The Variation of Vibration Amplitudes with Temperature in Some Molecular Crystals

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The theory of the translational and rotational vibrations of molecules in molecular crystals is discussed. Characteristic lattice frequencies for translational and rotational vibrations, derived from X-ray and Raman studies, are used to predict the variation of the molecular vibration amplitudes with temperature in benzene, naphthalene and anthracene. There will be little gain in using temperatures below about 25° K. for studies of the fine details of the electron density of these molecules.

1. Introduction

The simple Debye–Waller theory of the variation with temperature of the amplitude of vibration of an atom in a monatomic cubic crystal is well known. In this theory the frequency ν of a lattice vibration is assumed proportional to the reciprocal wave length $|\mathbf{k}|$ of the vibration, and a characteristic temperature Θ_M is defined in terms of the maximum lattice frequency ν_M by $\Theta_M = h\nu_M/k$. The mean square amplitude of atomic vibration $\overline{u^2}$ is (James, 1948, equation (5·69))

$$\overline{u^2} = \frac{3h^2 T}{4\pi^2 mk\Theta_M^2}\left\{\Phi(x)+\frac{x}{4}\right\}, \qquad (1)$$

where m is the mass of the atom,

$$\Phi(x) = \frac{1}{x}\int_0^x \frac{\xi d\xi}{e^\xi-1}, \qquad (2)$$

and $x = \Theta_M/T$. For $T > \Theta_M$, (1) may be approximated by

$$\overline{u^2} = \frac{3h^2 T}{4\pi^2 mk\Theta_M^2}. \qquad (3)$$

If Θ is known from calorimetric or elastic measurements, $\overline{u^2}$ may be calculated from (1) as a function of T. Alternatively, if $\overline{u^2}$ is known from an X-ray structure determination at one temperature, Θ_M may be calculated and hence $\overline{u^2}$ estimated for any other temperature.

Two extra factors have to be considered in the theory of the vibrations of crystals of general symmetry composed of rigid molecules (e.g. Fruhling, 1951). First, account must be taken of the lattice vibrations involving rotational oscillations of the molecules. These vibrations belong to 'optic' branches, as distinct from the 'acoustic' translational branches, because the vibration frequencies do not tend to zero as the reciprocal wave vector $\mathbf{k} \to 0$. A triclinic crystal with

one molecule per unit cell has three such rotational optic branches, each of which involves oscillations about one of the principal axes of inertia of the molecule (Rousset, 1947). Secondly, if there is more than one molecule in a unit cell, account must be taken of additional translational and rotational optic branches. If there are two molecules in a unit cell, there will be three translational optic branches and three additional rotational optic branches, all corresponding to vibrations in which the two molecules in a cell are (almost) out of phase.

A correct calculation of the rigid-body vibrations of a molecule in a crystal must take into account the distribution of frequencies in each of these branches. Another complication is that in general the mean square translational vibration of a molecule is anisotropic and may be represented by a tensor, whereas a formula of the type (1) yields only a scalar amplitude. It is therefore convenient to restrict the discussion of translational vibrations to directionally averaged amplitudes.

For definiteness, consider a crystal of orthorhombic or lower symmetry having two molecules in a unit cell. The simplest method of treating its optic translational branches is to suppose that the frequency in each is a constant, and further that these frequencies are the same. With these approximations, the mean square amplitude of translational vibration of the centre of mass of a molecule is

$$(\overline{u^2})_{\text{trans.}} = \tfrac{1}{2}\left\{\frac{3h^2 T}{4\pi^2 mk\Theta_M^2}\left\{\Phi(x)+\frac{x}{4}\right\} + \frac{h}{8\pi^2 m\nu}\coth\left(\frac{1}{2}\frac{h\nu}{kT}\right)\right\}, \qquad (4)$$

the first term giving the contribution from the acoustic branches and the second the contribution from the vibrations of frequency ν in the optic branches (Bloch, 1932).

