Temperature Dependence of Thermal Motion in Crystalline Naphthalene

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Abstract

Single-crystal data for naphthalene have been measured at five temperatures between 90 and 240 K. Positional and thermal parameters for C and H atoms at each temperature were refined by conventional least-squares techniques. The effect of varying the weighting scheme was examined. Contributions of internal molecular modes to the motions of the atoms turn out to be important. They were estimated for the C atoms at each temperature from a standard force field and subtracted from the experimental U_{ij} values. The corrected U_{ij}'s were then analysed to determine rigid-body translational and librational tensors for the naphthalene molecule. The absolute magnitudes and temperature dependence of these quantities have been compared with values calculated from atom–atom potentials and from spectroscopic data.

Introduction

Twenty-five years have passed since Cruickshank (1956c) presented a model for predicting the temperature dependence of translational and librational motion in molecular crystals, a model requiring only knowledge of librational frequencies or of atomic vibrational amplitudes at a single temperature. Cruickshank made specific predictions for benzene, naphthalene, and anthracene, but these seem to have never been tested experimentally so far. This is surprising because it would seem desirable to check the validity of such an appealingly simple theory, at least for crystals uncomplicated by disorder or pronounced anharmonicity. The only structure for which this appears to have been done is hexamethylenetetramine, a cubic crystal with one molecule per lattice point (Becka & Cruickshank, 1963).

Only two papers on experimental determinations of the vibrational amplitudes in crystalline naphthalene or anthracene by diffraction methods have appeared since Cruickshank's (1956b, 1957) work: for naphthalene, an X-ray study by Ponomarev, Filipenko & Atovmyan (1976, hereafter PFA), based on diffractometer measurements at 123 K, and, for anthracene, an X-ray

analysis by Mason (1964), based on visual intensity measurements collected at 95 and 290 K. In addition, there is a neutron-diffraction analysis by Pawley & Yeats (1969) of perdeuteronaphthalene at 295 K. Thus we know of no attempt to make a systematic study of the temperature dependence of the experimental vibrational parameters in crystalline naphthalene or anthracene. In fact, a search of the Cambridge Crystallographic Database shows that there have been very few such studies for molecular crystals in general.

Although studies of temperature dependence are rare, vibrational parameters (or thermal or temperature-factor parameters, as they are variously called) have been determined at a single temperature, mostly ambient, for many thousands of molecular crystal structures, and molecular diagrams showing atomic vibrational ellipsoids (Johnson, 1965) are commonplace. Opinion may differ concerning the physical significance of these parameters, which are undoubtedly sensitive to many kinds of error. At one extreme, they can be interpreted as quantitative measures of atomic vibration. At the other, they can be regarded merely as convenient parameters introduced in order to improve the least-squares agreement, but not endowed with much physical significance. The Commission on Journals of the IUCr seems more inclined to the latter view, judging from its edict of 1977 (see *Acta Cryst.* A**33**, 347) whereby anisotropic thermal parameters from routine crystal structure analyses are consigned to the depositories of the British Library Lending Division, a fate that, for all practical purposes, must be close to oblivion.† If the more optimistic of these two views is

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correct, then the temperature dependence of the vibrational parameters should also have physical significance.

Temperature-dependent rigid-body translational and librational tensors can also be calculated using the atom–atom-pair-potential approximation. Simple calculations may be based on the Einstein model in which neighboring molecules remain static (*e.g.* Shmueli & Kroon, 1974); more complicated ones include a summation over the Brillouin zone (Pawley, 1967). Confidence in these lattice-dynamical calculations has grown to the point that several authors (Filippini, Gramaccioli, Simonetta & Suffritti, 1973; Vovelle, Chedin & Dumas, 1978, hereafter VCD) have expressed the opinion that vibrational parameters can be calculated more accurately than they can be measured. They tested this proposition for several rigid hydrocarbons, notably naphthalene and anthracene, but the uncertainties in the experimental values and the absence of temperature-dependent measurements made it difficult to draw conclusions.

In this paper we describe new results on the temperature dependence of the vibrational parameters in crystalline naphthalene and compare them with results obtained from various models. The X-ray diffraction data are of a quality typical of a modern crystal structure analysis but with no pretensions to extraordinary accuracy. While we would have liked to obtain better data extending further out in reciprocal space, significant improvement would have been excessively time-consuming because of the scattering characteristics of our crystals.

A parallel study of anthracene is under way.

Data collection and refinement

All measurements were made with the same crystal specimen. A large flat plate, grown by slow evaporation of an ethanol solution, was shaped by dissolution in ethanol to give an approximate sphere with a diameter of ~0·35 mm. To prevent sublimation, the crystal was encased in epoxy resin. Polymerization of the adhesive was carried out at *ca* 240 K because at room temperature dissolution of the naphthalene crystal prevented hardening.

