SINGLE CRYSTAL X-RAY DIFFRACTION

X-ray optics: optimization of divergence and intensity

White Paper 529

Introduction

The role of the X-ray optic is to increase the intensity of X-rays at the sample by increasing the divergence of the X-ray beam. That is, the optic collects X-rays that would have otherwise 'missed' the sample and refocuses them onto the sample.

One should always choose to have the highest feasible divergence on the sample as this will lead to the highest signal-to-noise ratio and thus the best crystallographic results. Thus, X-ray mirrors are designed to have the highest feasible divergence angle to maximize the intensity at the sample.

However, at the maximum divergence angle adjacent spots may sometimes overlap which makes it impossible to index and integrate properly. In such cases it may be necessary to move the detector back farther from the sample or decrease the divergence of the optic (or both).

In this note, we look at the best practices for avoiding spot overlap while simultaneously achieving the highest intensity for both small molecule and macromolecular samples.

Figure 1
X-ray optics collect X-rays and refocus them onto the sample in order to increase the diffraction signal.

Intensity versus divergence

Intensity is the number of X-rays per unit area per unit time at the sample position. Since the diffracted signal is proportional to the intensity it is desirable to maximize the intensity at the sample.

Intensity is related to the brightness of the source by the well-known Liouville's theorem

$$I = BRa^2 \qquad (1)$$

Where I is the intensity (in X-rays/mm^2-sec), B is the brightness of the source (in X-rays/mm^2-mrad^2-sec), R is the reflectivity of the optics, and a is the divergence angle of the optics.

The intensity at the sample increases as the square of the divergence of the X-ray optic. Therefore, as noted above, it is usual to employ the highest divergence possible as this leads to the highest intensity at the sample.

Maximum resolvable unit cell versus divergence

The use of X-ray optics allows one to increase the number of X-rays focussed onto the sample (and thus the diffracted X-ray signal) but if the divergence angle is too high then adjacent spots may overlap. How much divergence is acceptable is sample dependent. since crystals with longer unit cells or higher mosaicity will have more closely spaced reflections and are thus more prone to overlap.

The maximum resolvable axis cell axis is given by

$$d_{max} = \frac{\lambda}{\sqrt{\alpha_{div}^2 + \alpha_{mos}^2 + (\text{atan}\,(s/x))^2}} \qquad (2)$$

where d_{max} is the maximum unit cell axis that can be resolved for a crystal with a mosaicity of α_{mos}, α_{div} is the divergence angle of the beam and λ is the wavelength of the X-rays. The term $atan(s/x)$ is the resolution function where x is the sample to detector distance and s is the geometric convolution of the detector point spread function and the sample size, that is, $s=\sqrt{p^2 + a^2}$ where p is the detector point spread function and a is the sample size.

This expression is plotted in Figures 2 and 3 below for a 100 µm sample with a typical mosaicity of 0.3° assuming that the detector point spread is 100 µm.

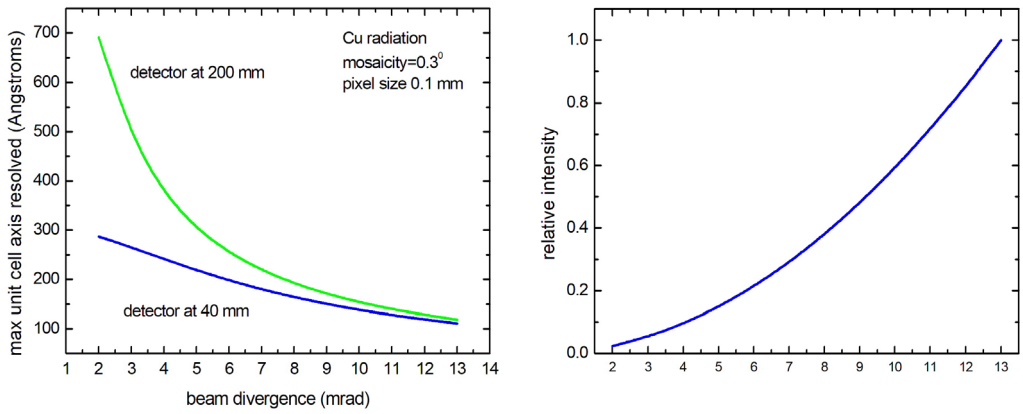

Figure 2
The maximum resolvable cell axis at two detector distances, 40 and 200 mm versus the divergence of the X-ray beam assuming Cu radiation and a 0.3-degree crystal mosaicity (left). The relative intensity of the X-ray beam versus divergence for Cu radiation with a 13 mrad mirror (right). 13 mrad is currently the highest divergence possible for Cu radiation using multilayer mirrors.

