

Use of scattered radiation for absolute x-ray energy calibration

Julie O. Cross^{a)}

Naval Research Laboratory, Code 6685, Washington, D.C. 20375

Anatoly I. Frenkel^{b)}

Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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A small, simple, and effective x-ray energy monitor has been built for use in energy-sensitive experiments where normal transmission monitoring is not an option. The instrument uses x rays scattered elastically from air, thin polymer films, or other featureless scatterers as a secondary source for measuring the transmission versus energy through a calibrated x-ray spectroscopy standard. In general, this type of energy monitor can be made from many combinations of detectors and scatterers, including ultrahigh vacuum compatible components. We show experimental results from a miniature, *p-i-n* diode-based monitor, which fits unobtrusively anywhere along the optical path of the experiment, and can be made easily from inexpensive and readily available parts.

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I. INTRODUCTION

Changes in the chemical state of atoms, or in their local structural environment, are often revealed by small shifts of the energy position, shape, and magnitude of specific features in the x-ray absorption and elastic scattering spectra near core electron resonance. Resonant x-ray techniques, such as x-ray absorption fine-structure (XAFS), x-ray absorption near-edge spectroscopy (XANES) and diffraction anomalous fine-structure (DAFS) spectroscopy, that measure small changes in the position of spectral features around resonance, require accurate absolute x-ray energy calibration. If the energy is properly calibrated in the experiment, the energy resolution is defined by the monochromator crystal spectral purity, which can be as good as $\Delta E/E \sim 10^{-5} - 10^{-6}$.¹ However, the energy of the prepared incident beam can deviate considerably from the energy defined by the Bragg angle of the monochromator due to several effects, such as thermal loading of the monochromator crystals, loss of steps in the monochromator motor, slipping or sticking in the monochromator linkage, orbit shifts, and more subtle effects such as the influence of the energy dependent transmission function of the beamline optics,² and inelastic scattering. These energy shifts are often unpredictable, therefore, a precise *in situ* energy calibration method is needed for spectroscopy experiments.

The energy calibration methods used for x-ray spectroscopies include (1) calibrating to sharp drops or Bragg “glitches” in the primary beam intensity, due to the excitation of secondary Bragg reflections in the monochromator,³ (2) measuring the transmission extended XAFS (EXAFS) of a standard sample, with known absorption edge features at tabulated energies, and (3) measuring the Bragg angle using an analyzer crystal.⁴ The Bragg glitches can serve as an energy reference because they always occur at the same mono-

chromator angle, however, they are not always convenient, since the energies at which the glitches occur may lie far outside the energy range of the spectroscopy experiment. Measurement of the absorption coefficient of a calibrated standard, simultaneously with the unknown sample, is the most common energy calibration method used in transmission and fluorescence XAFS experiments. A foil is placed downstream from the sample, in line between the transmitted beam detector $I_T(1)$ and an additional reference detector $I_T(2)$ [Fig. 1(a)], and the reference absorption coefficient $\mu_{T\text{ref}} = \ln[I_T(1)/I_T(2)]$ is compared against the sample absorption coefficient $\mu_{T_s} = \ln[I_0/I_T(1)]$, where t_{ref} and t_s are the reference and sample thicknesses, respectively. This method is not applicable to samples that are too absorbing, e.g., in fluorescence experiments where the samples or the substrates are too thick, or where the experimental geometry blocks the transmitted beam completely, e.g., in DAFS experiments. The third method listed above, use of a diffraction analyzer, also requires access to the beam downstream from the sample, and is considerably more complicated, since it requires additional alignment and calibration of the analyzer crystal, and puts restrictions on the experimental geometry.³

In this article, we report a simple and reliable method for calibrating the absolute x-ray energy based on the transmission calibration method commonly used in x-ray absorption spectroscopy (XAS). We have used x rays elastically scattered out of the incident beam (I_0), scattered either by air or by a weak scatterer such as kapton or Al foil, as a secondary source of x rays [Fig. 1(b)]. The elastically scattered x rays, which have the same energy as the incident beam, are detected through an XAS transmission standard giving the characteristic drop in transmission across the absorption edge which is used to set an energy fiducial. Since the scattered x rays propagate away from the primary optical path, this method can be used in experiments where the beam is stopped at the sample and in-line reference methods are not possible.