Data at five temperatures (92, 109, 143, 184, and 239 K) were measured with an Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å) and an LT-1 low-temperature device. Initially the crystal was cooled to 92 K, and the data sets were then measured in order of increasing temperature. Temperatures were monitored with a chromel–alumel thermocouple positioned in the nitrogen cold stream ahead of the crystal; stability and reproducibility were estimated to be about 1 K at the lower, and about 2 K at the higher temperatures. Previous calibrations with a second
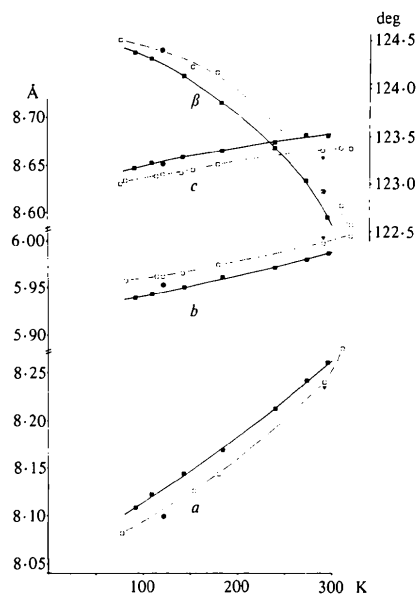

Fig. 1. Temperature dependence of lattice parameters in naphthalene. Our values are indicated by solid squares (■) with edge roughly equal to one standard deviation. Parameters determined by Ryzhenkov & Kozhin (1968) (□); Abrahams, Robertson & White (1949) (▼); and Ponomarev, Filipenko & Atovmyan (1976) (●) are also shown. In this graph and in all subsequent ones the smooth curves drawn are intended merely as guides to the eye and have no additional significance.

Table 1. *Lattice dimensions of naphthalene at seven temperatures*

T (K)	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)
92	8·1080 (53)	5·9397 (16)	8·6472 (46)	124·379 (43)	343·70
109	8·1224 (51)	5·9430 (19)	8·6525 (43)	124·322 (41)	344·94
143	8·1433 (39)	5·9512 (15)	8·6594 (33)	124·128 (31)	347·38
184	8·1686 (30)	5·9617 (12)	8·6654 (27)	123·860 (25)	350·42
239	8·2128 (22)	5·9727 (13)	8·6745 (18)	123·388 (18)	355·28
273	8·2425 (21)	5·9506 (9)	8·6814 (18)	123·042 (17)	356·94
296	8·2606 (66)	5·9872 (20)	8·6816 (77)	122·671 (80)	361·44

thermocouple placed at the crystal site have shown that the temperature difference between the two locations is not more than a degree or two.

For consistency the $P2_1/a$ orientation used by earlier authors (Abrahams, Robertson & White, 1949) was kept. Cell constants were determined at each temperature from the setting angles for nine Friedel pairs, all but one having $\theta > 10°$. By working quickly it was also possible to measure cell constants at two temperatures above 250 K, but after a short time at room temperature the crystal shattered; cell constants at this temperature are based on only four pairs of reflections. Unit-cell dimensions are given in Table 1 and plotted in Fig. 1, together with some other values including the temperature-dependent cell constants obtained by Ryzhenkov & Kozhin (1968) using very high-angle reflections measured on film. The temperature dependence of the two sets of observations is similar but the

Table 2. *Some experimental data and agreement factors*

Temperature (K)	92	109	143	184	239
Number of reflections measured	787	791	796	804	820
Number of reflections observed ($I > 3\sigma_I$)	696	697	694	687	657
R (exp. weights)	0·038	0·040	0·038	0·038	0·035
R_w	0·051	0·051	0·050	0·050	0·043
Coefficient a for modified weights (Å^2)	9	10	12	14	16
R (modified weights)	0·047	0·050	0·051	0·053	0·050
R_w	0·050	0·050	0·045	0·042	0·043

differences between the absolute values are considerably larger than the standard deviations estimated by the CAD-4F system.

Intensities of all reflections in a quadrant of reciprocal space were measured out to $\sin\theta/\lambda = 0.65 \text{ Å}^{-1}$ (27·5° θ for Mo $K\alpha$) with an ω scan of 1·5° and variable counting times which depended on the results of a prescan (target signal-to-noise ratio 50:1, maximum counting time 200 s). The total time required for data collection was 14 days. The data were processed in the usual way. No absorption correction was made since absorption errors for this crystal are negligible ($\mu = 0.63 \text{ cm}^{-1}$). Least-squares refinements with weights derived from counting statistics and omitting reflections with $I < 3\sigma(I)$ started from Cruickshank's (1957) room-temperature parameters. All crystallographic calculations were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and various local programs. Conventional agreement factors for these refinements (anisotropic C, isotropic H, 62 parameters total) are given in Table 2 along with the total numbers of reflections measured and observed. Extinction errors were found to be unimportant and were neglected in subsequent calculations.

Weighting system

Parameters determined by least-squares analysis depend on the weights assigned to the observations; vibrational parameters are particularly sensitive. In the absence of extensive high-order data, it may be advantageous to multiply the experimental weights, derived from counting statistics, by a function which increases with $\sin\theta/\lambda$ (Dunitz & Seiler, 1973). In order to choose the modifying function in a consistent way across the five data sets, it was necessary to develop a criterion for evaluating its performance.

