Electron yield: total, Auger and photoemission

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The depth sensitivity and collection efficiency of various electron-detection schemes for X-ray absorption fine structure are discussed with examples taken from the literature. Enhanced surface sensitivity is demonstrated with an example in which monolayer specificity from a single-crystal surface is achieved.

X-ray absorption fine structure (XAFS) refers to the modulations in the X-ray absorption cross section due to the electronic or atomic structure about an absorbing atom. Any method of detection that is proportional to the number of core holes created per unit of photon flux is therefore a measure of XAFS, whether it is direct, as in measuring the number of photons absorbed in a transmission experiment, or indirect, as in counting the number of fluorescence photons emitted as a result of core-hole decay.

Of particular importance to the technique is the ability to measure the intensity of nonradiative processes, i.e. the direct photoelectron channel (PES), in addition to partial electron yield (PEY), total electron yield (TEY) and elastic Auger electron yield (EAY). With the exception of TEY, which can be measured by recording the sample drain current in either rough vacuum or a gas-flow detector (Shevchik & Fischer, 1979), electron detection in general necessitates the use of an energy-discriminating detector that is enclosed in either a high- or ultrahigh-vacuum chamber. The detector can be as simple as an electron multiplier placed behind a series of isolated grids that can be either negatively biased to reject low-energy electrons (PEY) or positively biased to accept the total electron current (TEY) (Stöhr, 1992). The detector can also be as complicated, as in the modern, high-resolution electron spectrometer shown in Woicik & Pianetta (2023), which can be tuned to accept the energy and width of a specific Auger transition (EAY).

In general, the simplest and most straightforward method to measure XAFS is transmission. However, due to the large background encountered in these measurements, transmission is only feasible for concentrated samples (>500 p.p.m.). It also typically cannot take advantage either of sample geometry, such as glancing incidence, to achieve surface sensitivity or synchrotron-beam polarization to probe sample anisotropy and/or the dipole/quadrupole nature of electronic transitions. Transmission also cannot take advantage of the different electron-escape depths and hence surface sensitivities of the various electron de-excitation channels that occur at different kinetic energies. Electron-detection XAFS also becomes important at low photon energies where the branching ratio of Auger electron decay surpasses fluorescence decay (Krause, 1979). In addition, low-energy photons have a much shorter...
attenuation length than high-energy photons, making transmission measurements difficult for photon energies below 1000 eV. The fact that electrons do not travel far in matter is also beneficial for the study of concentrated samples in any photon-energy range as fluorescence yield is likely to suffer from self-absorption and thickness effects. X-ray penetration depths are typically of the order of 100 times greater than electron-sampling depths, making TEY the method of choice for measuring XAFS from concentrated and/or single-crystal samples.

Fig. 1 illustrates the radiationless de-excitation of a 1s core hole created by K-edge absorption in silicon through Auger electron emission (Woicik et al., 1989). In general, deep holes will ‘bubble up’ through Auger decays that involve both normal and satellite events. The TEY current emitted from a sample will therefore include both direct photoelectrons resulting from the creation of the core hole and numerous different elastic Auger electrons due to its de-excitation. All such electron emissions contribute to the secondary-electron cascade of inelastically scattered low-energy electrons that can also give a measure of XAFS (Stöhr et al., 1984). It should be noted, however, that measurement of the direct core-level photoelectron signal without full 4π sr angular integration can result in a signal that is strongly affected by photoelectron diffraction (Lee, 1976).

The electron inelastic mean free paths (IMFPs) for 41 elemental solids have been calculated (Powell & Tanuma, 2016; Tanuma & Powell, 2022). The IMFP is a basic material parameter and for a given kinetic energy it is the average distance that an electron travels between inelastic collisions. Consequently, it determines the information depth (ID) that an elastic photoelectron or Auger electron provides. As seen from these calculations, electrons with energies of 100 eV travel approximately 5 Å before they are inelastically scattered, while electrons with energies of 10 000 eV travel up to 100 Å. Before IMFP calculations had reached their current level of sophistication and accuracy, experimentally determined IMFP curves for a wide range of materials were often combined to give what was then called the ‘universal’ IMFP curve that described the overall trends (Lindau & Spicer, 1974); however, as the calculations now show, the variation between different materials can be quite large. For surface and near-surface studies, to minimize the background signal from either the substrate or other concentrated elements in the sample, it is often necessary to measure the intensity of an elastic Auger peak (EAY) to obtain XAFS with good signal-to-background ratio on account of both its elemental specificity and surface sensitivity (Stöhr, 1992).

