Recent Advances in Fluorescence XAFS Using High-brilliance Photon Sources

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Recent advances in fluorescence X-ray Absorption Fine Structure (XAFS) techniques, in particular, rapid and sensitive measurements using a tunable x-ray undulator, will be reported. One of the advantages of high-brilliance photon sources (i.e., x-ray undulator-based sources) is that one can study the local and dynamical atomic arrangements around optically excited atoms within ~8 Å using "pump and probe" XAFS techniques. A snapshot of local lattice distortion, relaxation, and, in some cases, bond alteration as a result of electronic excitation can be obtained from a fluorescence yield *in-situ* at low temperature using a tunable undulator and a densely packed solid-state detector array. In this paper, the recent advances in fluorescence XAFS techniques and studies of atomic rearrangements caused by optical pumping at low temperature are described. One of the serious limitations in optical pumping experiments used to be the "depth mismatch" between x-ray probing and optical excitation. Sample concentrations have been therefore severely limited in order to achieve an optimum absorption of pump photons in the visible wavelength region. If a highly parallel x-ray beam is available, however, the extinction length can be reduced by orders of magnitude to match that of optical excitation. Utilizing a grazing-incidence fluorescence excitation technique, one can probe the local structure of optically excited region using a concentrated specimen. For example, in the photosynthetic water oxidation catalyzed by the tetranuclear Mn cluster in the photosystem II (PS II), stable intermediate reaction states induced by four photons were studied by X-ray Absorption Near Edge Structure (XANES) using dilute specimens (200-300 mM). It is expected that more concentrated specimens can be studied using a flat x-ray/optical window. Applications to chalcogenide glasses have demonstrated the potential of pump and probe XAFS providing the evidence of photo-induced local melting phenomena. In this paper, we describe the design and performance of the high-brilliance XAFS station BL10XU of SPring-8. An undulator gap and a fixed-exit double crystal monochromator with a rotated-inclined geometry were successfully controlled to cover a wide energy range (5-25 keV). Although asymmetric Si(111) reflections in a (+,-) configuration with a "rotated-inclined" geometry broaden the rocking curve by a factor of two, because of an advantage of ultra-low emittance, the observed energy resolution is expected to be less than 1 eV at 9 keV. Such a high energy resolution is advantageous for XANES studies of heme proteins in relation to spin states, such as oxy-forms of cytochrome P-450, horseradish peroxidease (HRP), and myoglobin (Mb). With the support of spin-dependent multiple scattering theoretical calculations, one can now quantitatively study the local structure of heme irons including the ligand orientation. For high efficiency fluorescence data acquisition, a 100-element monolithic solid state detector array and digital signal processors are used. In a monolithic approach, a packing ratio around 90% is expected. In this design, each element is 2 mm thick and has an effective area of 22 mm^2. A typical energy resolution is 240 eV at 5.9 keV for 1 msec peaking time. Although this novel detector array is currently under development, preliminary results using undulator gap tuning are presented and the feasibility of pump and probe experiments will be discussed.