The criterion we adopted is based on an extension (Rosenfield, Trueblood & Dunitz, 1978) of Hirshfeld's (1976) rigid-bond postulate. If a molecule is assumed to be rigid, then for each atom-pair the mean-square amplitudes of the two atoms along the interatomic vector must be equal. To the extent that this equality

does not hold, it may be inferred that the experimental vibrational tensors are contaminated by systematic or random errors. We therefore choose as optimal that weighting system which minimizes $\langle \Delta^2_{A,B} \rangle^{1/2} = \langle (z^2_{A,B} - z^2_{B,A})^2 \rangle^{1/2}$, where $z^2_{A,B}$ is the mean-square amplitude of atom A in the direction of atom B. In fact, as will be discussed below, the carbon skeleton of the naphthalene molecule is not rigid, but the contributions to the $\Delta_{A,B}$'s from the internal vibrations are small relative to the other errors and do not seriously affect the validity of the test.

Modified weighting functions, $w' = w_{\text{exp}}f(s)$, $s = \sin\theta/\lambda$, were examined in detail for the 92 K data. Three functional forms were tried: (1) $f(s) = 1$ for $s \geq a$, $f(s) = 0$ for $s < a$; (2) $f(s) = \exp(as^2)$; and (3) $f(s) = \exp(as^2)/[b + \exp(as^2)]$. The second (Dunitz & Seiler, 1973) gave better results than the other two and was used for all further refinements. The dependence of the rigid-body-test quantity $\langle \Delta^2_{A,B} \rangle^{1/2}$ on the coefficient a was also investigated for the third and fifth data sets. The optimal value of a increases with temperature (see Fig. 2). Coefficients for the second and fourth data sets were chosen by interpolation. In all cases $\langle \Delta^2_{A,B} \rangle^{1/2}$ for the optimal weighting scheme is approximately the same as the estimated standard deviation in U^{ij} (see Table 3). Final weighting coefficients a and agreement factors are given in Table 2, and atomic positional and vibrational parameters are given in Table 3.[*]

It is gratifying to note that while the final weighting schemes were chosen with reference to the rigid-body test, they also satisfy other criteria. Difference maps for the 92 K data set after refinement with
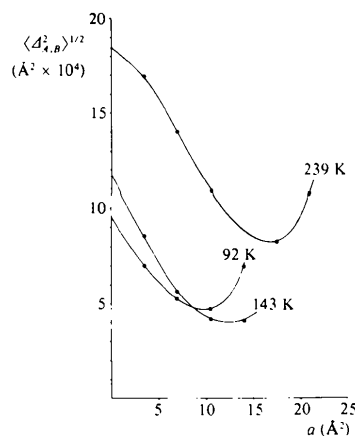
Fig. 2. Comparison of modified weighting schemes. Dependence of the root-mean-square value of $\Delta_{A,B}$ on coefficient a ($w' = w_{\text{exp}}e^{as^2}$) for the first, third and fifth data sets.

Table 3. *Positional and vibrational parameters* ($Å^2$) (*all* $\times 10^4$ *with e.s.d.'s in parentheses*) *for the results of the analyses at five temperatures*

See Fig. 3 for the atom numbering.

