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Vibrational Modifications of the Electron Distribution in Molecular Crystals. II. Mean Square Amplitudes of Thermal Motion

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The calculation of the mean square amplitude of thermal motion of an atom in a molecular crystal is discussed. It is shown that, with certain simplifying assumptions concerning the form of the force field, there should be a linear relation between the mean square amplitude and the square of the distance of the atom from the molecular centre of mass. The relation is found to hold approximately for naphthalene and anthracene, and its validity and limitations are discussed.

1. Introduction

In the first paper of this series (Higgs, 1953; to be referred to henceforth as I) the effective electron density derived from the Laue scattering of X-rays by a crystal was shown to be identical with the thermal average of the density at the temperature of the experiment. An expression (equation I-18) was derived which related this density to the electron distribution in a lattice of stationary atoms and to the mean square amplitudes and mean products of amplitudes of thermal vibration of the atoms in the actual crystal. The peak density at the centre of a carbon atom was computed as a function of its r.m.s. amplitude of vibration, a Hartree field being assumed for the distribution in the stationary atom and the thermal motion being taken to be isotropic.

In this paper the problem of calculating r.m.s. amplitudes for atoms in molecular crystals is considered, with particular reference to naphthalene and anthracene. In § 2 two different kinds of contribution to the total mean square amplitude $\overline{u^2}$ are distinguished: that of the 'rigid-body' vibrations in which each molecule moves as an almost rigid unit, and that arising from the internal normal modes of each molecule, interaction constants between these two types of displacement being neglected. In § 3 the rigid-body vibrations are classified further into translational and rotational modes, further interaction constants being neglected, and an expression for their contribution to the mean square amplitude is derived from a simple model of the intermolecular force field. The calculation of the contribution from the internal modes of the molecule is discussed in § 4.

In § 5 use is made of some unpublished results of Cruickshank (1953) to obtain values of $\overline{u^2}$ in naphthalene and anthracene derived from the published X-ray analyses (Abrahams, Robertson & White, 1949*a*, *b*; Mathieson, Robertson & Sinclair, 1950*a*, *b*). It is found that the variation of $\overline{u^2}$ from one atom to another within each molecule is roughly consistent with a thermal motion composed mainly of translation (lattice vibrations) and isotropic rotation (librations). The validity and limitations of this interpretation are discussed in § 6.

The Appendix contains the derivation of some formulae used in the body of the paper.

2. Internal and rigid-body contributions to $\overline{u^2}$

In any discussion of the vibrations of a molecular crystal it is useful to distinguish between coordinates describing the internal distortion of the molecules and those describing their relative motion. If we consider a general small displacement of the n atoms in a single molecule from their equilibrium configuration, we may completely specify the internal distortion by the $3n-6$ components ($3n-5$ for a linear molecule) of a column vector $\mathbf{y}$ and the movement of the molecule as a whole by the 6 components (5 for a linear molecule, of a column vector $\boldsymbol{\eta}$. The former consist of extensions of bonds, distortions of bond-angles, torsions of bonds, etc.; the latter of translations and rotations of the whole molecule. An alternative description is provided by another column vector $\mathbf{x}$, whose $3n$ components specify the atomic displacements relative to a triad of Cartesian axes fixed in space: we adopt the convention that the components $x_j (j = 3i-2,\ 3i-1,\ 3i)$ refer to the ith atom and denote these briefly by the 3-vector $\mathbf{u}_i$.

For small displacements the alternative systems are related linearly by a coordinate transformation which may be written as

$$\mathbf{x} = \mathbf{a}\mathbf{y}+\boldsymbol{\alpha}\boldsymbol{\eta}\,, \tag{1}$$

or as the inverse equations,

$$\mathbf{y} = \mathbf{b}\mathbf{x}\,, \tag{2}$$

$$\boldsymbol{\eta} = \boldsymbol{\beta}\mathbf{x}\,. \tag{3}$$

As is shown in the Appendix, the rectangular matrices

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$\boldsymbol{\alpha}$ and $\mathbf{b}$ may be written down immediately in terms of the geometry of the molecule. If the transformation is completed by the definitions,

$$\mathbf{a} = \mathbf{M}^{-1}\mathbf{b}'\mathbf{G}^{-1}, \tag{4}$$

$$\boldsymbol{\beta} = \boldsymbol{\Phi}^{-1}\boldsymbol{\alpha}'\mathbf{M}\,, \tag{5}$$

where $\mathbf{M}$ is the diagonal matrix of atomic masses ($M_{jj} = m_i$, for $j = 3i-2,\ 3i-1,\ 3i$) and

$$\mathbf{G} = \mathbf{b}\mathbf{M}^{-1}\mathbf{b}', \tag{6}$$

$$\boldsymbol{\Phi} = \boldsymbol{\alpha}'\mathbf{M}\boldsymbol{\alpha}\,, \tag{7}$$

then the kinetic energy splits up into two independent parts, the one arising from internal distortion, the other from motion of the molecule as a rigid body:

$$T = \tfrac{1}{2}\dot{\mathbf{y}}'\mathbf{G}^{-1}\dot{\mathbf{y}}+\tfrac{1}{2}\dot{\boldsymbol{\eta}}'\boldsymbol{\Phi}\dot{\boldsymbol{\eta}}\,. \tag{8}$$

