

Femtosecond Electron Diffraction Study of the Spin Crossover Dynamics of Crystalline $[\text{Fe}^{\text{II}}(\text{bpy})_3][\text{PF}_6]_2$

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Abstract: The atomic motions involved in spin crossover dynamics of crystalline $[\text{Fe}^{\text{II}}(\text{bpy})_3][\text{PF}_6]_2$ are investigated by femtosecond electron diffraction (FED). The experiment was performed by an ultrabright femtosecond electron source using 3.0×10^5 electrons per pulse with 400 fs temporal instrument response function.

OCIS codes: 320.7130 Ultrafast processes in condensed matter, including semiconductors; 320.7120 Ultrafast phenomena

1. Introduction

Spin crossover (SCO) dynamics, a conversion from low spin (LS) ground state to high spin (HS) excited state (or visa versa) due to temperature change or light absorption^[1,2], has been extensively studied for its potential applications in optical memory and photo switchable devices^[3]. Among the compounds with SCO dynamics, the group of ferrous Fe(II) metal compounds with an FeN_6 coordination environment is the largest^[4]. After the Fe(II) compounds absorb light, the LS $^1\text{A}_1(\text{t}_{2g}^6)$ ground state changes to the HS $^5\text{T}_2(\text{t}_{2g}^4\text{e}_g^2)$ excited state by 2 paired electrons in the t_{2g} sublevel entering the e_g sublevel as unpaired electrons. Fig. 1 shows that the Fe-N bond distance in the HS state is elongated by $\sim 0.2 \text{ \AA}$ because of the transfer of two electrons to the antibonding e_g and loss of π -backbonding from the t_{2g} ^[5].

Iron(II)-tris(bipyridine) ($[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$) is a model system for Fe(II) metal compounds. Aqueous iron(II)-tris(bipyridine) has been well studied by X-ray absorption spectroscopy^[6] and femtosecond fluorescence and transient absorption^[5]. Fig. 2 shows the population mechanism of quintet states in Fe(II) metal compounds is identified as a sample two intersystem crossing process, $^1\text{MLCT}$ - $^3\text{MLCT}$ - $^5\text{T}_2$ from the initially excited state^[6]. However, the SCO behavior of crystalline iron(II)-tris(bipyridine) is still unknown. Here we use FED diffraction to study the structural dynamics of $[\text{Fe}^{\text{II}}(\text{bpy})_3][\text{PF}_6]_2$ SCO in crystalline form. We use our ultrabright UED source to closely follow the dynamics of the Fe-N bonding coordinate from the LS to the HS state.

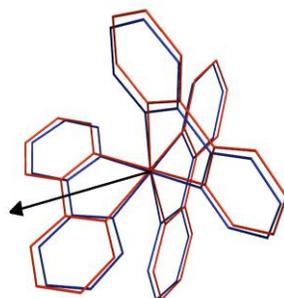


Fig. 1. For aqueous $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$, the Fe-N bond length of low spin state is 1.97 \AA ^[7] and it increases 0.2 \AA to high spin state^[5].

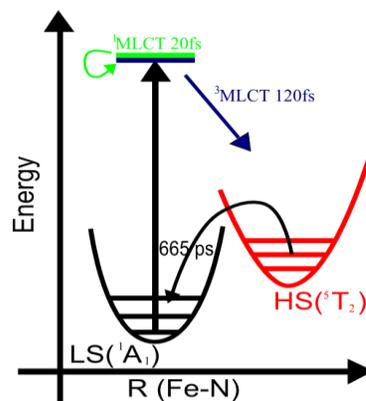


Fig. 2. Simplified energy level of aqueous $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ is determined by femtosecond fluorescence and transient absorption^[6]

2. Experimental Setup

In this study, a 95 keV hybrid DC-RF electron source is employed to generate ultrabright femtosecond electron pulses as an ultrafast structural probe^[9]. We generate 3.0×10^5 electrons per pulse with a spot size of $300 \mu\text{m}$ FWHM and a repetition rate of 10 Hz. To investigate the SCO dynamics of $[\text{Fe}^{\text{II}}(\text{bpy})_3][\text{PF}_6]_2$, we employed 60 fs pump pulses centered at 400nm. At the sample position, the pulse energy was $8 \mu\text{J}$ per pulse and the pulse size was $520 \mu\text{m}$. The incident excitation fluence was $1.31 \text{ mJ}/\text{cm}^2$.

3. Result and discussion

Fig. 3 shows preliminary results of the study. The diffraction pattern of the LT state of $[\text{Fe}^{\text{II}}(\text{bpy})_3][\text{PF}_6]_2$ is shown on Fig.3A. The important point is the high quality of the diffraction data for an organic system. We have numerous crystal orientations and have conducted in parallel fs transient absorption studies of these same single crystals to provide complementary information on the excited state dynamics to enable separation of the electronic and nuclear aspects to the spin cross over dynamics. Fig. 3B shows the 100 ps dynamics observed for just one diffraction order with the full structural dynamics and improved signal to noise on the atomically resolved structural dynamics to be reported at the meeting.

Further FED study of $[\text{Fe}^{\text{II}}(\text{bpy})_3][\text{PF}_6]_2$ is still in progress.

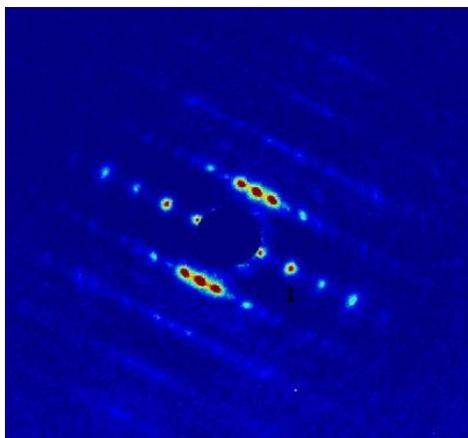


Fig. 3A. Diffraction pattern of LT state of $[\text{Fe}^{\text{II}}(\text{bpy})_3][\text{PF}_6]_2$ was obtained at room temperature. Single pulse electron number was 3.0×10^5 , and 10 electron pulses were used to generate one diffraction pattern.

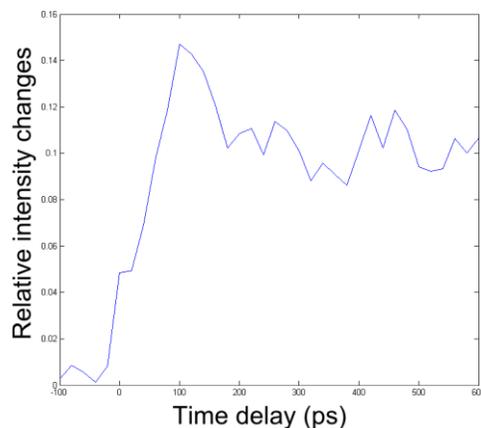


Fig.3B. Relative intensity change of selected diffraction spot 1 from Fig.3A. A 100 ps period dynamical process is shown. The excitation fluence was $1.31 \text{ mJ}/\text{cm}^2$

4. References

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