	x	y	z	U^{11} or U	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
(a) 92 K									
C(1)	824 (2)	189 (2)	3288 (1)	165 (5)	202 (6)	140 (5)	14 (3)	94 (4)	2 (3)
C(2)	1132 (2)	1638 (2)	2233 (1)	136 (5)	138 (5)	157 (5)	−9 (3)	85 (4)	−25 (3)
C(3)	479 (1)	1055 (1)	371 (1)	100 (5)	110 (5)	144 (5)	6 (3)	79 (4)	3 (3)
C(4)	770 (1)	2521 (2)	−756 (1)	128 (5)	113 (5)	183 (5)	−1 (3)	102 (4)	15 (3)
C(5)	134 (2)	1906 (2)	−2545 (2)	166 (5)	179 (5)	187 (5)	18 (4)	127 (4)	40 (4)
H(1)	1229 (35)	572 (38)	4471 (33)	280 (47)					
H(2)	1798 (29)	3067 (34)	2726 (27)	190 (39)					
H(4)	1412 (30)	3883 (36)	−253 (29)	201 (39)					
H(5)	323 (36)	2916 (41)	−3289 (34)	314 (51)					
(b) 109 K									
C(1)	826 (2)	189 (2)	3286 (1)	186 (5)	230 (6)	158 (5)	15 (4)	105 (4)	2 (4)
C(2)	1134 (2)	1635 (2)	2230 (1)	154 (5)	157 (5)	168 (5)	−10 (3)	92 (4)	−27 (4)
C(3)	479 (1)	1054 (1)	370 (1)	113 (5)	114 (5)	157 (5)	4 (3)	86 (3)	1 (3)
C(4)	769 (1)	2518 (2)	−758 (1)	144 (5)	125 (5)	207 (5)	1 (3)	115 (4)	20 (3)
C(5)	131 (2)	1903 (2)	−2547 (2)	187 (5)	200 (5)	209 (5)	22 (4)	141 (4)	50 (4)
H(1)	1210 (37)	545 (40)	4458 (36)	304 (49)					
H(2)	1795 (30)	3054 (34)	2708 (27)	180 (38)					
H(4)	1411 (31)	3884 (36)	−243 (29)	204 (39)					
H(5)	309 (36)	2912 (42)	−3288 (34)	304 (50)					
(c) 143 K									
C(1)	828 (2)	184 (2)	3280 (1)	243 (5)	290 (6)	193 (5)	19 (4)	129 (4)	3 (3)
C(2)	1137 (1)	1629 (2)	2228 (1)	191 (5)	199 (5)	207 (5)	−18 (3)	107 (4)	−40 (3)
C(3)	481 (1)	1051 (1)	370 (1)	139 (4)	142 (5)	190 (5)	4 (3)	98 (3)	1 (3)
C(4)	766 (1)	2511 (2)	−759 (1)	182 (5)	155 (5)	260 (5)	0 (3)	141 (4)	26 (3)
C(5)	128 (2)	1901 (2)	−2545 (2)	240 (5)	249 (5)	258 (5)	28 (4)	173 (4)	62 (4)
H(1)	1207 (40)	538 (44)	4435 (38)	385 (53)					
H(2)	1783 (31)	3050 (36)	2707 (28)	241 (40)					
H(4)	1400 (30)	3884 (35)	−238 (28)	233 (38)					
H(5)	290 (37)	2894 (43)	−3270 (35)	348 (50)					
(d) 184 K									
C(1)	832 (2)	180 (2)	3273 (2)	321 (5)	393 (6)	249 (5)	26 (4)	166 (4)	1 (4)
C(2)	1139 (2)	1618 (2)	2222 (1)	259 (5)	260 (5)	262 (5)	−23 (4)	135 (4)	−52 (4)
C(3)	481 (1)	1047 (1)	367 (1)	182 (4)	179 (5)	251 (5)	2 (3)	126 (3)	−3 (3)
C(4)	766 (1)	2502 (2)	−759 (1)	245 (5)	205 (5)	334 (5)	0 (3)	178 (4)	34 (4)
C(5)	123 (2)	1893 (2)	−2545 (2)	319 (5)	336 (6)	324 (5)	31 (4)	218 (4)	81 (4)
H(1)	1198 (47)	508 (52)	4404 (45)	495 (62)					
H(2)	1797 (36)	2980 (42)	2712 (33)	344 (46)					
H(4)	1396 (31)	3858 (37)	−268 (30)	283 (39)					
H(5)	280 (46)	2844 (53)	−3281 (43)	491 (63)					
(e) 239 K									
C(1)	838 (2)	176 (3)	3263 (2)	471 (7)	551 (8)	355 (5)	37 (5)	237 (5)	−2 (5)
C(2)	1146 (2)	1607 (2)	2216 (2)	372 (6)	372 (6)	382 (6)	−32 (4)	192 (4)	−73 (4)
C(3)	482 (1)	1039 (2)	364 (1)	254 (5)	251 (5)	360 (5)	2 (3)	176 (4)	−10 (4)
C(4)	762 (2)	2489 (2)	−767 (2)	354 (6)	287 (5)	490 (7)	−7 (4)	257 (5)	39 (4)
C(5)	116 (2)	1884 (3)	−2543 (2)	468 (6)	472 (7)	474 (6)	44 (5)	316 (5)	122 (5)
H(1)	1251 (51)	498 (60)	4440 (50)	630 (72)					
H(2)	1778 (36)	3014 (43)	2671 (33)	411 (47)					
H(4)	1381 (37)	3856 (45)	−289 (35)	443 (50)					
H(5)	217 (52)	2809 (61)	−3334 (50)	642 (76)					

experimental ($a = 0$) and exponentially modified ($a = 9\ Å^2$) weights are shown in Fig. 3; the bonding-density peaks are much more convincing in the latter. The isotropic U values of the H atoms (Table 3) are relatively insensitive to the weights and seem reason- able with respect both to absolute magnitude and to agreement between chemically equivalent pairs. The C—H bond lengths obtained with the final weights (Table 4) are consistent among themselves, but are uniformly shorter by several standard deviations than

Table 4. *Bond distances* (Å) *for the naphthalene molecule at five temperatures*

Values in parentheses are corrected for librational motion. E.s.d.'s are about 0·002 Å for C—C and 0·03 Å for C—H.

