Energy calibration and intensity normalization in high-resolution NEXAFS spectroscopy

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Abstract

Using high-brilliance synchrotron radiation and an ultrahigh-resolution monochromator a wealth of new fine structures can be observed in near-edge X-ray absorption spectra. The potential information gain, however, requires an accurate calibration of the energy scale and a perfect intensity normalization in order to avoid erroneous results, e.g., the occurrence of spurious peaks. By means of the most problematic C 1s edge it is shown how large these effects can be and how appropriate energy calibration and intensity normalization can be achieved.

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1. Introduction

The near-edge X-ray absorption fine structure (NEXAFS) technique has become a powerful technique to analyse interesting new materials, adsorbates, and thin films [1]. This method is particularly useful for the investigation of organic substances, for at least three reasons. First, the excitation of core electrons into unoccupied molecular orbitals yields important information on the electronic structure involving chemical shifts of the core levels as well as significant fine structure in the unoccupied valence states. Both are sensitive to the chemical bonding and responsible for electron transport [2–5]. Secondly, NEXAFS is a local probe that monitors the local distribution of valence states at the different core holes that can be selected by the energy dependence of the absorption cross section [6]. Thirdly, NEXAFS is ideally suited to investigate the molecular orientation based on the linear NEXAFS dichroism [3,7–9]. A detailed understanding of the rich fine structure is backed by appropriate calculations [1,10–13]. These advantages of NEXAFS are best illustrated by a very recent example obtained in our group, the observation of detailed fine structure in highly-ordered thin films of various organic substances which is due to various electronic transitions and their coupling to vibrations [14]. It is emphasized that such fine structures can only be observed by using a high-brilliance beamline with a high
energy resolution monochromator at a third generation synchrotron source.

It is obvious that energy calibration and intensity normalization become more important as more fine structure is resolved. Of course, a beamline, i.e., the monochromator, has to be energy-calibrated before being used. It is less well known that the energy calibration should be checked routinely—e.g., twice during each fill—in particular when a very accurate energy scale is required. The reason is that mechanical movements, positions of optical elements, the position of the electron beam after each refill, and changes of the heat load on optical elements and hence thermally induced deformations frequently lead to changes of the photon energy scale. Most experimenters hence rely on typical structures in the transmission or flux ($I_0$) curve for a routine recalibration of their data since the $I_0$ signal is usually recorded simultaneously. This is particularly the case for the C 1s edge at which two very prominent “dips” in the flux curve appear at about 284 and 291 eV (see Fig. 1). However, as we will show in the following, there are severe problems with this procedure since the $I_0$ structures also may change and since it may be impossible to record a useful $I_0$ signal simultaneously, e.g., when using a high-brilliance beamline with a small focal spot.

Such changes of the $I_0$ curve may also be disastrous for the intensity normalization of the spectra which is required because the primary photon flux usually has a significant energy dependence. This intensity variation as a function of the photon energy can be as much as 98%, at the C 1s edge due to the absorption by photolytically dissociated carbon impurities on the optical elements. In such a case the intensity normalization will fail if only small changes in the $I_0$ curve occur. In the following we will give examples how large these effects can be and by which means these problems can be solved. Thus, after a short experimental section, we will first discuss the energy calibration and will then move on to the intensity normalization problem.

2. Experimental

Most of the data presented here were taken at the U49/1-PGM beamline of BESSY II. It consists of an 84-period undulator of 49 mm period length, a vertically collimating cylindrical mirror (M1), a plane grating monochromator (PGM) with a plane mirror (M2) and a plane grating (G1), two focusing mirrors, i.e., one vertically (cylindrical mirror M3) and one horizontally (spherical mirror M4), and an exit slit [15,16]. It is noted that the electron beam in the undulator defines the source, i.e., the beamline has no entrance slit and is hence sensitive to the electron beam position. The photon energy ranges from 100 to 1500 eV. An energy resolving power of more than $E/\Delta E=10\,000$ could be demonstrated at the N K-edge at 401 eV with a photon flux of about $3\times10^{10}$ ph/s/100 mA (fixed-focus constant $c_{\text{ff}}=10$, exit slit 10 $\mu$m). In March 2002 the horizontally polarizing undulator U49/1 was replaced by a new APPLE-II type 79-period undulator with 52 mm period length, which provides either elliptical or linear polarization with variable direction of the polarization plane.

