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X-ray natural linear dichroism of graphitic materials across the carbon K-edge: Correction for perturbing high-order harmonics

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Abstract. Reflectivity measurements on graphitic materials such as graphene at energies across the carbon K-edge are frustrated by significant intensity loss due to adventitious carbon on beamline mirrors. Such intensity reduction enhances effects due to perturbing high-order harmonics in the beam. These effects distort the actual structure of the reflectance curve. In order to overcome this limitation, a correction technique has been developed and demonstrated first with measurements for highly ordered pyrolytic graphite. The same approach may be applied to other graphitic materials such as graphene and it may be used with other synchrotron beamlines. The fraction of high-order harmonics was determined by passing the incident beam through a 87 nm thin silicon nitride absorber that can be well modeled. Using the corrected measurements the x-ray natural linear dichroism of the sample has been determined.

1. Introduction

The technology perspectives offered by graphene and other graphitic materials have triggered significant research activity [1],[2]. Two different types of molecular bonds are important for electronic and structural properties of such materials. While π -bonds, which are perpendicular to the basal plane, are important for electronic transport properties, in-plane oriented σ -bonds are important for structural properties [1]. The orthogonal orientation of both types of bonds can be investigated by resonant excitation across the carbon K-edge between 280 eV-300 eV using linearly polarized synchrotron radiation (SR). P-polarized light, with the electric field vector parallel to the π -bonds, excites unoccupied π -orbitals, predominantly at 285 eV. S-polarized light with the electric field vector aligned with the σ -bonds excites unoccupied σ -orbitals above 291 eV.

Measurements at soft x-ray beamlines suffer from the fact that optical components become contaminated with adventitious carbon [3]. This contamination is unavoidable due to residual organic molecules being adsorbed on beamlines optical elements [4]. At certain energies near the carbon K-edge the adventitious carbon on optical elements can lead to huge decreases in intensity of up to two orders of magnitude [3] and a drastic increase of the relative amount of high-order radiation with respect to first order radiation. High-order harmonics are produced in the monochromator and cannot be avoided due to the optical laws of grating diffraction



[5],[6]. They thus act as an unwanted background that creates artefacts that are superimposed on the actual reflection and transmission spectra and obscure resonance structures. Moreover, the unwanted absorption of incident light I_0 by contaminated beamline optical elements is polarization sensitive.

Measurements were performed at BESSY II, Berlin, at the elliptical undulator beamline UE56-2 with a plane grating monochromator PGM-2 [5] using the BESSY polarimeter [7]. Incoming, linearly polarized light with vertical polarization vector (Fig 1: I_{0ver} , closed symbols) predominantly excites unoccupied σ -orbitals of adventitious carbon on contaminated optical elements at 290 eV, thus causing a strong intensity dip at this energy. Linear polarized light with horizontal polarization vector (Fig 1: I_{0hor} , open symbols) excites mainly unoccupied π -orbitals at 284 eV leading to an intensity minimum at this energy [3].

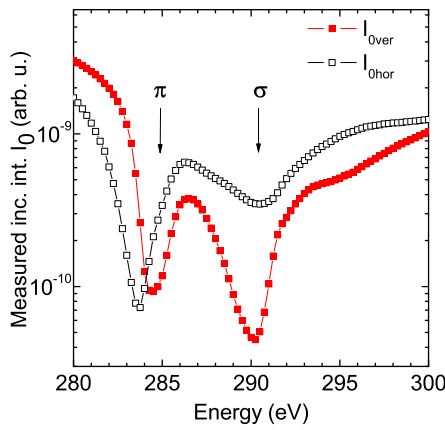


Figure 1. Intensity of incoming light for vertically and horizontally polarization with respect to the laboratory system.

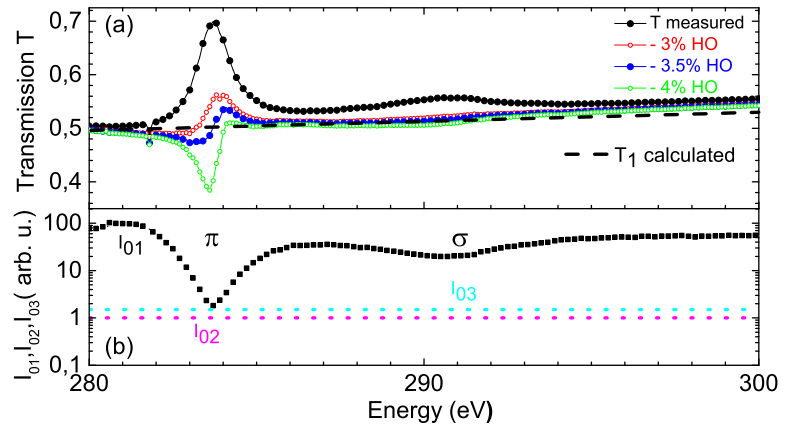


Figure 2. (a) Measured transmission T for a 87 nm Si_3N_4 -absorber, using I_{0hor} and corrections with different amounts of high-order SR. (b) Amount of first order SR I_{01} according to Eq. 1 and high-order harmonics I_{02} , I_{03} .

