Development of light-modulated XAFS spectroscopy

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The light-modulation method was applied to XAFS spectroscopy as a useful tool for electronic and structural studies of light-excited states. The visible light for electronic excitation was modulated by an optical chopper and the concomitant change in the X-ray absorbance was extracted by a lock-in amplifier. It is essential to reduce any noise arising from several sources, especially those generated by the X-ray monochromator. Fe and Co *K*-edge XANES and EXAFS spectra were measured using the present approach for spin transition compounds. The light-modulated XAFS method is found to be applicable to systems with an excited-state ratio of less than several percent. Detailed discussion is also given concerning quantitative measurements, including the signal amplitude and phase shift information.

Keywords: XAFS; photomodulation method; light-induced excited-state spin transitions; spin-crossover complex; relaxation.

1. Introduction

Structural and electronic change upon photoexcitation has attracted much attention and various methods have been developed to study this subject. X-ray absorption fine structure (XAFS) spectroscopy is one of the most useful tools for obtaining direct information on local structures and electronic properties, especially in the case of materials without long-range ordering. However, it trails behind other spectroscopies in the study of short-lived photoexcited states.

There are two serious inherent problems in the application of the XAFS method to photoexcited states. One problem is the large difference between the absorption coefficients of visible light and X-rays. In general, the penetration depth of X-rays of a coloured sample is much larger than that of visible light, and the sample thickness appropriate for the visible-light absorption is much thinner than that for the XAFS measurement. Another problem is that the X-ray absorption energy is almost the same for ground and photoexcited states. Therefore conventional XAFS measurements of short-lived photoexcited species under continuous light irradiation often result in a spectrum that is hardly distinguishable from the ground state, and extraction of information of the photoexcited state is very difficult. Thus, it is essential to find or create a suitable system in which the photoexcited state is dominant. In fact, several techniques have been developed for the studies of photoexcited states. The rapid-flow experiment combined with an intense laser irradiation is one such technique with a microsecond resolution, as Thiel *et al.* (1993) performed for a diplatinum complex and Chance *et al.* (1993) performed for biological samples. For longer-lifetime species the energy-dispersive XAFS method is available (Dent, 2002; Chen *et al.*, 1999). Pump–probe time-resolved XAFS measurements were first performed by Mills *et al.* (1984) using X-ray and laser pulses, and more recently by Chen (2001), and allows the study of the photoexcited transient states with a time resolution of 14 ns. They are indeed powerful, but very elaborate and time-consuming, even when using state-of-the-art techniques and facilities. Furthermore, the contribution of the remaining ground-state species cannot be avoided. A simpler and more effective method should be developed for the study of photoexcited species.

The photomodulation method, or the phase-sensitive detection method, is one of the more popular methods for detecting small spectral changes (Lakowicz, 1983). It is widely used in microwave, IR and UV/vis absorption and fluorescence spectroscopies, in which light is modulated periodically, making the signal follow the modulation to be detected by a lock-in amplifier, with only the synchronizing component being extracted. It allows weak signals to be obtained on strong backgrounds without any subtraction of spectra. The purpose of the present study is to apply the photomodulation method to XAFS spectroscopy by modulating the visible excitation light and detecting the concomitant X-ray absorbance change for two light-induced spin-transition compounds. It is expected to be one of the more useful tools for photoexcitation studies, as mentioned previously by Emura & Maeda (1995). Hereafter we will call this method the 'light-modulation' method in order to distinguish the pumping visible light from the probing X-rays.

2. Principle and experimental

The principle of the light-modulated XAFS method is schematically shown in Fig. 1. Light irradiation on a photoactive sample causes some change in the X-ray absorbance A at a certain photon energy due to the changes of the electronic state and/or of the structure. If the excitation light is modulated, the X-ray absorbance should follow the modulation, and that can be detected by a lock-in amplifier, giving a difference spectrum between the ground and the photoexcited states by plotting the outputs as a function of X-ray energy. It is more reliable than the conventional method in which the ground-state spectrum is subtracted from the photoexcited-state spectrum.