The beamline is equipped with an ultrahigh-vacuum spectroscopy chamber with a SCIENTA XES200 electron energy analyzer for photoemission experiments and a retarding field analyzer for partial electron yield detection. Thus, photoemission and NEXAFS with Auger yield detection can be compared with partial yield NEXAFS and/or with total

Fig. 1. (a) Photon flux of the U49/1-PGM beamline at BESSY II recorded by a photodiode using the first undulator harmonic (monochromator setting: fix focus constant $c_{\text{ff}}=2.25$; exit slit: 30 $\mu$m). (b) (Inset) Comparison of the flux curves of the PM1 and U49/1-PGM beamlines at BESSY II around the carbon K-edge plotted on nominal (not recalibrated) energy scales.
yield NEXAFS if the sample current is being recorded.

For comparison we will also present data recorded at the PM-1 dipole (bending magnet) beamline at BESSY II. This beamline uses a Petersen-type SX-700 monochromator to select photon energies in the range from 20 to 2000 eV with an energy resolving power of about \( E/\Delta E = 3000 \) and a photon flux of about \( 1 \times 10^{10} \) ph/s/100 mA at 400 eV \( (\varepsilon_n = 2.08, \text{exit slit 50 } \mu\text{m}) \). Also this beamline has no entrance slit. A detailed description of the beamline and performance can be found elsewhere [17].

3. Energy calibration

The energy scale of a monochromator has to be calibrated at several points, even if a good description of the energy/wavelength dependence on mechanical parameters (e.g., angle of the grating) is available. Of course, the energy scale depends on all mechanical parameters like positions and angles of the grating, the various mirrors, and the exit slit, and therefore has to be calibrated carefully. The calibration, once established, can be influenced by mechanical clearance of the monochromator drives, faults of the angle decoders, mechanical shocks, exchange of gratings, by bake-outs of the UHV chambers, and even by the temperature increase of optical elements in the high photon flux after injection. The energy scale also depends on the position of the electron beam, especially for beamlines without entrance slit. This position may change after modifications of the storage ring or of the orbit parameters, and it may vary from run to run, after new injections, or even during data recording. Hence it is important to check the energy calibration routinely, i.e., at the beginning of each beamtime, after each refill, and perhaps even before and after each new experiment (see below).

There are at least three different approaches for this calibration check. (1) The most accurate and most general method is the use of very precisely known photoemission lines and an accurately calibrated photoelectron spectrometer. (2) If standard samples have been previously measured by NEXAFS using a calibrated beamline their NEXAFS spectra can be used as calibration standards in the future.

Using gaseous samples with well known absorption spectra, e.g., He, Ar, N\(_2\), Ne and Xe, this is a common way of energy calibration. Relatively simple experimental requirements, sharp absorption features and a wide energy range \( (10 \rightarrow 10^5 \text{ eV}) \) make it the most popular method for beamline commissioning in the VUV and soft X-ray range [18]. For in-situ calibration near the carbon edge carbonaceous gases such as CO\(_2\), CO and acetylene can also be applied [19]. (3) Similarly, if the flux (transmission) vs. energy curve of the monochromator, usually called the \( I_0 \) curve, has sharp and stable structures, these can also be used as calibration points. This third method is commonly applied near the C 1s edge at which the \( I_0 \) curve always has two very pronounced dips. It is well established—though very dangerous (see below)—to set the photon energy at these dips to 284.7 and 291.0 eV, respectively [1].

The last point is illustrated in Fig. 1a which shows a typical transmission \( (I_0) \) curve of a soft X-ray beamline (U49/1-PGM at BESSY II) with the dominant double-dip at about 290 eV. This dip is due to absorption by carbon contaminants deposited on the optical elements by photolytical processes. In the case of the U49/1-PGM with five optical elements the photon flux drops from about \( 4 \times 10^{11} \) ph/s/100 mA at 230 eV to \( 8 \times 10^9 \) ph/s/100 mA at 290 eV. Of course, such a pronounced structure in the \( I_0 \) curve is disadvantageous because of the intensity loss (factor 50) and the problem of normalization (see below). However, it is commonly believed that the dips can be used for routine and accurate energy calibration. The inset (Fig. 1b) provides a zoomed view of the dip region of two different monochromators using their nominal energy scale. It demonstrates that the flux curves can differ in both, energy and shape for these different beamlines (here: PM1 and U49/1-PGM). As mentioned, the common way of (re-)calibration would be to set the energies of the dips to 284.7 eV and 291.0 eV, respectively [1]. However, it can be derived from the inset of Fig. 1b that this method is not sufficient since the energy separation of both dips may vary, for instance between 5.5 and 6.3 eV in the present case.