This equation was first derived by Wilson (1939) for the special case, $\boldsymbol{\eta} = \mathbf{0}$.

The potential energy of a free molecule depends only on its internal distortion and may be written in the first (harmonic) approximation as

$$V = \tfrac{1}{2}\mathbf{y}'\mathbf{F}_0\mathbf{y}\,, \tag{9}$$

where $\mathbf{F}_0$ is a matrix of force constants and interaction constants. It is obvious from inspection of equations (8) and (9) that the normal coordinates for molecular vibrations fall into two distinct sets: the first set, $\mathbf{q}_1$, consists of linear combinations of $\mathbf{y}$ and corresponds to frequencies ν_0 which are solutions of the secular equation for internal vibrations,

$$|\mathbf{G}\mathbf{F}_0-4\pi^2\nu_0^2\mathbf{I}| = 0; \tag{10}$$

the second, $\mathbf{q}_2$, is formed from $\boldsymbol{\eta}$ and describes free rigid-body motion ($\nu = 0$).

When the molecule is situated in a crystal, equation (9) is no longer valid: the potential energy is, in the harmonic approximation, of the more general form,

$$V = \tfrac{1}{2}\sum_{\varrho,\sigma=1}^{N}\{\mathbf{y}_\varrho'\mathbf{F}_{\varrho\sigma}\mathbf{y}_\sigma+\boldsymbol{\eta}_\varrho'\mathbf{K}_{\varrho\sigma}\boldsymbol{\eta}_\sigma+2\mathbf{y}_\varrho'\mathbf{k}_{\varrho\sigma}\boldsymbol{\eta}_\sigma\}\,, \tag{11}$$

in which the vectors $\mathbf{y}_\varrho$ and $\boldsymbol{\eta}_\varrho$ refer to the ϱth molecule of the N which constitute the crystal. The intermolecular forces are here represented by the matrices $\mathbf{K}_{\varrho\sigma}$, $\mathbf{k}_{\varrho\sigma}$ (all ϱ, σ), $\mathbf{F}_{\varrho\sigma}$($\varrho \neq \sigma$) and ($\mathbf{F}_{\varrho\varrho}-\mathbf{F}_0$). In general, owing to the presence of the last term in (11), it is no longer possible to separate the normal modes rigorously into internal and rigid-body vibrations of the molecules. However, there is ample spectroscopic evidence that most of the vibration frequencies of many organic molecules do not depend to any large extent on the physical state of the substance. That is, as one would expect, the intermolecular forces are much weaker than the intramolecular forces: in (11) $\mathbf{F}_{\varrho\varrho} \fallingdotseq \mathbf{F}_0$, $\mathbf{F}_{\varrho\sigma} \fallingdotseq \mathbf{0}\,(\varrho \neq \sigma)$ and the elements of $\mathbf{k}$ are small compared with those of $\mathbf{F}_0$. Therefore it seems reasonable to neglect $\mathbf{k}$ and use the simplified potential,

$$V = \tfrac{1}{2}\sum_{\varrho=1}^{N}\mathbf{y}_\varrho'\mathbf{F}_0\mathbf{y}_\varrho+\tfrac{1}{2}\sum_{\varrho,\sigma=1}^{N}\boldsymbol{\eta}_\varrho'\mathbf{K}_{\varrho\sigma}\boldsymbol{\eta}_\varrho\,. \tag{12}$$

The separation of the normal coordinates into $\mathbf{q}_1$ and $\mathbf{q}_2$ is now valid once more.

