XAFS data collection: an integrated approach to delivering good data

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Energy scale calibration and reliable intensity measurement are the main issues related to the collection of good spectroscopy data. The accurate determination of the energy scale is often established by using foils of optimum thickness to calibrate the monochromator. However, mechanical issues with the mono-chromator, movement of the source, or even the resolution of the spectrometer can have an effect on the measured energy scale. For the issue of accurate intensity measurements, calibrated detectors are necessary to ensure a reliable measurement of the spectroscopic signal, both in transmission and fluorescence detection modes. In this paper a review of the most common techniques used for energy calibration and for collecting X-ray absorption spectroscopy data is given, together with a brief description of the factors that have an impact on the intensity of the measured signal. A brief description of the versatile X-ray absorption spectroscopy beamline, I20, at Diamond Light Source is also presented, giving particular emphasis on how the beamline design has been undertaken to tackle these key issues. In particular, the use of a four-bounce monochromator will be discussed, highlighting the advantages of the device for the measurement of spectroscopy data.

1. Introduction

X-ray absorption spectroscopy is a very powerful technique that provides local structural information around an absorbing atom (Bunker, 2010). The technique is widely applied to a range of systems, from crystalline or amorphous solids to liquids and gaseous systems. The experimental information is contained in the variation of the absorption coefficient of the sample as a function of energy. For measurements obtained in transmission mode, the spectrum is obtained by measuring the intensity of the radiation before and after the sample as a function of the energy of the incident radiation, at which point the logarithm of the ratio between the incident and trans-mitted signals is taken. For those samples where the absorbing element is found in very low concentration or is embedded in a very absorbing support matrix, it is advantageous to measure the intensity of the characteristic fluorescence line as a func-tion of the incident energy, as the ratio of this with the incident intensity is proportional to the absorption coefficient.

In order to collect reliable data, two conditions need to be fulfilled. First, the energy of the radiation impinging on the sample needs to be known and, second, the intensity of the radiation needs to be determined with good enough accuracy and free of any spurious contributions that can affect the data quality.

In this paper the state-of-the-art methods of collecting XAS data with good energy calibration are discussed, highlighting the advantages and the drawbacks of each of them. The main considerations to be taken when performing experiments both in transmission and fluorescence modes to collect meaningful intensities are also reviewed. A brief description of beamline I20 at Diamond Light Source is also presented, giving special emphasis to the design steps that have been followed to tackle the issues required for good spectroscopy data.

1.1. Energy calibration

X-ray absorption spectroscopy techniques require accurate energy calibration. Together with the intensity and the shape, the absolute energy position of particular features in the absorption spectrum contains valuable information for the determination of electronic and geometrical structural para-meters of the species under study. In addition, a precise energy scale is essential in order to obtain accurate values for interatomic distances from the absorption spectrum.

Nowadays at modern synchrotrons, the energy of the radiation impinging on a sample is, in most cases, selected by the use of a double-crystal monochromator. By using the Bragg law, the energy of the monochromatic beam is calcu-lated if the d-spacing of the crystal and the angle of incidence

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are known. As it is not easy to know these two values with high precision, the most commonly used method to calibrate a monochromator is by measuring the absorption spectrum of a metal foil as a known standard. The foil spectrum is compared with tabulated and known spectral features, and the monochromator is thus calibrated. The quality of this calibration is dependent on the accuracy of the tabulated spectral reference data (Bearden & Burr, 1967; Kraft *et al.*, 1996), as these are used to calculate the incidence angle. Once the angle of the monochromator crystals is determined, angular increments are then calculated by measuring the steps of the motor of the monochromator or, in more modern devices, with angular encoders.

It is always good practice to calibrate the monochromator with a known reference measurement before starting an experiment, or, in any case, after a large angular movement of the monochromator, that is often required when moving to study a different elemental absorption edge present in the sample.

