

Development of Time-Resolved Soft X-Ray Absorption Spectroscopy for Photoreactions in a Liquid Cell

Time-resolved soft X-ray absorption spectroscopy (TR-SXAS) is an effective technique to elucidate elementary processes of photoreactions on metal complexes, organic molecules, and biomolecules. To apply this technique to various photochemical reactions in solutions, we have developed the TR-SXAS system including a liquid cell by the combination of laser pump and soft X-ray probe pulses. We have observed photo-induced spin transition of iron phenanthroline ($[\text{Fe}(\text{phen})_3]^{2+}$) in aqueous solution by using the TR-SXAS. The lifetime of the relaxation process from the high spin state induced by the laser excitation to the ground state has been determined from the ligand side using the nitrogen K-edge.

Time-resolved soft X-ray absorption spectroscopy (TR-SXAS) is an effective method to elucidate elementary processes of photoreactions such as relaxation and charge transfer processes on metal complexes, organic molecules, and biomolecules since the soft X-ray region below 2 keV includes K-edges of typical light elements and L-edges of transition metals. Photochemical processes of liquid and thin film samples with time scales of sub-nanoseconds have been revealed by the TR-SXAS technique by the combination of laser pump pulses and synchrotron radiation (SR) probe pulses with the pulse width of 10–100 ps. The TR-SXAS measurements using a liquid cell would be applied to the photoreactions of chemical and biological samples in solutions because the sample environments such as temperature, pH,

electrode potential, *etc.* are controlled by sealing liquid samples with membranes. However, there has been no significant development in more than 10 years after the first report [1] due to the experimental difficulties.

Recently, soft X-ray absorption spectra of liquid samples have been measured by using a transmission-type liquid cell, where the liquid layer is sandwiched between two Si_3N_4 membranes and the liquid thickness is precisely controlled by adjusting the helium pressure outside the liquid cell [2]. In this study, we have developed the TR-SXAS system using this transmission-type liquid cell at BL-13A for observing various photoreactions of chemical and biological samples in solutions. We have applied the TR-SXAS system to the photoreactions of iron phenanthroline ($[\text{Fe}(\text{phen})_3]^{2+}$) aqueous

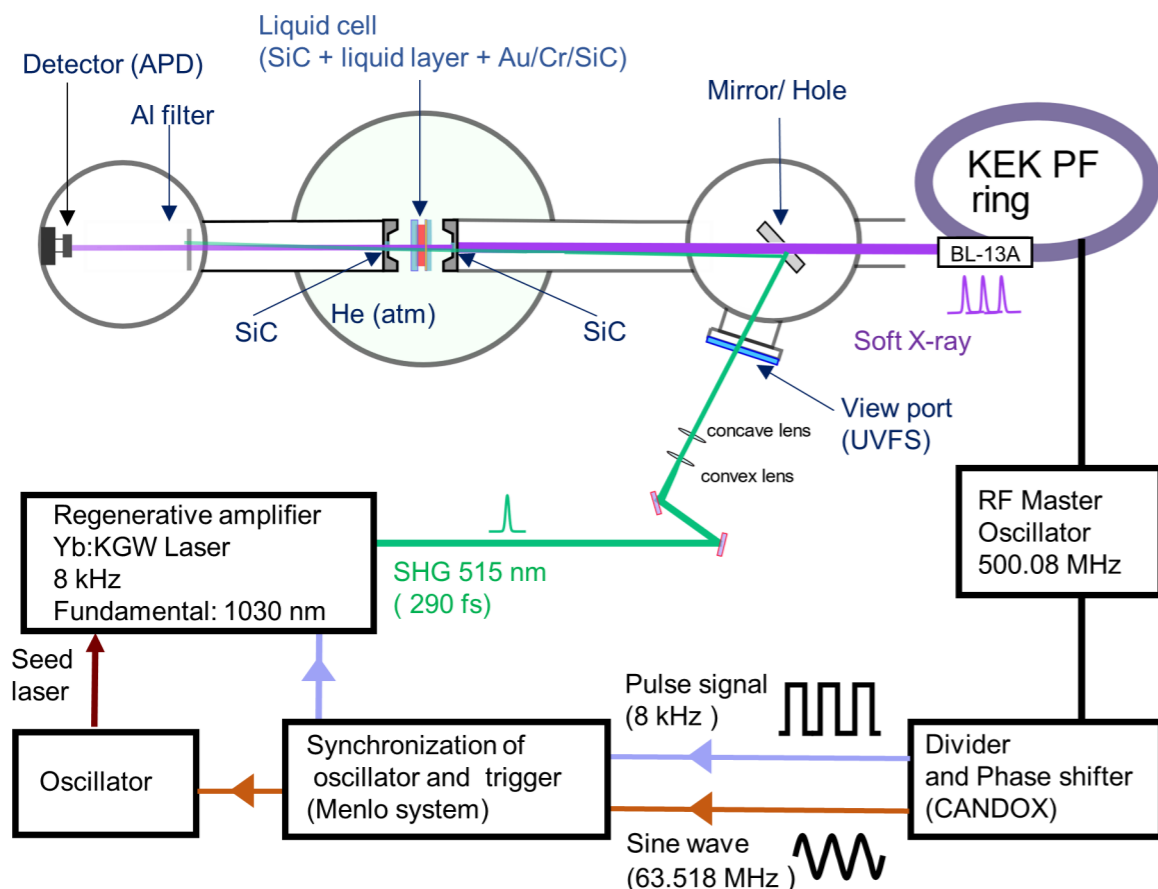


Figure 1: The schematic view of the TR-SXAS system developed at BL-13A.

