

Irradiated Volume in Weissenberg and Precession Techniques

BY A. S. PARKES AND R. E. HUGHES

Department of Chemistry and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia 4, Pennsylvania, U.S.A.

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Small but systematic correction factors are derived to account for changes in reflection intensities due to variations in volume associated with motion of the crystal in the X-ray beam. Cylindrical and plane lamina crystals of essentially infinite extent are considered for both Weissenberg and precession techniques.

Introduction

In many crystallographic studies, including analyses of crystalline fibers and crystals grown *in situ* in capillaries at low temperature, it is often convenient or necessary to make intensity measurements from a sample too large to be bathed completely in the X-ray beam. Techniques involving moving crystals will, in general, introduce errors into these intensity measurements since the irradiated volume will not be constant for all reflections. If the crystal has the shape of a cylinder or plane lamina and is essentially infinite in extent, it is possible to reduce the observed intensities to a common relative basis. It is the purpose of this article to present the required correction factors for both Weissenberg and precession techniques.

If the axis of a cylindrical X-ray beam intersects the axis of a cylindrical crystal of arbitrary radius, the volume common to the two cylinders will be a function of the common volume when the cylinders are perpendicular and, also, of the relative orientation of the cylinders. Similarly, the volume common to a cylindrical X-ray beam and a plane lamina crystal is a function of the common volume when the cylinder is normal to the plane and of the orientation of the plane relative to the cylinder.

It is convenient to define a unit vector \mathbf{J} which, in the case of a cylindrical crystal, is coincident with the cylinder axis and which, for a plane lamina, lies in the plane of the crystal along the normal projection of the X-ray beam. The volume common to the X-ray beam and the crystal can then be written as

$$V = V_0 / \sin \psi, \quad (1)$$

where ψ is the angle between the X-ray beam and \mathbf{J} , and V_0 is the minimum common volume corresponding to normal incidence. In the limit of normal incidence, in the case of a plane, ψ is defined as $\pi/2$.

The orientation of the crystal with respect to the camera is specified by two angles. The angle between the spindle rotation axis and the crystal cylinder axis (or the normal to the plane lamina) is given by λ ,

where $\cos \lambda = \cos \gamma_i \cos \gamma_o$; in this expression γ_i and γ_o are the changes in setting of the inner and outer goniometer arcs required to reduce λ to zero. The rotation of \mathbf{J} about the spindle axis is described by the angle ω , with a fiducial zero set when \mathbf{J} lies in the plane of the X-ray beam and the spindle axis.

Weissenberg method

Calculation of the required intensity correction factor for the Weissenberg method at an equi-inclination angle μ is now quite straightforward. From Fig. 1 it can be seen that $\cos \psi = \cos \lambda \sin \mu + \sin \lambda \cos \mu \cos \omega$, and from equation (1) the corrected intensity expression becomes

$$I_{\text{corr}} = I_{\text{obs}} \sin [\cos^{-1} (\cos \lambda \sin \mu + \sin \lambda \cos \mu \cos \omega)]. \quad (2)$$

The correction can be calculated for each reflection directly from the instrumental settings and the film coordinates in a simple computer program.

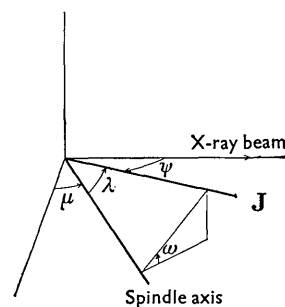


Fig. 1. The relationship of \mathbf{J} to the X-ray beam and the spindle axis for the Weissenberg camera at an equi-inclination angle μ .

Precession method

The correction factor for the precession method is more complex, since the observed intensity is the sum of two reflections; one when the reciprocal lattice point enters the sphere of reflection and another

when it leaves. Characterizing these reflections with the angles ψ_1 and ψ_2 , equation (1) becomes

$$V = \frac{1}{2} V_0 \left(\frac{1}{\sin \psi_1} + \frac{1}{\sin \psi_2} \right). \quad (3)$$

In order to calculate the two values of ψ for a given reciprocal lattice point, it is convenient first to calculate the corresponding values of Ωt , the angle which describes the rotation of the camera about the precession axis, and then to calculate ψ as a function of Ωt .