Similarly, each of the rotational branches may be

approximated by a constant frequency, so that if ν_1 and ν_2 are the frequencies of the in-phase and out-of-phase branches for the oscillations about an axis with moment of inertia I, the mean square amplitude of angular oscillation in radians² is

$$(\overline{\varphi^2})_I = \frac{h}{8\pi^2 I}\left\{\frac{1}{2\nu_1}\coth\left(\frac{1}{2}\frac{h\nu_1}{kT}\right) + \frac{1}{2\nu_2}\coth\left(\frac{1}{2}\frac{h\nu_2}{kT}\right)\right\}. \quad (5)$$

Equations (4) and (5) have the disadvantage that they cannot be used to determine characteristic lattice frequencies from the $(\overline{u^2})_{\text{trans.}}$ and the three $(\overline{\varphi^2})_I$ found at one temperature, since each involves two parameters, Θ_M and ν, and ν_1 and ν_2, respectively. However, as the characteristic temperatures $h\nu/k$ of the optic translational branches are higher than Θ_M, it is often adequate to treat the whole of the translational motion by the Debye–Waller formula (1), using an apparent Θ_M somewhat higher than the true Θ_M of the acoustic branches. Indeed, the resulting frequency distribution may be more correct. For the rotational motions, there is often little difference between ν_1 and ν_2, so that (5) can be used to determine an average frequency for the oscillations about each axis. At sufficiently high temperatures the relation between $(\overline{\varphi^2})_I$ and the corresponding average frequency ν is

$$(\overline{\varphi^2})_I = \frac{kT}{4\pi^2 I \nu^2}. \quad (6)$$

Once the lattice frequencies have been found, the appropriate formula may be used to determine the variation of the vibration amplitudes with temperature.

It is sometimes possible to determine the frequencies of some of the long-wave lattice vibrations ($\mathbf{k} = 0$) by spectroscopic methods (e.g. Rousset, 1947). Further, by using orientated single crystals with polarized light, it may be possible to identify both the axis of oscillation and the coupling of the molecules within the unit cell which are responsible for a given frequency (e.g. naphthalene, Kastler & Rousset, 1941). The information available is limited by selection rules, e.g. the optic translational vibrations of centrosymmetric molecules sited at centres of symmetry are inactive in Raman spectra.

2. Anthracene

In the recent three-dimensional X-ray crystallographic analysis of the anisotropic thermal motion of anthracene at room temperature (Cruickshank, 1956) values were found for $(\overline{u^2})_{\text{trans.}}$ and the three $(\overline{\varphi^2})_I$ for the anthracene molecules. Anthracene crystallizes in the space group $P2_1/a$, with two molecules per unit cell. The value for $(\overline{u^2})_{\text{trans.}}$, averaged over all directions, was $3\cdot13\times10^{-2}$ Å². Using the approximation of treating all the translational motion by the Debye–Waller formula (1), this gives $\Theta_M = 87°$ K.

