REVIEWS OF MODERN PHYSICS VOLUME 30, NUMBER 1 JANUARY, 1958

On the Lattice Vibrations of Benzene, Naphthalene, and Anthracene

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1. DESCRIPTION OF THE MOLECULAR VIBRATIONS

In the preceding two papers, Professors E. G. Cox and J. M. Robertson have described the x-ray crystal structure analyses of benzene, naphthalene, and anthracene. Besides the customary atomic positions and bond lengths, these analyses have yielded the individual anisotropic vibration tensors $\mathbf{U}^r$ of the carbon atoms at the temperatures of the experiments. The present paper shows how these tensors can be interpreted in terms of the rigid-body vibrations of the molecules, and then relates the x-ray results on the molecular vibrations to the thermodynamic data for the crystals and to the low-frequency Raman lines of the crystals.

The symmetric 3×3 tensors $\mathbf{U}^r$ are defined so that the mean square amplitude of vibration of an atom in a direction $\mathbf{l}$ is

$$\bar{u}^2 = \sum_{i,j=1}^{3} U^r{}_{ij} l_i l_j.$$

The internal vibrations of the molecules are sufficiently small for the atomic vibration tensors to be interpreted in terms of the rigid-body vibrations of the molecules. These rigid-body vibrations can be expressed in terms of two symmetric 3×3 tensors, $\mathbf{T}$ giving the anisotropic translational vibrations of the mass center, and $\boldsymbol{\omega}$ the anisotropic angular vibrations about axes through the center. The value of the mean square amplitude $\bar{u}^2$ in a direction $\mathbf{l}$ at a point $\mathbf{r}$ in the molecule is then

$$\sum_{i,j=1}^{3} U_{ij} l_i l_j = \sum_{i,j=1}^{3} \{T_{ij} l_i l_j + \omega_{ij} (\mathbf{l}\times\mathbf{r})_i (\mathbf{l}\times\mathbf{r})_j\}.$$

Given the $\mathbf{U}$ tensors for the atoms of a molecule, the best values of the $\mathbf{T}$ and $\boldsymbol{\omega}$ tensors may be found by the method of least squares.[1]

For naphthalene,[2] for example, the values of the $\mathbf{T}$ and $\boldsymbol{\omega}$ tensors at room temperature are

$$\mathbf{T} = \begin{bmatrix} 5.0 & -0.3 & 0.1 \\ & 4.0 & -0.1 \\ & & 3.4 \end{bmatrix} \times 10^{-2}\ \text{A}^2,$$

and

$$\boldsymbol{\omega} = \begin{bmatrix} 19.5 & 2.2 & 2.6 \\ & 14.0 & 0.8 \\ & & 17.7 \end{bmatrix} \text{deg}^2.$$

The tensors are referred to the natural molecular axes: 1 down the length of the molecule, axis 2 the short axis, and axis 3 perpendicular to the molecular plane. The off-diagonal elements are not significantly different from zero, so that the principal axes of $\mathbf{T}$ and $\boldsymbol{\omega}$ can be considered to coincide with the natural molecular axes. The rms amplitudes of the translational vibration of naphthalene along these axes, obtained from the square roots of the diagonal elements of $\mathbf{T}$, are 0.22, 0.20, and 0.19 A, respectively. The greatest amplitude of translational vibration is along the long axis of the molecule, so that the molecule moves most easily in the direction in which it presents the least area of resistance. The rms amplitudes of angular vibration obtained from $\boldsymbol{\omega}$ are 4.4°, 3.7°, and 4.2°. The estimated standard deviations of these, estimated from the least-squares equations, are ~0.8°, 0.3°, and 0.2°.

The results for anthracene[3,4] are entirely similar. The rms amplitudes of translational vibration are 0.20, 0.16, and 0.16 A, and the amplitudes of the angular vibrations are 3.8°, 2.2°, and 3.1°.

An unambiguous determination of all the elements of $\mathbf{T}$ and $\boldsymbol{\omega}$ for benzene is not possible[5] as the three carbon atoms of the planar asymmetric unit give insufficient U_{ij}'s to solve the least-square equations. However, the rms amplitude of angular vibration about the axis normal to the plane is unambiguously found to be 7.9°.