|	92 K	109 K	143 K	184 K	239 K
C(1)—C(2)	1·376 (1·377)	1·376 (1·378)	1·374 (1·377)	1·372 (1·375)	1·368 (1·373)
C(4)—C(5)	1·376 (1·378)	1·377 (1·379)	1·376 (1·378)	1·377 (1·381)	1·374 (1·380)
C(2)—C(3)	1·425 (1·426)	1·424 (1·426)	1·425 (1·428)	1·423 (1·428)	1·425 (1·431)
C(3) C(4)	1·422 (1·424)	1·422 (1·424)	1·421 (1·423)	1·418 (1·421)	1·419 (1·424)
C(1)—C(5)'	1·415 (1·417)	1·414 (1·416)	1·412 (1·415)	1·409 (1·413)	1·407 (1·413)
C(3)—C(3)'	1·422 (1·424)	1·423 (1·425)	1·423 (1·426)	1·423 (1·427)	1·420 (1·426)
C(1)—H(1)	0·91	0·90	0·89	0·87	0·90
C(5)—H(5)	0·95	0·95	0·92	0·91	0·92
C(2)—H(2)	0·97	0·96	0·96	0·94	0·95
C(4)—H(4)	0·93	0·93	0·94	0·92	0·93

(a)

(b)
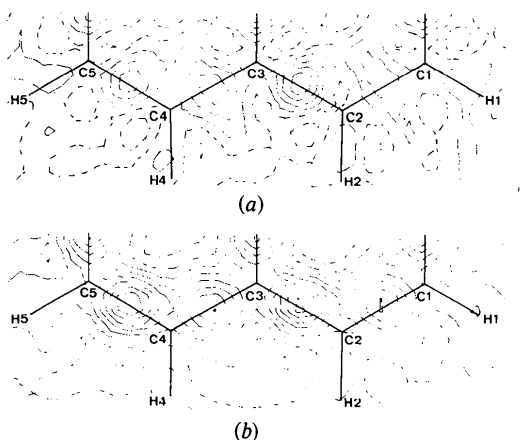
Fig. 3. Difference electron-density maps for naphthalene at 92 K: (a) refinement with experimental weights; (b) refinement with w' = $w_{exp} e^{as^2}$, a = 9·0 Å^2. The contour interval is 0·075 e Å^{-3}, and regions of negative density are indicated by broken lines.
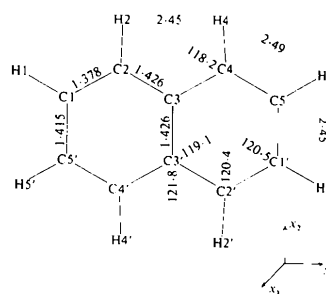

Fig. 4. Diagram of a naphthalene molecule showing atom numbering, inertial axes, and some distances and angles averaged over assumed D_{2h} molecular symmetry and over the five determinations. Standard deviations for the means are about 0·002 Å for C—C, 0·04 Å for H···H, 0·2° for C—C—C, and 0·6° for C—C—H.

those determined with experimental weights. Conversely, the C—C bond lengths increase by about 2σ on going from experimental to final weights. The distributions of $\langle w(\Delta F)^2 \rangle$ with sin θ/λ are not markedly affected by the changes in weights. For the 239 K data set, which is most strongly affected, $\langle w(\Delta F)^2 \rangle$ over five equally populated ranges of sin θ/λ varies by a factor of 2 when a = 0, and a factor of 3·5 when a = 16 Å^2.

1976), although the C—C bond lengths determined in this study are marginally longer. Also shown in Fig. 4 are the intramolecular H···H contacts calculated after lengthening the C—H vectors to 1·08 Å. The essential equality of these three distances indicates that the H···H repulsions around the ring are balanced at the expense of small deformations in the H—C—C angles. Note that the *peri* H atoms are bowed slightly inward.

The arrangement of the molecules in the unit cell is shown in Fig. 5.

Molecular geometry

With increasing temperature the apparent bond lengths (Table 4) get shorter, especially those more distant from the molecular center. When corrections are made for the effects of rigid-body librational motions, this trend disappears. Corrected bond lengths and angles are practically the same at all five temperatures. Values averaged over the chemically equivalent atoms and over the five determinations are shown in Fig. 4; they agree well with those published previously (Cruickshank, 1957; Pawley & Yeats, 1969; PFA,
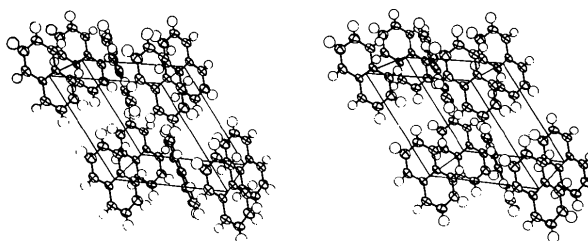

Fig. 5. Stereoscopic view of the unit cell of naphthalene at 239 K. The a axis is approximately horizontal, and the b axis points into the plane of the paper. The ellipsoids are drawn at the 50% probability level (Johnson, 1965).

Thermal-motion analysis

The tensors describing rigid-body motion for the naphthalene molecule were obtained by the usual procedure (Cruickshank, 1956a); that is, the 30 independent components U_n^{ij} of the five independent atomic vibrational tensors U_n were determined by least-squares analysis and were then themselves used as the observations in a second least-squares procedure to determine the 12 components of the molecular translational (T) and librational (L) tensors (S vanishes because of the crystallographic site symmetry). All analyses of the U_n^{ij} values were carried out with Trueblood's (1978) program THMB.