Moreover, the shape, the energy separation, and in particular the energy positions of the dips of a calibrated beamline may change as a function of

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**Footnotes:**

time. This is shown in Fig. 2 which displays the \( I_0 \) curves taken at three different runs (continuous black line and grey lines) within about one year using the same U49/1-PGM monochromator. The monochromator was carefully calibrated each time according to the procedure given below. While the second (because of its shallow shape less suited) dip remained constant in energy, the first sharp \( I_0 \) dip shifted from 284.3 to 283.4 eV, i.e., by nearly 1 eV! The deviation of 1.3 eV of the here measured first dip (dashed grey curve) from the literature value is unacceptable and nearly two orders of magnitude worse than the possible accuracy of calibration. We note that the origin of this shift is a proceeding contamination of the first mirror, since a cleaning of this mirror in March 2002 brought the shape of the flux curve and hence also the dip positions almost completely back to the initial state of December 2000 (compare black curves in Fig. 2). This result also shows, that the applied cleaning procedure of mixed oxygen/argon plasma etching [20] is an appropriate method to remove contaminants. Note also, that the replacement of the undulator U49/1 by the new UE52 in March 2002 had no significant effect on the shape of the flux curve.

Now we briefly describe an accurate calibration method that can be used as standard procedure. In a first step this requires the accurate calibration of an electron spectrometer. By using the well-known energies of a laboratory X-ray source and of prominent photoemission or Auger lines of clean noble metals (see Table 1) [21,22] one can exactly determine the deviation \( \Delta \) of the used spectrometer over the full range of kinetic energies. This is done by recording at least two peaks that are as far as possible apart from each other on the kinetic energy scale. Their energy positions are carefully evaluated yielding \( E_{\text{Kin}}^{\text{meas}} \) and subtracted from the corresponding calibration values (\( E_{\text{Kin}}^{\text{cal}} \) or \( E_B^{\text{cal}} \), see Table 1) according to:

\[
\Delta = E_{\text{Kin}}^{\text{cal}} - E_{\text{Kin}}^{\text{meas}} = (h\nu - E_B^{\text{cal}}) - E_{\text{Kin}}^{\text{meas}}
\]  

(1)

The deviation \( \Delta \) is then plotted versus the real kinetic energy resulting in a straight line (a nonlinear behaviour of the spectrometer is usually not found [21,22]) which can then be used as calibration curve for this particular spectrometer. This calibration should be checked routinely, say at least twice a year or—better—for each run. With our SCIENTA XES200 analyzer at the U49/1-PGM we measured the 3d\(_{3/2}\) and M\(_{1,3}\)VV lines of a carefully cleaned Ag(111) sample with Mg K\(_\alpha\) and Al K\(_\alpha\) excitation (to cover a sufficiently wide kinetic energy range, 350–1120 eV) and obtained a constant deviation (offset) of \( \Delta = 0.22 \) eV. Of course, the Fermi edge of s-metals (e.g., Cu, Ag, Au) is also a good calibration point.

In the next step the photon energy scale of the monochromator is calibrated by recording photoemission lines with accurately known binding energies, for instance those of Table 1, using photon energies in the energy range of interest. For example, for the spectral range of the C 1s NEXAFS measurements we recorded the Ag Fermi edge using the
Table 1
Calibration values for some photoemission binding energies and Auger kinetic energies of the clean metals Cu, Ag, Au, Ni, and Ru using Al and Mg Kα excitation and calibrated energies of the Al and Mg Kα excitation lines

