

Femtosecond time-resolved X-ray absorption spectroscopy by a multichannel spectral detection using a hard X-ray free electron laser

Yuki Obara,¹ Tetsuo Katayama,² Yoshihiro Ogi,³ Takayuki Suzuki,^{1,4} Naoya Kurahashi,⁵ Shutaro Karashima,⁵ Yuhei Chiba,¹ Yusuke Isokawa,¹ Tadashi Togashi,⁶ Yuichi Inubushi,⁶ Makina Yabashi,⁶ Toshinori Suzuki,^{3,5} and Kazuhiko Misawa^{1,4}

¹Department of Applied Physics, Tokyo University of A & T, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

²Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

³Molecular Reaction Dynamics Research Team, RIKEN Center for Advanced Photonics, 2-1 Hirosawa, Wako 351-0198, Japan

⁴Interdisciplinary Research Unit in Photon-nano Science, Tokyo University of A & T, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

⁵Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

⁶RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

obayu@cc.tuat.ac.jp

Abstract: We have performed the first time-resolved X-ray absorption spectroscopy using the SPring-8 Angstrom Compact Free Electron laser (SACLA) with a dual X-ray beam dispersive detection method. The test compound is aqueous 0.5 M ammonium iron(III) oxalate trihydrate solution. The photoexcited iron complex exhibits a red shifted iron K-edge with a rise time constant of 260 fs. The X-ray absorption difference spectra between the presence and absence of pump pulses are independent of time delay between 1.5 and 100 ps, indicating that the photoexcited species is long-lived.

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1. Introduction

Time-resolved X-ray absorption spectroscopy (TRXAS) is useful for investigating the ultrafast electronic and structural dynamics of materials, because it enables element-selective observation of electronic states and the local geometrical structures in real time [1]. TRXAS is becoming more accessible with the advent of X-ray free electron lasers (XFELs) such as Linac Coherent Light Source (LCLS) and SPring-8 Angstrom Compact Free Electron laser (SACLA). The first TRXAS experiment using LCLS [2] monitored the total X-ray fluorescence as a function of the photo-energy of monochromatized X-ray radiation. However, the efficiency of XFELs using monochromatized X-ray radiation is limited by considerable spectral fluctuations and low repetition rates. Recently, we proposed an alternative approach, i.e., direct X-ray absorption spectroscopy with a dual-beam dispersive detection method, which exploits the broadband radiation from an unseeded FEL [3].

Here we present the first femtosecond TRXAS of $\text{Fe(III)(C}_2\text{O}_4)_3^{3-}$ in aqueous solution by multichannel spectral detection. Although the compound has been investigated in previous TRXAS studies using a laser-plasma X-ray source [4], the iron oxalate complex [5, 6] was selected because its photo-induced dynamics are not well understood. The data acquisition, storage, and analysis were fully optimized in the new approach, and the pump-induced absorbance change was successfully detected up to the order of 10^{-3} .

2. Experimental

Femtosecond TRXAS was performed using the 400 nm second harmonic of a Ti:sapphire laser with a commercial regenerative amplifier supplemented by a home-made double-pass power amplifier. Since the repetition rate of the 400 nm laser was 10 Hz, the 400 nm pump pulses excited the sample at every other X-ray probe pulse emitted from SACLA at 20 Hz. The pulse energy at the sample position was 1.1 mJ. The temporal jitter between the laser pulse and X-ray pulses was determined as 166 ± 8 fs. Considering the 400 nm laser pulse width of 100 fs, the FWHM of the instrumental response function (IRF) was estimated as 200 fs.

An aqueous solution of 0.5 M ammonium iron(III) oxalate trihydrate was discharged into air from a fused silica capillary with an inner diameter of 100- μm at a discharge flow rate was 5 mL/min. All experiments were performed at room temperature under atmospheric pressure.

The spectra were measured by a dispersive spectrometer comprising an ultra-precisely configured elliptical mirror, a flat silicon (111) crystal as a diffraction grating, and a multi-port charge-coupled device detector. The spectral range and resolution of the spectrometer was 67 eV and 1 eV, respectively. To compensate for pulse fluctuation induced by stochastic processes in the self amplified stimulated emission XFEL, the signal and reference spectra were simultaneously measured in the dual beam scheme [3]. Averaging over 500 shots reduced the spectral fluctuations by two orders of magnitude. The absorption spectra with and without pump pulses were individually averaged over at least 500 shots and their difference calculated as $\Delta A^{\text{ave}} = A_{\text{w/pump}}^{\text{ave}} - A_{\text{w/o pump}}^{\text{ave}}$.

3. Results

Figure 1(a) shows the difference X-ray absorption spectra of the $\text{Fe(III)(C}_2\text{O}_4)_3^{3-}$ complex at several pump-probe time delays in the 7.10–7.26 keV energy region. Each difference spectrum is merged from five spectra measured at different undulator settings, and is calculated from absorption spectra with and without the pump pulses, accumulated over 10000 shots. Figure 1(b) shows the temporal dependence of the absorbance change integrated over 7.120 ± 0.006 keV. Allowing for the IRF of 200 fs, least squares fitting of the experimental data yields a rise time of 260 ± 50 fs. The spectral profile is essentially invariant, even at time delays as high as 100 ps.

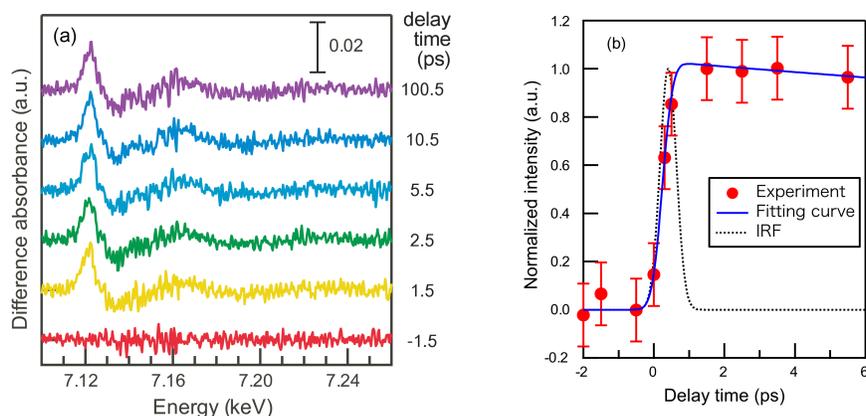


Fig. 1. (a) Time-resolved difference absorption spectra in the 7.10–7.26 keV X-ray energy region. (b) Temporal dependence of the absorbance change integrated over 7.120 ± 0.006 keV. Solid line is the result of least squares fitting to the experimental data.

4. Discussion and conclusion

Our result indicates a similar geometrical structure of the ground state complex, and a long lifetime (exceeding 100 ps), of the transient species. Light-induced electron transfer is considered to reduce the Fe(III) complex to the Fe(II) complex [5]. Indeed, the photodynamics of $\text{Fe(III)(C}_2\text{O}_4)_3^{3-}$ may proceed by intramolecular ligand-metal electron-transfer [6]. An alternative proposal is photodissociation while the complex maintains its +3 oxidation number [4]. In any case, the observed red-shift of the K-edge indicates that the electron density of the excited Fe(III) is higher than in the ground state. The limited experimental evidence in our study precludes an assignment of this transient species. To understand the chemical nature of this compound, we require further information from transient infrared absorption spectra, lifetime measurements and kinetic analysis, and improved time resolution in TRXAS. In conclusion, we performed the first time-resolved X-ray absorption spectroscopy by a multichannel spectral detection using SACLA.

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