In order to appreciate the probing depth of an XAFS experiment using electron detection, Fig. 2 shows the IMFP calculated from the semi-empirical Tanuma–Powell–Penn equation (Tanuma et al., 2003), the effective electron attenuation length (EAL) that also includes the instrumental configuration and elastic scattering effects, and the effective information depth (ID) for 90% (ID-90) and 99% (ID-99) of the signal. The latter is defined as the depth normal to the surface from which the percentage of detected elastic signal is obtained. The calculations were performed for SiO₂ measured at an 85° electron take-off angle (Weiland et al., 2016). At low kinetic energy the EAL and IMFP differ significantly, but as the kinetic energy increases elastic scattering effects are minimized and the EAL and IMFP effectively become equivalent. Note that 90% of the elastic Auger signal arises from within approximately twice the EAL, and 99% of the elastic Auger signal from within approximately four times the EAL.

Although it is fairly straightforward to calculate the ID for elastically detected electrons, it is more complicated to estimate the ID for TEY. In this case, the ID is determined primarily by the penetration range Rₑ over which the various Auger electrons deposit their energy to the solid through inelastic scattering (Erbil et al., 1988). This range is generally much larger than the IMFP, as the TEY signal is dominated by the low-energy inelastic tail of the secondary-electron cascade.

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**Figure 1**
Nonradiative core-hole decay illustrated for crystalline silicon. (a) Standard LVV decay following 2p photoionization. (b) Standard KLL decay together with satellite L*VV decay following 1s photoionization. The doubly ionized L* shell and the corresponding satellite L*VV electron are marked with an asterisk. Note that standard LVV decay will follow satellite L*VV decay. KVV, KLV and fluorescence (radiative) decay are not shown.

**Figure 2**
Comparison of IMFP, EAL and ID for 90% and 99% of information (ID-90 and ID-99, respectively) calculated for SiO₂ measured at an 85° electron take-off angle.
that peaks at low but finite energy due to the sample work function. TEY is still surface-sensitive compared with fluorescence yield because electrons generated at too great a depth will not escape the surface-potential barrier because they have lost too much energy. Several experimental estimates of the TEY sampling depth for electrons travelling through a variety of materials at different absorption-edge energies have been given in the literature, with the caveat that gas-flow detection may produce different values to vacuum detection (Erbil et al., 1995; Kasrai et al., 1992; Girardeau, 1983; Bouldin et al., 1992; Girardeau et al., 1992; Vogel & Sacchi, 1994; Schroeder et al., 1995; Kasrai et al., 1996; Frazer et al., 2003). The NIST Stopping-Power and Range Tables for Electrons, Protons, and Helium Ions may be used to determine the Auger penetration range for a variety of materials as a function of electron kinetic energy (Berger et al., 2017). Additional information may be found in the X-ray Data Booklet published by the Center for X-ray Optics and Advanced Light Source, Lawrence Berkeley National Laboratory (Pianetta, 2009).

Clearly, it is advantageous for surface and near-surface studies, where either the surface species or the dilute element of interest resides on or within the surface region of a concentrated sample, to use electron detection to increase the signal-to-background ratio of the XAFS signal. However, this increased signal to background does not come without considerable cost. For example, the collection efficiency of an energy-discriminating cylindrical mirror analyzer (CMA), as used in the original experiments (Stöhr, 1992; Citrin et al., 1978), is as low as 7% of 4π sr, increasing to only 11% of 4π sr for a modern analyzer operating with a wide-acceptance objective lens (Kobayashi et al., 2013). Consequently, it is often advantageous to collect the PEY signal instead of the EAY by setting the retarding energy of a gridded detector to just below the energy of an elastic Auger transition. PEY detectors can in principle be as efficient as 50% of 4π sr, but this benefit comes with a significant decrease in signal to background due to the large amount of high-energy secondary electrons that are not discriminated. TEY, while giving the highest signal, has the worst signal-to-background ratio since there is no advantageous element-specific energy discrimination. Note that elastic photo-peaks originating from either the element of interest or the substrate will often sweep through the energy window in an EAY experiment, limiting the k-range of useful XAFS data. This problem can be partially mitigated by using PEY instead of EAY together with a judicious choice of low-energy cutoff. Differential electron yield (DEY) has also successfully been demonstrated for low-Z elements (Isomura et al., 2016).

To illustrate the depth sensitivity that can be achieved through electron detection, Fig. 3 shows P K-edge XAFS data recorded from a clean, ultrahigh-vacuum cleaved InP(001) surface (Woicik et al., 1992). The data were collected by simultaneously monitoring the intensity of the low-energy P LVV Auger decay that occurs at 120 eV kinetic energy and the TEY drain current. From the clear reduction in higher frequency signal, the surface-sensitive EAY data directly measure the reduced coordination around the P atoms on the clean, single-crystal surface. Similar electron-detection methods have been utilized to study the surface-versus-bulk crystallization of sputter-damaged silicon surfaces (Comin et al., 1985), the surface-versus-bulk orientation of polystyrene (Wu et al., 2003) and the surface-versus-bulk chemical oxidation of aluminium surfaces (Jones & Woodruff, 1982), all with great success. It is interesting to note that analogous changes in surface coordination and chemistry have been observed in modern-day transmission experiments of crystalline nanoparticles both as a function of nanocrystallite size and chemical preparation (Carter et al., 1997; Elsen et al., 2015).

References