The values for the r.m.s. amplitudes of angular oscillation were $3\cdot9°$, $2\cdot2°$ and $3\cdot0°$ about axes 1, 2 and 3 respectively, axis 1 being the long axis of the molecule, axis 2 the short axis and axis 3 normal to the molecular plane. The e.s.d.'s of these determinations were about $0\cdot2°$ for axes 2 and 3, but about $1\cdot0°$ for axis 1. Using estimated moments of inertia of 1846, 391 and 2237×10^{-40} g.cm.$^{-2}$, (5) gives the average rotational lattice frequencies as 81, 65 and 43 cm.$^{-1}$. These frequencies may be compared with the lattice frequencies at $\mathbf{k} = 0$ of 120 ± 8, 68 ± 5 and 48 ± 4 cm.$^{-1}$ determined by Fruhling (1951) in his Raman spectra investigations, no separation into doublets being observable. The Raman frequencies for axes 2 and 3 agree nicely with those inferred from the X-ray results, while the difference for axis 1 is quite compatible with the large X-ray e.s.d. for this axis. Conversely, using (5), the Raman frequencies imply angular oscillations of r.m.s. amplitudes $2\cdot6°$, $2\cdot1°$ and
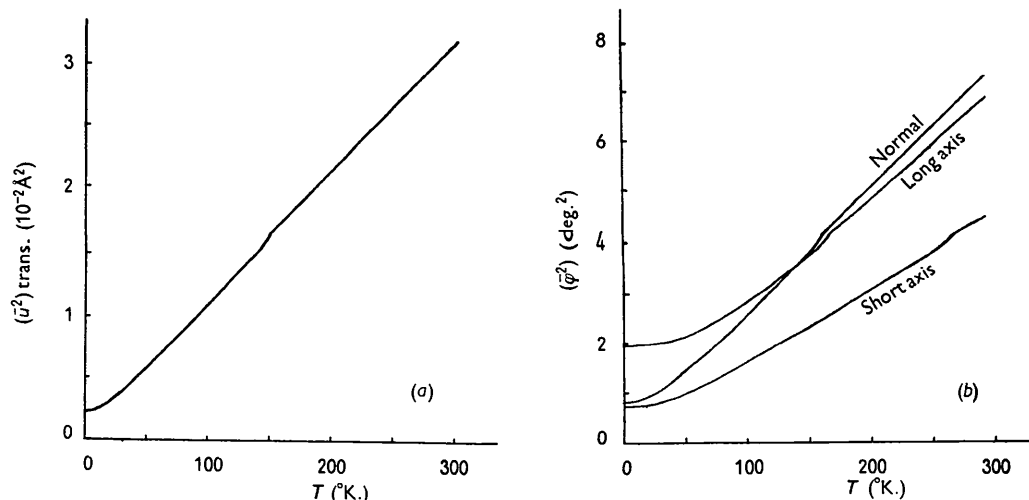

Fig. 1. (a) $(\overline{u^2})_{\text{trans.}}$ for anthracene. (b) $(\overline{\varphi^2})$ for anthracene.

2·7° at room temperature, which also agree satisfactorily with the X-ray values.

Supposing that the Raman values are better for the rotational frequencies, and using $\Theta_M = 87°$ K. for the translational motion, we can now estimate the variation with temperature of the amplitudes of the molecular motions of anthracene from (1) and (5). Fig. 1(a) shows the variation of $\overline{(u^2)}_{\text{trans.}}$, and Fig. 1(b) the variation of the $\overline{(\varphi^2)}$'s. The characteristic temperatures $(\Theta = h\nu/k)$ for the rotational oscillations about the three axes are 173, 98 and 69° K. (numerically, if ν is in cm.$^{-1}$, $\Theta = 1\cdot44\nu$). Examination of Fig. 1 shows that at temperatures above the characteristic temperatures the mean square amplitudes vary linearly with T in the classical manner, as in (3) and (6). At lower temperatures the quantum effects are clearly marked. At 0° K. the estimated r.m.s. amplitudes of angular oscillation are 1·4, 0·8 and 0·9°, and $\overline{(u^2)}_{\text{trans.}}$ is $0\cdot23 \times 10^{-2}$ Å^2.

As a check on the effect of treating the translational motion by (1) using an artificially high Θ_M, alternative calculations were carried out with (4) assuming $\Theta_E = h\nu/k = 1\cdot2\Theta_M$. With this assumption, the room temperature $\overline{(u^2)}_{\text{trans.}} = 3\cdot13 \times 10^{-2}$ Å^2 corresponds to $\Theta_E = 82°$ K. ($\nu = 57$ cm.$^{-1}$) and $\Theta_M = 68°$ K. The variation of $\overline{(u^2)}_{\text{trans.}}$ with T then calculated from (4) differed insignificantly from the results shown in Fig. 1(a).

3. Naphthalene

The most serious defect of calculations of the preceding type is that they make no allowance for the variation of the lattice frequencies with temperature. No suitable data for anthracene appear to be available, but Ichishima (1950) has measured the variation of the lattice rotational frequencies for naphthalene between $+25°$ C. and $-190°$ C. It is therefore worth while

considering the lattice vibrations of naphthalene in some detail.