The experimental set-up for the fluorescent X-ray yield mode is shown in Fig. 2. In principle, the transmission mode is also compatible with the light-modulated method; in practice, however, this does not work well because the sample concentration appropriate for visible-light absorption is too low to obtain reliable XAFS spectra in the transmission mode. Visible light from the source was modulated using an optical chopper (Oriel Instruments) and introduced to the sample through a PET window of the cryostat. The light source was either a

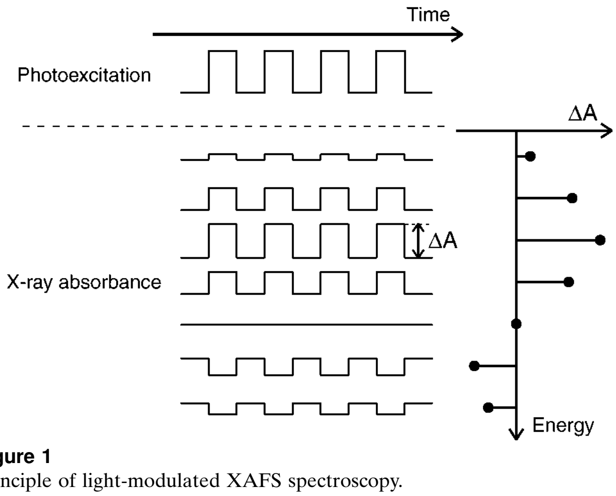

Figure 1
Principle of light-modulated XAFS spectroscopy.

Xe-arc lamp [350–700 nm using an IR cut filter (Kenko HA-50), supplying a power of 300 W, and a total light power of ~1 W] or a Nd-doped solid-state CW laser (532 nm, ~60 mW), with a spot diameter of 3–5 mm at the sample position. Incident X-rays, I_0, were also introduced simultaneously with a smaller spot size (typically <1 mm × 1 mm), and the fluorescent X-rays were detected using a Lytle detector (Lytle *et al.*, 1984). The signal from the Lytle detector, I_f, was divided into two after pre-amplifying with a picoammeter (Keithley 427). One signal was introduced directly to a V/F converter (VFC, Tsuji Electronics NVF-02/02B) as the normal I_f signal, and the other was introduced to a lock-in amplifier (NF Corporation 5600A, typical sensitivity $\simeq$ 10 mV) to extract and amplify the synchronizing component with the visible-light modulation, followed by conversion of the output range from −10–10 V to 0–10 V, and then to a V/F converter. Finally, all signals, I_0, I_f and $I_{\rm mod}$ (the output from the lock-in amplifier, *i.e.* the light-modulated component of I_f), were introduced to a counter/timer (Ortec 974) and then to a PC.

Owing to the large difference between the absorption coefficients of X-rays and visible light, the light-modulated XAFS signal intensity becomes very small. Thus, much effort was needed to keep the noise level as low as possible. The Lytle detector was set in a soundproof box on a heavy base with vibration insulators made of silicone rubber, and connected to the picoammeter with a low-noise cable to avoid vibration and electric noises, respectively. It was also essential to avoid signal fluctuations at each step of the energy scanning caused by the monochromator. For this purpose, the signal counter was controlled by an external timer circuit, waiting until the signal became stable (for about 15 s when the time constant of the lock-in amplifier was 1 s). This elongated the measurement time, but improved the spectrum quality drastically.

Light-induced spin-transition compounds, $Fe(pic)_3Cl_2{\cdot}C_2H_5OH$ (Sorai *et al.*, 1976, 1977), **1**, and $K_{0.4}Co_{1.3}[Fe(CN)_6]{\cdot}4.2H_2O$ (Sato *et al.*, 1997; Yokoyama, Ohta *et al.*, 1998), **2**, were prepared according to the literature. They both show spin transitions from low-spin (LS) to high-spin (HS) states induced by heat or light at low temperatures, as summarized in Fig. 3, accompanied by large changes of electronic and local structures. They were used in powder form dispersed on Scotch tape.