Before considering the temperature dependence of the derived tensors T and L it is useful to examine the behavior of the observed U_n^{ij} values. The variation with temperature of $\frac{1}{3}\mathrm{Tr}(U_n)$, which is coordinate-system independent as long as it is referred to orthonormal axes, for the five C atoms (Fig. 6) is smooth but decidedly nonlinear. While the curves for chemically equivalent atoms lie close together, they are not superimposed, an indication that the principal axes of L do not coincide with the molecular inertial axes. All the second derivatives are positive throughout.

The two most useful coordinate systems for presenting the results of the thermal-motion analysis are a Cartesian crystal system c [in our case $x_1(c)$ ‖ a; $x_2(c)$ ‖ b], and the inertial system i [$x_1(i)$, long molecular axis; $x_3(i)\perp$ molecular plane; see Fig. 4]; within each of these systems the tensors may be specified either by

Fig. 7. Principal components of T and L at five temperatures in the Cartesian crystal coordinate system (x_1 ‖ a, x_2 ‖ b). The lengths of the error bars correspond to one estimated standard deviation.

components or by eigenvalues and eigenvectors. Standard deviations, however, are available only for the components. None of these four ways of representing the tensors provides a consistent basis for comparison across the five determinations since the coordinate systems themselves vary with temperature, but, in practice, the variations are small.

The $T^{ii}(c)$ and $L^{ii}(c)$ values are plotted against temperature in Fig. 7. The three curves for the translations have similar slopes and curvatures, and so do the three curves for the librations. Relative to the total variation with temperature, the uncertainties in $L^{ii}(c)$ are larger than those in $T^{ii}(c)$. The greatest uncertainties are associated with the $L^{33}(c)$ values because $x_3(c)$ points nearly along $x_1(i)$, the inertial axis associated with the smallest moment of inertia. The magnitudes of $T^{ii}(c)$ and $L^{ii}(c)$ are sensitive to the weighting scheme, the shapes of the curves are not. An increase in the weights of the high-order reflections generally leads to a decrease in the translational and librational components of up to about 3–4 e.s.d.'s for the T^{ii} and at most one e.s.d. for the L^{ii} values.

The eigenvalues and eigenvectors of T and L expressed in the inertial coordinate system are given in Table 5. Measures of goodness of fit for the rigid-body model are also given. The eigenvectors are reasonably independent of temperature and do not coincide with the inertial axes. Note that $T^{11}(i) > T^{22}(i) > T^{33}(i)$ and that the smallest diagonal component of L is $L^{22}(i)$.

Corrections for internal motion

Rigid-body analyses of atomic vibrational tensors usually ignore the effect of internal vibration. If the agreement is good and the rigid-body criterion satisfied (e.g. Rosenfield, Trueblood & Dunitz, 1978), as is certainly the case for our analysis, the T and L tensors obtained are considered to represent external, rigid-body motion of the molecule. However, calculations by
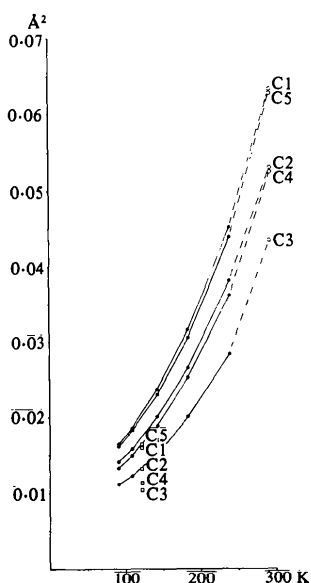

Fig. 6. Temperature dependence of $\frac{1}{3}\mathrm{Tr}(U)$ for the five carbon atoms. The sizes of the solid circles roughly correspond to the estimated standard deviations. Values determined by Cruickshank (1957) (O) and by Ponomarev, Filipenko & Atovmyan (1976) (□) are also shown.
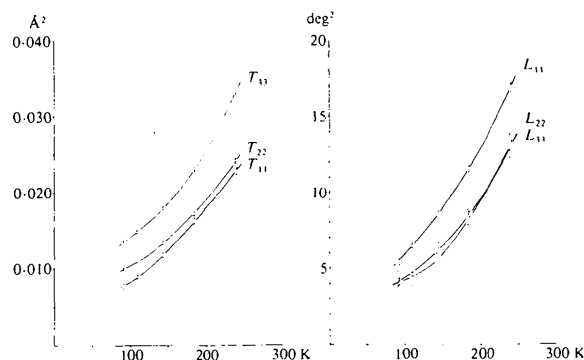
Table 5. *Eigenvalues and eigenvectors of* T ($\text{Å}^2 \times 10^4$) *and* L (deg^2) *with respect to the inertial axes defined in Fig. 4*