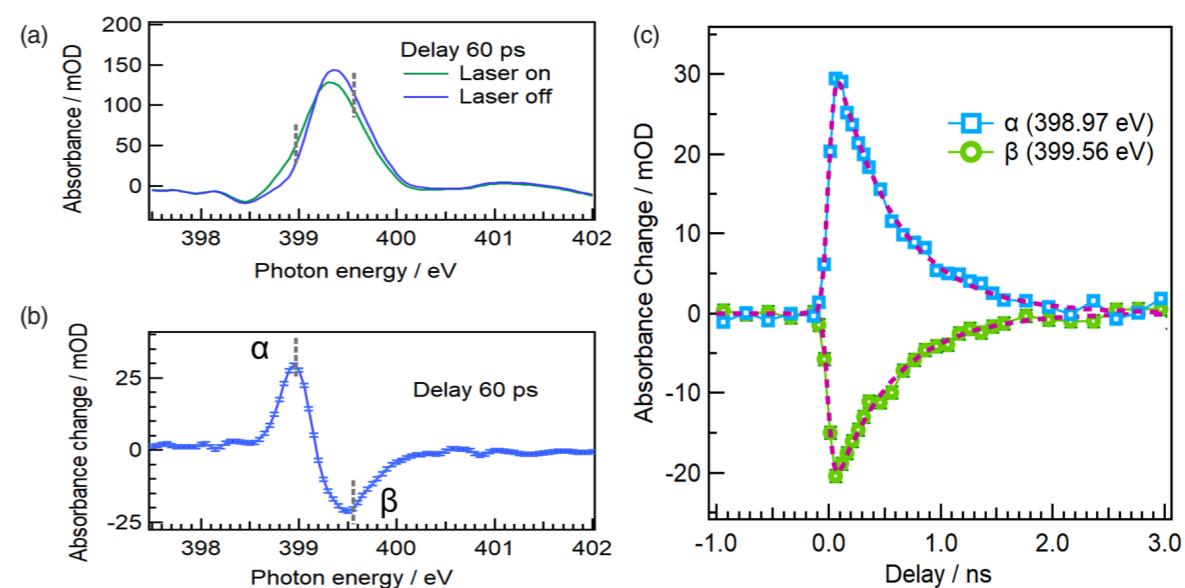


Figure 2: (a) N K-edge XAS spectra of $[\text{Fe}(\text{phen})_3]^{2+}$ aqueous solution in the low spin state (laser off) and the high spin state (laser on). (b) The differential spectrum of the high spin state relative to the low spin state. (c) The temporal evolutions of the peak intensity differences at α (398.97 eV) and β (399.56 eV) shown in (b).

solutions, which are typical photo-induced spin transition processes ($S = 0$, low spin $\rightarrow S = 2$, high spin), from the ligand side of the iron complexes using the nitrogen K-edge [3].

Figure 1 shows a schematic view of the TR-SXAS system developed at soft X-ray beamline BL-13A. The SR probe pulses were taken from single bunches of the hybrid mode. The excitation laser pulse was a second harmonic generation of Yb:KGW laser (515 nm, 8 kHz), which is focused onto the liquid cell by a mirror with a center hole. The SR pulses passed through the hole in the mirror and was irradiated the liquid cell almost coaxially with the laser pulses. The overlap of the laser and SR was matched at the sample position with an accuracy of $29 \times 29 \mu\text{m}^2$. Laser pulses were electrically synchronized with SR pulses by a trigger clock delay system (84DgR5C03, CANDOX) and a frequency synchronization module (Menlo systems), enabling us to scan the delay within the time range of 10^{-12} – 10^{-6} s.

The liquid cell consists of a liquid layer sandwiched between gold coated SiC and bare SiC membranes. A gold coated SiC membrane was used for preventing the laser irradiation damage such as coloration and adhesion and shows nine times more durability with the laser irradiation compared to the bare SiC membrane. Transmitted soft X-ray pulses through the liquid cell were detected by using an avalanche photodiode (APD) with high sensitivity. An aluminum filter ($t = 150$ nm) was placed in front of the detector for removing the laser pulses.

Figure 2(a) shows the N K-edge spectra of a 50 mM aqueous solution of $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ at the ground state (low spin) and the laser excited state (high spin) after 60 ps from the laser irradiation. The peak around 399.5 eV is assigned as the transition of N 1s electrons to $\text{C}=\text{N} \pi^*$

unoccupied orbitals. Figure 2(b) shows the differential spectrum of the high spin state relative to the low spin state, indicating the lower energy position of the high spin state. Figure 2(c) shows the temporal evolutions of the peak intensity differences shown in Fig. 2(b) obtained by scanning the delay time of SR pulses from laser pulses. The lifetimes of the relaxation processes from the high spin states to the ground states are about 550 ps at the energy positions of both α (398.97 eV) and β (399.56 eV). This result is close to that obtained by the central metal side from the time-resolved Fe K-edge measurement in the hard X-ray regions [4].

The TR-SXAS utilizing the liquid cell is expected to be applied to *Operando* measurements of biological samples such as pigment-protein complexes in photo-system to reveal the processes of energy and charge transfer during photoreactions.

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BEAMLINE

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