A simple method for determining linear polarization and
energy calibration of focused soft X-ray beams

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Abstract

Although critical to quantitative linear dichroism studies of molecular orientation, the degree of linear polarization of focused soft X-ray beams delivered by X-ray microscopes has not been previously measured. Here, we present a scaled-down version of a recently developed technique in which the $\pi^*$ near edge X-ray absorption fine structure (NEXAFS) resonance of highly oriented pyrolytic graphite (HOPG) is used to probe the electric field intensity in each direction and hence deduce the degree of linear polarization of the incident X-ray beam. Applying this technique to the soft X-ray microscope at beamline 5.3.2 of the Advanced Light Source in Berkeley, CA, yielded a measured value of 79 $\pm$ 11\%, for the first Stokes parameter of 0.79 $\pm$ 0.11 or as a St"ohr $P$ factor of 0.89 $\pm$ 0.06. It is expected that the error margin could be significantly reduced via the use of an in-vacuum rotation actuator. We have also calibrated the energy of the graphite exciton to be 291.65 $\pm$ 0.025 eV, improving the utility of graphite as an energy calibration standard for NEXAFS and allowing the convenience of both energy calibration and polarization determination with a single inexpensive sample.

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1. Introduction

To date, a number of linear dichroism studies of molecular orientation have been carried out using scanning transmission X-ray spectromicroscopes (STXMs) that included materials such as Kevlar [1,2], linear alkane crystals [3,4], polyethylene [5], crystals of polycyclic aromatic hydrocarbons [6] and phenyl urea [7], thermoplastic/liquid crystalline polymer blends [8], block-copolymer, coke [9] and silk [10]. The number of X-ray linear dichroism applications has been much smaller than the number of applications that seek to quantify composition with near edge X-ray absorption fine structure (NEXAFS) microscopy [11,12]. This is due to a number of factors: (i) the intrinsic number of possible applications, (ii) the non-linearity and non-orthogonality of the STXMs imaging systems available [1,2,13,14] had made quantitative analysis of two orthogonal sample orientations difficult, and (iii) the uncertainty in the degree of linear polarization of the focused soft X-ray beam of a STXM and its reproducibility and stability over time also degraded quantitative analysis capabilities and decreased productivity. Recent instrument developments based on laser interferometers have now vastly improved the linearity and orthogonality of STXM technology [14]. Furthermore, STXM is a technology that is now implemented at a number of synchrotron facilities at bending magnets and undulators. The need to reliably perform quantitative dichroism measurement remains and with it, the need to measure the degree of linear polarization of a STXM, particularly those that are operated at bending magnet beamlines.

The zone plate optical element utilized in a STXM complicates the use of these instruments for dichroic measurements. The zone plate is usually overfilled (see Fig. 1) in order to stabilize the transmitted flux and therefore also acts as an aperture, spatially truncating the beam. The incident beam is thus not necessarily representative of the transmitted beam and the location of the zone plate relative to the beam greatly affects the polarization of the transmitted beam. Hence, inevitable changes in alignment over time lead to changes in the degree of polarization, greatly reducing accuracy and reproducibil-
ity. Measurement of the polarization in STXM is challenging for two reasons. Firstly, as discussed above, measurements upstream of the zone plate are not representative of the transmitted beam, and secondly, the short focal distance of the zone plate requires that the order selecting aperture (OSA) and sample be situated within a short distance of the order of a few millimeters, providing little space for the inclusion of additional equipment. Thus, conventional macroscopic methods for measuring the degree of polarization of a soft X-ray beam cannot be easily applied to soft X-ray microscopes. However, knowledge of the degree of linear polarization is critical for fully quantifying the degree of molecular alignment observed in a sample.

A recently developed polarimetry technique [15] utilizes the π+ near edge X-ray absorption fine structure (NEXAFS) resonance of highly oriented pyrolytic graphite (HOPG) to deduce the degree of linear polarization of the incident X-ray beam. This method may be summarized in three steps:

- Firstly, NEXAFS spectra of the sample HOPG crystal are recorded at normal X-ray incidence, which provide a measure of non-ideality of the sample crystal. The principle behind this measurement lies in the fact that in a perfect HOPG crystal, all of the C 1s → π+ transition moment vectors are aligned with the surface normal and hence are perfectly orthogonal to the electric field vector of a normally incident X-ray beam, resulting in zero NEXAFS resonance intensity. Therefore, any NEXAFS resonance intensity observed near 285 eV in a normal incidence geometry can be entirely attributed to defects and contaminants in the HOPG crystal. Note that since the resonance intensity is proportional to the squared sine of the angle between the X-ray beam axis and the crystal surface normal (or more precisely, the squared cosine of the angle between the electric field vector of the X-ray beam and the transition moment vector [16]), the normal incidence measurement is not very sensitive to small errors in sample orientation.