	92 K	109 K	143 K	184 K	239 K
(a) Before correction for internal motion					
T_1	137 0·89, −0·38, −0·25	150 0·89, −0·39, −0·24	183 0·93, −0·34, −0·15	235 0·95, −0·29, −0·13	340 0·96, −0·25, −0·12
T_2	103 0·32, 0·92, −0·24	110 0·33, 0·91, −0·26	136 0·30, 0·92, −0·24	177 0·29, 0·96, −0·04	246 0·25, 0·97, −0·04
T_3	76 0·32, 0·13, 0·94	89 0·32, 0·15, 0·94	114 0·22, 0·18, 0·96	155 0·14, 0·00, 0·99	215 0·12, 0·01, 0·99
L_1	5·4 −0·57, −0·20, −0·80	6·5 −0·36, −0·13, −0·92	8·7 −0·53, −0·17, −0·83	11·5 0·45, 0·23, 0·86	17·2 0·65, 0·23, 0·73
L_2	5·0 −0·72, −0·34, 0·60	5·4 −0·79, −0·48, 0·38	7·4 −0·68, −0·50, 0·53	10·2 −0·77, −0·38, 0·51	15·4 −0·65, −0·34, 0·68
L_3	3·3 −0·39, 0·92, 0·05	3·5 −0·49, 0·87, 0·07	4·6 −0·51, 0·85, 0·15	6·6 −0·45, 0·90, −0·01	10·4 −0·40, 0·91, 0·07
$\langle \Delta U^2 \rangle^{1/2}$ (Å^2)	4×10^{-4}	3×10^{-4}	3×10^{-4}	4×10^{-4}	5×10^{-4}
$\langle \Delta^2_{A,B} \rangle^{1/2}$ (Å^2)	5×10^{-4}	4×10^{-4}	4×10^{-4}	5×10^{-4}	8×10^{-4}
(b) After correction for internal motion					
T_1	122 0·90, −0·39, −0·18	135 0·90, −0·41, −0·17	169 0·93, −0·35, −0·11	220 0·95, −0·29, −0·09	326 0·96, −0·26, −0·09
T_2	89 0·37, 0·92, −0·15	96 0·39, 0·91, −0·13	122 0·33, 0·94, −0·12	163 0·28, 0·96, −0·03	231 0·25, 0·97, −0·03
T_3	40 0·22, 0·07, 0·97	52 0·21, 0·05, 0·98	74 0·14, 0·08, 0·99	105 0·10, 0·07, 1·00	156 0·09, 0·00, 1·00
L_1	7·0 0·96, 0·24, 0·13	7·6 0·91, 0·27, 0·31	10·0 0·89, 0·28, 0·36	13·7 0·94, 0·27, 0·21	19·0 0·95, 0·26, 0·17
L_2	5·3 0·10, 0·11, −0·99	6·2 0·29, 0·13, −0·95	8·1 0·29, 0·26, −0·92	11·3 0·21, 0·04, −0·98	16·4 0·15, 0·09, −0·98
L_3	3·8 −0·25, 0·96, 0·08	4·1 −0·30, 0·95, 0·04	5·3 −0·35, 0·93, 0·15	7·6 −0·27, 0·96, −0·02	11·6 −0·27, 0·96, 0·04
$\langle \Delta U^2 \rangle^{1/2}$ (Å^2)	4×10^{-4}	3×10^{-4}	3×10^{-4}	4×10^{-4}	5×10^{-4}
$\langle \Delta^2_{A,B} \rangle^{1/2}$ (Å^2)	5×10^{-4}	4×10^{-4}	4×10^{-4}	5×10^{-4}	10×10^{-4}

Cyvin, Cyvin, Hagen, Cruickshank & Pawley (1972) show that the internal motion of the naphthalene molecule is by no means negligible. In fact, interpolation of their results at 0 and 298 K suggests that mean-square amplitudes associated with internal motion might account for up to 40% of the atomic $U_n^{ij}(i)$ values at around 100 K. We therefore decided to examine the effect of internal-motion corrections on the T and L tensors.

Although the correction terms $U_n^{ij}(i)_{\text{int}}$ at 0 and 298 K were available in the literature, we needed values at intermediate temperatures. These were estimated by using the normal-coordinate analysis program *ASYM20* (Hedberg, Iijima & Hedberg, 1979) and a standard force field (Neto, Scrocco & Califano, 1966; Evans & Scully, 1964) to reproduce the 48 observed frequencies and hence to obtain the associated eigenvectors in the inertial coordinate system. The mean-square amplitudes of the C atoms $[U_n^{ij}(i)_{\text{int}}]$ were then calculated at the five temperatures as outlined by Cyvin (1968). The resulting values at 92 and 239 K are shown in Fig. 8. Results for 0 and 298 K were in substantial agreement with those of Cyvin *et al.* (1972), the minor discrepancies being attributable to the differences between the force fields used.

Fig. 8 shows that the in-plane $U_n^{ii}(i)_{\text{int}}$ values are smaller than the out-of-plane components and also increase more slowly with temperature. Since the $\langle \Delta^2_{A,B} \rangle^{1/2}$ test for naphthalene contains no contri-

butions from out-of-plane vibrations, it is insensitive to the presence of important internal motion. The contributions to this test from the in-plane mean-square amplitudes shown in Fig. 8 are 1·6 and 1·8 × 10^{-4} Å^2 at 92 and 239 K, respectively (compare with values shown in Fig. 2).

