

Femtosecond time-resolved X-ray absorption spectroscopy using SACLA: Dual beam direct absorption and X-ray fluorescence

X-ray absorption spectroscopy (XAS) interrogates inner-shell electrons strongly bound to nuclei, enabling element-specific investigations of the electronic and geometrical structures of molecules. The ionization energy of an inner-shell electron, which is observed as the absorption edge, varies with the atomic number and exhibits a “chemical shift,” revealing the oxidation state and/or chemical bonding of the atom. An X-ray absorption spectrum also displays oscillatory features, termed the extended X-ray absorption fine structure (EXAFS), in the post-edge region owing to scattering of a photoelectron by neighboring atoms. EXAFS analysis provides the bond lengths around the atom of interest. SACLA generates an X-ray pulse as short as 10 fs with a pulse energy on the order of μJ , opening new avenues for femtosecond X-ray spectroscopy. Considering the low repetition rates of SACLA (30 – 60 Hz), time-resolved XAS (TRXAS) is one of the best-suited techniques.

We started our project supported by the “X-ray Free Electron Laser Priority Strategy Program” of the Ministry of Education, Culture, Sports, Science, and Technology of Japan (MEXT) in 2012, and have succeeded in TRXAS using a dual beam multiplex detection method as shown in Fig. 1 in 2013 [1,2]. In this method, a transmission grating splits a hard X-ray pulse (FWHM = 30 eV) into two equally intense beams. One of which is transmitted through a sample solution and used as a signal beam. The signal beam and the reference beam, which does not pass through the sample, are spectrally dispersed and simultaneously recorded on a shot-to-shot basis. From these signal and reference spectra, an X-ray direct absorption spectrum is obtained for the entire

30 eV spectral bandwidth of the X-ray pulse.

While the simultaneous measurement of an absorption spectrum for a 30-eV wide energy region provides a high efficiency, the direct absorption method inherently suffers from low sensitivity. Therefore, we have implemented TRXAS using X-ray fluorescence detection method, which provides an order of magnitude higher detection sensitivity than the dual beam method (Fig. 2) [3]. X-ray radiation from SACLA is monochromatized to 1.3 eV using a Si(111) X-ray monochromator, and focused on the sample using Kirkpatrick-Baez mirrors down to a spot diameter of 1.5 μm . A sample is photoexcited with a femtosecond UV pulse (268 nm) generated by a Ti:sapphire regenerative amplifier, and a transient X-ray absorption spectrum of the excited species is measured by scanning the photon energy of the time-delayed X-ray pulse while monitoring X-ray fluorescence with a multi-port charge-coupled device sensor.

Figure 3(a) shows the transient X-ray absorption spectra, which are observed using X-ray fluorescence, of aqueous 0.1 M ammonium iron(III) oxalate trihydrate solution at selected pump-probe delay times. The spectra reveal a clear change that occurs instantaneously upon UV irradiation, while the subsequent spectral evolution is rather small. The difference spectra shown in Fig. 3(b) were calculated from the spectra shown in Fig. 3(a) by subtracting the spectrum measured at -3 ps from those measured at positive time delays. The difference spectra reveal that the largest spectral change upon UV irradiation is the red-shift of the *K*-edge. Magnification of the *K*-edge region, shown in Fig. 3(c), reveals that the