The precession method is conveniently described (Waser, 1951) in terms of three orthogonal coordinate systems, all centered at the origin of the reciprocal lattice. One set of axes, $[x_1, x_2, x_3]$, is fixed in space with the x_3 axis directed upward along the vertical camera axis and the x_1 axis horizontal in such a way that the coordinates of the center of the sphere of reflection are $[0, \bar{1}, 0]$. A second set, $[y_1, y_2, y_3]$, moves with the reciprocal lattice, coupled through the geometry of the camera so that y_1 lies in the $x_1 x_2$ plane and y_2 is at a constant angle $\bar{\mu}$ to x_2 while precessing about x_2 . The coordinate transformation is given by the expression

$$\mathbf{X} = \begin{vmatrix} \cos \alpha & \sin \alpha \cos \beta & -\sin \alpha \sin \beta \\ -\sin \alpha & \cos \alpha \cos \beta & -\cos \alpha \sin \beta \\ 0 & \sin \beta & \cos \beta \end{vmatrix} \mathbf{Y},$$

where the angles α and β are related to the instrumental parameters Ωt and $\bar{\mu}$ through the expressions

$$\begin{aligned} \sin \alpha &= \sin \bar{\mu} \cos \Omega t (1 - \sin^2 \bar{\mu} \sin^2 \Omega t)^{-\frac{1}{2}} \\ \cos \alpha &= \cos \bar{\mu} (1 - \sin^2 \bar{\mu} \sin^2 \Omega t)^{-\frac{1}{2}} \\ \sin \beta &= \sin \bar{\mu} \sin \Omega t \\ \cos \beta &= (1 - \sin^2 \bar{\mu} \sin^2 \Omega t)^{-\frac{1}{2}}. \end{aligned}$$

The transformations

$$y_1 = \xi \cos \tau, \quad y_2 = \zeta, \quad y_3 = \xi \sin \tau,$$

define the third useful coordinate set $[\xi, \tau, \zeta]$. This is a reciprocal lattice set directly relating to film coordinates; ξ and τ are the plane polar radius and the azimuthal angle for a reciprocal lattice point, and ζ is the n th level coordinate.

The two required values of Ωt can now be obtained

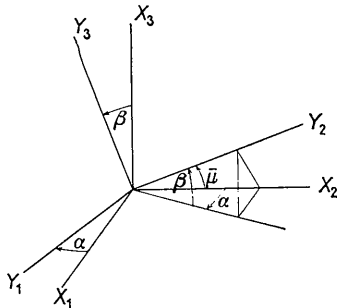


Fig. 2. The angular relationship between the X and Y sets of axes for the precession camera.

in terms of experimentally accessible parameters by transforming the coordinates of the center of the sphere of reflection, $[0, \bar{1}, 0]$, to the set $[\xi_0, \tau_0, \zeta_0]$ and calculating the reflection conditions in terms of $[\xi, \tau, \zeta]$. We can write $\tan \tau_0 = \tan \Omega t \cos \bar{\mu}$ and, from the reflection conditions, we find that $\tau_{\text{refl}} = \tau_0 \pm \eta$, where

$$\cos \eta = (\xi^2 + \zeta^2 + 2\zeta \cos \bar{\mu}) / 2\xi \sin \bar{\mu}.$$

The required expression which yields the two values of Ωt therefore becomes,

$$\tan \Omega t = \frac{\tan \{ \tau \pm \cos^{-1} [(\xi^2 + \zeta^2 + 2\zeta \cos \bar{\mu}) / 2\xi \sin \bar{\mu}] \}}{\cos \bar{\mu}}. \quad (4)$$

Now, the relationship of ψ to Ωt must be calculated. The angle ψ between \mathbf{J} and the X-ray beam can be obtained from the scalar product of \mathbf{J} with a unit vector along the x_2 axis, which of course is simply the x_2 component of \mathbf{J} . The components of \mathbf{J} along the x axes can be obtained from the transformation matrix above. In particular, the x_2 component becomes,

$$x_2 = - \frac{(y_1 \cos \Omega t + y_3 \cos \bar{\mu} \sin \Omega t) \sin \bar{\mu}}{(1 - \sin^2 \bar{\mu} \sin^2 \Omega t)^{\frac{1}{2}}} + y_2 \cos \bar{\mu}, \quad (5)$$

for which we can write

$$\psi = \cos^{-1} x_2. \quad (6)$$

The components of \mathbf{J} along the y axes can easily be expressed in terms of the experimentally determined parameters λ and ω :

$$\begin{aligned} y_1 &= \cos \lambda \\ y_2 &= \sin \lambda \cos \omega \\ y_3 &= \sin \lambda \sin \omega. \end{aligned} \quad (7)$$

The expression for the corrected intensity becomes, from equation (3),

$$I_{\text{corr}} = 2I_{\text{obs}} \left(\frac{1}{\sin \psi_1} + \frac{1}{\sin \psi_2} \right)^{-1}. \quad (8)$$

This equation can be applied in the following manner. From the reciprocal lattice coordinates corresponding to each reflection, the two values of Ωt are calculated from equation (4). These values, along with the appropriate values from equations (7), determine two values of x_2 in equation (5). The corresponding values of ψ are calculated from equation (6) and inserted into equation (8) to yield the corrected intensity. The sequence of operations can easily be programmed for a small computer.