- Second, the HOPG crystal is mounted, at some fixed tilt angle, on an azimuthally rotatable stage so that the crystal’s surface normal can be precessed about the X-ray beam axis, as shown in Fig. 1. Recording NEXAFS spectra at a range of azimuthal angles then reveals a trend in the π+ NEXAFS resonance intensity, showing maxima and minima when the crystal normal is aligned, respectively parallel and perpendicular to the synchrotron plane.

- Lastly, the π+ NEXAFS resonance intensity trend with azimuthal angle is plotted against the squared sine of the azimuthal angle to produce a straightline trend, as demonstrated in Fig. 8. From this plot, we can determine the gradient, \( m \), and intercept, \( b \), of the trend which, when combined with the resonance intensity observed at normal X-ray incidence, \( I_\perp \), can calculate the Stöhr polarization factor [16], \( P \), using the equation:

\[
P = \frac{[(m/b - I_\perp)] + 1}{[(m/b - I_\perp)] + 2}
\]

Measurements performed at a number of beamlines demonstrated that the linear polarization of bending magnet beamlines can vary significantly, especially due to design and alignment issues, and demonstrate the need to experimentally determine polarization. Here, we present a scaled-down version of this polarimeter experiment and use the adapted technique to determine the degree of linear polarization of a STXM instrument.

Furthermore, we will also accurately determine the energy position of the HOPG exciton resonance peak (observed in NEXAFS spectra near 291 eV) by comparison of the NEXAFS spectra of HOPG and CO2 gas. HOPG is a common standard for calibrating the photon energy scale of NEXAFS spectra, but typically the wider and more asymmetric π+ peak near 285 eV is used. Use of the more narrow exciton peak will improve the utility of HOPG as a secondary energy standard. In combination with the polarimetry methods described in this work, a precise energy standard for HOPG spectra enables the simultaneous evaluation of both the energy scale and linear polarization of a soft X-ray beam.

2. Experiment

Initial samples were prepared by rubbing a TEM grid (1000 mesh; Gilder Grids, Grantham, UK) with a piece of HOPG (GRBS/1.2; NanoTech America, Allen, TX). While the method was found to also work with grids of other sizes, coarser TEM grids were found to result in graphite sections oriented at strong angles to the plane of the mesh so that the crystal quality could not be accurately assessed (i.e. difficult to achieve normal X-ray incidence) and the grid bars of finer TEM grids tended to interfere with the measurement. Rubbing with HOPG tends to leave a lot of graphite stuck to the TEM grid, but much of it is either too thick for the transmission of soft X-rays or highly crumpled and...
therefore of far too poor crystal quality to be of use in the experiment. Different rubbing techniques produced varying amounts of graphite on the TEM grid, however the creation of appropriately thin and flat graphite sections appears to be an essentially random occurrence. Excessive rubbing does not tend to improve the chance of finding an appropriate graphite section since they tend to be fragile and are easily destroyed by successive strokes.

Finding appropriately thin and flat sections of graphite on the grids is relatively simple with an optical microscope. Appropriate thickness can be assessed by the transparency of the graphite section (when illuminated in transmission) and crystal quality can be roughly assessed by how uniform it appears when illuminated in transmission and reflection. Promising candidates were then introduced into the beamline 5.3.2 STXM instrument [14] at the Advanced Light Source, CA for further inspection via images at 285.3 eV (corresponding to the HOPG π* resonance) and 292.3 eV (corresponding to maximum C 1s → σ* resonance) as well as line-spectra covering the full C K-edge energy range (270–340 eV). Fig. 2 shows representative images of a thin graphite section viewed with both optical and soft X-ray microscopes. As discussed in Section 1, any NEXAFS resonance intensity observed near 285 eV indicates that the sample crystal is either not ideal (i.e. contains defects, contaminant species, etc.) or is incorrectly oriented (i.e. not quite at normal incidence). Another possible source of normal incidence NEXAFS resonance intensity is significant divergence of the probing X-ray beam. However, the current 5.3.2 STXM zone plate has a diameter of 155 μm and focal length of 1225 μm and therefore the focused X-rays are less than 3.63° off-axis, which corresponds to a maximum 0.4% increase in π* intensity for normal incidence HOPG spectra.