2. THEORY OF LATTICE VIBRATIONS

These x-ray results, derived from the intensities of the Bragg reflections, give only the average amplitudes of vibration of the molecules. To interpret them further and to relate them to the thermodynamic and spectroscopic data we must consider how these average amplitudes are built up from contributions from all the lattice vibrations.

In the simple Debye-Waller theory for the amplitude of vibration of an atom in a monatomic cubic crystal, the frequency of an "acoustic" lattice vibration is assumed proportional to the reciprocal wavelength $|\mathbf{k}|$ of the vibration, and a characteristic temperature Θ_M is defined in terms of the maximum lattice frequency ν_M by $\Theta_M = h\nu_M/k$, where k is Boltzmann's constant. The mean square amplitude of the atomic vibration is

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[1] D. W. J. Cruickshank, Acta Cryst. **9**, 754 (1956).

[2] D. W. J. Cruickshank, Acta Cryst. **10**, 504 (1957).

[3] D. W. J. Cruickshank, Acta Cryst. **9**, 915 (1956).

[4] D. W. J. Cruickshank, Acta Cryst. **10**, 470 (1957).

[5] Cox, Cruickshank, and Smith (to be published).

then a function of the mass m, the temperature T, and Θ_M.

Two extra factors have to be considered in the theory of the vibration of crystals of general symmetry composed of rigid molecules (see, e.g., Fruhling[6]). Firstly, account must be taken of the lattice vibrations involving rotational vibrations of the molecules. These vibrations belong to "optic" branches, as distinct from the three "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 vibrations about one of the principal axes of inertia of the molecule.[7] 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. However, to avoid too many complications, it is necessary to make a number of approximations. First, the mean square translational vibration of a molecule is anisotropic and is represented by a tensor, whereas the simple Debye-Waller formula yields only a scalar amplitude. To use this formula it is therefore necessary to restrict the discussion of translational vibrations to directionally averaged amplitudes. Second, if a crystal of low symmetry has two molecules in a unit cell there will be both acoustic and optic translational branches. The simplest method of treating the optic branches is to suppose that the frequency in each is a constant. If the frequencies for $\mathbf{k}=0$ are known spectroscopically we may take these as the branch frequencies. But if no observations are available (or if the lines are forbidden by the selection rules, as in the Raman spectra of benzene, etc.) we have to guess the optic frequencies in relation to the acoustic ν_M. In such circumstances it is usually simplest, and probably sufficiently accurate, to treat the whole translational motion by the Debye-Waller formula, using an apparent ν_M somewhat higher than the true ν_M of the acoustic branches. This apparent ν_M will be close to the average frequency of the optic translational branches. We shall use the Debye-Waller formula for the translational motion of benzene, naphthalene and anthracene.

Each rotational branch 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 vibrations about an axis with moment of inertia I, the mean square amplitude of angular vibration in radians^2 is

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

Conversely, if $(\bar{\phi}^2)_I$ is known from the x-ray results, we can determine an average frequency for the vibrations about that axis.

3. NAPHTHALENE

For naphthalene, rather extensive experimental results are available. Of the Raman investigations, the single crystal studies of Kastler and Rousset[8] 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 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,[9] the substitution of these frequencies in (1) gives the rms amplitudes of vibration as 3.2°, 3.1° and 4.0°, respectively.[10] These compare satisfactorily with the x-ray values of 4.4±0.8, 3.7±0.3, and 4.2±0.2°. Conversely the x-ray values imply mean frequencies for each axis of 84, 62, and 47 cm^{-1} respectively. After allowance for the small effects of the internal vibrations, the x-ray results give the directionally averaged mean square amplitude of translational vibration as 4.0×10^{-2} A^2, which corresponds to $\Theta_M = 91°$K ($\nu_M = 63$ cm^{-1}).

These frequencies could be used to predict the variation of the vibration amplitudes and of the entropy of the crystal with temperature, but a more precise discussion is possible since Ichishima[11] has measured the variation of the rotational frequencies between +25°C and −190°C. He gives the frequencies between +25°C and −190°C as

$\nu_4 = 125 - 0.0634T$ cm^{-1}: (106),
$\nu_5 = 145 - 0.0633T$: (126),
$\nu_3 = 91 - 0.0593T$: (74),
$\nu_1 = 60 - 0.0433T$: (47),
$\nu_2 = 75 - 0.0800T$: (52),

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[6] A. Fruhling, Ann. phys. **6**, 401 (1951).

