

Ultrafast Dynamics of Single Crystal $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$

R. L. Field^{1,2}, L. Liu^{1,2}, C. Lu¹, Y. Jiang^{1,2}, W. Gawelda³, R. J. D. Miller^{1,2,a}

¹ Departments of Chemistry and Physics, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6, Canada

² Max Planck Institute for Structural Dynamics, Centre for Free Electron Laser Science, Bld. 99, Luruper Chaussee 149, 22761 Hamburg, Germany

³ European XFEL, Albert-Einstein-Ring 19, 22761 Hamburg, Germany

^a Email: dwayne.miller@mps.fel.de

Abstract: Transient absorption spectroscopy is used to characterize the ultrafast spin-transfer process in single crystal iron(II)-tris(bipyridine)-bis(hexafluorophosphate). Preliminary data analysis shows evidence of the formation of a high spin state and oscillatory signals on multiple time scales.

OCIS codes: (300.6530) Spectroscopy, ultrafast; (300.6250) Spectroscopy, condensed matter

1. Introduction

Transition metal complexes (TMC) are molecules in which central metal atoms or ions are bound to a surrounding array of organic molecules (ligands). Some TMCs have been observed to undergo a phenomenon known as spin crossover (SCO) where a transition from a low-spin (LS) state to a high-spin (HS) state is induced upon photoexcitation or temperature change.

Iron(II)-tris(bipyridine) (figure 1A, inset) is a complex that has been extensively studied with regard to the SCO phenomenon. Studies have used fluorescence up-conversion and transient absorption (TA) spectroscopy in the visible [1], UV [2], and X-ray regimes to elucidate the relaxation cascade leading to SCO in aqueous iron(II)-tris(bipyridine) ($[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$) [3]. Upon absorption of a 400 nm photon, the complex is excited from the LS ground state to a metal-to-ligand-charge-transfer singlet state (¹MLCT) from which it rapidly (20 fs) populates a triplet state (³MLCT) via intersystem crossing (ISC). The system then relaxes within 120 fs, again via ISC, to the HS quintet state from which the LS ground state is repopulated with a time constant of 665 ps [1,3]. This is illustrated schematically in figure 1A. Additionally, using a 520 nm pump, oscillations with a 254 fs period were observed in the excited state absorption (ESA) region of the UV TA spectrum [2]. These oscillations were ascribed to a vibrational wave packet on the HS surface.

The extremely fast spin transitions observed defy conventional descriptions of spin-orbit coupling. The nuclear motions coupled to the MLCT band are thought to play a role. Femtosecond electron diffraction studies are in progress to separate the nuclear dynamics from electronic effects. However, the excited state dynamics must be characterized within the single crystal environment needed for adequate spatial resolution to resolve this intriguing issue. Crystal contacts and the difference in medium polarizability could affect these dynamics. Here, we present preliminary data of the first TA studies on single crystal iron(II)-tris(bipyridine)-bis(hexafluorophosphate) ($[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$).

2. Experimental Methods

The data presented was collected using a home-built pump-probe spectrometer. The setup used a commercial Ti:Sapphire regenerative amplifier laser system (Coherent Legend) outputting 40 fs pulses at 1 kHz, centered at 800 nm. A fraction of the output beam was used to generate a 400 nm pump beam via second harmonic generation. This beam was passed through an acousto-optic pulse shaper used to compress the pulse to near the transform limit. The pulse duration was characterized using a home-built transient-grating frequency-resolved optical gating (TG FROG) spectrometer. A 52 fs pulse duration was retrieved. The 195 nJ excitation pulses were focused at the sample position, resulting in a fluence of 2.5 mJ/cm². A white-light continuum ranging from 360 nm to 625 nm was used as a probe. The continuum was generated using a small fraction of the 800 nm beam that was focused into a 2 mm thick CaF₂ window. The instrument response function was estimated to be 100 fs by fitting the measured Kerr effect signal in MeOH.

Optical choppers were used in both the pump and probe beams, with the probe beam being chopped at half the frequency of the pump beam. This allowed for the signal from pump scattering to be isolated and largely removed. All pump-probe data shown were corrected to compensate for group velocity dispersion in the probe beam. The $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$ samples were microtomed to 400 nm in thickness and placed on thin glass microscope slides for measurement.