Conclusion

Although the correction factors can be large in individual cases, for the usual experimental conditions they average less than 5 or 10%. While it

might appear that such errors could frequently be absorbed in the random errors in intensity measurement, it must be noted that they are calculable, systematic errors which can generate measurable effects upon the refined structure. In a particular case where the corrections were applied (Parkes & Hughes, 1963), there resulted not only an improvement

in R but also a statistically significant change in the structure.

References

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Stereochemistry of Arsenic. X. Tri-*p*-xylylarsine*

BY J. TROTTER

Department of Chemistry, University of British Columbia, Vancouver 8, B. C., Canada

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Crystals of tri-*p*-xylylarsine are monoclinic, with four molecules in a unit cell of dimensions $a = 10.81$, $b = 33.4$, $c = 5.72$ Å, $\beta = 96^\circ 28'$, space group $P2_1/a$. The structure has been determined from projections along the a and c axes. Within experimental error the molecule has symmetry C_3 , the arsenic being pyramidal with mean C-As-C angles of 102° , and each ring being rotated about its As-C bond, in the same sense, 37° from the position it would occupy in an ideal model with maximum interaction between the lone pair and the aromatic π -electrons. Overcrowded intramolecular distances are thereby increased to the usual van der Waals separations. Values of the bond distances, valency angles and intermolecular contacts have been obtained.

Introduction

Tri-*p*-xylylarsine has methyl substituents *ortho* to the arsenic atom, and its structure has been investigated for comparison with that of tri-*p*-tolylarsine, which has no *ortho* substituents (Trotter, 1963).

Experimental

Crystals of tri-*p*-xylylarsine are colourless prisms elongated along the c axis. The density was measured by flotation in aqueous potassium iodide, and the unit cell dimensions and space group were determined from various rotation, oscillation, Weissenberg ($Cu K\alpha$) and precession ($Mo K\alpha$) films.

Crystal data

Tri-*p*-xylylarsine, $C_{24}H_{27}As$; $M = 390.4$; m.p. $161^\circ C$.
 Monoclinic, $a = 10.81$, $b = 33.4$, $c = 5.72$ Å; $\beta = 96^\circ 28'$.
 Volume of the unit cell = 2052 Å³.

D_x (with $Z = 4$) = 1.256 , $D_m = 1.24$ g.cm⁻³.

Absorption coefficients for X-rays, $\lambda = 1.542$ Å,

$\mu = 24$ cm⁻¹.

$\lambda = 0.7107$ Å, $\mu = 17$ cm⁻¹.

$F(000) = 816$.

Absent spectra: $h0l$ when h is odd, $0k0$ when k is odd. Space group is $P2_1/a$.

$hk0$ (Weissenberg films, $Cu K\alpha$) and $0kl$ (precession films, $Mo K\alpha$) intensity data were recorded and

* Part IX. Camerman & Trotter (1963).

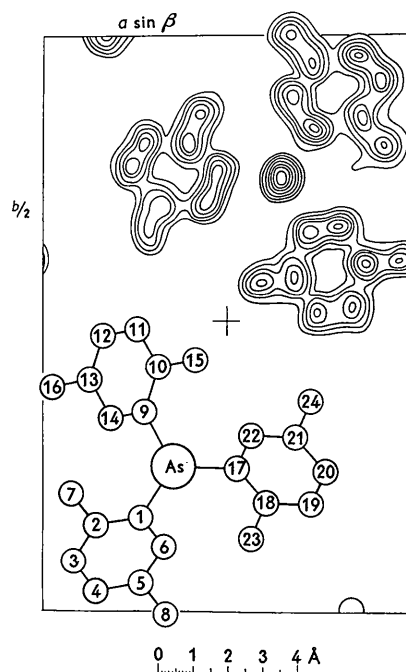


Fig. 1. Electron-density projection along the c axis. Contours at intervals of 1 e.Å^{-2} (starting at 2) for the C atoms, and 5 e.Å^{-2} for the As atom.

estimated visually, and the structure amplitudes derived. No absorption corrections were applied, and the absolute scale was established later by correlation