[7] A. Rousset, *La Diffusion de la Lumiere par les Molecules Rigides* (Gauthier-Villars, Paris, 1947).

[8] A. Kastler and A. Rousset, J. phys. radium **2**, 49 (1941).

[9] G. M. Barrow and A. L. McClellan, J. Am. Chem. Soc. **73**, 573 (1951).

[10] D. W. J. Cruickshank, Acta Cryst. **9**, 1005 (1956).

[11] I. Ichishima, J. Chem. Soc. Japan (Pure Chem. Sec.) **71**, 607 (1950).

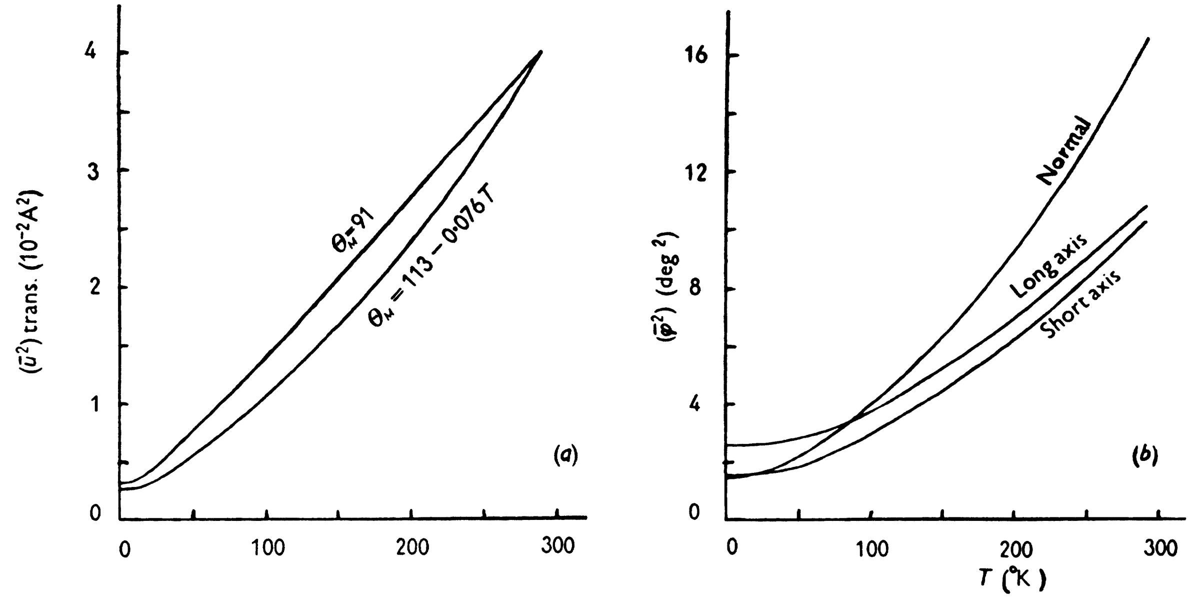

FIG. 1. (a) $(\bar{u}^2)_{\text{trans}}$ for naphthalene. Upper curve with $\Theta_M=91$°K, lower curve with $\Theta_M=113$–$0.076T$. (b) $(\bar{\phi}^2)$ for naphthalene.

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

If for simplicity we assume that Ichishima's formulae hold down to 0°K, we can use (1) to determine the variation with temperature of the $(\bar{\phi}^2)_I$ for naphthalene with allowance for the change in the lattice frequencies. The results are shown in Fig. 1(b).

No direct evidence is available as to the variation of the translational lattice frequencies of naphthalene with temperature, so it is simplest to assume that they also vary linearly with temperature. If Ichishima's rotational frequencies are written in the form $\nu=\nu_0(1-\alpha T)$, the mean value of $a=0.00067$. Assuming the same value of a, Θ_M must be taken as

$$\Theta_M=113-0.076T \text{ °K}$$

to give the x-ray value of $\Theta_M=91°$ at 293°K. The corresponding variation of $(\bar{u}^2)_{\text{trans}}$ with temperature is shown in Fig. 1(a), as is also the variation if Θ_M is assumed constant and equal to 91°.

At absolute zero, the rms amplitude of translational vibration of naphthalene is estimated to be 0.055 A (using the variable Θ_M) and the rms angular vibrations are estimated to be 1.6°, 1.2°, and 1.2°.