Once the calibration of the monochromator has been addressed, the reproducibility of the energy scale has to be ensured. It is common to compare samples during an experiment, and changes in the position of given features such as the absorption edge are usually interpreted as changes in the chemical state of the absorbing atom or its local structural environment. It is thus extremely important that the energy scale is reproducible over the course of a series of repeated measurements.

The main factors affecting the reproducibility of the energy scale are:

(i) Mechanical issues with the monochromator. Any loss of steps of the angular motor in the monochromator or any sticking and slipping in the monochromator linkage will have a detrimental effect on the reproducibility of the energy scale. This is less of an issue nowadays, as modern monochromators use very precise encoders that greatly reduce these problems.

(ii) Incidence angle of the X-rays in the first crystal of the monochromator. Any angular movement of the optical elements placed upstream of the monochromator, or orbit changes in the synchrotron, will have an effect on the incidence angle of the X-rays on the first crystal of the monochromator, and thus affect the energy scale.

(iii) Temperature of the monochromator crystals. As the *d*-spacing of the crystal planes depends on the temperature, it is important to keep this constant throughout the measurements, although care must be taken as changes in conditions of the upstream optics or decay of the current in the synchrotron will unavoidably affect the thermal stability. Nowadays this last effect is less common as most modern synchrotrons work in top-up mode to keep the power load on the beamline optical elements as constant as possible. In addition, many modern monochromators use silicon crystals cooled to liquid-nitrogen temperatures to minimize the effects of thermal expansion in the crystal lattice.

(iv) Resolution of the spectrometer. The energy resolution of the spectrometer affects the measured position of sharp spectral features such as the absorption edge and pre-edge features, so it is important to keep this constant during the experiment if reliable comparative studies are to be performed.

Even if care is taken to avoid all the issues listed above, the use of 'in situ' energy calibration methods is often necessary when performing spectroscopy measurements. There are three main methods of achieving the internal energy calibration.

The first method is to use secondary reflections or glitches that appear in the absorption spectrum at specific energies to calibrate the energy scale (Arthur, 1989). This is not always convenient, as it is possible that the energy of these reflections appears far away from the angular range that is scanned during the spectroscopy experiment.

The second method consists of recording a reference spectrum simultaneously with the sample under study (Goodin *et al.*, 1979). A schematic of the experimental set-up is shown in Fig. 1 (top panel). A reference sample containing the same absorption element, usually a foil if available, is placed downstream of the sample, in the path of the X-rays and after the transmitted intensity monitor, I_t. An additional intensity monitor is then placed after the reference sample, I_{ref}, and the absorption spectrum is directly obtained by taking the natural logarithm between I_t and I_{ref}. As the reference sample energy scale should not change with time, the energy position of the known features in the spectrum is used as calibration for the experiment. This method is the most commonly used, although it cannot be applied if there is no intensity transmitted by the sample such as when the samples under study are very absorbing and the detection method used is fluorescence, or when the experimental set-up blocks the path of the transmitted X-ray beam.
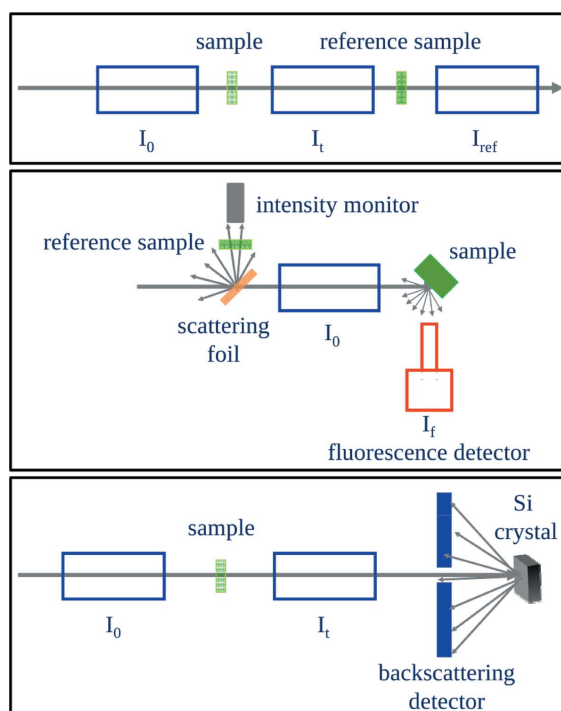

Figure 1
Schematic of the most common experimental set-ups used for internal energy calibration during absorption scan collection (see text for details).