Naphthalene also crystallizes in the space group $P2_1/a$, with two molecules per unit cell. The author's three-dimensional X-ray crystallographic analysis of the anisotropic thermal motion of naphthalene at room temperatures is not yet complete, but the preliminary results (quoted by Higgs (1955)) give $\overline{(u^2)}_{\text{trans.}} = 4\cdot03 \times 10^{-2}$ Å^2. Using (1), this implies $\Theta_M = 91°$ K. The preliminary X-ray results do not give the amplitudes of the individual angular oscillations, but these may be inferred from the Raman investigations of Kastler & Rousset (1941) and Ichishima (1950). The single crystal studies of Kastler & Rousset are particularly noteworthy, as these authors were able to identify both the axis and the coupling responsible for each rotational frequency. They give the room-temperature frequencies as

Axis 1,	S	109,	A	127;
Axis 2,	S	74,	A	76;
Axis 3,	S	46,	A	54 cm.$^{-1}$,

where the numbering of the axes is the same as for anthracene (1 is the long axis, 2 the short and 3 is the normal), and S or A denotes whether the two molecules in a unit cell are vibrating in or out of phase. Using estimated I's of 267, 667 and 935×10^{-40} g.cm.^{2} (Barrow & McClellan, 1951), the substitution of these frequencies in (5) gives the r.m.s. amplitudes of vibration as 3·2, 3·1 and 4·0° respectively.

Ichishima gives the frequencies between $+25°$ C. and $-190°$ C. as

$$\nu_4 = 125 - 0\cdot0634T: \quad (106),$$
$$\nu_5 = 145 - 0\cdot0633T: \quad (126),$$
$$\nu_3 = 91 - 0\cdot0593T: \quad (74),$$
$$\nu_1 = 60 - 0\cdot0433T: \quad (47),$$
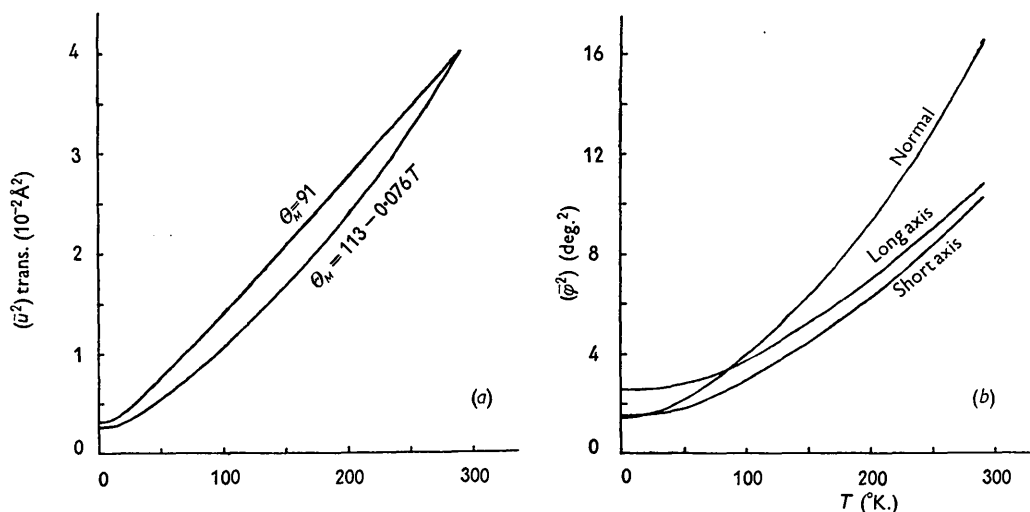$$\nu_2 = 75 - 0\cdot0800T: \quad (52),$$

Fig. 2. (a) $\overline{(u^2)}_{\text{trans.}}$ for naphthalene. Upper curve with $\Theta_M = 91°$ K., lower curve with $\Theta_M = 113 - 0\cdot076T$.
(b) $\overline{(\varphi^2)}$ for naphthalene.

where T is in °K., and the figures in brackets are the values given by these formulae at $+20°$ C. If we suppose that Ichishima's ν_3 is an unresolved doublet involving the two oscillations about axis 2, we see that his results agree closely with those of Kastler & Rousset.

If, for simplicity, we assume that Ichishima's formulae hold down to 0° K., we can use (5) to determine the variation with temperature of the $\overline{(\varphi^2)}_l$ for naphthalene with allowance for the change in the lattice frequencies. The results are shown in Fig. 2(b).