In these circumstances it is possible to effect a corresponding decomposition of $\overline{u_i^2}$, the mean square amplitude of thermal motion of the ith atom in any molecule: for $\mathbf{u}_i$ is related to $\mathbf{q}_1$ and $\mathbf{q}_2$ by a linear transformation,

$$\mathbf{u}_i = \mathbf{c}_{i1}\mathbf{q}_1+\mathbf{c}_{i2}\mathbf{q}_2\,,$$

from which it follows that

$$\overline{u_i^2} = \text{trace}\,\{\mathbf{c}_{i1}\overline{\mathbf{q}_1\mathbf{q}_1'}\mathbf{c}_{i1}'+\mathbf{c}_{i2}\overline{\mathbf{q}_2\mathbf{q}_2'}\mathbf{c}_{i2}'\} \tag{13}$$

($\mathbf{q}_1$ and $\mathbf{q}_2$ being different sets of normal coordinates, $\overline{\mathbf{q}_1\mathbf{q}_2'} = \mathbf{0}$). The two terms of (13) may be interpreted as the contributions from internal and rigid-body modes respectively:

$$\overline{u_i^2} = (\overline{u_i^2})_{\text{int.}}+(\overline{u_i^2})_{\text{r.-b.}}\,. \tag{14}$$

The intermolecular forces being comparatively weak, the second term of (14) is by far the larger of the two. and to the first may be assigned the value appropriate to a free molecule.

3. An approximate expression for $(\overline{u_i^2})_{\text{r.-b.}}$

It is shown in the Appendix that the rigid-body term in the kinetic energy (8) may be written (as in A14) as the sum of independent terms arising from translation of the centre of mass ($\boldsymbol{\eta}_\text{t}$) and rotation about that centre ($\boldsymbol{\eta}_\text{r}$). Let us assume a model for the intermolecular potential such that there is no interaction between translation and rotation, i.e.

$$V_{\text{r.-b.}} = \tfrac{1}{2}\sum_{\varrho,\sigma}\{\boldsymbol{\eta}_{\text{t}\varrho}'\mathbf{K}_{\text{t}\varrho\sigma}\boldsymbol{\eta}_{\text{t}\varrho\sigma}+\boldsymbol{\eta}_{\text{r}\sigma}'\mathbf{K}_{\text{r}\varrho\sigma}\boldsymbol{\eta}_{\text{r}\sigma}\}\,. \tag{15}$$

There being now no cross-terms in either the kinetic or the potential energy, $(\overline{u_i^2})_{\text{r.-b.}}$ is the sum of two terms, one arising from translation (the lattice or 'acoustic' modes), the other from restricted rotation (libration):

$$(\overline{u_i^2})_{\text{r.-b.}} = (\overline{u_i^2})_\text{t}+(\overline{u_i^2})_\text{r}\,. \tag{16}$$

Let us consider the dependence of these two terms on the position of atom i in the molecule. Whatever the form of the first term of (15) may be, it is obvious that $(\overline{u_i^2})_\text{t}$, arising as it does from translation, is the same for all atoms:

$$(\overline{u_i^2})_\text{t} = A\,, \tag{17}$$

where A is some function of the temperature.

On the other hand $(\overline{u_i^2})_\text{r}$ varies from atom to atom in a way which depends on the form of the second term of (15). In view of the present scarcity of evidence concerning this force field for libration it seems to be necessary to adopt some simple model. Let us assume that each molecule rotates in a time-independent external field, which may be regarded as an average of that due to interaction with its neighbours, and that this field does not depend on the direction of the axis of rotation. Then the second term of (15) contains no cross-terms between the coordinates of different molecules, and the potential for rotation of a single molecule may be written as

$$V_{\mathrm{r}} = K_{\mathrm{r}}\boldsymbol{\eta}_{\mathrm{r}}'\boldsymbol{\eta}_{\mathrm{r}}\,, \tag{18}$$

where K_{r} is a force constant for libration.

In order to calculate $(\overline{u_i^2})_{\mathrm{r}}$ we require an expression for the thermal average $\overline{\boldsymbol{\eta}_{\mathrm{r}}\boldsymbol{\eta}_{\mathrm{r}}'}$. The general expression for such a matrix is that of (I-8); it leads to the formula

$$\overline{\boldsymbol{\eta}_{\mathrm{r}}\boldsymbol{\eta}_{\mathrm{r}}'} = \tfrac{1}{2}\hbar(K_{\mathrm{r}}\boldsymbol{\Phi}_{\mathrm{r}})^{-\frac{1}{2}}\coth\,(\hbar K_{\mathrm{r}}^{\frac{1}{2}}\boldsymbol{\Phi}_{\mathrm{r}}^{-\frac{1}{2}}/2kT)\,, \tag{19}$$

in which T is the thermodynamic temperature, $\hbar$ and k have their usual significance and $\boldsymbol{\Phi}_{\mathrm{r}}$ is defined by (A13). Now the spectroscopic evidence indicates that the libration frequencies of molecular crystals are quite low, usually in the region of 100 cm.$^{-1}$ (see, for example, Rousset, 1948). Since these frequencies are the solutions of the secular equation,

$$|K_{\mathrm{r}}\mathbf{I}-4\pi^2c^2\tilde{\nu}^2\boldsymbol{\Phi}_{\mathrm{r}}| = 0\,,$$

the argument of the function in (19) is essentially $hc\tilde{\nu}/2kT$. At ordinary temperatures ($T \sim 290°$ K.) and with $\tilde{\nu} \sim 100$ cm.$^{-1}$ this quantity is small enough for the approximation $\coth x \fallingdotseq x^{-1}$ to be a good one; (19) becomes

$$\overline{\boldsymbol{\eta}_{\mathrm{r}}\boldsymbol{\eta}_{\mathrm{r}}'} \fallingdotseq kT\mathbf{I}/K_{\mathrm{r}}\,. \tag{20}$$