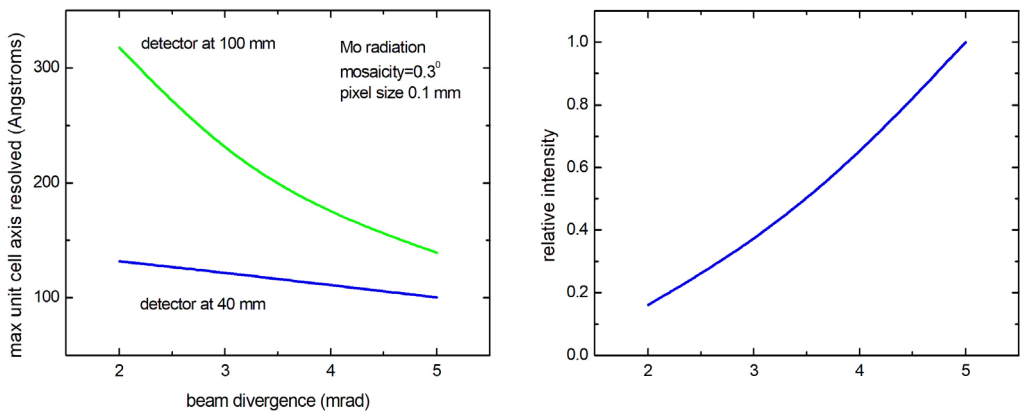

Figure 3
The maximum resolvable cell axes versus the divergence of the X-ray beam at two sample to detector distances assuming Mo radiation a 100 µm sample with 0.3-degree crystal mosaicity (left). The relative intensity of the X-ray beam versus divergence for Mo radiation with a 5 mrad mirror (right). 5 mrad is currently the largest divergence angle possible for Mo radiation using multilayer mirrors.

Optimization of divergence for macromolecules

To minimize spot overlap it is best practice to always first move the detector back for long unit cell axes and then only decrease the divergence, if necessary, since moving the detector back does not significantly increase the reflection intensities while reducing the divergence does lead to a strong reduction intensity.

Referring to Figure 2, macromolecules with small unit cells (<100 Å) should usually be run at full divergence (13 mrad) to achieve the highest possible intensity. For large unit cell axes, it is necessary to reduce the divergence, and also moving the detector back becomes increasingly crucial.

For example, integrating a 300 Å unit cell could be accomplished either by running the sample at a sample-to-detector distance of 80 mm with a beam divergence of about 1 mrad or by moving the detector back to 200 mm and using a beam divergence of about 5 mrad. Both configurations would eliminate spot overlap but the latter configuration benefits from 25 times higher intensity and thus is strongly preferred.

This advantage of large sample-to-detector distance for long unit cells is of course the reason why large detectors are usually preferred for macromolecular crystallography. That is, a large detector can be moved back to deal with long unit cells without sacrificing crystallographic resolution or completeness.

Optimization of divergence for small molecules

The longest unit cell axes of small molecules typically are less than about 35 Å. Figures 2 and 3 above show that a 35 Å unit cell can be easily resolved with the full beam divergence for both Cu (13 mrad) and Mo (5 mrad). Therefore, since the maximum divergence gives the highest intensity there is usually not a good reason to decrease the beam divergence for chemical crystallography for the majority of samples.

However, there are less-common cases in chemical crystallography where spot overlap can become an issue. For example, twinned samples or samples with modulated structures may be prone to overlapping reflections. In these cases, the best practice is to first move the detector back and, if this is not sufficient to separate the adjacent reflections, then decrease the beam divergence.

Optimization of divergence for small molecules

It is best practice for most samples to use the full X-ray divergence of the optic as this results in the best signal-to-noise ratio.

However, for some samples (for example, macromolecules with long unit cell axes or some twinned samples) spot overlap may occur.

In these cases, the best practice is to first move the detector back as far as possible as this separates the spots without reducing the intensity. As a second step, divergence should be reduced as little as possible to separate the spots.

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