

## Ultrafast Photo-Switching of Molecular Magnet Revealed by 100-Picosecond Time Resolved XAFS

Understanding and controlling dynamic magnetic properties has attracted much research interest in recent years. However, in disordered magnetic systems, it is particularly hard to study the spin dynamics directly with conventional optical methods. The transient spin state dynamics coupled with electronic and structural modifications were directly observed for the first time in a disordered system using a pulsed hard X-ray beam from PF-AR.

Molecular magnetic systems such as nanomagnets and biological systems have attracted much research interest in recent years [1]. In disordered magnetic systems, where the spin system does not have macroscopic magnetization, it is crucial to directly observe the transient spin states to aid in the understanding and controlling of the dynamic magnetic properties. In studies of ultrafast spin dynamics, pico- and femtosecond timescales are now accessible with advanced optical pump-probe measurement using two ultrafast lasers. However, it is not a trivial task to deconvolute the dynamics of the spin state from the transient optical signal. Although the magneto-optical effect has been applied to macroscopic magnetization, it is difficult to apply in disordered magnetic systems. To overcome these difficulties, we utilized a pulsed hard X-ray as a probe for the dynamics of the inner-atomic transitions.

The pump-probe time-resolved X-ray absorption fine

structure (XAFS) experiments were conducted at the undulator AR-NW14A [1]. A Ti:Sapphire femtosecond laser, synchronized with the x-ray pulse, was used as a pump source. The XAFS spectra were collected in the fluorescence mode using a fast scintillation detector.

The sample was composed of aqueous solutions of the divalent iron phenanthroline complex ( $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ ), where an iron atom is coordinated to six nitrogen atoms and is in the low-spin (LS) configuration in the ground state. This complex exhibits strong absorption around 430 nm due to a metal-to-ligand charge transfer. Based on the optical spectrum, the photoreactive intermediate state has been assumed to be a quintet high-spin (HS) state generated as a result of the spin crossover (SC), and has been called a photo-excited HS state. However, no direct evidence for the transient changes in spin state has been reported, even though the spin dynamics are the essence of ultrafast SC phenomena.

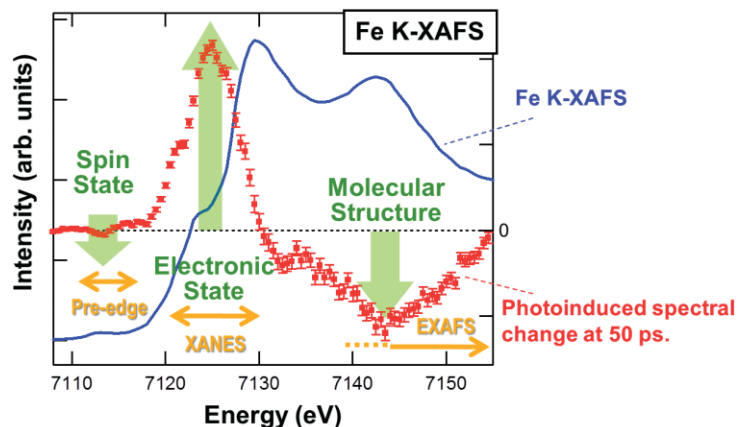


Figure 1  
Fe K-XAFS of  $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$  in the aqueous solution (solid line) and the transient difference 50 ps after the laser excitation (square).

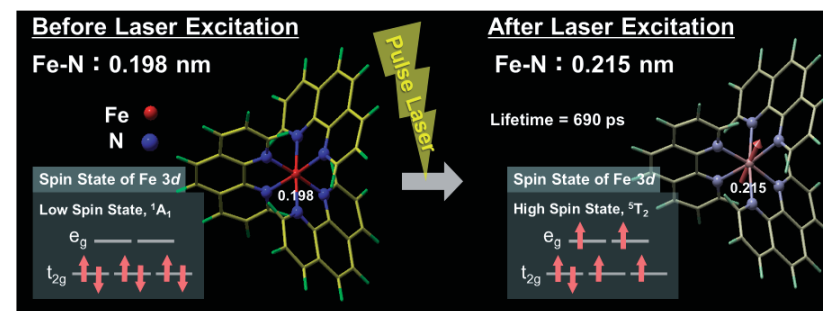


Figure 2  
Photoinduced ultrafast spin crossover reaction accompanied by the structural change.

The Fe  $K$ -edge of XAFS can be classified into three regions: pre-edge, X-ray absorption near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS). These mainly contain information about the spin state, the electronic state, and molecular structure, respectively. The pre-edge peaks reveal information about the spin state of the 3d electrons in the metal ion as the peaks are attributed to the  $1s$ - $3d$  quadrupole transition. Therefore, time-resolved XAFS uniquely probes the spin dynamics. In addition to this, the electronic and molecular configurations can be tracked simultaneously for a particular excited state. This is the greatest advantage of using hard X-rays, as electronic and molecular structural modifications can be studied in depth, provided there is a redistribution of the 3d electrons.

The ground state of the Fe  $K$ -edge XAFS spectrum and transient difference at 50 ps are shown in Fig. 1. The photoinduced SC transition was directly observed by detecting the evolution of the  $1s$ - $3d$  transition in the pre-edge region. In addition, large modifications in the electric state were observed in the XANES region due to 3d electrons occupying an antibonding  $e_g$  orbital in the photo-excited HS state. Furthermore, in the EXAFS region, spectral changes are caused by modulation of the resonant effect in the multiple scattering of photoelectrons when the bond length of Fe-N is increased.

Spectral analyses by reference samples and EXAFS analysis using the Fourier transform method yielded detailed dynamic information of transient SC transitions and variations in molecular structure as shown in Fig. 2. By time-resolved XAFS, the SC transition, with a lifetime of 690 ps, from  $^1A_1$  LS to  $^5T_2$  HS states accompanied by the molecular structural change with the Fe-N bond elongation of 0.017 nm has been directly observed on a picosecond timescale [2].

### REFERENCES

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### BEAMLINE

AR-NW14A

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