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Development of light-modulated XAFS spectroscopy

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Structural and electronic changes upon photo-excitation have been studied by various methods. In the case of materials with no long-range ordering, XAFS is one of the most useful tools to obtain direct information on local structures and electronic properties. However, it is quite difficult to observe dynamic behaviours by the conventional XAFS method. The purpose of this study is to apply the light-modulation method, which is widely used for Raman, IR, and UV-vis spectroscopies, to x-ray absorption spectroscopy.

All measurements were carried out in the fluorescence mode at BL-9A with a double-crystal Si(111) monochromator detuned by ~40%. The incident x-rays were detected by an ionization chamber filled with N_2 and fluorescent x-rays by a Lytle detector filled with Ar. Experimental setup is shown in Fig. 1. A focused Xe lamp (300 W, 350-700 nm) was used as the light source. Some efforts were needed to reduce the noise level as low as possible. To avoid noises caused by the signal fluctuations after moving the monochromator, the signal counter was controlled by an external timer circuit. To avoid vibration, the Lytle detector was set on silicone rubber insulators. Light-induced spin transition samples with strong and well-known spectroscopic changes were selected for examining the performance: $Fe(pic)_3Cl_2\cdot C_2H_5OH$ (pic=2-aminomethylpyridine)[1], **1**, and $K_{0.4}Co_{1.3}[Fe(CN)_6]\cdot 4.2H_2O$[2], **2**. They both show spin transitions from low-spin (LS) to high-spin (HS) states induced by heat or light at low temperatures. Sample powders were dispersed on Scotch tapes and cooled in a refrigerator. All spectra were normalized to the edge jumps, and outputs of the lock-in amplifier were corrected to the original order.

Figure 2 shows the Fe *K*-edge XANES and EXAFS spectra of **1** at about 15 K. Differential shapes expected from the spectra upon continuous irradiation were well reproduced in the light-modulated spectra even in the EXAFS region. Figure 3 shows the Co *K*-edge XANES spectra of **2**. The trapped excited state of **2** is stable at very low temperatures (Fig. 3, dashed line) but rapidly relaxes to the ground state above 100 K, and the difference becomes too small to obtain difference spectra accurately. However, the light-modulated spectrum has an accurate shape, especially around the inflection point, despite of very small spectral change (~10ppm relative to the edge jump).

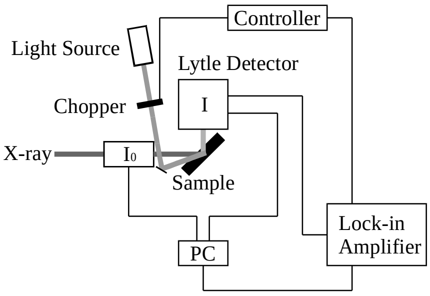

Fig. 1. Experimental setup for light-modulated XAFS.

Present study demonstrates the applicability of the light-modulated XAFS spectroscopy as a convenient method to study short-lived photo-excited states.

[1] L. X. Chen et al. J. Phys. Chem. 99, 7958 (1995).
[2] T. Yokoyama et al. Phys. Rev. B 60, 9340 (1999).

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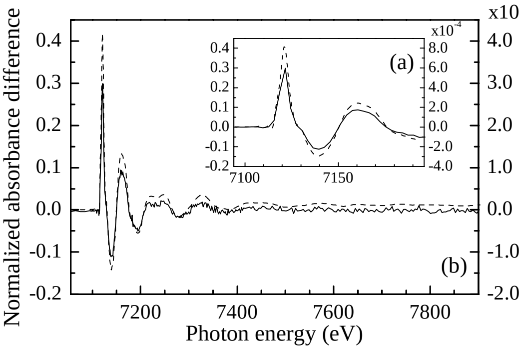

Fig. 2. Fe *K*-edge XANES (a) and EXAFS (b) difference spectra of **1** obtained by the light-modulated method (modulation frequency of 5.0 Hz, solid lines, right Y axis) and by continuous irradiation (dashed lines, left Y axis).

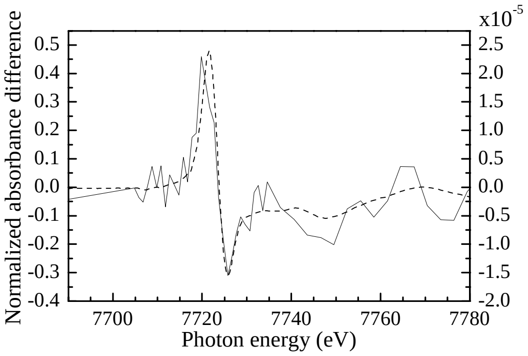

Fig. 3. Co *K*-edge XANES difference spectra of **2** obtained by the light-modulated method (modulation frequency of 4.1 Hz, solid line, right Y axis) and by continuous irradiation at 100 K (dashed line, left Y axis) .