

Spin-Crossover Dynamics in Solution Studied with a Newly-Developed Picosecond Time-Resolved Fluorescence XAFS Technique

The experimental strategy and setup for a new picosecond time-resolved fluorescence X-ray absorption fine structure technique (TR-XAFS) is presented. X-ray positional active feedback combined with a figure-of-merit (FOM) scan of the laser beam position is employed as a key technique. It is shown that pump-probe TR-XAFS using the pulsed X-ray structure of synchrotron radiation sources is a powerful tool for investigating the dynamics of the electronic state and molecular structure of non-crystalline samples. A TR-XAFS study of a photo-induced spin-cross-over reaction of the tris(1,10-phenanthroline)iron(II) complex in water is presented.

Recently, time-resolved X-ray measurements are becoming powerful tools for exploring structural dynamics in the fields of materials and biological sciences [1-7]. Time-resolved X-ray absorption fine structure (TR-XAFS) can be used to provide information on the electronic state and molecular structure of non-crystalline samples with a temporal resolution equal to the pulse-width of the X-rays.

In order to conduct successful TR-XAFS measurements in the pump-probe mode, a precise spatial and temporal overlap of the X-ray and laser pulses is essential. However, maximizing the incident X-ray beam intensity makes it difficult to maintain spatial overlap during the experiment, since a high intensity X-ray beam leads to a large heat load, mainly on the monochromator and mirror. This then destabilizes the X-ray beam position. In order to maintain the spatial overlap during data collection, the X-ray beam position must be stabilized using active positional feedback. At the same time, the spatial overlap must be reproducibly tuned dur-

ing the data collection period to avoid mismatch of the X-ray and laser beam positions due to positional drift of the two beams. The most effective check is a laser positional scan using the photo-induced X-ray signal itself as a figure of merit (FOM) of the spatial overlap. We have newly developed an effective TR-XAFS measurement system equipped with stable alignment of the X-ray and laser beam positions at AR-NW14A [8]. Figure 1 shows the experimental layout for liquid TR-XAFS [9]. The 794 kHz X-ray pulses from the undulator are delivered to a Si(111) double crystal monochromator (DCM) with a pulse duration of 60 ps (rms). The X-ray position is monitored with a position-sensitive ion chamber (PSIC) downstream of the DCM, and its output is converted to a positional signal. The beam position is stabilized by a feedback system which monitors the difference between the positional signal and the standard beam position. The feedback system stabilizes the X-ray beam position and intensity to within 1 μm and 1% respectively.

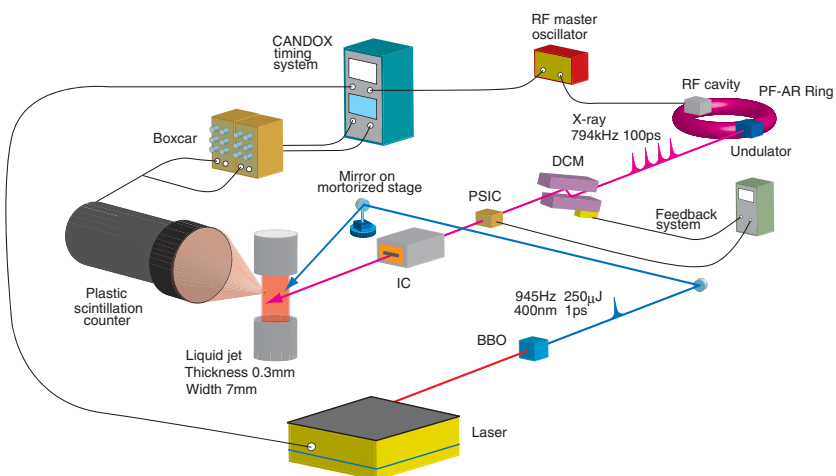


Figure 1
The experimental setup for liquid TR-XAFS at AR-NW14A. The 945 Hz frequency and the delay time between the laser and X-ray pulses was generated by CANDOX systems which consist of frequency dividers, IQ modulator phase shifters, and digital counters with less than 3 ps jitter.

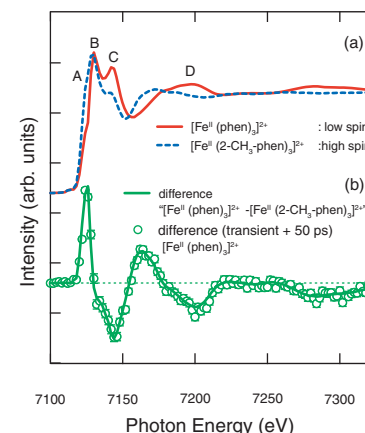


Figure 2
(a) Fe K-edge XANES spectra of a 50mM aqueous solution of $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ (solid line) and $[\text{Fe}^{\text{II}}(2\text{-CH}_3\text{-phen})_3]^{2+}$ (dashed line). (b) The static difference spectrum between $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ and $[\text{Fe}^{\text{II}}(2\text{-CH}_3\text{-phen})_3]^{2+}$ (solid line). The transient difference spectrum between before excitation (-1.3 μs) and after excitation (+50 ps) of $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ (circle).

The position of the laser beam is controlled by a mirror on a motorized stage near the sample. The two motorized stages enable spatial overlap of the X-ray and laser beams to be achieved by FOM scanning using the X-ray signal itself. The spatial overlap is optimized in this manner to within 0.1 mm. The details of the setup and the sample environment are described in Ref. [9].

This novel TR-XAFS system was readily applied to study the photo-induced spin-cross-over reaction of the tris(1,10-phenanthroline)iron(II) complex in water. Photo-excitation of the Metal to Ligand Charge Transfer (MLCT) band at 400nm induces a high spin state 5T_2 . Before photo-irradiation, the spin state of this compound is the low spin state 1A_1 . The decay time of the relaxation from the high spin state to the low spin state has been estimated to be ~680 ps based on a spectroscopic measurement [10]. Figure 2 (a) shows the steady-state XAFS spectra of $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ in the low-spin state, and also of $[\text{Fe}^{\text{II}}(2\text{-CH}_3\text{-phen})_3]^{2+}$ which is used as a high-spin reference sample. The difference spectrum of these states is shown in Fig. 2 (b) (solid line). The open circles, which show the transient difference spectrum between the low-spin $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ and photo-excited intermediate species observed at 50 ps after laser excitation, perfectly coincide with the reference low-spin/high-spin difference spectrum. This result clearly shows that the photo-excited intermediate species at 50 ps after laser excitation is very similar to the high-spin

reference sample. The steady-state difference spectrum is scaled by 0.06, which accounts for the 6% photo-excitation yield of the ground-state species in solution by laser irradiation.

Features A and B arise from the 1s to 4p transition. Features C and D are attributed to multiple scattering processes of the photo-electron. Spectral feature B directly reflects the change in distance between the Fe and N atoms, since the Fe 4p orbital is hybridized with the N 2p orbital [4, 6]. Therefore, the intensity enhancement of the differential spectrum at this feature suggests that photo-induced elongation of the Fe-N bond distance accompanies the spin transition.

We have demonstrated that X-ray positional feedback of the monochromator and FOM scanning of the laser beam position are powerful tools for successful TR-XAFS measurements. We are now applying this powerful technique to other photo-reactions of metal complexes which are related to photo-catalysis and solar-energy conversion.

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