The TEM grids holding the most promising graphite sections were then mounted on a STXM sample plate with rotatable mounts (to allow rotation in the final measurement step), introduced into the STXM and the identified high-quality graphite sections were analyzed with line spectra. These line spectra constitute the normal incidence (I⊥) measurement discussed in Section 1 and it is important to acquire spectra of sufficient resolution and statistics for any graphite sections selected for use in the polarization measurement because the following step of deforming the TEM grid will make it extremely difficult to re-acquire a normal incidence orientation afterwards.

As discussed in Section 1, this method of linear polarization measurement requires that the graphite planes be oriented such that the surface normal is tilted away from the incident beam axis by a significant angle. To this end, the TEM grid in the area

![Fig. 2. Images of the graphite section in (A) optical reflection, (B) optical transmission, (C) X-ray transmission (292.3 eV) at normal incidence and (D) X-ray transmission after TEM grid deformation (tilt angle, θ, of approximately 50°). The image widths are coincident with the TEM grid bar spacing of 19 μm. The dark, horizontal line appearing in (D), but not (C), is the result of radiation damage from an excessively long duration line-scan.](image-url)
The sample TEM grid and rotatable STXM mount plate were then introduced to the beamline 5.3.2 STXM instrument [14] at the Advanced Light Source, California, as detailed in Fig. 1. Carbon K-edge spectra of the graphite section shown in Fig. 2 were obtained at azimuthal angles over a range of about $130^\circ$. The entrance, dispersive exit and non-dispersive exit slits were set to 60 $\mu$m, 10 $\mu$m and 60 $\mu$m, respectively, corresponding to normal operation of the 5.3.2 STXM. Note that only the non-dispersive exit slit impacts the vertical acceptance angle of the bending magnet source and hence the polarization of the accepted radiation. Since the sample mount was limited to manual rotation, the STXM chamber was vented between each recorded spectrum. All spectra were normalized as discussed by Watts et al. [17].

Further spectra were acquired in the presence of a few mTorr of CO$_2$ gas in order to accurately calibrate the photon energy scale of the HOPG spectra. Since the sharpest peak in the NEXAFS spectrum of graphite, the exciton peak near 291 eV, is covered by the large C=O $\pi^*$ resonance of CO$_2$, the energy calibration required the acquisition of separate $I_0$, graphite and CO$_2$ spectra as an interlaced series to allow isolation of the resonance peaks while ensuring against a possible drift in the photon energy between spectra. This is a modified version of a previously described STXM energy calibration method successfully employed to calibrate NEXAFS spectra of polymers [18,19]. The energy calibration spectra were collected with the entrance, dispersive exit and non-dispersive exit slits set to 25 $\mu$m, 10 $\mu$m and 60 $\mu$m, respectively, which was previously determined to correspond to a photon energy resolution of 0.075 eV through the Gaussian part of Voight line-shapes fitted the vibrational lines of the CO$_2$ carbon K-edge spectrum [20].

3. Results and discussion

All graphite spectra presented here were recorded from the graphite section illustrated in Fig. 2, using the STXM instrument.
on ALS beamline 5.3.2. The different intensity levels of the large zones seen in Fig. 2(C) and (D) were found to indicate variations in sample thickness only, since no variation in spectral features were observed. While such variations do not interfere with the polarization measurement, measurements were restricted to the large, thicker zone to the right of centre. The dark spots observed in these images were found to vary in spectral features, therefore representing contaminant material that could interfere with the polarization measurement and hence were carefully avoided.

NEXAFS spectra measured at a range of azimuthal angles are shown in Fig. 5. As expected for the HOPG carbon K-edge, these spectra show strongly angle-dependent $\pi^*$ and $\sigma^*$ resonance peaks at photon energies of 285.3 eV and 292–310 eV, respectively. The sharp exciton resonance peak near 291.5 eV and broad EXAFS oscillations in the higher energy region are also characteristic of the HOPG NEXAFS spectrum. The small peaks observed near 288 eV suggest a small amount of oxidation of the graphite [21], which is not extensive enough to significantly influence the polarization measurement. Further, as discussed in the previous polarimetry article [15], the spectral contamination of the oxidation would only affect the polarization measurement if it created bonds that were aligned in some preferred direction, which is unlikely in highly symmetric materials such as HOPG. Note that the black spectrum with the weakest $\pi^*$ resonance intensity was measured at normal X-ray incidence before the supporting TEM grid was deformed. Further, utilizing the spectra in Fig. 6 and reference values for the spectral peaks of CO$_2$ [22], the position of the HOPG exciton peak has been determined to be 291.65 ± 0.025 eV, in agreement with the value previously reported by Brüthwiler et al. [23]. This new measurement of the exciton peak position represents the most precise calibration to date of the often referenced graphite NEXAFS spectrum. Brüthwiler et al. did not quote any precision to accompany their exciton peak position measurement, merely a photon energy resolution of 0.3 eV was quoted. For compari-