2. Estimating high-order contributions

In order to determine the high-order fraction of I_0 across the carbon K-edge, we recorded transmission spectra for a 87 nm thin Si_3N_4 -foil that acts as a differential discriminator of different high-order harmonics to determine the high-order fractions in the resonance region and outside at 300 eV.

The high-order fraction of light at soft x-ray PGM beamlines outside the resonances can be determined as suggested by Follath [6]. The author utilized the line structure of undulator radiation at a PGM beamline similar to the arrangement used here with UE56-2 PGM-2 for different fix-focus constants (c_{ff}), which is the ratio of the angle of mirror and grating. Follath worked in high resolution mode ($c_{ff}=2.25$) and in high-order suppression mode ($c_{ff}=1.4$) [6]. For the high resolution mode he found a ratio of second to first order SR of $I_{02}(270 \text{ eV})/I_{01}(135 \text{ eV}) = 0.0014$ and of third to first order of $I_{03}(405 \text{ eV})/I_{01}(135 \text{ eV}) = 0.0022$. Furthermore, for $c_{ff}=1.4$ high-order SR was completely suppressed. Due to similarities of the set-ups, our analysis was guided by Follath's results.

Incoming light of intensity I_0 is transmitted by the filter and is detected as I_t by a GaAs photo diode [7]. The thickness of the Si_3N_4 -filter was determined as (87 ± 2) nm and its theoretical transmission (Fig. 2(a), dashed line) was simulated with the computer code REFLEC [8] using tabulated data [9]. The measured transmission spectrum $T = I_t/I_0$ (Fig. 2(a)) shows local maxima near 284 eV and 290 eV. These maxima are caused by high-order contributions and result from the energy dependent transmittance of the Si_3N_4 -filter, which differentially suppresses first order SR with respect to second and third order radiation. The

theoretical transmission coefficients have been determined using REFLEC as $T_1(284\text{ eV}) = 0.50$, $T_2(568\text{ eV}) = 0.74$, $T_3(852\text{ eV}) = 0.90$, respectively. Correcting the transmission spectrum from high-order contributions should result in a straight line as indicated in Fig. 2(a), (dashed line), neglecting possibly existent adventitious carbon on the filter. In order to correct for the artificial maxima the incoming light is separated into first order I_{01} and high-order components I_{02} , I_{03} . The measured transmitted intensity is then given by $I_t = I_0 T = T_1 I_{01} + T_2 I_{02} + T_3 I_{03}$. The amount of first order SR with respect to high-order components is given according to

$$I_{01} = ((-I_t/I_0 + T_2)I_{02} + (-I_t/I_0 + T_3)I_{03})/(I_t/I_0 - T_1). \quad (1)$$

Assuming only weak energy dependence of high-order SR, the ratio at 300 eV was taken as constant with a ratio of $I_{03}/I_{02} = 1.5$, in agreement with Follath [6], gives an I_{01} contribution according to Eq. 1 as shown in Fig. 2(b). One can clearly see the huge loss of first order radiation I_{01} with respect to the amount of high-order harmonics at the resonances down to 42% of the total incoming intensity I_0 at 284 eV. At 300 eV the summed fraction of high-order harmonics $I_{02}+I_{03}$ in I_0 amounts to 3.5%. That is a magnitude higher than determined by Follath, possibly caused by different amounts of adventitious carbon on optical components in the respective beamlines.

3. High-order correction

The measured transmitted intensity I_t has been corrected across the complete spectrum according to:

$$T_1 = \frac{I_t - T_2 I_{02} - T_3 I_{03}}{I_0 - I_{02} - I_{03}}. \quad (2)$$

A correction with a fraction of $(3.5 \pm 0.5)\%$ high-order radiation gives the best agreement with expectation (Fig. 2(a)).

For reflection spectroscopy we used highly ordered pyrolytic graphite (HOPG) with 0.4° mosaicity and recorded reflection spectra under an angle of incidence $\theta = 20^\circ$ using again the BESSY polarimeter [7] with exactly the same beamline settings as used for the transmission measurements. The corrected reflectance R_1 is obtained by subtracting high-order contributions from the measured intensity I_r according to:

$$R_1 = \frac{I_r - R_2 I_{02} - R_3 I_{03}}{I_0 - I_{02} - I_{03}}. \quad (3)$$

The theoretical reflection coefficients for s- and p-polarized light R_1, R_2, R_3 for the respective higher order are again calculated by REFLEC as $R_{p2}(568\text{ eV}) = 2.5 \cdot 10^{-5}$, $R_{p3}(852\text{ eV}) = 4.9 \cdot 10^{-6}$, $R_{s2}(568\text{ eV}) = 4.3 \cdot 10^{-5}$, $R_{s3}(852\text{ eV}) = 8.3 \cdot 10^{-6}$, respectively. Experimentally deduced reflectances R_p , R_s (filled symbols) and their