In these cases the method used for internal calibration consists of inserting a thin scattering foil just before the incident intensity monitor (Cross & Frenkel, 1999). The scattered radiation is then allowed to pass through a reference sample, and an intensity monitor, usually a pin diode, is used to measure the radiation absorbed by the sample (Fig. 1, middle panel). The sharp decrease in absorption due to the absorption edge can be detected by this method, and the energy of the feature used as a calibration point for the experiment.

In both cases mentioned above, a linear correction of the experimental data collected following the edge position of the reference sample is usually enough to achieve an accurate energy scale. However, if the shift is significant, this correction can introduce distortions in the energy scale, as the angle of the monochromator and the energy selected do not follow a linear relationship. This effect is shown in Fig. 2. The top and middle panel show the effect that a linear energy scale correction of 10 eV, ΔE_{edge}, has on an iron foil that has been collected with an angular misalignment of $0.0233°$ (corresponding to the offset at E_{edge}). The bottom panel shows the non-linearity of the energy scales by representing the difference between the original energy scale and the energy scale linearly corrected.

In order to address this, some authors have proposed alternative methods that can provide the energy calibration of an XAFS spectrum by using more than one point in the scan. Pettifer & Hermes (1985) built a device that collects the Laue diffraction pattern from a perfect silicon crystal as the absorption scan is measured. A scheme of this set-up is shown in Fig. 1 (bottom panel). In the case of Acrivos et al. (1982) and Stümpel et al. (1991), a bond-diffractometer was utilized. In both cases the collection time of the absorption spectrum increased considerably.

A possible solution to these issues would be to calibrate the reference sample absorption spectrum that is collected simultaneously with the sample with a foil measured with a very highly accurate energy scale, as is the case of measurements that have been performed by Kraft et al. (1996). Once the calibration parameters have been found, they can be applied to the real sample, so not only a linear correction is performed.

It is important to highlight that, for most of the cases, the collection of the absorption spectrum of a reference sample at the same time as the measurement of the sample signal, and the application of a linear correction, is generally sufficient to extract the information sought in the experiment. All that this requires are the available tabulated edge energies for metal foils. However, the availability of a database of reference foils absorption spectra collected with very high energy accuracy is advisable. If this were done, and if it is necessary for the experiment, a multipoint energy scale calibration can be performed, and not just a linear correction extrapolated from a single fixed point. This database would also be very useful for the calibration of the absorption spectra collected on energy-dispersive spectrometers (Ferrero et al., 1997; Ruffoni & Pettifer, 2006).
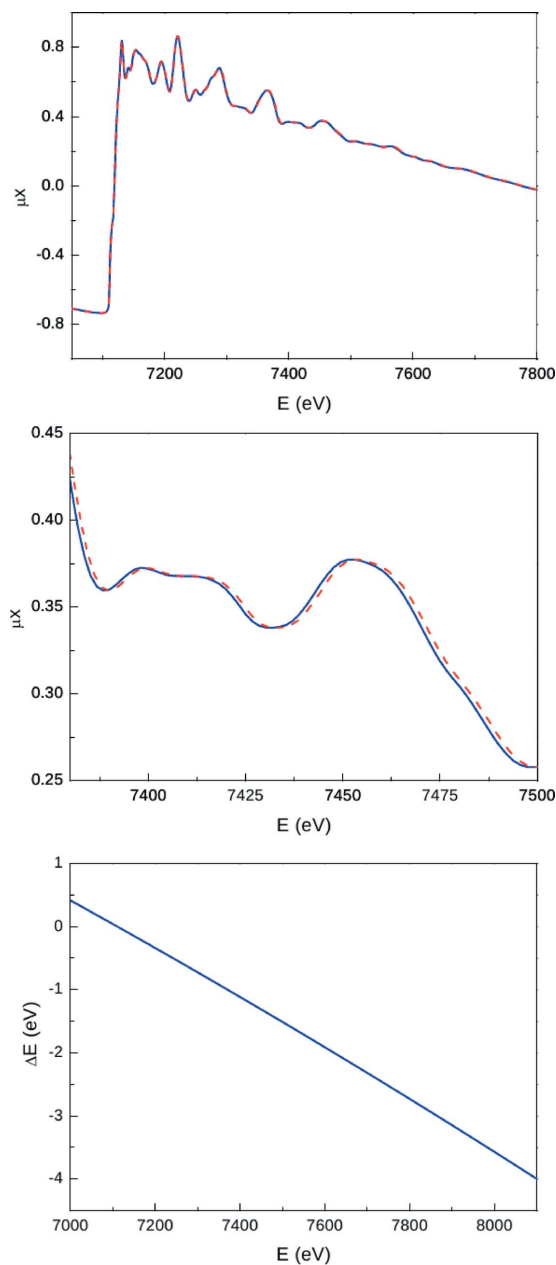