Fe and Co K-edge XAFS experiments were carried out at beamlines 9A (Nomura & Koyama, 1999) and 12C (Nomura & Koyama, 1989) at the Photon Factory, Institute of Materials Structure Science (KEK-PF; operation energy 2.5 GeV, stored current 450–300 mA), using double-crystal Si(111) monochromators detuned by ~40%, and at BL01B1 (Uruga *et al.*, 1999) at SPring-8, Japan Synchrotron Radiation Research Institute (operation energy 8 GeV, stored current 70–50 mA), using a double-crystal Si(111) monochromator and Rh-coated mirrors. The incident and transmitted X-rays were detected by ion chambers filled with N_2 and the fluorescent X-rays by a Lytle detector filled with Ar. Two types of Lytle detector were used in the experiments: a conventional type with three grids and an applied voltage of 45 V, and a fast type with seven grids and an applied voltage of 300 V recently developed by Suzuki *et al.* (2002). Temperature was controlled using a closed-cycle He cryostat and an electric furnace monitored with an Si diode thermometer. In the light-modulated measurements, the detection phase at the lock-in amplifier was shifted to give a maximum signal at the photon energy where a large positive change was expected. The shifted value was usually small, and changing the X-ray energy for phase determination affects only the signs of the obtained spectra. Data acquisition times were 2 and 8 s per point for the conventional XANES and EXAFS measurement, respectively, and 20 s per point for the light-modulated spectra.

The light-induced difference of the fluorescent X-ray intensity, ΔI_f, is related to the lock-in-amplifier output, $I_{\rm mod}$, with the following correction,

$$\Delta I_f = \left(\frac{s\,[V]}{10\,[V]} \times 2 \times 2^{1/2} \times 2\right) I_{\rm mod}, \qquad (1)$$

where s denotes the sensitivity of the lock-in amplifier. The three factors in (1) represent corrections of the amplification and output as

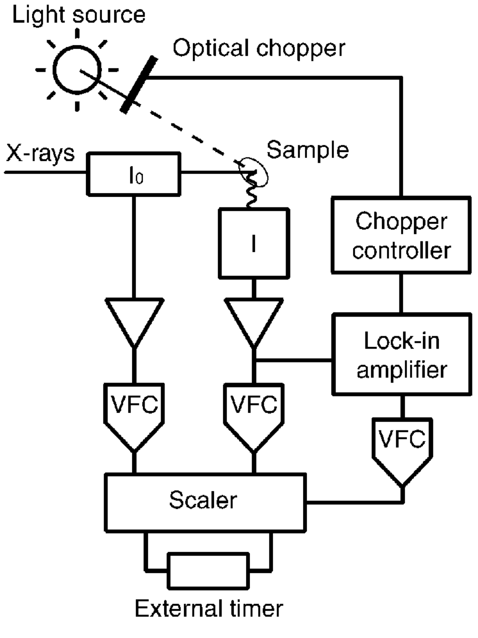

Figure 2
Set-up for the light-modulated XAFS measurement.