(This approximation is essentially that of classical mechanics, $\hbar = 0$.)

From equations (20) and (A1) it follows that

$$(\overline{u_i^2})_{\mathrm{r}} = 2kTR_i^2/K_{\mathrm{r}}\,, \tag{21}$$

where R_i is the distance of atom i from the molecular centre of mass.

Combining (16), (17) and (21) we obtain for the total contribution from rigid-body modes

$$(\overline{u_i^2})_{\mathrm{r.\text{-}b.}} = A+BR_i^2\,, \tag{22}$$

in which A and B are temperature-dependent.

4. The calculation of $(\overline{u_i^2})$ int

It is evident from equations (1), (8), (9) and (I-8) that the formula from which $(\overline{u_i^2})_{\mathrm{int.}}$ must be calculated is

$$(\overline{u_i^2})_{\mathrm{int.}} = \sum_{j=3i-2}^{3i}\mathbf{a}_j\overline{\mathbf{yy}'}\mathbf{a}_j'\,, \tag{23}$$

in which

$$\overline{\mathbf{yy}'} = \tfrac{1}{2}\hbar(\mathbf{GF}_0)^{-\frac{1}{2}}\coth\,\{\hbar(\mathbf{GF}_0)^{\frac{1}{2}}/2kT\}\mathbf{G}\,, \tag{24}$$

where $\mathbf{G}$ is defined by equation (6), and $\mathbf{a}_j$ is the jth row of $\mathbf{a}$. Using (4) and (24), we transform (23) into the form

$$(\overline{u_i^2})_{\mathrm{int.}} = \tfrac{1}{2}\hbar m_i^{-2}\sum_{j=3i-2}^{3i}\mathbf{b}_j'\mathbf{G}^{-1}(\mathbf{GF}_0)^{-\frac{1}{2}} \times \coth\,\{\hbar(\mathbf{GF}_0)^{\frac{1}{2}}/2kT\}\mathbf{b}_j\,, \tag{25}$$

where $\mathbf{b}_j$ is the jth column of $\mathbf{b}$. If the vibration frequencies ν_0, found by solving equation (10), are low ($h\nu_0/kT \ll 1$), we may use the approximation $\coth x \fallingdotseq x^{-1} (x \ll 1)$ to simplify (25) as follows:

$$(\overline{u_i^2})_{\mathrm{int.}} \fallingdotseq kTm_i^{-2}\sum_{j=3i-2}^{3i}\mathbf{b}_j'(\mathbf{GF}_0\mathbf{G})^{-1}\mathbf{b}_j\,. \tag{26}$$

Conversely, if the frequencies are high ($h\nu_0/kT \gg 1$), the asymptotic relation $\coth x \sim 1 (x \to \infty)$ leads to the approximate formula

$$(\overline{u_i^2})_{\mathrm{int.}} \fallingdotseq \tfrac{1}{2}\hbar m_i^{-2}\sum_{j=3i-2}^{3i}\mathbf{b}_j'\mathbf{G}^{-1}(\mathbf{GF}_0)^{-\frac{1}{2}}\mathbf{b}_j\,. \tag{27}$$

Equations (26) and (27) are respectively the classical and zero-point limits of (25). These results enable us to calculate $(\overline{u_i^2})_{\mathrm{int.}}$ from the geometry of the molecule, as expressed by the transformation matrix $\mathbf{b}$, and any hypothetical force field $\mathbf{F}_0$.

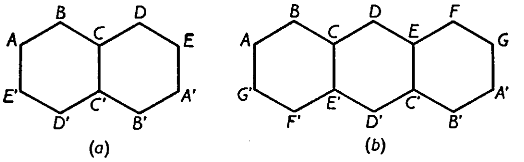
The choice of $\mathbf{F}_0$ depends upon two considerations: on the one hand we have ideas concerning the general form of the field based on quantum-theoretical treatments of the electronic structure; on the other hand we want the solutions ν_0 of equation (10) to agree as closely as possible with the fundamental vibration frequencies determined spectroscopically. In practice, a compromise is usually attempted, for most of the *a priori* quantum mechanical calculations carried out so far do not lead to very good quantitative agreement with the observed spectra.