Figure 2
Illustration of the imperfect nature of a single-point energy calibration to correct for an angular offset in a typical monochromator. The top panel shows two spectra that have been corrected in energy to the E_{edge}, one of a perfect calibrated monochromator and the other from a monochromator with a $0.0233°$ angular offset. The middle panel highlights the energy offset that develops when the correction is based on a simple linear realignment of the edge position. The bottom panel shows the magnitude of this offset over the scan range.

1.2. Intensity calibration

In most cases, absolute values of the intensity of the radiation used in the absorption experiments are not necessary, although it is often interesting to know the number of photons reaching the sample during the experiment. However, to obtain meaningful information from the absorption data it is imperative that the measured intensity is proportional to the number of photons reaching the detectors. In addition, the two

detectors used to collect the absorption spectrum need to be linear, and changes in the intensity of the radiation must give the same response in both detectors. In the case of fluorescence or electron yield experiments, it is very important that the measured secondary process is proportional to the main process.

If the detectors used are ionization chambers, there are two main factors that have to be addressed (Rossi & Staub, 1949; Sharpe, 1964; Knoll, 1999; Pettifer et al., 1999). First of all, the ionization chamber needs to operate in the 'saturation' regime where the voltage applied to the chamber has to be high enough to separate the electrons from the positively charged gas atoms before they recombine (Knoll, 1999). This ensures that the measured signal just depends on the number of photons reaching the chamber, the energy of the photons, and the nature of the gas selected to fill the chamber. A second important issue is to ensure that a measurement of the dark current is taken and subtracted from the data, and it is good practice to take a dark-current measurement before every measurement.

The main issue with multi-element fluorescence detectors that are used to collect data in fluorescence mode is the so-called 'dead-time', i.e. when two events reach the detector separated by a very short time, the detector cannot process the two events (Knoll, 1999). Dead-time effects can cause the features in the XANES region of the absorption spectrum to be damped (Woicik et al., 2010). As the amplitude of the EXAFS signal is reduced, so the structural information extracted is not accurate. This is illustrated in Fig. 3. The top panel shows the absorption spectra of an iron-containing sample collected at different count rates. The lower panel shows the extracted EXAFS signal for the collected spectra (data courtesy of beamline I18 at Diamond Light Source). The relation between the counts processed by the detector and the counts reaching the detector moves further away from linearity the higher the count rate, so it is advisable that dead-time effects are kept below 15–20% so that they can be corrected with reasonable accuracy.