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Ni</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2s</td>
<td>1097.05</td>
<td></td>
<td></td>
<td>4f_{1/2}</td>
<td>83.98*</td>
</tr>
<tr>
<td>2p_{1/2}</td>
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<td>3d_{5/2}</td>
<td>374.27</td>
<td>2p_{1/2}</td>
<td>869.99</td>
</tr>
<tr>
<td>2p_{3/2}</td>
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<td></td>
<td></td>
<td>2p_{3/2}</td>
<td>852.75</td>
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<td>3p_{3/2}</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3p_{1/2}</td>
<td>66.30</td>
</tr>
</tbody>
</table>

Auger $E_a$ (eV)

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Ni</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s/VV</td>
<td>918.62*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2s/VV</td>
<td></td>
<td></td>
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<tr>
<td>3s/VV</td>
<td></td>
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</table>

Excitation energies of common laboratory sources

Al Kα = 1486.58±0.03 eV*  
Mg Kα = 1253.56±0.03 eV*

The data indicated by asterisks (*) were taken from Refs. [21] and [22] (accuracy = 0.02 eV). The other data [unpublished] were acquired by Höfer, Hudecek, Wurth and Umbach using a calibrated VG ESCALAB MkI instrument (accuracy <0.05 eV).

nominal photon energies $h\nu=270$ and 320 eV, respectively, and determined the exact values of $h\nu$ by taking the analyzer deviation $\Delta$ at 270 (320) eV kinetic energy into account. In this way an accuracy of the absolute energy scale of <50 meV can be obtained. The error bar mainly depends on the quality of the calibration values and on the evaluation of the measured photoemission/Auger lines. Of course, the relative accuracy is significantly better, for instance better than 10 meV, depending on the resolution of analyzer and monochromator. This relative accuracy turned out to be of prime importance also for the intensity normalization as discussed in the next section.

The experimenters should be aware, that a recalibration by simply shifting the energy might lead to a distorted energy scale. This is because energy is inversely proportional to the wavelength and for most monochromators the miscalibration is typically due to an offset in wavelength. However, for small recalibrations within a small energy range, e.g., 100 meV in the range 270 to 320 eV, non-linearity effects in the energy scale are negligible. For larger deviations one has to re-calibrate the wavelength and recalculate the energy scale to maintain linearity.

We note, that in addition to the energy calibration procedures described above a new method, that can be utilized for plane-grating monochromators with the freedom to change the fixed-focus constant $c_{ff}$, has been developed at BESSY [23]. In combination with the in-vacuum angular encoders of the new BESSY PGM generation, that allow highly accurate measurements of the mirror and grating angles [24], this method shows an absolute accuracy of the calibrated energy in the $10^{-4}$ range.

4. Intensity normalization

As mentioned above NEXAFS spectra have to be normalized since the photon flux varies as a function of energy and time. This normalization is often performed by dividing the sample signal $I_{sample}(h\nu)$ simply by the flux curve $I_f(h\nu)$. A better normalization procedure which applies to very thin films or adsorbates takes the substrate signal $I_{substrate}(h\nu)$ into account, according to:

$$I(h\nu) = \frac{I_{sample}(h\nu) - fI_{substrate}(h\nu)}{I_f(h\nu)}$$

$$I(h\nu) = \frac{I_{sample}(h\nu)}{I_f(h\nu)} - f\frac{I_{substrate}(h\nu)}{I_f(h\nu)}$$

(2)

Here $I_{sample}$ contains the photon energy dependent signals from the adsorbate (or deposited thin film) and from the (attenuated) substrate, while $I_{substrate}$
stems from the clean substrate. When this is subtracted one has to consider that $I_{\text{substrate}}$ is attenuated by the overlayer resulting in a material, coverage, angle and energy dependent factor $f \ll 1$. The sample and substrate signals may be recorded in total, partial or Auger yield mode [1] which should be chosen according to the experimental requirements and available equipment. It is emphasized that for each method different offsets due to higher-order contributions, dark currents, stray light, secondary electrons, etc., may occur which also have to be taken into account by subtracting offsets from both signals. The attenuation factor $f$ is usually not sufficiently known and hence is used as a free parameter.