In the main, force fields are constructed by semi-empirical procedures having as their point of departure the 'simple valence force field' introduced by Bjerrum (1914): $\mathbf{F}_0$ is taken to consist mainly of force constants which may be transferred between similar structural units of related molecules, and small off-diagonal interaction constants are postulated to account for details of the spectra. These extra constants have been interpreted theoretically by Coulson, Duchesne & Manneback (1948) in terms of resonance effects, changes of hybridization and interactions between non-bonded atoms. Such procedures are quite successful in dealing with molecules built from simple atomic groupings linked by chains of single bonds, but less so in coping with conjugated systems, where the form of the field is determined largely by the mobile electrons and the resulting interaction constants are large. It is in describing fields of the latter type that a theoretical approach is most helpful: for example Coulson & Longuet-Higgins (1948) have shown how these fields may be obtained by the simple molecular-orbital technique in terms of such quantities as the mobile orders and the self and mutual polarizabilities of the bonds.

A calculation of the type described in this section has been carried out on the carbon skeleton of naphthalene in order to find the relative magnitudes of $(\overline{u_i^2})_{\text{int.}}$ for the various carbon atoms: the details of this calculation were described in the author's M. Sc. thesis (Higgs, 1952, chap. 4). The assumed force field was that given by Coulson & Longuet-Higgins (1948) with the addition of force constants for bending of the skeleton; the same field for in-plane vibrations was used by Jacobs (1951) in her calculation of the A_g frequencies. The formula employed was (26), although at 20° C., the temperature at which the X-ray measurements of Abrahams, Robertson & White (1949*a*) were carried out, the ratios $h\nu_0/kT$ could hardly be called small (see Higgs, 1952); nevertheless, it was thought that the simple classical approximation would give some indication of the variation of $(\overline{u_i^2})_{\text{int.}}$ over the molecule. The results of the calculation are given in Table 1 (see Fig. 1(*a*) for labelling of atoms).

Table 1. *Mean square amplitudes in naphthalene*

Atom	$(\overline{u_i^2})_{\text{int.}}$ (Å²)	$\overline{u_i^2}$ (Å²)	$(\overline{u_i^2})_{\text{r.-b.}}$ (Å²)	R_i^2/l^2
A	0·005	0·180	0·175	3·25
B	0·006	0·159	0·153	1·75
C	0·004	0·129	0·125	0·25



(*a*) (*b*)

Fig. 1. (*a*) Naphthalene. (*b*) Anthracene.

5. Experimental values of $\overline{u_i^2}$: naphthalene and anthracene

In order to test the validity of equation (22) let us consider the values of $\overline{u_i^2}$ in naphthalene and anthracene at 20° C., for which the detailed results of X-ray analyses are available (Abrahams, Robertson & White, 1949*a*, *b*; Mathieson, Robertson & Sinclair, 1950*a*, *b*). Ahmed & Cruickshank (1952) have refined the crystal and molecular structures by a method which minimizes the mean difference between the observed structure factors and those calculated from a model with atoms arranged in roughly the expected configuration. In their earlier calculations they assigned to the various carbon atoms the same isotropic vibration amplitude, but more recently (Cruickshank, 1953) they have used a more flexible method which allows for different isotropic thermal motions. Values of $\overline{u_i^2}$ derived from Cruickshank's B values are given in Tables 1 and 2. (The B value for an atom is a parameter in its temperature factor, isotropic thermal motion being assumed. In the notation of I it is defined by the relation

$$g_i = f_i \exp\left(-B_i \sin^2\theta/\lambda^2\right) \tag{28}$$

connecting the scattering factor for a vibrating atom with that for a stationary one. It follows from equations (28), (I-9) and (I-11*a*) that

$$\overline{u_i^2} = 3B_i/8\pi^2.)$$

Table 2. *Mean square amplitudes in anthracene*

Atom	$\overline{u_i^2}$ (Å²)	R_i^2/l^2
A	0·152	7
B	0·131	4
C	0·096	1
D	0·108	1

We may now find $(\overline{u_i^2})_{\text{r.-b.}}$, for naphthalene at least, by subtracting from each $\overline{u_i^2}$ the appropriate value of $(\overline{u_i^2})_{\text{int.}}$ calculated in § 4; these quantities are also tabulated in Table 1. The corresponding values of R_i^2 are calculated on the assumption that the carbon atoms lie at the vertices of coplanar regular hexagons (Fig. 1(*a*)). When $(\overline{u_i^2})_{\text{r.-b.}}$ is plotted against R_i^2/l^2, where l is the C–C bond length, the three points (A, B, C) lie reasonably close to a straight line (Fig. 2, middle graph).

