Acta Cryst. (1956). 9, 757

Errors in Bond Lengths Due to Rotational Oscillations of Molecules

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(*Received* 24 *February* 1956)

Angular oscillations of molecules cause displacements of the electron-density peaks. A formula is given relating the displacements to the amplitudes of small angular oscillations.

The preceding paper (Cruickshank, 1956*a*) has described how the thermal anisotropic vibrations of atoms in molecular crystals may be interpreted in terms of the anisotropic translational and rotational oscillations of the molecules. In the course of detailed analyses of several crystals, particularly of benzene (Cox, Cruickshank & Smith, 1956), angular oscillations with r.m.s. amplitudes as large as 8° have been found. An immediate consequence of these angular oscillations is that the maxima of the atomic peaks in the electron density are closer to the centre of rotation than they would be otherwise. The purpose of the present note is to give a simple formula relating the errors in position to the amplitudes of angular oscillation.

In Fig. 1, let P be the rest position of an atom. If the atom performs translational vibrations only, the maximum of the electron-density map will remain at P (supposing that finite-series and peak-overlapping effects are allowed for as usual). If the molecule makes rotational oscillations with O as centre, the atom will vibrate over the surface of the sphere through P whose centre is O. This causes a positional error, whose order of magnitude can easily be obtained from a highly simplified theory. Suppose that the motion of the atom is confined to the plane of the figure and that it vibrates along the arc of the circle, spending half its time at Q and half at Q'. Then the time average electron density will have its maximum at B, and the atom will appear too close to O by

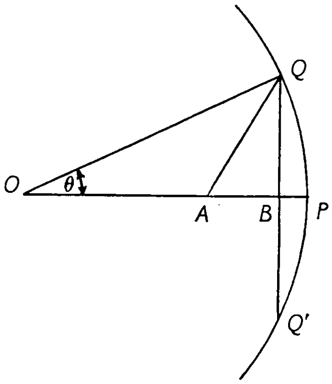

Fig. 1. Peak displacements in angular oscillations.

$$BP = r(1-\cos\theta) \sim \tfrac{1}{2}r\theta^2, \quad \text{for small } \theta\,.$$

For $\theta = 8°$ and $r = 1{\cdot}39$ Å, the error is 0·014 Å. Such an error is important in accurate structure determinations.

A more complete calculation for small oscillations will now be given. We may suppose that the shape of the atomic peak, including finite-series effects and the spread due to translational but not rotational oscillations of the molecule, is represented by a Gaussian function

$$\varrho(x) \propto \exp -\{(x)^2/2q^2\}\,, \tag{1}$$

where x is the distance from the centre of the atom and q^2 is a breadth parameter for the peak. The final formula for the error will show that this assumption of a spherical peak is a sufficiently good approximation. The use of a Gaussian function is certainly satisfactory, as Fourier map peaks have often been shown to be approximately Gaussian for at least $\frac{1}{2}$ Å from their centres.

If the molecule makes harmonic angular oscillations the atom will move on the surface of the sphere with P as its middle position and with the maximum of its time average density lying along OP. The problem is thus to calculate the variation of the time average density along OP and to find its maximum.

If the atom is stationary at Q the density at a point A along OP will be

$$\varrho \propto \exp -\{AQ^2/2q^2\}\,. \tag{2}$$

We need be concerned only with the oscillations of the molecule about axes in the plane through O perpendicular to OP, since angular oscillations about OP do not move an atom at P. Let φ and ψ be the angles of rotation about the principal axes in this plane which move the atom from P to Q and let s^2 and t^2 be the mean square amplitudes of oscillation of the atom for rotations about these axes. Then, for harmonic vibrations and φ and ψ small, the fraction of time the atom spends near Q will be proportional to

$$\exp -\{r^2\varphi^2/2s^2+r^2\psi^2/2t^2\}\,. \quad (3)$$

Combining (2) and (3), the time average density along OQ will be

$$\varrho \propto \iint \exp -\{AQ^2/2q^2+r^2\varphi^2/2s^2+r^2\psi^2/2t^2\}d\varphi d\psi\,. \quad (4)$$