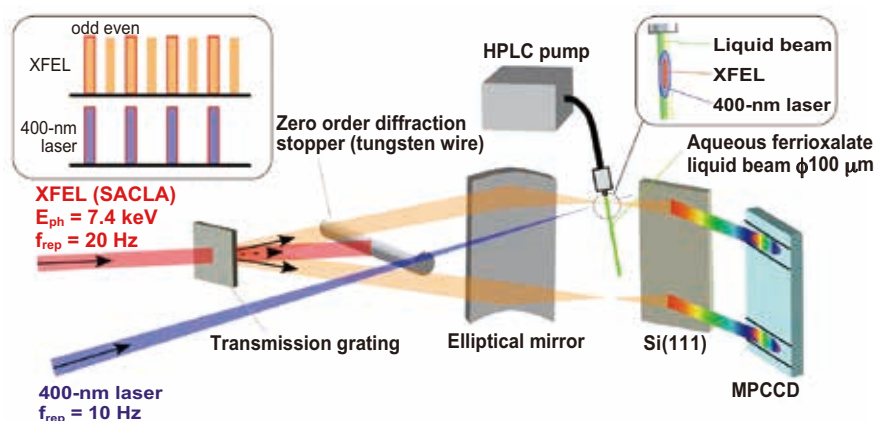


Fig. 1. Dual beam multiplex detection method.

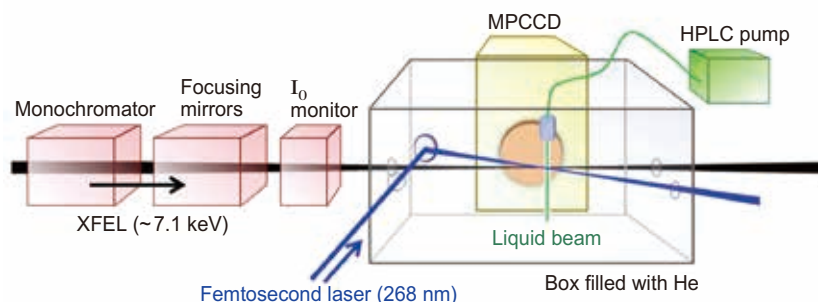


Fig. 2. X-ray fluorescence method.

red-shift of the *K*-edge diminishes by more than 2 eV within 3 ps.

From the transient spectra, we extracted the spectrum of photochemical reaction product. The red-shift of Fe *K*-edge indicates that Fe(III) is reduced to Fe(II) by the ligand-to-metal charge transfer, and

the reduction of the oscillatory feature in the product spectrum suggests that one ligand dissociates within 5 ps after the pump pulse. This method can be used to study the carrier dynamics and redox reactions of various samples. We are also planning to improve the sensitivity further for biological samples.

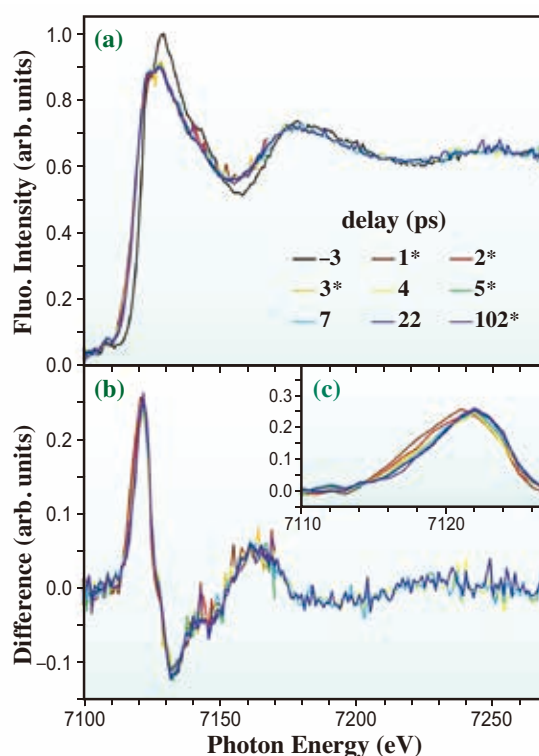


Fig. 3. (a) Time-resolved X-ray absorption spectra of an aqueous $[\text{Fe}(\text{III})(\text{C}_2\text{O}_4)_3]^{3-}$ solution observed at various time delays. Excitation wavelength is 268 nm. (b) Difference spectra between positive delay times and -3 ps. (c) Enlarged view of the reddest part of the difference spectra, which reveals that the magnitude of the red-shift diminishes within 3 ps.

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References

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