Since no calculations of $(\overline{u_i^2})_{\text{int.}}$ have been made for anthracene, we cannot plot values of $(\overline{u_i^2})_{\text{r.-b.}}$ for this molecule. However, as is shown in Fig. 2 (topmost graph), the $(\overline{u_i^2})_{\text{int.}}$ values for naphthalene vary so little—they are in any case only about 4% of the total $\overline{u_i^2}$—that the graph of $\overline{u_i^2}$ itself against R_i^2/l^2 is nearly linear. So we may expect that if, as is very likely, the anthracene $(\overline{u_i^2})_{\text{int.}}$ values vary only slightly over the molecule, the graph of $\overline{u_i^2}$ against R_i^2/l^2 will again

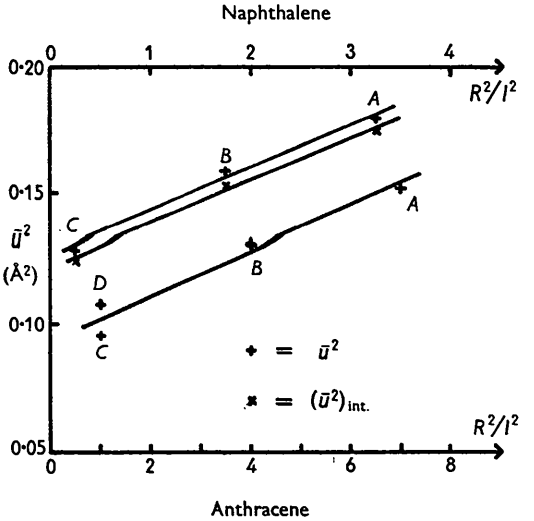


Fig. 2. Variation of $\overline{u^2}$ with R^2.

be nearly linear: this is indeed what happens (Fig. 2, bottom graph; the data are taken from Table 2, and the labelling of the atoms is illustrated in Fig. 1(*b*)).

6. Discussion

It appears from the foregoing considerations that, for naphthalene and anthracene at least, the formula (22) provides quite a good approximate description of the thermal motion: the implication is that most of the variation in the carbon peak densities noticed by Abrahams *et al.* may be accounted for in terms of Fourier-series termination errors (allowed for by the methods of Ahmed & Cruickshank) and thermal libration. However, it must be stressed that this conclusion is only provisional. The data supplied by Cruickshank are the results of preliminary work and may be modified slightly by further calculations. Besides, these data are scarcely sufficient to establish the linearity of the $\overline{u^2}$ versus R^2 relation.

Finally, there are a few comments to be made on the deviations of the experimental points from strict linearity, if in fact these are significant: in particular we may note that atoms C and D in anthracene, having the same value of R_i, do not have equal $\overline{u_i^2}$ values. The calculated $(\overline{u_i^2})_{\text{int.}}$ values are so small compared with the total $\overline{u_i^2}$ that we may probably discount internal molecular vibrations as a cause of these deviations. A much more likely explanation is that they are due to anisotropy of the librations, for to assign an isotropic force field (equation (18)) to a molecule in such an anisotropic environment as a polyacene crystal is really a drastic oversimplification; no doubt further work on the anisotropy of the atomic motions, as revealed by the X-ray data, will throw some light on this matter. Moreover, to return to the problem which provided the starting point for this investigation, there must be some error in the $\overline{u_i^2}$ values deduced from the X-ray data due to the use of scattering factors for isolated atoms; any redistribution of electronic charge occurring during bonding will give rise to departures from linearity in the graph of apparent $\overline{u_i^2}$ versus R_i^2. There is an obvious need for further investigations to distinguish decisively between the effects of thermal motion and those of charge transfer.

I am greatly indebted to Prof. C. A. Coulson for his advice and encouragement during the course of this work and to Dr D. W. J. Cruickshank for much helpful correspondence and for his permission to quote unpublished results.

APPENDIX

Given the definition of the quantities $\mathbf{y}$, we may write the matrix $\mathbf{b}$ of equation (2) in terms of the geometry of the molecule. General formulae for several commonly used types of internal coordinate have been given by Wilson (1939, 1941): for example, if a particular coordinate y is the extension of the bond connecting atoms i and j, then y is related to $\mathbf{x}$ by the formula (in 3-vector notation),

$$y = \frac{(\mathbf{U}_i-\mathbf{U}_j)\,.\,(\mathbf{u}_i-\mathbf{u}_j)}{|\mathbf{U}_i-\mathbf{U}_j|}\,,$$

where $\mathbf{U}_i$ is the 3-vector defining the equilibrium position of atom i relative to the origin of the Cartesian coordinates.