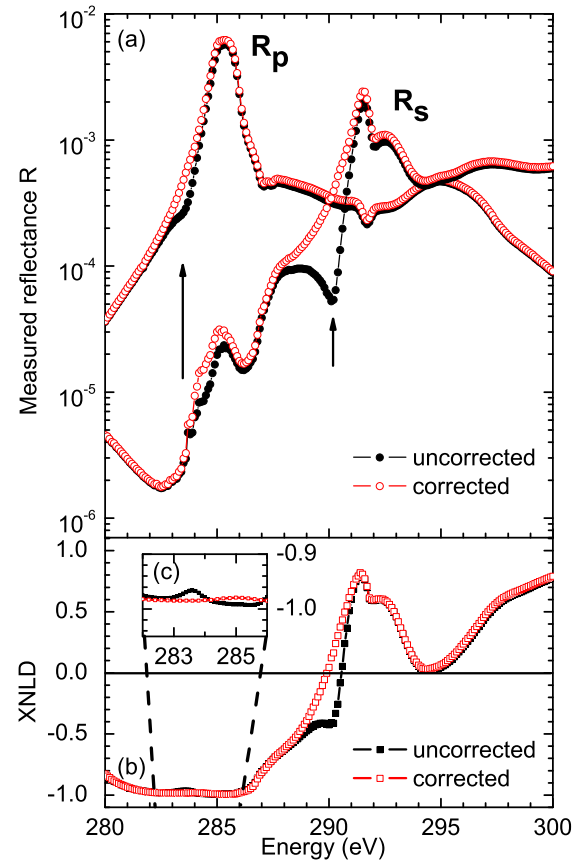


Figure 3. (a) Measured reflection spectra of HOPG 0.4° for p-polarized light (using I_{0hor}) and s-polarized light (using I_{0ver}) with $c_{ff}=1.4$.

(b), (c) XNLD of HOPG 0.4° .

corrected spectra (open symbols) are shown for the high-order suppression mode with $c_{ff}=1.4$ in Fig. 3(a). While reflection measurements performed with p-polarized light (R_p) show a huge peak at 285 eV, originating from the excited π -states of HOPG, measurements with s-polarized light (R_s) show a feature around 291.5 eV at the σ -states of HOPG. One can clearly see remarkable differences between uncorrected and corrected spectra in Fig. 3(a). In the resonances of the adventitious carbon on the beamline optical elements around 284 eV and 290 eV this difference is especially huge. At these energies, I_0 shows minima (Fig. 1) with a large amount of high-order SR with respect to first order SR. This leads to minima in uncorrected reflection spectra. Those artificial structures could easily be misinterpreted as resonant excitations.

Although working in the high-order suppression mode with $c_{ff}=1.4$, artificial minima still occur around 284 eV and 290 eV, showing that even a small c_{ff} -value is not able to reduce high-order contributions completely in this energy range. In order to avoid noise-introduced, non-physical negative reflectances between 282 eV-285 eV, the reflection coefficients R_2, R_3 for R_s in Eq. 3 were set to zero only in this energy range.

Reflection spectra of s- and p-polarized light (R_s, R_p) play a crucial role in the x-ray natural linear dichroism (XNLD) [2] according to

$$XNLD = (R_s - R_p)/(R_s + R_p).$$

These spectra can directly be compared to polarization spectra to demonstrate the correlation of XNLD and birefringence [2]. Uncorrected reflection spectra lead to distorted XNLD signals as shown in Fig. 3(b),(c). In the minima of I_0 (Fig. 1) around 284 eV and 290 eV two artefacts occur. After correcting the reflection spectra R_s and R_p , the feature at 290 eV in the XNLD signal completely vanishes and the peak's intensity at 284 eV is strongly reduced.

4. Conclusions

We determined the fraction of high-order harmonics in the energy range 280 eV- 300 eV across the carbon K-edge for linearly polarized light in beamline UE56-2 PGM-2 at BESSY II. The technique we have demonstrated using transmission measurements with a Si_3N_4 -absorber foil gives a fraction of high-order harmonics in I_0 of up to 58% in the 284 eV resonance, of about 10% at the 290 eV resonance and of 3.5% out of the resonance region at 300 eV. The high-order fraction has been shown to affect the measured transmission, reflectance and XNLD spectra, since artefacts are introduced. Such artefacts may result in the misinterpretation of resonance structures in the spectra. Through the energy-dependent measurement of the high-order fraction of incident light, a correction of spectra is possible, as it has been demonstrated. The importance of correcting reflection spectra to determine the correct x-ray natural linear dichroism of HOPG has become evident. The procedure may be applied similarly to other graphitic materials including graphene.

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