The measurement of the $I_0$ curve is the central issue for the normalization routine. Conventionally, $I_0$ is detected by measuring the photocurrent from a Au grid mounted behind the exit slit of the monochromator [1]. In order to avoid problems with contaminations on the $I_0$ detector one can regularly evaporate a fresh gold film onto the grid before data recording. However, monitoring the $I_0$ intensity of a state-of-the-art high-brilliance undulator beamline is more difficult since this may provide a much smaller beam size (<100 μm). Therefore the use of a conventional gold grid with a mesh size in the order of the magnitude of the beam size is not appropriate since even minor movements of the experimental chamber or the beam will drastically change the $I_0$ photocurrent signal from the grid and will hence make a correct normalization impossible. Also, measuring the photocurrent with a photodiode is not suitable, at least not for C–K NEXAFS experiments on thin films or monolayers, since the effect of carbon contaminations on the diode will lead to artifacts. In principle, one could use a gas cell inserted between exit slit and sample to record the $I_0$ curve. This has not been tried by us so far.

A proper alternative is to use the clean substrate spectrum for normalization, i.e.:

$$I_0(h\nu) - I_{\text{substrate}}(h\nu)$$

This is possible if the substrate does not show any specific absorption structures in the interesting energy range. Eq. (2) can then be reduced to:

$$I(h\nu) = c \cdot \left[ I_{\text{sample}}(h\nu)/I_{\text{substrate}}(h\nu) - f \right]$$

Of course, $I_{\text{sample}}$ and $I_{\text{substrate}}$ (from the clean substrate) can only be recorded sequentially. In this case the energy calibration has to be monitored carefully, since small changes in the electron orbit, that can occur, e.g., during injection, can slightly shift the photon energy, as discussed above. At the U49/1-PGM beamline we observed energy shifts of up to 100 meV between two subsequent injections.

It is shown in Fig. 3 what happens if this effect is not carefully taken into account. It displays the C–K NEXAFS spectrum of a 0.9 ML thick (0.9 monolayer thick) PTCDA (3,4,9,10-perylene-tetracarboxylicacid-dianhydride) film on Ag(111) after it was normalized to (a) a substrate spectrum as measured and (b) to an energy-corrected substrate spectrum. Actually both, the monolayer and the substrate spectrum, were calibrated to the correct energy in this latter case leading to a relative shift of both by

![C1s NEXAFS spectrum of 0.9 monolayers of PTCDA / Ag(111)](image-url)

**Fig. 3.** C 1s NEXAFS spectrum of 0.9 monolayers of PTCDA / Ag(111). (a) normalized by a clean substrate spectrum, as recorded; (b) after proper energy recalibration of sample and $I_0$ spectra (see text).
50 meV. It is emphasized that such an energy shift can already lead to strong artifacts in the final spectrum (compare spectrum a to spectrum b in Fig. 3), particularly in the region of the first sharp $I_0$-dip. Since the lowest $\pi^*$-resonances of many organic molecules appear exactly in this energy range, a very careful check of all structures in this particular energy range is advisable. In the present case the appearance or non-appearance of (a) structure(s) around 283.5 eV would have major implications since it provides information about the involvement of the lowest unoccupied molecular orbital (LUMO) in the bonding to the substrate. We further note that the (properly corrected) structures in this energy range are very different for similar molecules (e.g., PTCDA and NTCDA) in different bonding situations (e.g., different states or on different substrate surfaces) [25] indicating the great importance of an accurate energy calibration and intensity normalization.

5. Conclusions

High-brilliance, high-resolution undulator beamlines enable NEXAFS measurements with very distinct fine structures that are due to various electronic transitions and their coupling to vibrations. This detailed structure contains a variety of information about electronic, chemical and structural properties provided that both, the energy calibration as well as the normalization are carried out with great care.

In this report we discussed some of the problems that can arise at such beamlines and gave some procedures how to avoid them. Energy calibrations are easy to perform routinely thus achieving an accuracy of absolute energies of about 50 meV and of relative energies of about 10 meV. Also, the normalization requires accurate energy scales for both, the sample spectra and the corresponding normalization curves. Otherwise artifacts may arise that lead to incorrect interpretations. Of course, artifacts are particularly large for small signal-to-background ratios, e.g., for signals from monolayers. Thus for a proper normalization, it is strongly recommended to take energy calibration spectra (e.g., of the substrate Fermi edge or of a clean Au foil mounted on the sample holder) directly before or after each sample NEXAFS spectrum.

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