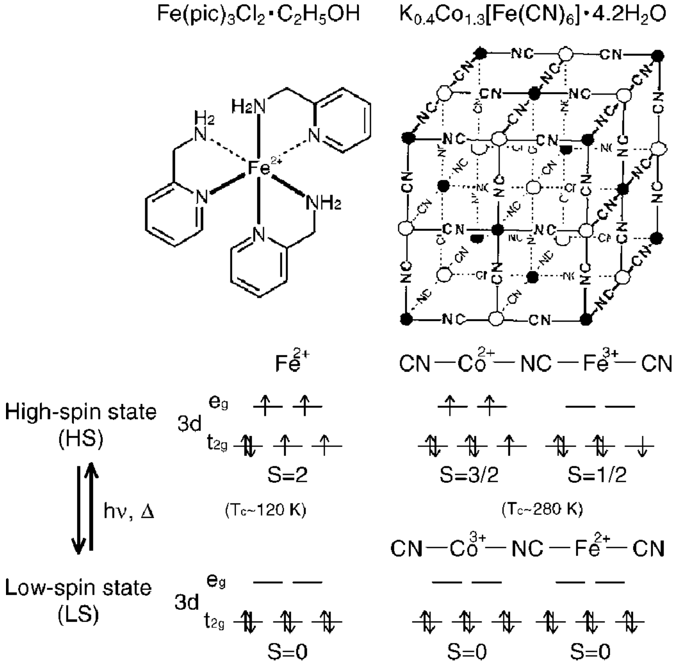

Figure 3
Structures and orbital models of $Fe(pic)_3Cl_2{\cdot}C_2H_5OH$, **1**, and $K_{0.4}Co_{1.3}[Fe(CN)_6]{\cdot}4.2H_2O$, **2**.

the AC effective value by the lock-in amplifier, and of the conversion of the output range.

On the other hand, ΔI_f is expressed using a simplified expression, $I_f = \eta I_0[1 - \exp(-\mu t)]$,

$$\begin{aligned}\Delta I_f = I_f^e - I_f^g &= \eta I_0\{\exp(-\mu t) - \exp[-(\mu + \Delta\mu)t]\}\\ &= \eta I[1 - \exp(-\Delta\mu t)],\end{aligned} \quad (2)$$

where I_0 and I are the incident and transmitted X-ray intensity, respectively, I_f^g and I_f^e represent the fluorescent X-ray intensity from the ground and excited states, respectively, η is the emission and detection efficiency of the fluorescent X-rays, $\Delta\mu$ is the light-induced change of the X-ray absorption coefficient μ, t is the sample thickness, and $I = I_0\exp(-\mu t)$ is the transmitted X-ray intensity. When $\Delta\mu t$ is sufficiently small, (2) becomes

$$\Delta I_f = \eta I \Delta\mu t, \quad (3)$$

and by the further approximation $I \simeq I_0$ (*i.e.* μt is negligibly small), then

$$\Delta\mu t = \Delta I_f/(\eta I_0). \quad (4)$$

This means that $\Delta\mu t$ is proportional to $\Delta I_f/I_0$ as long as the sample is thin and signal modulations are small. Finally, $\Delta I_f/I_0$ is normalized to the edge jump of I_f/I_0.

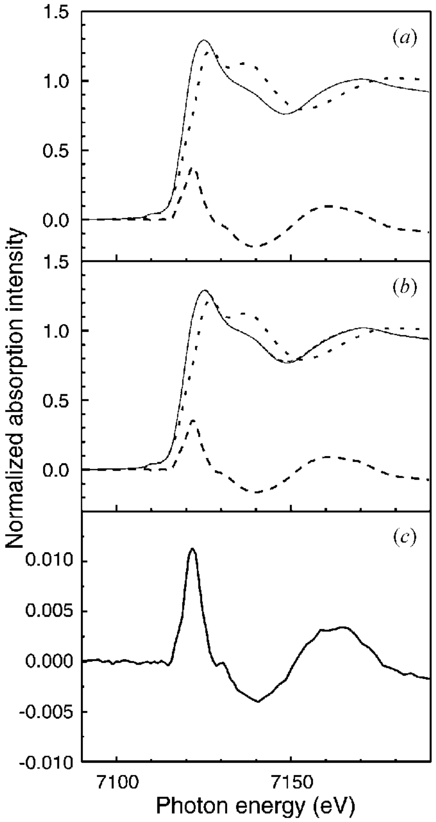

Figure 4
Fe-*K* XANES spectra of **1** (*a*) at 30 K (dotted line) and 300 K (solid line) in the dark, and their difference (dashed line), and (*b*) with and without Xe-lamp irradiation at 30 K (solid and dotted lines), and their difference (dashed line). The spectra at 30 K and 300 K are from pure LS and HS states, respectively. Continuous Xe-lamp irradiation converts the sample to the 88% HS state. (*c*) Spectrum obtained by the light-modulation method.