Comparisons of experimental and theoretical thermodynamic functions of crystals are usually carried out in terms of specific heats, but, as Guggenheim[12] has stressed, the entropy is really more suitable for such comparisons. It is the only simple thermodynamic function for which there is both a closed formula and an experimental value available from a single set of calorimetric measurements performed at constant pressure, whereas the comparison of specific heats involves the difference between C_p and C_v, which must be estimated from additional experiments.

The lattice frequencies already mentioned may be used to calculate the contributions to the entropy of naphthalene.[13] Column (2) of Table I shows the translational entropy calculated by a Debye entropy function using

$$\Theta_D=113-0.076T,$$

and column (3) shows the rotational entropy calculated from Ichishima's frequencies. Column (4) shows the entropy contributions of the internal molecular vibrations, using the frequencies given in the recent vibrational assignment by McClellan and Pimentel.[14] Column (5) gives the total calculated entropy.

TABLE I. Contributions to the entropy of naphthalene.

(1) T°K	(2) $S_{\text{trans.}}$	(3) $S_{\text{rot.}}$	(4) $S_{\text{int.}}$	(5) S_{total}
298.2	15.09	12.10	13.83	41.02
200	12.23	9.38	6.22	27.83
100	7.82	5.04	1.43	14.29
70	5.70	3.22	0.51	9.43
50	3.96	1.86	0.14	5.96
30	1.80	0.56	0.01	2.37
20	0.76	0.07	0.00	0.83
15	0.35	0.03	0.00	0.38

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[12] E. A. Guggenheim, *Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1949).

[13] D. W. J. Cruickshank, Acta Cryst. **9**, 1010 (1956).

[14] A. L. McClellan and G. C. Pimentel, J. Chem. Phys. **23**, 245 (1955).

Table II. Experimental and calculated entropies of naphthalene.

(1) T°K	(2) S_{calc}	(3) ΔS	(4) $S_{\text{expt.}}$	(5) ΔS	(6) S_{calc} (adjusted)
298.2	41.02	−1.05	39.97	−1.02	40.99
200	27.83	−0.62	27.21	−0.75	27.96
100	14.29	−0.24	14.05	−0.52	14.57
70	9.43	+0.05	9.48	−0.32	9.80
50	5.96	+0.13	6.09	−0.16	6.25
30	2.37	+0.18	2.55	−0.06	2.61
20	0.83	+0.16	0.99	+0.03	0.96
15	0.38	+0.05	0.43	−0.02	0.45

Southard and Brickwedde[15] have measured the specific heat C_p of naphthalene between 15.14°K and 294.68°K. The experimental entropy obtained from their results by integrating C_p/T as a function of T is shown in column (4) of Table II. The total calculated entropy is shown again in column (2) of Table II, and the differences between the observed and calculated values are given in column (3). The differences are gratifyingly small considering the diverse sources from which the information about the lattice frequencies has been drawn. In detail, the calculated entropy is rather too small at low temperatures and rather too large at higher temperatures. Some adjustment of the discrepancy at low temperatures seems possible, for the temperature dependence of the translational lattice frequencies was only guessed from the known behavior[11] of the rotational lattice frequencies. Θ_D is known from the x-ray results to be 91° at room temperature. If Θ_D is assumed to increase less quickly as T falls, and is taken as

$$\Theta_D = 106 - 0.0512T,$$

a better fit of the experimental entropy between 15° and 30°K can be obtained. The adjusted total calculated entropy is shown in column (6) of Table II, and the new differences in column (5). The calculated entropy now gradually rises above the experimental entropy at temperatures over 50°K.

This slight discrepancy at the higher temperatures may well be due to the many approximations used in calculating the lattice entropy, but it is interesting that it would probably disappear if any revision of the vibrational assignment of the molecule should substantially raise one of the low-frequency vibrations (176, 191, or 285 cm^{-1}).

4. ANTHRACENE

Fewer data are available for anthracene, though these give results very similar to those for naphthalene. The observed rotational Raman frequencies of 120±8, 68±5, and 48±4 cm^{-1} [6] imply angular vibrations of amplitudes 2.6°, 2.1°, and 2.7°, which compare satisfactorily with the x-ray determinations of 3.8±0.7, 2.2±0.2, and 3.1±0.1°. Conversely, the x-ray results imply mean frequencies for the rotational branches of 83, 64, and 42 cm^{-1}. The translational motion of the molecules corresponds to $\Theta_M = 85$°K at room temperature.