For small φ and ψ

$$AQ^2 = y^2+(r^2-yr)(\varphi^2+\psi^2)\,, \quad (5)$$

where $y = AP$. Collecting coefficients of φ^2 and ψ^2 in (4), we obtain

$$\varrho \propto \exp -(y^2/2q^2)\iint \exp -\{\alpha\varphi^2+\beta\psi^2\}d\varphi d\psi\,, \quad (6)$$

where

$$\alpha = (r^2-yr)/2q^2+r^2/2s^2 \quad (7a)$$

and

$$\beta = (r^2-yr)/2q^2+r^2/2t^2\,. \quad (7b)$$

For small oscillations we may take the limits of both integrations as $+\infty$ and $-\infty$. Expression (6) then integrates immediately to

$$\varrho \propto (\alpha\beta)^{-\frac{1}{2}} \exp -(y^2/2q^2)\,. \quad (8)$$

This is a maximum when $\partial\varrho/\partial y = 0$, or

$$(\alpha\beta)(-y/q^2)-\tfrac{1}{2}\partial(\alpha\beta)/\partial y = 0\,. \quad (9)$$

Now $\partial\alpha/\partial y = \partial\beta/\partial y = -r/2q^2$, hence (9) gives

$$-\alpha\beta y+\tfrac{1}{4}(\alpha+\beta)r = 0$$

or

$$y = \tfrac{1}{4}r(1/\alpha+1/\beta)\,. \quad (10)$$

Since y is small compared with r, we may now take

$$\alpha = r^2(1/2q^2+1/2s^2)$$

and

$$\beta = r^2(1/2q^2+1/2t^2)\,.$$

Hence

$$y = \frac{1}{2r}\left(\frac{s^2}{1+s^2/q^2}+\frac{t^2}{1+t^2/q^2}\right)\,. \quad (11)$$

This is the required formula connecting the error in atomic position with the amplitudes of the angular oscillations.

Equation (10) shows that the errors due to the two angular oscillations at right angles are additive. If there is no oscillation about one axis, $t^2 = 0$, say, and if q^2 is much larger than s^2, representing small oscillations of a broad peak, the error is $y = s^2/2r$ in agreement with the preliminary calculation of the order of magnitude.

A possible difficulty about the application of (11) is that q^2 is not obtainable from the peak shapes of the observed electron density, since it relates to the peak shapes without angular oscillations. In principle, q^2 can be obtained from an appropriate calculated electron-density map, but since q^2 is ordinarily several times as large as s^2 or t^2 it will usually be sufficient to derive approximate values of q^2 from the observed electron density.

For a carbon atom in benzene at $-3°$ C. (Cox *et al.*, 1956) $s^2 = 0{\cdot}036$ Å^2, $t^2 = 0{\cdot}016$ Å^2, $q^2 = 0{\cdot}13$ Å^2 and $r = 1{\cdot}39$ Å, giving $y = 0{\cdot}015$ Å, which was a significant correction to the C–C bond length. For one of the outer carbon atoms in anthracene (Cruickshank, 1956*b*) $s^2 = 0{\cdot}038$ Å^2, $t^2 = 0{\cdot}023$ Å^2, $q^2 = 0{\cdot}11$ Å^2 and $r = 3{\cdot}71$ Å, giving $y = 0{\cdot}006$ Å. As all the atoms in anthracene had to be moved slightly outwards, the maximum bond-length error did not exceed 0·004 Å. These results suggest that the positional corrections are most likely to be important in small molecules.

Equation (11) applies only when the angular oscillations are small. The integrals become much more complex for large oscillations, and numerical methods may have to be used if results are required in such cases.

References

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