3. Results and discussion

Fig. 4(*a*) shows the Fe *K*-edge XANES spectra of **1** at 300 K and at 30 K, corresponding to pure HS and LS phases, respectively (Sorai *et al.*, 1976, 1977). The spectrum of the trapped state by Xe-lamp irradiation in Fig. 4(*b*) is very similar to that of the room-temperature HS phase (Fig. 4*a*). It is reproduced as a linear combination of HS and LS spectra with an HS ratio of 0.88, assuming that the temperature dependence of XANES is negligible. Fig. 4(*c*) shows the spectrum obtained by the light-modulation method. It is in good agreement with the difference spectra in Figs. 4(*a*) and 4(*b*), together with the EXAFS difference spectra in Fig. 5. Nd-laser irradiation gave an identical result. It was revealed that the light-modulated XAFS spectrum is detectable using our experimental set-up not only for the XANES but also for the EXAFS regions where only a small change is expected. Further experiments were performed to examine the applicability of the light-modulated XAFS method, as discussed in the following sections.

3.1. Modulation frequency dependence

Figs. 6(*a*) and 6(*b*) show the frequency dependence of the light-modulated XANES difference spectra $\Delta I_f/I_0$ at 30 K and 60 K, respectively. Here, a fast-type Lytle detector was used for intensity comparison between different modulation frequencies. The signal intensity decreases monotonically upon faster modulation at 30 K, while at 60 K it is strongest at 10 Hz, becomes weaker at 20 Hz and stays the same at higher modulation frequencies. The behaviour at

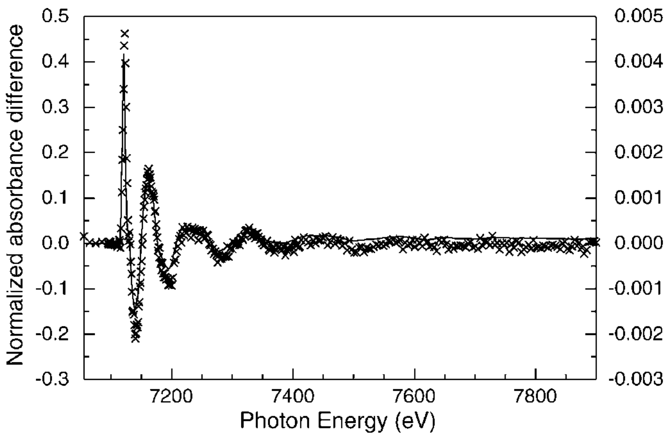

Figure 5
Fe-*K* EXAFS difference spectra of **1** at 30 K obtained by subtraction (solid line) and by the light-modulation method with a modulation frequency of 10 Hz (crosses). The light source was a Xe lamp.

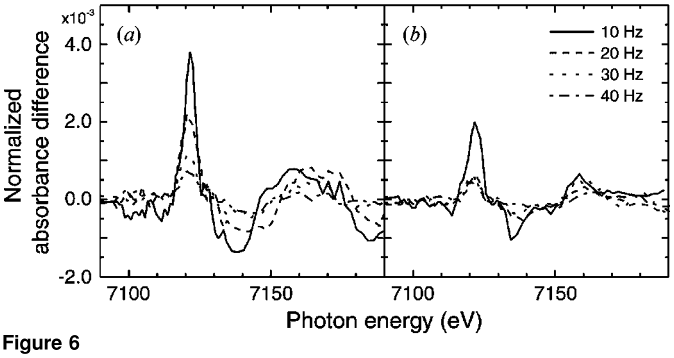

Figure 6
Modulation-frequency dependence of Fe-*K* XANES spectra of **1** at (*a*) 30 K and (*b*) 60 K. A fast-type Lytle detector was used with a phase shift of 180°.

