

Operando Time-Resolved Soft X-ray Absorption Spectroscopy for Photoexcitation Processes of Metal Complexes in Solutions

Fumitoshi Kumaki,¹ Masanari Nagasaka,^{2,3,*} Ryo Fukaya,^{1,4} Yasuaki Okano,² Shohei Yamashita,^{1,4} Shunsuke Nozawa,^{1,4} Shin-ichi Adachi,^{1,4} Jun-ichi Adachi^{1,4,*}

¹ Department of Materials Structure Science, School of High Energy Accelerator Science, SOKENDAI, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

² Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

³ Department of Functional Molecular Science, School of Physical Sciences, SOKENDAI, Myodaiji, Okazaki 444-8585, Japan

⁴ Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

1 Introduction

Operando time-resolved soft X-ray absorption spectroscopy (TR-SXAS) has the advantage to investigate photochemical reactions of metal complexes in solutions since soft X-ray region below 2 keV include K-edges of C, N, and O and L-edges of 3d transition metals. The TR-SXAS experiment at the Fe L-edge has been applied to the spin-state conversion of the iron polypyridyl complex in aqueous solution after the photoexcitation [1]. On the other hand, there are few reports on the TR-SXAS measurements of the ligands in metal complexes using the N K-edge compared to that of the central metal using the Fe L-edge.

Recently, we have developed the liquid cell for soft X-ray absorption spectroscopy (XAS) in transmission mode by controlling the liquid thickness precisely from 20 to 2000 nm [2]. In this study, we have developed the TR-SXAS system including our transmission-type liquid cell by synchronizing the soft X-ray probe pulses from the synchrotron radiation with the laser pump pulses and have measured the photoexcitation process of iron phenanthroline ($[\text{Fe}(\text{phen})_3]^{2+}$) aqueous solutions from the ligand side by using N K-edge XAS [3].

2 Experiment

The TR-SXAS system was developed at the soft X-ray beamline BL-13A. The experiments were performed during the hybrid mode of the PF ring. The laser pump pulses (515 nm, 290 fs) from the second harmonic generation of a Yb:KGW crystal laser (Pharos, Light Conversion) were focused on the liquid cell by using a center-holed aluminum mirror. Since soft X-rays pass through the hole of the mirror, the laser pulses were almost coaxially introduced to the liquid cell with soft X-ray pulses. A trigger clock delay system and a frequency synchronization module were used for the synchronization of the laser pump pulses with soft X-ray probe pulses. In the liquid cell, the liquid layer was sandwiched between the gold-coated SiC and the bare SiC membranes. XAS spectra were measured by detecting soft X-ray intensities with an avalanche photodiode detector. An aluminum filter was installed in the front of the detector for removing the laser beam.

3 Results and Discussion

Figure 1(a) shows the N K-edge XAS spectra of $[\text{Fe}(\text{phen})_3]^{2+}$ aqueous solutions in the ground (low spin) and photoexcited (high spin) states with the 60 ps delay time of soft X-ray probe pulses from the laser pump pulses. The C=N π^* peak in the high spin state is shifted to the lower photon energy compared to that in the low spin state. Figure 1(b) shows the difference spectrum of the high spin state from the low spin state obtained from the XAS spectra shown in Fig. 1(a). The difference spectrum clearly shows the increase of the peak at the lower energy side and the decrease of that at the higher energy side.

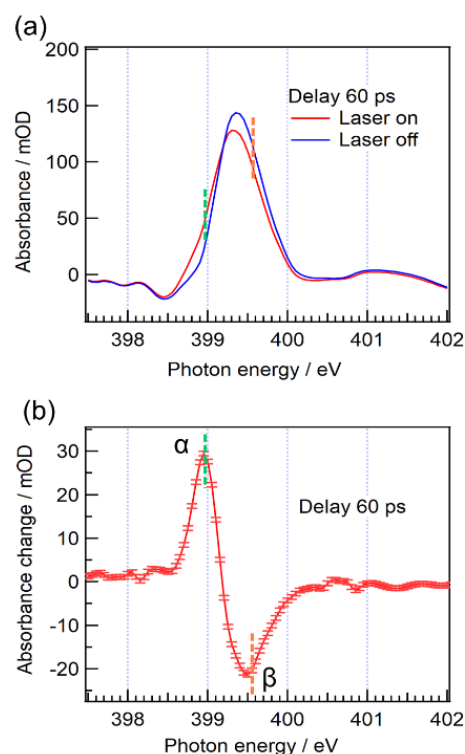


Fig. 1: (a) N K-edge XAS spectra of $[\text{Fe}(\text{phen})_3]^{2+}$ aqueous solutions in the ground state (laser off) and the photoexcitation state (laser on). (b) The difference spectrum of the photoexcitation state relative to the ground state obtained from the XAS spectra shown in (a).

Figure 2 shows the temporal evolution of the peak intensity difference at the energy position of α (398.97 eV), where the delay time of the soft X-ray probe pulses was scanned relative to the laser pump pulses. The time constant from the N K-edge XAS is 550 ± 12 ps, which is close to that obtained by the Fe K-edge XAS (690 ps) [4]. The slight deviations in the time constants might be caused by the differences in the absorption edges or the different thermal environments.

Since liquid cells are in an atmospheric condition and can control the reaction condition such as liquid temperature, electrode potential, etc., the present TR-SXAS system would be applied to various chemical and biological phenomena in solutions, such as photocatalytic reactions, photoelectrochemical reactions, and photochemical reactions of antenna pigment-protein complexes in photosystems.

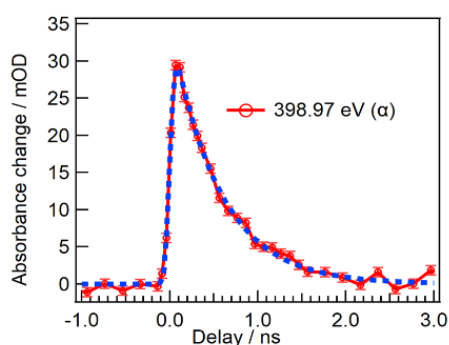


Fig. 2: The temporal evolution of the peak intensity difference at the energy position of α (398.97 eV) shown in Fig. 1(b).

References

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* nagasaka@ims.ac.jp

* jun-ichi.adachi@kek.jp