2C11 時間分解X線吸収分光による鉄オキサレート錯体の光化学反応の研究

(京大院理[1], 理研[2], 東京農工大[3], JASRI[4], Univ. of Chem. and Tech.[5])
○鈴木 俊法[1], 小城 吉寛[2], 小原 祐樹[3], 片山 哲夫[4], 鈴木 喜一[1], Liu Suet Yi[2],
Bartlett Nathaniel[2], 倉橋 直也[1], 唐島 秀太郎[1], 富樫 格[2], 犬伏 雄一[4], 矢橋 牧名[2],
三沢 和彦[3], Slavicek Petr[5]

Femtosecond time-resolved X-ray absorption spectroscopy of photochemical reaction of iron oxalate complex in aqueous solution

(Kyoto U., RIKEN, Tokyo U. of Agri. and Tech., JASRI, U. of Chem. and Tech.)
Toshinori Suzuki, Yoshihiro Ogi, Yuki Obara, Tetsuo Katayama, Yoshi-Ichi Suzuki,
Suet Yi Liu, Nathaniel Bartlett, Naoya Kurahashi, Shutaro Karashima, Tadashi Togashi,
Yuichi Inubushi, Makina Yabashi, Kazuhiko Misawa, and Petr Slavicek

X-ray absorption spectroscopy (XAS) interrogates inner-shell electrons strongly bound to nuclei, and it enables element-specific investigation of the electronic and geometrical structures of molecules. The ionization energy of an inner-shell electron, observed as the absorption edge, varies with the atomic number and exhibits a “chemical shift” that reveals the oxidation state and/or chemical bonding of the atom. Time-resolved XAS (TRXAS), which is based on the pump and probe method, utilizes the unique performance of XAS for studies of short-lived chemical species and transient states of matter. In this talk, we present a TRXAS study using SACLA with the total X-ray fluorescence yield (TFY) method. The focus of this work is the photochemistry of ferrioxalate, $[\mathrm{Fe(III)(C_2O_4)_3}]^{3-}$, in aqueous solution. Although the overall photochemical reaction of $[\mathrm{Fe(III)(C_2O_4)_3}]^{3-}$ in aqueous solution is known to be a photoreduction reaction, which is often expressed as $2[\mathrm{Fe(III)(C_2O_4)_3}]^{3-} + h\nu \rightarrow 2[\mathrm{Fe(II)(C_2O_4)_2}]^{2-} + 2\mathrm{CO_2} + \mathrm{C_2O_4}^{2-}$, the elementary steps of this reaction have not yet been elucidated.

Figure 1 schematically shows our experimental setup for TFY-TRXAS. The sample is an aqueous 0.1 M solution of ammonium iron(III) oxalate trihydrate, $\mathrm{(NH_4)_3[Fe(C_2O_4)_3]\cdot 3H_2O}$. The solution was pressurized using a gradient-flow high performance liquid chromatography (HPLC) pump and was discharged from a fused silica capillary with a 50 μm inner diameter. The central photon energy of the hard X-ray pulse was tuned for the Fe K-edge by adjusting the accelerator conditions and the undulator of SACLA. The X-ray bandwidth was decreased to 1.3 eV (FWHM) using a Si(111) X-ray monochromator. The monochromatized X-ray beam was focused on the sample solution by a pair of Kirkpatrick-Baez mirrors, which produced a focal spot diameter of 1.5 μm. The repetition rate of SACLA was 30 Hz. The X-ray fluorescence from the sample was detected using a multi-port charge-coupled device (MPCCD) sensor. The 268 nm excitation pulse (100 fs) was the third

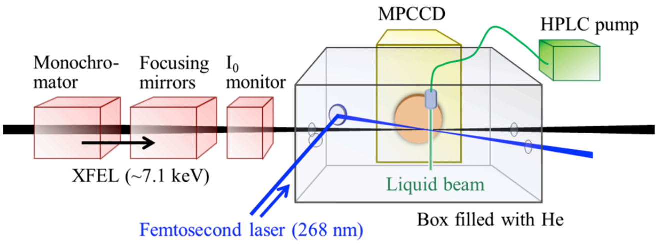

FIG. 1 Schematic diagram of our experimental setup.

harmonic of a Ti:sapphire laser, generated using two BBO crystals for frequency doubling and mixing. The pump beam was focused on the sample using an axisymmetric lens (*f* = 300 mm). The cross-correlation between the UV and X-ray pulses is estimated as 200 fs considering the timing jitter between SACLA and the synchronized laser, as well as an estimated UV pulse duration.

Figure 2(a) shows the observed X-ray absorption spectra of aqueous 0.1 M ammonium iron(III) oxalate trihydrate solution at selected pump-probe delay times. The spectra reveal a clear change upon UV irradiation, particularly in the region from the K-edge up to 7180 eV. The K-edge exhibits a distinct red-shift after the generation of transient species by the 268 nm pulse, which indicates that the K-edges of the transients are lower in energy than that of the parent. Figure 2(b) shows the difference spectra calculated from the observed spectra shown in Figure 2(a), obtained by subtracting the spectrum measured at -3 ps from those measured at positive time delays. Close examination of the blowup view of the K-edge region, presented as Figure 2(c), reveals that the magnitude of the red-shift of the K-edge subsequently diminishes within 3 ps. More detailed analysis of the time profiles yielded two time constants of 140 fs and 3 ps.

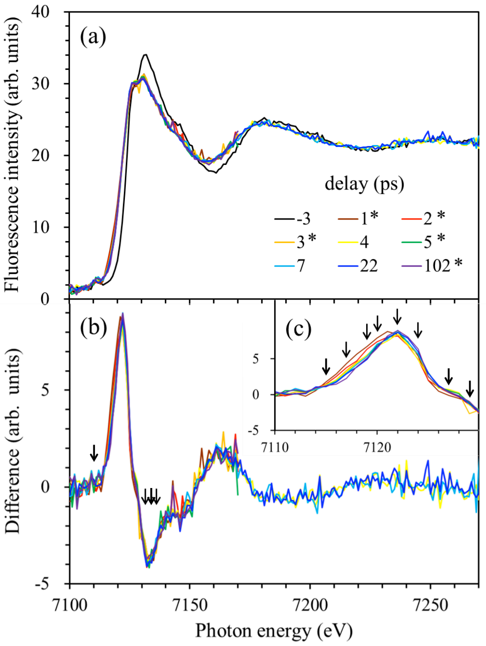

FIG. 2 (a) Time-resolved X-ray absorption spectra of an aqueous $[Fe(III)(C_2O_4)_3]^{3-}$ solution observed at various time delays. The excitation wavelength is 268 nm. (b) Difference spectra between those obtained at positive delay times and that measured at a delay of -3 ps. (c) Expanded views of the reddest region of the difference spectra, revealing a blue-shift.

The most robust experimental observation is the red-shift of the Fe K-edge energy. We have estimated the K-edge energies (the binding energies of the 1s electron) of different species using DFT with a dielectric continuum model and concluded the product is Fe(II) complex. The EXAFS feature also suggested dissociation of a metal-ligand bond. From the experimental and theoretical results, we concluded that UV excitation induces a ligand to metal charge transfer to reduce Fe(III) to Fe(II), and then the C-C bond of the oxalate ligand dissociates. This produces CO_2 fragment first and subsequently CO_2^-. Thus, finally $[Fe(II)(C_2O_4)_2]^{2-}$ complex is created in 3 ps.

Reference Structural Dynamics, 2, 034901 (2015)