30 K is understood simply as a consequence of relatively slow relaxation to follow fast light modulation. On the other hand, the spectra at 60 K can be interpreted as a superposition of two components with different relaxation rates. On increasing the modulation frequency, the slower component shows a more delayed signal than the faster component, resulting in a smaller amplitude and a larger phase shift (Johnston *et al.*, 1967). Thus the slower contribution is eliminated from $I_{\rm mod}$, and only the fast component remains at higher modulation frequency. In the present case, the slower component would be attributed to the thermally induced spin transition, and the faster component to the light-induced spin transition. The starting temperature of the spin transition of **1** is known to be ~80 K (Sorai *et al.*, 1976). The thermal spin transition does not occur on slight local heating caused by laser irradiation at low temperatures, but would partially occur at relatively high base temperatures. A rise in temperature causes the thermal spin transition, but its speed might be slower than that of the light-induced one. Thus, the light-modulation method with a higher frequency can eliminate the contribution from the thermal spin transition. These facts indicate that these two contributions can be discriminated by changing the modulation frequency. Fig. 7 shows the contribution from light- and thermally induced changes of XANES spectra obtained by subtracting the average of the 20, 30 and 40 Hz light-modulated spectra from the superposed spectrum at 60 K and 10 Hz modulation. Although the noise prevents a detailed comparison of these two spectra, the spectral shape remains almost unchanged, suggesting that the thermally and light-induced spin transition results in the same trapped HS state.

In the light-irradiation experiments, local heating of the samples is often a serious problem. It should be emphasized that the light-modulated XAFS method can eliminate this problem using fast modulation, also allowing the contributions with different time scales to be separated. This is one of the advantages of the light-modulated XAFS method.

3.2. Amplitude damping and phase shift information

The modulation method provides information on the relaxation of the excited states in amplitude and phase. Additionally, the phase shift determines the sign of the signal. If the phase value is shifted by 180°, the signal sign reverses, and thus a rough estimation should be carried out externally.

Before estimating the amplitude damping and phase shift due to the response delay of the samples, the contribution from the measurement system itself should be evaluated. The Keithley picoammeter was shown to follow the signal modulation perfectly with a sufficiently shortened rising time, as confirmed by using a function generator. On the other hand, the signals from the conventional Lytle detector with three grids and an applied voltage of 45 V showed large phase shifts and signal damping when the incident X-rays were chopped, while the practical values are near 0° in the light-modulated XAFS experiments (a phase shift of 0° means complete following to the modulation). This discrepancy became smaller when a paper chopper was used, through which the high-energy X-rays partially transmit. This shows that the conventional Lytle detector responds sufficiently fast to a small signal change, but not enough to a large oscillation amplitude, probably due to the slow recombination rate of the ionized gas and electrons.

These observations reveal that the phase shift setting near 0° is available for the qualitative measurements of the light-induced spectral change, as long as the signal is small. The relaxation study requires quantitative determination of the modulation amplitude and the phase shift originated from the sample. However, since the rising time of the conventional Lytle detector is 15 ms (Suzuki *et al.*, 2002), the signal intensity is seriously affected at higher modulation frequencies than 20 Hz. Faster response of the detector can be achieved by narrowing the grids and by applying a higher voltage between them. Recently, Suzuki *et al.* (2002) have developed a fast-type Lytle detector which has a rising time as fast as 0.2 ms. We used this detector for the present experiment as shown in Fig. 6 but, owing to large noise, could not obtain quantitative information of the phase shifts.

Although quantitative detection and analysis of the light-modulated spectra have not yet been achieved, the pure excited-state spectrum was obtained since the ground- and excited-state ratio and corresponding difference of the X-ray absorbance is known at a certain X-ray energy. The absorption difference between the HS and LS spectra at 7121 eV was used to normalize the amplitude of the light-modulated spectrum. Adding the normalized spectrum to that at 30 K, we constructed the $k^3\chi(k)$ spectrum of the purely light-excited state. It is roughly in good agreement up to $k \simeq 6$ Å^{-1}, as shown in Fig. 8. It is consistent with our EXAFS results that the light-induced phase has the same structure with the HS state at room temperature, together with the XANES and light-modulated XANES spectra shown above (Okamoto *et al.*, 2003). Although Tayagaki & Tanaka (2001) reported that the light-induced phase of **1** gives a Raman spectrum that is quite different from that of the HS state at room