Fig. 5. HOPG spectra recorded in the ALS-5.3.2 STXM instrument at a variety of azimuthal angles, $\phi$ (and fixed tilt angle, except for the normal incidence spectrum).

Plotting the measured values of $\pi^*$ resonance intensity at 285.3 eV against $\phi$ produce a sinusoidal trend, as shown in Fig. 7. This data was fitted to obtain the azimuthal offset, $\phi' = 22^\circ$, and the same $\pi^*$ resonance intensity data then plotted against $\sin^2(\phi - \phi')$ to demonstrate a linear trend, as shown in Fig. 8. The slope and intercept of the trend in Fig. 8 were then determined and used to calculate the linear polarization of the X-ray beam, via Eq. (1), as $79 \pm 11\%$ (Stöhr $P$ factor of 0.89 ± 0.06 or Stokes parameter of 0.79 ± 0.11). The 11% error quoted

![Figure 6](image6.png)  
Fig. 6. Overlay of measured HOPG spectrum (red), showing the $\pi^*$ peak, and the measured spectrum of CO$_2$ gas. The spectra were energy calibrated using literature values for the CO$_2$ peak positions [22] indicated with vertical lines. A wider energy range showing the full C K-edge spectra is displayed inset. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

![Figure 7](image7.png)  
Fig. 7. Plot of the normalized HOPG C 1s $\rightarrow \pi^*$ resonance peak intensity (blue crosses) and a fitted sine squared function (solid black line) against azimuthal angle, $\phi$. The angular position of the maximum intensity gives $\phi' = 22^\circ$, the angular scale offset. The dotted line across the bottom represents the resonance intensity at normal X-ray incidence.
for this measurement is derived from the 50% confidence level (assuming a normal distribution) of the least squares fit to the experimental data shown in Fig. 8. Note that this measurement only probes the linear polarization of the delivered X-ray beam and does not measure the circular polarization (though the design of the ALS beamline 5.3.2 makes significant circular polarization unlikely).

Conducting the experiment on a manually rotated sample mount introduced many complications. Firstly, the STXM chamber had to be vented and the mount plate removed in order to rotate the sample, then re-introduce it and pump down the chamber again. This meant that the sample position and focus had to be re-acquired, which was more onerous than usual owing to the fact that the unusual depth of the sample increased the likelihood of collision with the OSA. Utilizing an in-vacuum rotation actuator, such as that described by Hernández-Cruz et al. [24], would circumvent these issues, significantly reducing the time required to conduct the measurement and increasing its accuracy through improved sample stability and a greater utilization of beamtime for improved statistics.

4. Conclusions

A recently reported method for the determination of the degree of linear polarization of synchrotron radiation has been miniaturized and adapted for use in STXM instruments. The method uses the highly aligned C 1s → π* transition vector resonance from a thin graphite section, produced by rubbing HOPG against a TEM grid, to probe the polarization state of the focused X-ray beam near 285 eV. The degree of linear polarization of the focused X-ray beam delivered by the 5.3.2 STXM instrument at the ALS in Berkeley, California was determined to be 79 ± 11%. The large, 11% error of this measurement is thought to originate from complications associated with being limited to manually rotating the sample outside the STXM chamber and it is expected that the incorporation of an in-vacuum rotation actuator could significantly reduce this error as well as the amount of beamtime required to perform the measurement. This method could be feasibly implemented as a routine polarimetry measurement for quantitative soft X-ray spectromicroscopic studies of molecular orientation and alignment.

Also, the position of the graphite exciton peak has been determined to be 291.65 ± 0.025 eV by comparison to a CO2 gas standard. This precise measurement of the narrow spectral feature makes it an excellent secondary reference for energy scale calibration and furthermore allows the convenience of energy calibration and linear polarization determination via a single inexpensive sample.

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