculated LS and HS spectra reproduces the transient differential spectrum very well. Note that calculations for HS transitions beyond 401.5 eV suggest a stronger transition than observed which accounts for the only larger discrepancy within the calculated energy range.

From the good agreement between theory and experiment we conclude that the DFT calculations represent the structure and valence charge distribution of the HS state well. Isosurfaces of the corresponding highest occupied molecular orbitals (HOMO & HOMO-1) and the lowest unoccupied orbital (LUMO) are plotted in Fig. 2. The HOMOs are of σ -symmetry and strongly mixed with $\sim 40\%$ population of both the Fe- $3d(e_g)$ and the ligand- σ^* electrons (cf. Fig. 1A). The LUMO shows substantial mixing of π -symmetric Fe- $3d(t_{2g})$ and ligand- π^* in contrast to the localized Fe- $3d(t_{2g})$ charge density of the low-spin ground-state. This also reflects the partial occupancy of the

Fe-3d(t_{2g}) orbitals in the HS state. The theoretical result can be related to the spin cross-over reaction: Photo-induced MLCT excitation promotes an electron from the fully occupied Fe-3d(t_{2g}) manifold into a ligand-delocalized π^* orbital. The resulting charge distribution is formally Fe $3d^5L^{-1}$ [9]. The HS state has strong charge-transfer character with delocalized metal 3d-valence electrons extending onto unoccupied ligand orbitals, partially resembling the charge-transfer character of the MLCT state, although orbital symmetries are different (π vs. σ -symmetry). We conclude that the strong charge-transfer character of the high-spin state facilitates MLCT \rightarrow HS relaxation (but not necessarily bypassing the other metal-centered ligand-field states).

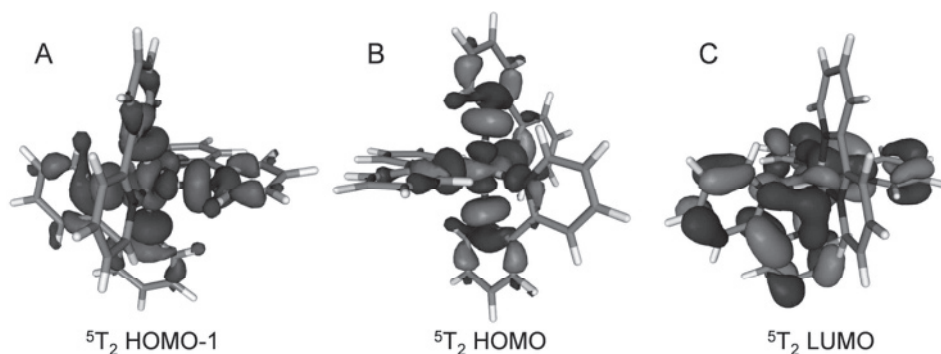


Fig. 2. Isosurfaces of valence electron density distributions for three orbitals of $[\text{Fe}(\text{bpy})_3]^{2+}$ in the high-spin 5T_2 state. **A** second to highest occupied molecular orbital, **B** highest occupied molecular orbital, and **C** lowest unoccupied molecular orbital.

In conclusion, we have used time-resolved core-level spectroscopy in the X-ray water window for the first time to measure transient N K-edge spectra, studying photo-induced SCO in a transition-metal complex in aqueous solution. Comparison with *ab initio* results provides new evidence for a strongly delocalized valence charge distribution despite 10% larger metal-ligand bond distances. The charge-transfer character of the transient high-spin state may facilitate ultrafast MLCT \rightarrow HS relaxation. We anticipate this type of solution-phase spectroscopy to soon be feasible with laser-based X-ray sources to study charge migration in solution on femtosecond time-scales and beyond.

References

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