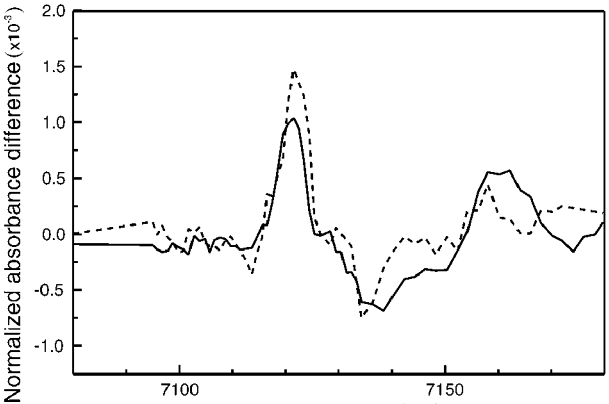

Figure 7
Light-induced (doubled, solid line) and thermally induced (dashed line) Fe-*K* XANES changes of **1** obtained by spectral analysis.

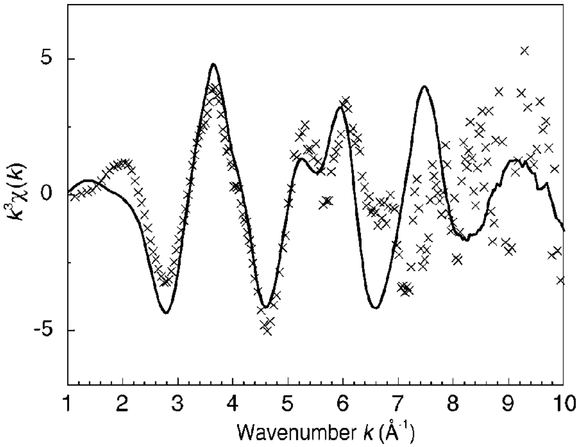

Figure 8
Fe-*K* EXAFS $k^3\chi(k)$ of the room-temperature HS state (solid line) and the constructed EXAFS spectrum of the light-induced state at 30 K (crosses).

temperature, no evidence of uniqueness is obtained about the electronic state and the local structure around the Fe^{2+} ion by XAFS spectroscopy.

The present case might be rather special because the excited-state spectrum is known. However, in principle, the following process would extract the EXAFS spectrum of an excited state: (i) The population ratio of the photoexcited state is estimated by other methods, such as the UV/vis absorbance measurement; (ii) X-ray absorbance difference is measured with and without light irradiation at a specific X-ray energy, possibly in the XANES region; (iii) the amplitude of the light-modulated spectrum is normalized at the photon energy to the X-ray absorption difference; (iv) the EXAFS spectrum of the pure excited state is obtained by addition of that of the ground state and the normalized light-modulated spectrum, taking into account the population ratio.