2. Beamline I20 at Diamond Light Source

The versatile spectroscopy beamline at Diamond Light Source, I20, consists of two branches that can be operated independently and simultaneously (Diaz-Moreno et al., 2009). To achieve this, a pair of canted wigglers are located in a 5 m diamond straight section. The two branches share the vacuum space in the optics hutch, but each has a completely independent experimental hutch. One branch of the beamline, the scanning XAS branch, will deliver monochromatic X-ray radiation of high spectral purity to one of the experimental hutches, whilst the other branch will constitute an energy-dispersive spectrometer.

The scanning branch of the I20 beamline is designed for the study of the local structure around a photoabsorbing atomic site that is present at a concentration of approximately 1.0 mM, and/or in an X-ray unfavourable heavy matrix (Diaz-Moreno et al., 2012). The energy range of the scanning branch
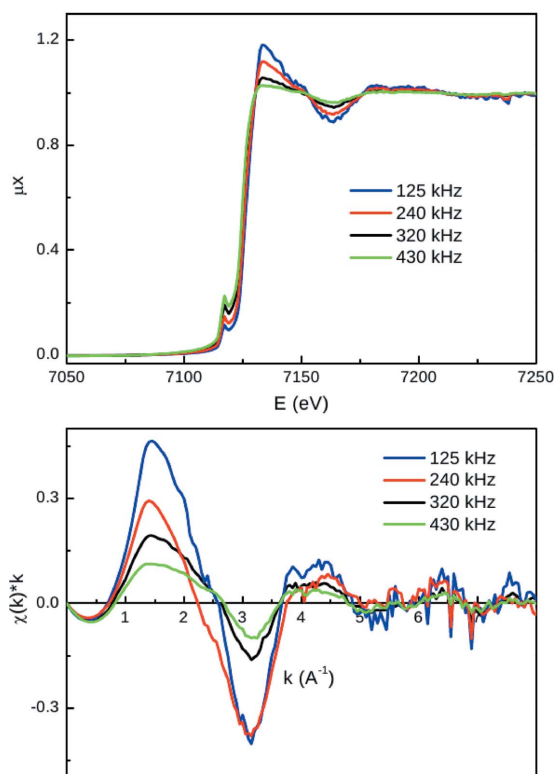

Figure 3
Raw collected data (top panel) and extracted EXAFS signal (bottom panel) for an iron-containing sample measured in fluorescence mode demonstrating the effect of different total count rates on a solid state detector [data courtesy of beamline I18 at Diamond Light Source, using a monolithic nine-element germanium detector (Ortec) coupled with the XSPRESS 2 data acquisition electronics (Farrow et al., 1995)].

is from 4 keV to 34 keV, providing access to the absorption edges of the entire periodic table from calcium upwards, via the K or the L edges.

The main design feature of the scanning branch of I20 is the use of a four-bounce monochromator (DuMond, 1937; Faigel et al., 1987; Tolentino & Rodrigues, 1992; Nakayama et al., 1973). The device is based on two counter-rotating axes, each one carrying a pair of crystals in a traditional double-crystal configuration. The two axes are set in a dispersive configuration. Currently there are two crystal sets installed in the monochromator: a Si(111) set to be used in the energy range from 4 keV to 19 keV, and a Si(311) crystal set to be used in the energy range from 7 keV to 34 keV. The monochromator is simply operated by counter rotating the two axes. This means that a real fixed exit is achieved without the need of any translations, in contrast with the constant exit beam height double-crystal monochromator designs (Lemonnier et al., 1978; Golovchenko et al., 1981; Mills & King, 1983; Goulon et al., 1983; Matsushita et al., 1986). These translational motions increase the chances of beam movement at the sample position, which is a particular problem when working with small beams and inhomogeneous samples.

The in-house design of the four-bounce monochromator has been extremely challenging (Sutter et al., 2008). Not only must the two axes be synchronized for the entire energy range

of the beamline but, more importantly in the case of an absorption beamline, the two axes must be kept synchronized while scanning to maintain the X-ray throughput during data collection. The repeatability needed for this design is $\pm 0.3\ \mu$rad for each axis, required for the case of the Si(311) crystal set at the highest energy range of the beamline, 34 keV.

