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Harmonic contamination and its effects on measurements

Christopher T. Chantler*

School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia. *Correspondence e-mail: chantler@unimelb.edu.au

Modern synchrotron beamlines often use standard techniques to eliminate harmonics from the beam. Use of an undulator gives sharp peaks and may avoid the corresponding harmonic. Most bending-magnet and wiggler beamlines use detuning of the second plane of the monochromator or an X-ray total reflection harmonic rejection mirror. Often the monochromator is, for example, monolithic Si(111) or Si(311) or Ge(111), and the second harmonic is forbidden. It is well known that these approaches do not fully eliminate harmonics, and in many cases a significant third harmonic remains in the beam at the sample, especially at lower X-ray energies. Harmonic components have completely different absorption and scattering coefficients to the main wavelength, which add baseline, noise and sometimes structure to the measurements. This prevents the direct measurement of absorption coefficients, which impacts the ability of theory to predict oscillation amplitudes and edge jumps. This chapter discusses the effect of harmonic contamination on transmission measurements.

A monochromator uses Bragg diffraction, following the law $n\lambda = 2d\sin\theta$, to select a particular wavelength from the X-ray beam. The monchromator is usually tuned to the fundamental wavelength, for $n = 1$, but harmonics occur when the energy is an integer multiple of the fundamental. For several popular monochromator diffraction planes, for example the (111) plane of Si or Ge, the second harmonic $n = 2$ is ‘forbidden’, so significant harmonic contamination will usually only occur for $n = 3$. Detuning and harmonic rejection mirrors effectively reduce the per cent harmonic contamination by at least two orders of magnitude. Detuning of course also lowers the propagated intensity, and shifts the beam energy by the order of the half width of the first-order diffraction peak. At lower X-ray energies (4–5 keV) the intensity of the third-order harmonic can be 30% of that of the fundamental, in which case suppression by a full two orders of magnitude still leaves a large harmonic contamination level of 0.3%. This can be observed in diffraction (Barnea & Mohyla, 1974), fluorescence and transmission. For energies around the K edge (X-ray absorption spectroscopy; XAS), third-order harmonics are in a region of minimal structure for the active absorbing element. For compounds, the harmonic may interact with the structure or edges of inactive species, adding structure, whereas for L edges the third-order harmonic can also interact with the structure (for example of a K edge).

In regions of absorption where harmonics have slowly varying structure, the main consequence for attenuation is the addition of background signal, which affects the pre-edge signal, the edge-jump ratios and background subtraction, which can also potentially be addressed by using suitable background-subtraction techniques. This may affect X-ray absorption fine-structure fitting of oscillations or fingerprinting of X-ray absorption near-edge and pre-edge structure,

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and can have a large effect on the determination of the attenuation coefficient, the absorption coefficient and the form factor.

Abe *et al.* (2018) illustrated major errors in structure, fitting and transforms caused by harmonic contamination from inadequate detuning or mirror optimization. Sayers (2000) recommended that

> Harmonics passing the X-ray monochromator should be evaluated *quantitatively*, and the methodology used to eliminate them should be reported. If possible a harmonic detector should be operated throughout the data collection.

The effect of harmonic contamination is a thickness effect (Bridges, 2024*a*; Best & Chantler, 2024), which is seen in spectral distortions caused by both the optics (Abe, 2024) and the sample (De Panfilis & Bardelli, 2024). This can often contribute as an unknown systematic error (Booth, 2024), and should ideally be treated under the general topic of calibration and diagnostics (Diaz-Moreno, 2024). Harmonic contamination is one of the four key systematic errors discussed in some textbooks (Bunker, 2010) under HALO: Harmonics, Alignment, Linearity, Offsets. The last three topics of HALO are important in all of measurement science and all four are important in XAS measurement and analysis.

The harmonic content, or the effective harmonic content, can be directly measured at the sample to very high precision and this is recommended not only for beamline characterization and control, but also for high-accuracy measurements (Chantler, 2024*a*). In general, harmonic diagnosis and measurement requires multiple samples (Chantler, 2024*b*). The samples or reference materials should be located either in a fast filter bank or in a daisy-wheel setup (Chantler, 2024*c*). Similarly, any energy distribution in the beam incident upon the sample will affect the structure because of the beam harmonics or the beam bandwidth at the sample (de Jonge *et al.*, 2004; Bridges, 2024*b*), as will any sample inhomogeneity or roughness (de Jonge *et al.*, 2024). These sorts of issues are collectively labelled as 'thickness effects' (Best & Chantler, 2024). These effects relate to wedge-shaped samples, pinholes, voids, roughness and defects and their impact in transmission or fluorescence, and to the systematic effect on the spectra of using the ideal, correct or incorrect sample thickness (for example, samples which are 'too thick' or 'too thin').

For an X-ray beam at the fundamental energy $E_{\rm F}$, with a higher-order harmonic energy $E_{\rm h}$, the intensity ratio at an ion chamber (with dark-current correction DC) is (Tran *et al.*, 2003; Glover & Chantler, 2009; Chantler *et al.*, 2012; Ekanayake *et al.*, 2021)

$$\begin{aligned}\frac{I_t - {\rm DC}_t}{I_0 - {\rm DC}_0} &= \exp\left\{-\left[\frac{\mu}{\rho}\right][\rho t]\right\}\\ &= (1-f_n)\exp\left\{-\left[\frac{\mu}{\rho}\right]_{\rm f}[\rho t]\right\} + f_n\exp\left\{-\left[\frac{\mu}{\rho}\right]_{\rm h}[\rho t]\right\},\end{aligned}\tag{1}$$

where f_n is the fraction of the harmonic contribution to the attenuation measurements. A recommended measurement approach to investigating this is presented in Chantler (2024*c*). This can be a fast and efficient monitor throughout the experiment and can be used for beamline characterization and diagnostics.

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