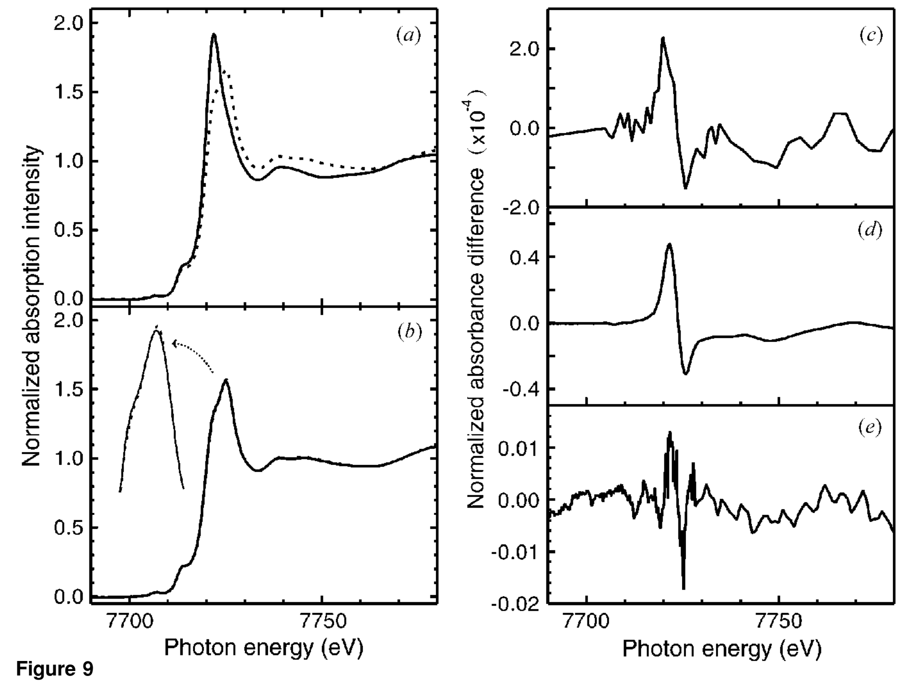

Figure 9
Left-hand side: Co-*K* edge XANES spectra of a prussian blue analogue **2** with and without the Xe-lamp irradiation (solid and dotted lines, respectively) at (*a*) 30 K and (*b*) 100 K. In (*b*) an enhanced view of the main peak is also shown. The HS ratios of the photoirradiated spectra are ~1 in (*a*) and <0.03 in (*b*). Right-hand side: Co-*K* XANES difference spectra obtained (*c*) by the light-modulation method at 100 K, and (*d*), (*e*) by subtraction of the XANES spectra in (*a*) and (*b*), respectively.

3.3. Detection limit

The detection limit of the light-modulation XAFS method was investigated using a prussian blue analogue, $K_{0.4}Co_{1.3}[Fe(CN)_6]\cdot 4.2H_2O$ (**2**). This compound shows the tautomeric spin transition from Co^{3+}(LS)Fe^{2+}(LS) to Co^{2+}(HS)Fe^{3+}(LS) by heating to 270 K or by irradiating visible light at low temperatures (Fig. 3). The trapped excited state of **2**, which is stable at very low temperatures (30 K, for example) but rapidly relaxes to the ground state above 100 K, has the same electronic state and structure with the room-temperature HS state as reported by Yokoyama, Murakami *et al.* (1998) and Yokoyama *et al.* (1999). The Co-*K* XANES spectra of **2** is shown in Fig. 9. Light-irradiation induces almost complete spin transition to the HS state at 30 K (see Fig. 9*a*), and the corresponding difference spectrum (Fig. 9*d*) should show the actual difference between the two spin states. The XANES spectrum at 100 K, on the other hand, stays almost unchanged by the photoirradiation, and the HS ratio is estimated to be less than 0.03 (Fig. 9*b*). The corresponding difference spectrum (Fig. 9*e*) is weak and noisy, and its shape depends on the method of normalization. The light-modulated spectrum at 100 K is shown in Fig. 9(*c*), which has a shape closer to that in Fig. 9(*d*) than that in Fig. 9(*e*), especially around the inflection point. It is noteworthy that the excited state is less than 1% and the obtained modulation intensity is of the order of 10^{-4} relative to the edge jump. This corresponds to 100 µV modulation on a 1 V I_f signal after amplification, which is slightly larger than the noise level at KEK-PF. This result demonstrates the superiority of the light-modulation method over the conventional subtraction method. As discussed in §3.2, a high noise level in the experimental hall still prevents quantitative measurements under the present conditions. However, we believe that the noise level from the detector can be further suppressed in the future, although noise from the X-ray beam itself cannot be avoided.

4. Conclusions

The present study demonstrates the applicability of the light-modulated XAFS spectroscopy as a method to study short-lived photoexcited states. Using two spin-transition compounds, changes caused by light-irradiation were detected successfully for both XANES and EXAFS, as a consequence of the elimination of various types of noise. Varying the modulation frequency showed the capability of studying the relaxation process and to distinguish two components with different relaxation rates. The light-modulation XAFS method has the following advantages: (i) a simple experimental set-up, which requires only a visible-light source, an optical chopper, a lock-in amplifier and a conventional XAFS beamline, and (ii) it is free from the ground-state components because the light-induced absorbance difference is directly detected. Although the current performance is sufficient for qualitative studies, more technical improvements are required for quantitative discussions such as the relaxation kinetics and detailed EXAFS analysis of light-induced structural changes.

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