There is no direct evidence available as to the variation of the translational lattice frequencies of naphthalene with temperature, so that it is simplest to assume that they also vary linearly with temperature. If Ichishima's rotational frequencies are written in the form $\nu = \nu_0(I - aT)$, the mean value of a is 0·00067. Assuming the same value of a, Θ_M must be taken as

$$\Theta_M = 113 - 0.076T$$

to give the X-ray value of $\Theta_M = 91°$ K. at 293° K. The corresponding variation of $(\overline{u^2})_{\text{trans.}}$ with temperature is shown in Fig. 2(a), as is also the variation if Θ_M is assumed constant and equal to 91° K.

Comparison of the two curves in Fig. 2(a) shows that the vibration amplitudes estimated with variable Θ_M fall off rather more quickly as T decreases than those estimated with constant Θ_M. For instance, at 90° K. constant Θ_M gives $(\overline{u^2})_{\text{trans.}} = 1.26 \times 10^{-2}$ Å^2, while variable Θ_M gives $(\overline{u^2})_{\text{trans.}} = 0.94 \times 10^{-2}$ Å^2. At absolute zero the values are 0.31×10^{-2} Å^2 and 0.25×10^{-2} Å^2. The differences between the two curves are not, however, very large, so that the assumption of constant lattice frequencies may be used as a rough first approximation. On this basis, the values shown in Fig. 1 for anthracene may be used for rough predictions.

Comparison of the magnitudes of the angular oscillations of naphthalene and anthracene shown in Figs. 1(b) and 2(b) is interesting (the assumption of constant frequencies for anthracene must be borne in mind). At all temperatures the angular oscillations of naphthalene are rather larger than those of anthracene. For both molecules the smallest oscillation is about the short axis, and at room temperature the largest oscillation is about the normal. At very low temperatures the low-frequency normal-axis oscillations have about the same magnitude as the short-axis oscillations, while the high-frequency long-axis oscillations have the largest amplitudes. For naphthalene (using Ichishima's frequencies) the r.m.s. angular oscillations fall from 3·3, 2·2 and 4·1° at room temperatures to 1·6, 1·2 and 1·2° at 0° K.

The relative contributions of the translational and angular oscillations of a molecule to the total oscillation of any particular atom are of interest. For naphthalene the mean square tangential oscillation of the carbon atom farthest from the centre due to the

normal-axis oscillation is 3.20×10^{-2} Å^2 at room temperature, compared with the molecular translational contribution of 4.03×10^{-2} Å^2. At 0° K. the magnitudes are 0.27×10^{-2} Å^2 and 0.25×10^{-2} Å^2, respectively. The effects of the normal-axis oscillation are smaller for atoms nearer the centre, as are the effects of oscillations about other axes. For the outermost hydrogen the mean square tangential oscillation is about twice that of the outermost carbon.

4. Benzene

It is not possible to give as complete an account of the vibration amplitudes of benzene as of naphthalene or anthracene, for neither the X-ray nor the Raman analyses are complete. On the one hand, the X-ray analysis of the anisotropic thermal motion (Cox, Cruickshank & Smith, 1957) does not determine one of the parameters involved in the rigid-body motions perpendicular to the molecular plane, and on the other hand some of the Raman lines are missing. Benzene crystallizes in the space group $Pbca$ with 4 molecules per unit cell, so that four rotational lattice frequencies, corresponding to different molecular couplings, should be obversable for each axis in the Raman spectra (Fruhling, 1951). Of the twelve possible rotational lattice frequencies only six have been found, and there is doubt as to the axes to which these frequencies correspond (Cruickshank, 1957). Accordingly, it seems best for the present to omit the Raman frequencies from a discussion of the vibration amplitudes of benzene, and to use only the unambiguous part of the X-ray results. Fortunately, this allows a discussion of the motions in the plane of the molecule, including the large oscillation about the hexad axis.