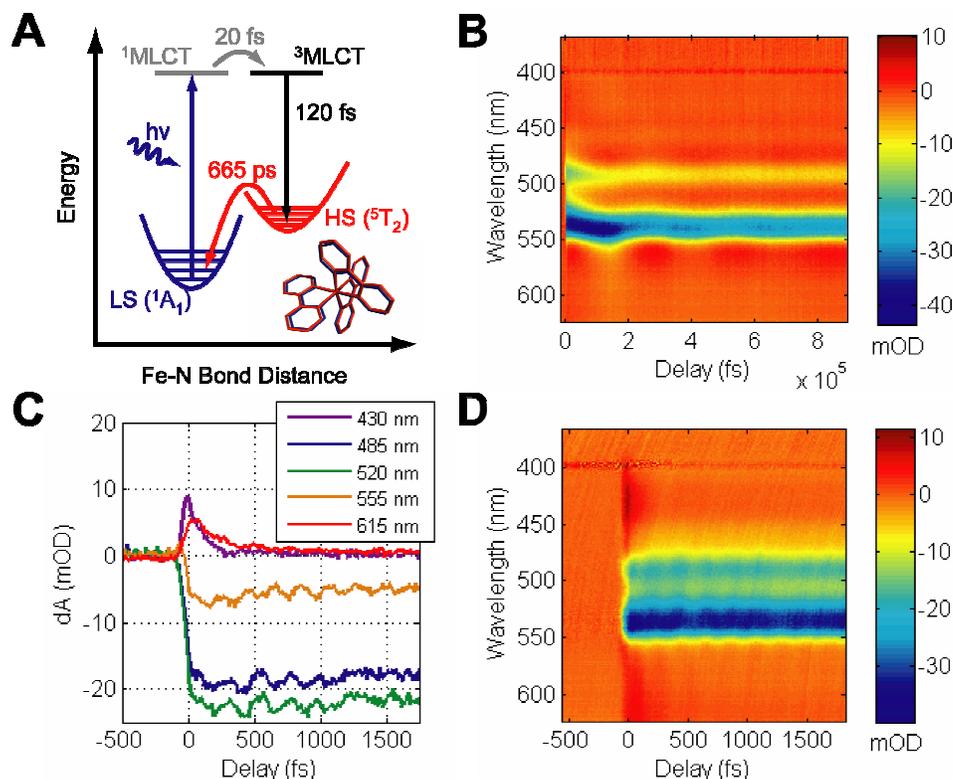


Fig. 1. (A) Schematic of relaxation of aqueous $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ after photoexcitation. Proposed mechanism and time scales are taken from [1,3]. Inset: Molecular conformation of $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ in LS (blue) and HS (red) states. (B) TA scan of single crystal $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$ from -10 ps to 900 ps. (C) Cross-sections of TA data at early times after excitation. (D) TA scan of single crystal $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$ from -500 fs to 1750 fs.

3. Results and Discussion

Preliminary TA data is shown for long and short times after excitation in figures 1B and 1D respectively. The data show generally good agreement with those reported in [1-3]. Spectral signatures of ESA are present between 400-460 nm and 560-625 nm, and a strong GSB signal is present from 460-560 nm. The ESA at 430 nm can be fit well with a single exponential with a time constant of ~ 116 fs. This is consistent with the decay time of the $^3\text{MLCT}$ state given in [1,3]. The ESA at 615 nm shows a small, positive offset after the initial decay, suggesting population of the HS state. The long-time scan (figure 1B) shows that the GSB signal persists well beyond 850 ps. However, the sample almost fully recovers to the ground state within 1 ms, as evidenced by the negligible background signal before the zero delay. In contrast to [1], no GSB is observed at wavelengths below 450 nm.

Cross-sections of the short time scan (Figure 1C), show clear oscillations in the GSB signal. Fourier analysis of these oscillations gives a period of ~ 230 fs. Although the cause of these oscillations is yet to be determined, we note that the period is similar to that assigned to vibrational wave packets under solution phase conditions (254 fs) in [2]. In the long-time scan, large oscillations with a period of ~ 290 ps are observed. This period is consistent with oscillations of an acoustic phonon in the bulk crystal under certain boundary conditions. Further research is in progress to elucidate the origin of the observed oscillations, and to fully understand the differences in the ultrafast dynamics between the single crystal and aqueous phases of $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$.

4. References

- [1] W. Gawelda, A. Cannizzo, V. T. Pham, F. Mourik, C. Bressler, M. Chergui, "Ultrafast Nonadiabatic Dynamics of $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ in Solution," *J. Am. Chem. Soc.* **129**, 8199-8206 (2007).
- [2] C. Consani, M. Prémont-Schwarz, A. ElNahas, C. Bressler, F. Mourik, A. Cannizzo, M. Chergui, "Vibrational Coherences and Relaxation in the High-Spin State of Aqueous $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$," *Angew. Chem.* **121**, 7320-7323, (2009).
- [3] C. Bressler, C. Milne, V. T. Pham, A. ElNahas, R. M. van der Veen, W. Gawelda, S. Johnson, P. Beaud, D. Grolimund, M. Kaiser, C. N. Borca, G. Ingold, R. Abela, M. Chergui, "Femtosecond XANES Study of the Light-Induced Spin Crossover Dynamics in an Iron(II) Complex," *Science*, **323**, 489-492, (2009).