Similarly, in (1) the matrix $\boldsymbol{\alpha}$ may be written in terms of the molecular geometry: if η_1, η_2, η_3 (3-vector $\boldsymbol{\eta}_t$) are the Cartesian components of the displacement of a certain point in the molecule during a small rigid-body motion ($\mathbf{y} = \mathbf{0}$), and η_4, η_5, η_6 (3-vector $\boldsymbol{\eta}_r$) are the components relative to the Cartesian axes of the rotation of the molecule during such a motion, then during the motion the displacement of atom i is (in 3-vector notation)

$$\mathbf{u}_i = \boldsymbol{\eta}_t+\boldsymbol{\eta}_r\times\mathbf{R}_i\,, \tag{A1}$$

in which

$$\mathbf{R}_i = \mathbf{U}_i-\mathbf{U}_0\,, \tag{A2}$$

where $\mathbf{U}_0$ is the equilibrium position of the reference point relative to the Cartesian origin. Equation (*A*1) constitutes rows $3i-2$, $3i-1$, $3i$ of (1) with $\mathbf{y} = \mathbf{0}$, thus defining $\boldsymbol{\alpha}$.

We now have $\mathbf{y}$ defined generally and $\boldsymbol{\eta}$ defined only for rigid-body motion; to define the coordinates completely we need to generalize the definition of $\boldsymbol{\eta}$, that is, to find the matrix $\boldsymbol{\beta}$ of (3): the matrix $\mathbf{a}$ of the inverse equation (1) will then be defined uniquely. So far the only known relations between the unknown matrices, $\mathbf{a}$, $\boldsymbol{\beta}$, and $\boldsymbol{\alpha}$, $\mathbf{b}$ are those expressing the reciprocal nature of (1) and (2), (3):

$$\mathbf{ab} + \boldsymbol{\alpha\beta} = \mathbf{I}; \tag{A3}$$

$$\left.\begin{aligned} \mathbf{ba} &= \mathbf{I}_1,\ \mathbf{b}\boldsymbol{\alpha} = \mathbf{0}\,, \\ \boldsymbol{\beta}\mathbf{a} &= \mathbf{0},\ \boldsymbol{\beta\alpha} = \mathbf{I}_2\,, \end{aligned}\right\} \tag{A4}$$

where $\mathbf{I}_1 . \mathbf{I}_2$ are the unit matrices of orders $(3n-6)$, 6 respectively. These equations are not sufficient to define $\mathbf{a}$, $\boldsymbol{\beta}$ uniquely.

To make the problem soluble uniquely we add the requirement that the kinetic energy shall be expressible as the sum of independent contributions from the velocities $\dot{\mathbf{y}}$ and $\dot{\boldsymbol{\eta}}$. In Cartesians the kinetic energy is

$$T = \tfrac{1}{2}\dot{\mathbf{x}}'\mathbf{M}\dot{\mathbf{x}};$$

using (1) we express it in terms of $\dot{\mathbf{y}}$ and $\dot{\boldsymbol{\eta}}$ as

$$T = \tfrac{1}{2}\dot{\mathbf{y}}'(\mathbf{a}'\mathbf{Ma})\dot{\mathbf{y}}+\tfrac{1}{2}\dot{\boldsymbol{\eta}}'(\boldsymbol{\alpha}'\mathbf{M}\boldsymbol{\alpha})\dot{\boldsymbol{\eta}}+\dot{\mathbf{y}}'(\mathbf{a}'\mathbf{M}\boldsymbol{\alpha})\dot{\boldsymbol{\eta}}\,. \tag{A5}$$

We require the cross-term in (*A*5) to be identically zero:

$$\mathbf{a}'\mathbf{M}\boldsymbol{\alpha} = \mathbf{0}\,. \tag{A6}$$

Equation (*A*6) may be regarded as a set of $3n-6$ relations between the rows of $\boldsymbol{\alpha}$; so also may the second equation of ($A4$). Since the 6 coordinates $\boldsymbol{\eta}$ are linearly independent, the $3n\times 6$ matrix $\boldsymbol{\alpha}$ is of rank 6, so there are precisely $3n-6$ linearly independent relations between its rows. Thus the sets of ($A4$) and ($A6$) must be equivalent ways of writing the same relations, that is, $\mathbf{a}'\mathbf{M}$ must be expressible in terms of $\mathbf{b}$:

$$\mathbf{a}'\mathbf{M} = \mathbf{A}\mathbf{b}\,, \tag{A7}$$

where $\mathbf{A}$ is a regular $(3n-6)^2$ matrix. All that remains now is to determine $\mathbf{A}$; this is done by using ($A7$) and the first equation of ($A4$):

$$\mathbf{b}\mathbf{M}^{-1}\mathbf{b}'\mathbf{A}' = \mathbf{I}_1\,,$$

whence

$$\mathbf{A} = \mathbf{G}^{-1}\,, \tag{A8}$$

where $\mathbf{G}$, defined in (6), is Wilson's inverse kinetic energy matrix. Equations (4) and (8) now follow from $A(5)$, ($A7$) and ($A8$); equation (5) is obtained by premultiplying ($A3$) by $\boldsymbol{\alpha}'\mathbf{M}$ and using ($A6$).