^{a)}Electronic mail: jox@pnc.aps.anl.gov

^{b)}Electronic mail: frenkel@bnl.gov

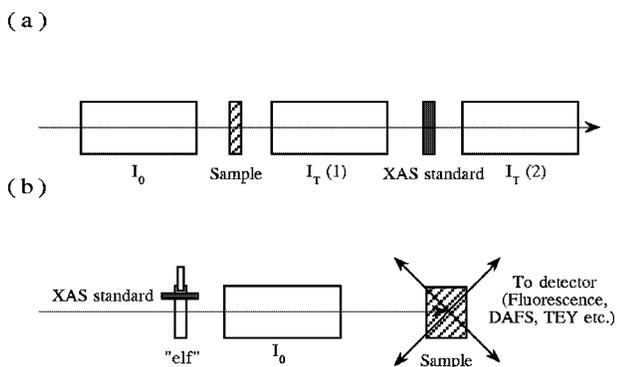


FIG. 1. XAS experiments using metal foil standards for calibrating the position of the absorption edge: (a) transmission and (b) fluorescence, DAFS, TEY etc. experiments using the monitor described in this work.

II. EXPERIMENT

In general, the energy monitor simply comprises three parts: (1) x rays scattered elastically out of the incident beam, (2) an XAS transmission standard, typically a thin metal or oxide foil, and (3) a detector with a monotonic response over the energy range of the experiment. The elastic scattering can be from air or other gases, or from any low Z material with a smooth cross section over the energy range of the experiment, with the object of obtaining a signal through the XAS standard in the monitor without incurring a significant losses in I_0 . The place where the beam passes through the scatterer serves as an extended point source of secondary x rays with the same energy as the incident beam. The XAS standard and the detector are placed as close as is practical to this point in order to maximize the solid-angle acceptance of the monitor. It is important to prevent contaminating other detectors in the experiment with stray fluorescence from the XAS standard, however, this is easily accomplished by judicious arrangement and shielding of the components.

The Compton (inelastically) scattered photons, which are shifted downward in energy from the incident beam, will also excite the absorption edge once the incident energy reaches the absorption edge energy plus the Compton shift. The angular dependence of the Compton shift is given by

$$\lambda_s - \lambda_{in} = h/mc(1 - \cos \theta), \tag{1}$$

where λ_{in} and λ_s are the incident and scattered wavelengths, respectively, h is Planck's constant, m is the electron rest mass, c is the speed of light, and θ is the angle between the incident and scattered photon wave vectors. Reexcitation of the edge by the Compton scattered photons does not affect the position of the spectral features used for calibration, provided that the calibration detector is positioned at sufficiently large wave vector transfer that the Compton shift is larger than the range needed for calibration, typically 30–50 eV. With the detector placed at $\theta=90^\circ$, the Compton shift in eV at 9659 eV for the Zn K-edge XAFS data shown in Fig. 2 below was approximately 180 eV.

Scintillation detectors, e.g., NaI(Tl) detectors, placed normal to the incident beam direction, counting the photons scattered from air or low Z materials, are commonly used as beam intensity monitors in both laboratory and synchrotron x-ray experiments. We first tested our energy monitoring