The X-ray results at $-3°$ C. give $(\overline{u^2})_{\text{trans.}} = 5.77 \times 10^{-2}$ Å^2 (averaged in the molecular plane) and an r.m.s. amplitude of 7·9° about the hexad axis. Formally the translational vibrations are divided among three acoustic and nine optic branches. However, the frequency distribution implied by treating the whole translational motion by (1) will probably be as good as that implied by the appropriate generalization of (4) with assumed relations between Θ_M and the ν's of the optic branches. On the former assumption (1) gives $\Theta_M = 93°$ K. By (5), using $I = 295 \times 10^{-40}$ g.cm.^{2}, the hexad axis r.m.s. amplitude of 7·9° corresponds to a mean frequency of 43 cm.$^{-1}$ for the four optic branches involving oscillations about this axis.

Ichishima & Mizushima (1950) have given the variation of the observable lattice frequencies between $-10°$ C. and $-195°$ C. in the form $\nu = \nu_0(1 - aT)$. Taking their mean value for $a = 0.0011T$, we may write

$$\Theta_M = 132 - 0.145T \quad (\text{°K.})$$

and, for the mean frequency of the hexad axis oscillations,

$$\nu = 62 - 0.068T \quad (\text{cm.}^{-1}) .$$

Fig. 3 shows the corresponding m.s. amplitudes of oscillation, the angular oscillation being shown in terms of the tangential movement of a carbon atom
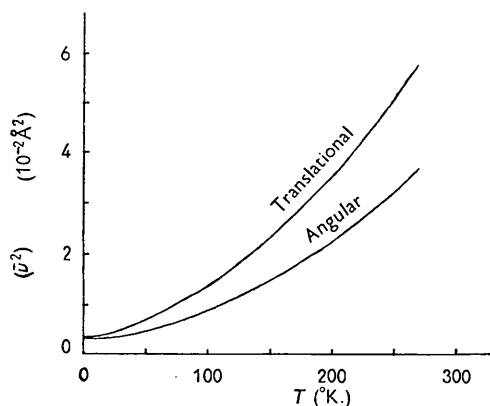

Fig. 3. Contributions to the total tangential movement of a carbon atom in benzene from the translational and angular oscillations.

1·39 Å from the centre of the molecule. The r.m.s. amplitude of the translation motion of the molecule in the molecular plane falls from 0·24 Å at 270° K. to 0·06 Å at 0° K., and the angular oscillation about the hexad axis from 7·9 to 2·2°.

5. General comments

The advantages of the use of low temperatures in detailed studies of molecular structures by X-ray crystallography are well known (e.g. Hirshfeld & Schmidt, 1954). The present theoretical work provides some quantitative data on which to decide at what temperatures particular studies of the fine details of molecular electron densities should be carried out. For instance, Fig. 3 shows that the total m.s. amplitude of a carbon atom in benzene in a tangential direction is $9·45 \times 10^{-2}$ Å² at 270° K., $2·02 \times 10^{-2}$ at 90° K., $0·79 \times 10^{-2}$ at 25° K. and $0·65 \times 10^{-2}$ at 0° K. Accordingly the thermal motion of benzene can be very considerably reduced by using liquid nitrogen as a coolant (giving, say, 90° K.), and still further reduced by using liquid hydrogen (giving, say, 25° K.). Rel-

atively little further reduction is obtainable at lower temperatures. There would thus be little gain in using temperatures below about 25° K. for studies of the electron density in benzene. The same conclusion holds for naphthalene and anthracene.

This conclusion about a minimum worth-while temperature can be expressed in a more general form. For rotational branches, the corresponding oscillation decreases relatively little for temperatures below about $0·4\Theta$, $\Theta = hv/k$ being the characteristic temperature of the branch. For translational branches, the minimum is effectively reached by about $0·2\Theta_M$. The latter in general determines the minimum worth-while temperature.

One final comment may be made. In all the figures shown it is the squares of the amplitudes rather than the amplitudes themselves which have been plotted. This is primarily because the square amplitudes occur naturally in the formulae. It is also convenient because the peak heights of an electron-density or difference map vary roughly with an inverse power of the amplitude, the power lying between the square and the cube (e.g. Higgs, 1953). The figures thus give a fair idea of the variation of the reciprocal peak heights.

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