From equation ($A1$) we may derive the explicit form of the 'total inertia matrix' $\boldsymbol{\Phi}$, defined in (7). If we denote the jth row of $\boldsymbol{\alpha}$ by $\boldsymbol{\alpha}_j$, then by comparing (1) and ($A1$) we find

$$\begin{pmatrix}\alpha_{3i-2}\\ \alpha_{3i-1}\\ \alpha_{3i}\end{pmatrix} = \begin{pmatrix}1, & 0, & 0, & 0, & Z_i, & -Y_i\\ 0, & 1, & 0, & -Z_i, & 0, & X_i\\ 0, & 0, & 1, & Y_i, & -X_i, & 0\end{pmatrix},$$

where X_i, Y_i, Z_i are the Cartesian components of $\mathbf{R}_i$. Equation (7) now becomes

$$\boldsymbol{\Phi} = \sum_{i=1}^{n} m_i \times \begin{pmatrix} 1, & 0, & 0, & 0, & Z_i, & -Y_i\\ 0, & 1, & 0, & -Z_i, & 0, & X_i\\ 0, & 0, & 1, & Y_i, & -X_i, & 0\\ 0, & -Z_i, & Y_i, & Y_i^2+Z_i^2, & -X_iY_i, & -X_iZ_i\\ Z_i, & 0, & -X_i, & -Y_iX_i, & Z_i^2+X_i^2, & -Y_iZ_i\\ -Y_i, & X_i, & 0, & -Z_iX_i, & -Z_iY_i, & X_i^2+Y_i^2 \end{pmatrix}. \tag{A9}$$

It is obvious on inspecting ($A9$) that $\boldsymbol{\Phi}$ may be simplified by choosing the centre of mass as the reference point for defining $\boldsymbol{\eta}_t$, that is,

$$\mathbf{U}_0 = m^{-1}\sum_{i=1}^{n} m_i\mathbf{U}_i\,, \tag{A10}$$

where

$$m = \sum_{i=1}^{n} m_i\,. \tag{A11}$$

Equation ($A10$) may be written as

$$\sum_{i=1}^{n} m_i\mathbf{R}_i = \mathbf{0}\,,$$

so ($A9$) becomes

$$\boldsymbol{\Phi} = \begin{pmatrix} m\mathbf{I}, & \mathbf{0}\\ \mathbf{0}\,, & \boldsymbol{\Phi}_r\end{pmatrix}, \tag{A12}$$

in which $\boldsymbol{\Phi}_r$ is the tensor of moments and products of inertia relative to the centre of mass:

$$\boldsymbol{\Phi}_r = \sum_{i=1}^{n} m_i \begin{pmatrix} Y_i^2+Z_i^2, & -X_iY_i, & -X_iZ_i\\ -Y_iX_i, & Z_i^2+X_i^2, & -Y_iZ_i\\ -Z_iX_i, & -Z_iY_i, & X_i^2+Y_i^2\end{pmatrix}. \tag{A13}$$

The rigid-body term in the kinetic energy (8) now splits up again into two terms:

$$T_{\text{r.-b.}} = \tfrac{1}{2}m\dot{\boldsymbol{\eta}}_t'\dot{\boldsymbol{\eta}}_t + \tfrac{1}{2}\dot{\boldsymbol{\eta}}_r'\boldsymbol{\Phi}_r\dot{\boldsymbol{\eta}}_r\,. \tag{A14}$$

The definition (3) of $\boldsymbol{\eta}$ may be written explicitly in 3-vector notation ($\boldsymbol{\Phi}_r$ being regarded as a dyadic) as

$$\boldsymbol{\eta}_t = m^{-1}\sum_{i=1}^{n} m_i\mathbf{u}_i\,, \tag{A15}$$

$$\boldsymbol{\eta}_r = \boldsymbol{\Phi}_r^{-1}\left\{\sum_{i=1}^{n} m_i\mathbf{R}_i\times\mathbf{u}_i\right\}: \tag{A16}$$

these vectors are now the displacement of the centre of mass and the mean rotation about that centre respectively, and $\mathbf{R}_i$ is the vector from that point to atom i in the equilibrium configuration.

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