5. BENZENE

Benzene crystallizes with 4 molecules in each unit cell. There are accordingly 4 optic branches for the rotational oscillations about each principal axis, so that 12 Raman lines are possible. However, in his extensive single crystal studies Fruhling[6] detected only 6 lines. Their polarization characteristics enabled him to decide whether they arose from vibrations in which all 4 molecules in a cell vibrate in phase (type *SSS*) or from vibrations in which 2 molecules are in phase, and 2 out of phase (types *SAA*, *ASA*, and *AAS*). The lowest frequency he observed was 35 cm^{-1} (type *SSS*). (His assignments of the oscillation axes are unfortunately vitiated by a misreading of Cox's[16] description of the crystal structure.)

As has already been mentioned the x-ray analysis, giving the vibration tensors of the 3 independent carbon atoms, does not permit an unambiguous determination of all the molecular vibrations. The rms amplitude about the hexad axis is 7.9°, which corresponds to an average frequency of 43 cm^{-1} in the appropriate rotational branches. With a plausible estimate of the relative contributions of the angular and translational oscillations to the motions normal to the plane, the vibrations about the two axes in the molecular plane are approximately 3.8° and 6.2° (78 and 128 cm^{-1}) and the rms amplitude of translational vibration is 0.23 A ($\Theta_M = 96$°). Unambiguous values for these latter vibrations will be obtainable when a neutron diffraction investigation gives the hydrogen vibration tensors.

A full discussion of the differing assignments of the Raman frequencies made by various investigators in recent years would be out of place here. A few points may however be made. The mode of packing of the molecules in the crystal, described by Professor E. G. Cox, makes it very likely that of the 4 branches involving oscillations of the molecules about their hexad axes, 2 will correspond to rather low frequencies (the in-phase gear wheel motions) and 2 to considerably higher frequencies (the out-of-phase motions). The x-ray average frequency of 43 cm^{-1} nicely allows the assignment of the Fruhling's 35 cm^{-1} *SSS* line to the fully in-phase motion, (and would require an unobserved *SAA* frequency ~35 cm^{-1}) and suggests out-of-phase motions (*ASA* and *AAS*) with frequencies 60–100 cm^{-1}.

These considerations make it difficult to accept the recent suggestion of Hexter and Dows[17] of a libration frequency of 16 cm^{-1}, which would imply (if there are

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[15] J. C. Southard and F. G. Brickwedde, J. Am. Chem. Soc. **55**, 4378 (1933).

[16] E. G. Cox, Proc. Roy. Soc. (London) **A135**, 491 (1932).

[17] R. M. Hexter and D. A. Dows, J. Chem. Phys. **25**, 504 (1956).

2 branches of about this frequency) an rms amplitude of vibration of about 15°. In the opposite sense, Ichishima and Mizushima's[18] assignment of the relatively high frequency,

$$\nu_4 = 141 - 0.128T \text{ cm}^{-1},$$

to the hexad axis would give far too small an angular vibration (if this were the only frequency for that axis).

Despite their uncertainties, the frequencies mentioned above derived from the x-ray results give calculated entropies which fit the observed entropies over the range 4–270°K about as well as the corresponding results for naphthalene.* The introduction of an optic branch with $\nu = 16$ cm^{-1} would not give a good fit with the observed entropy.

6. CONCLUSION

Despite the various approximations and simplifications, the agreement between the results derived from the x-ray, calorimetric, and Raman data is reasonably good and is an encouragement to further studies of this kind on molecular crystals. The three experimental techniques are complementary. The Raman data yield definite values of the lattice frequencies at $\mathbf{k} = 0$ for some or all of the optic branches, though the motions responsible may be only partially identifiable. The x-ray data give average frequencies for identifiable sets of branches, but not in general for individual branches. These average frequencies may help to identify the branches responsible for the Raman lines. The calorimetric data at very low temperatures yield the Debye parameter for the acoustic branches, and at higher temperatures indicate possible sets of frequencies for the optic branches, but without any identification of the motions responsible.

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[18] I. Ichishima and S. Mizushima, J. Chem. Phys. **18**, 1686 (1950).

* The variations of the rotational frequencies with T were taken as $\nu_0(1-0.0011T)$, and the Debye parameter as $\Theta_D = 117 - 0.076T$.