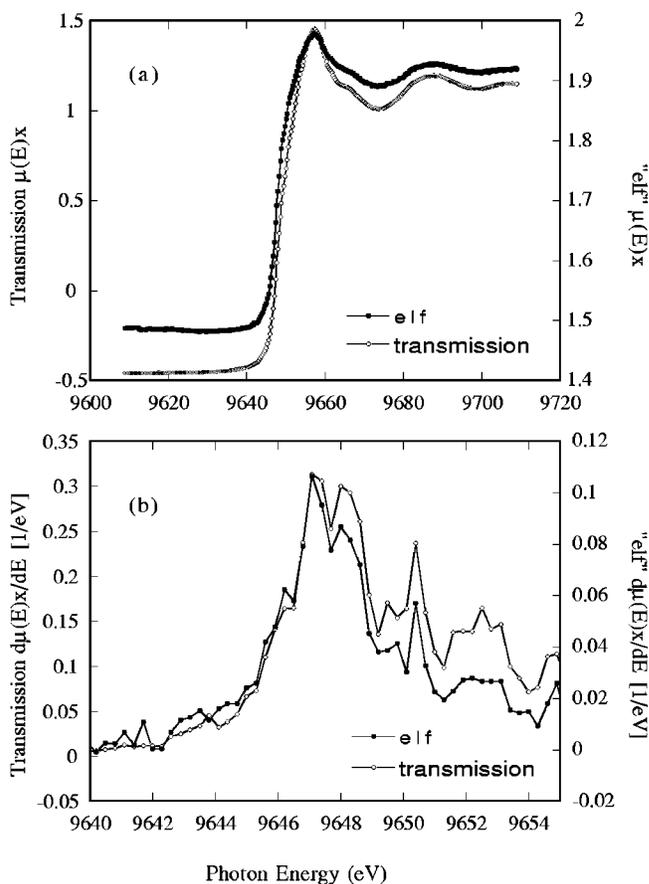


FIG. 2. Comparison of energy calibration using a Zn foil standard measured simultaneously in transmission (open circles) and elf (solid circles) modes. Shown are (a) the absorption coefficients and (b) the first derivatives of the Zn K-edge XANES.

method by placing a pure Fe foil standard in front of a Bicron detector configured as an intensity monitor in order to calibrate E_0 in a DAFS experiment on magnetite Fe_3O_4 .⁵ A similar arrangement has been used by Sansone and Devries⁶ for low energy x-ray spectroscopy using He scattering as the elastic source, and for measuring the transmission through an oxide or foil filter into a Lytle-type fluorescence detector, with a ~ 10 cm aperture. Both of these arrangements provide excellent energy calibration and monitoring, however, the size of these highly sensitive detectors may compromise the experimental geometry and, unless their use is warranted by low count rates, a more compact instrument would be preferred.

A miniaturized version of the energy monitor was built using kapton tape as the elastic scatterer and a 2.5 mm diam windowless *p-i-n* diode (EG&G UV-100) as the detector. An aluminum block was used to house the diode, and the housing was designed to accommodate the 1×2 in. transmission standards available from the National Synchrotron Light Source (NSLS) XAFS equipment pool. The diode was mounted normal to the incident beam and faced downward, co-axial with an optical mounting post for easy alignment. *p-i-n* diodes have been used as x-ray detectors previously,⁷ and have the advantage over many other kinds of x-ray detectors of being inexpensive and small. For convenience, and because they provide accurate edge location via elastic scat-

tering, these unobtrusive and useful energy monitors are referred to as elves, with a single monitor appropriately dubbed an elf.

Figures 2(a) and 2(b) show the XANES spectrum and first derivatives, respectively, of a pure Zn XAS transmission standard (NSLS XAFS equipment pool, Goodfellow Metals) measured at the Zn *K* edge using elf and transmission detection modes simultaneously. Gas ionization chambers of 5 and 15 cm, flowing a 1:1 mix of N₂ and Ar gases, were used as the *I*₀ and transmission detectors, respectively. The elf signal was normalized to *I*₀. No energy shift, within the accuracy of the 0.3 eV energy increment in the experiment, was observed between the elf and the transmission XANES [Fig. 2 (b)]. Although the signal intensity is low, due to the small 2.5 mm active area of the diode on hand at the time this experiment was performed, it is sufficient for monitoring the edge position, as Fig. 2 demonstrates.

III. DISCUSSION

The energy monitoring method we have described is simple and effective, and requires very little sacrifice of incident beam intensity. A basic “elf” monitor can be assembled quickly from components found at most synchrotron beamlines, and the size of the instrument is limited only by the size of the detector-filter combination used, and the amount of shielding required for the specific experimental geometry and energy range. The *p-i-n* diode based elf, because of its simplicity and its small size, can easily be integrated, e.g., into a slit assembly or into the end cap of a beam pipe.

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