In order to achieve the required repeatability, five main design characteristics have been implemented in the design of the I20 four-bounce monochromator. These are:

(i) The use of an air bearing for the main axes rotations. This offers excellent performance in terms of run-out, stiction (static friction that needs to be overcome to enable relative motion of stationary objects in contact), friction and repeatability.

(ii) A large-diameter direct drive motor is selecting the Bragg angle: there is no gear system.

(iii) A ferrofluidic seal is used to separate the vacuum. It adds a damping term which makes control at very tight tolerances more straightforward. Because there are no sliding or wiping joints the seal introduces no friction or stiction.

(iv) A large-diameter in-vacuum encoder ring is installed on each axis. The encoder features 20 μm line spacing, giving a total of 63800 lines over the 360° of the encoder, but is further interpolated by a factor of 2000, giving a minimum step size of 50 nrad. The control system then permits control to three interpolated steps.

(v) Four encoder heads placed at 12, 3, 6 and 9 o'clock positions are used, and the position of the axis is controlled by the average of the signal from the four encoders.

The choice of a four-bounce monochromator for the I20 beamline was partly made to address the issues described in §1.1 that affect the energy scale of the absorption spectrum. Thus, in the four-bounce monochromator configuration, movements of the source or any optical element upstream of the monochromator are translated into intensity variations of the transmitted beam. The energy calibration and the position of the beam on the sample become fixed. Following the same principle, the energy of the beam transmitted by the four-bounce monochromator does not vary if the temperature of the first axis changes, as the beam still has to travel through the second axis. In addition, the energy resolution is solely given by the Darwin width of the crystal set and is independent of all other factors such as divergence of the incident beam or mode of operation of the synchrotron.

Another important characteristic of the four-bounce monochromator is the reduction of the tails in the reflectivity curves. This will enable thick samples to be studied without distorting the XAS spectrum collected (Stern & Kim, 1981; Kraft *et al.*, 1996; Pease *et al.*, 1979). As can be seen in Fig. 4, the tails of the reflectivity curve are greatly reduced when four bounces are used, in contrast with the case when one or two crystals are used.

3. Conclusions

The use of features of known energy in reference samples such as metallic foils is commonly used for the calibration of the
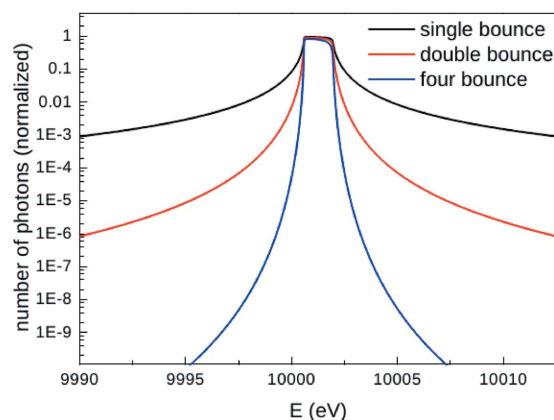

Figure 4
Comparison of the normalized photon flux transmitted by a single-crystal (black line), a double-crystal (red line) and a four-crystal system (blue line) at 10 keV for a Si(111) cut, calculated assuming a perfectly collimated incident beam.

monochromator. As for the reproducibility of the energy scale during an experiment, the use of internal calibrations is normally the best solution.

In general, and for most experiments, a linear shift of the spectrum is sufficient. However, some experiments will benefit from an absolute energy calibration. This can be achieved by measuring the energy of the radiation impinging on the sample at more than one point, although the acquisition time increases considerably. An alternative option is to compare the reference sample measured during the experiment with the absorption spectrum of the same sample measured with absolute energy calibration, extracting the energy scale relationship that has to be applied to the data.

Regarding the intensity of the measured radiation, exhaustive characterization of the detectors, ionization chambers and/or fluorescence detectors is necessary to obtain reliable structural information from the absorption data.

There are other factors affecting the amplitude of the EXAFS signal but, as they are sample dependent, they fall out of the scope of this paper.

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