Thermal-motion analysis corrected for internal motion

The tensors T and L were redetermined after subtraction of the calculated values of $U_n^{ij}(i)_{\text{int}}$ at each temperature from the corresponding $U_n^{ij}(i)$ (crystallographic vibrational parameters referred to the inertial coordinate system). Results are given in Tables 5 and 6 and Fig. 9. The effects of the corrections, even for a molecule as rigid as naphthalene, are profound. The T tensor, which describes that motion shared equally by all the atoms, shrinks. The largest change, nearly 50% at the lowest temperature, is in $T^{33}(i)$, *i.e.* in the direction perpendicular to the molecular plane. Conversely, the L tensor, which measures a more complicated correlation between atomic motions, expands. The largest increase is in $L^{11}(i)$. From casual consideration, one might expect to find the largest increase in $L^{22}(i)$ where the influence of the low-frequency out-of-plane deformations (*e.g.* butterfly mode) might appear to be the greatest, but this is not the case.

Table 6. *Components of* T ($Å^2 \times 10^4$) *and* L (deg^2) *relative to the inertial coordinate system after correction for internal motion*

Effective frequencies (cm^{-1}) calculated from L^{ii} [eq. (1)] and $\frac{1}{3}$ Tr(T) [eq. (2)] are also shown.

|	T			v_M	L			v_{eff}
92 K	114 (2)	−13 (2)	−16 (2)		6·74 (107)	0·74 (22)	0·23 (40)	86 (7)
		94 (3)	−1 (3)	78 (2)		4·05 (31)	−0·06 (23)	69 (3)
			44 (6)				5·34 (23)	50 (1)
109 K	126 (2)	−15 (2)	−15 (2)		7·22 (78)	0·94 (16)	0·42 (29)	90 (5)
		102 (2)	0 (2)	81 (1)		4·42 (23)	0·03 (17)	71 (2)
			55 (4)				6·38 (16)	49 (1)
143 K	162 (2)	−16 (2)	−12 (2)		9·24 (85)	1·36 (17)	0·73 (32)	89 (4)
		128 (2)	−2 (2)	81 (1)		5·89 (25)	−0·19 (19)	70 (1)
			76 (5)				8·29 (18)	49 (1)
184 K	214 (2)	−16 (2)	−10 (3)		13·17 (113)	1·58 (23)	0·47 (42)	83 (4)
		167 (3)	1 (3)	80 (1)		8·10 (33)	0·20 (25)	67 (1)
			106 (6)				11·37 (24)	47 (1)
239 K	318 (3)	−23 (3)	−15 (4)		19·32 (157)	2·12 (32)	0·64 (58)	78 (3)
		237 (4)	2 (4)	75 (1)		12·18 (46)	−0·04 (54)	62 (1)
			158 (9)				16·55 (33)	44 (1)
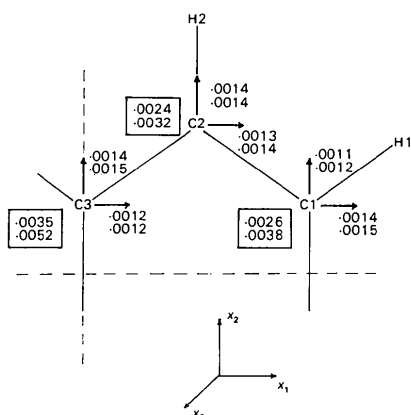
Fig. 8. Mean-square amplitudes U^{ii} ($Å^2$) at 92 and 239 K of internal vibration calculated for the chemically independent C atoms of naphthalene along the inertial axes (U^{33} values are enclosed in boxes). The cross-terms U^{12} are +0·0001, +0·0002, and 0 $Å^2$ for C(1), C(2), and C(3) respectively.

Fig. 9. Principal components of T and L in the inertial coordinate system before (solid lines) and after (broken lines) correction for internal motion. Cruickshank's (1957) uncorrected values (O) and those derived from the data of Ponomarev, Filipenko & Atovmyan (1976) (□) are also shown. Error bars correspond to estimated standard deviations. Note that while $T^{11} > T^{22} > T^{33}$ for all sets, the order of L^{ii} differs.

Another result of the corrections is that the principal axes of L become more nearly parallel to the inertial axes, L_1 along $x_1(i)$, L_2 along $x_3(i)$, and L_3 along $x_2(i)$. However, before correction the two larger eigenvalues differed by less than 10%, so that their eigenvectors were not well determined. The correction also reverses the order of $L^{11}(i)$ and $L^{33}(i)$ so that the largest component of the libration tensor is now associated with the smallest moment of inertia.

Judged by purely statistical criteria, the rigid-body fit does not improve as a result of the corrections. The main reason may be that the rigid-body model can absorb a considerable amount of internal motion into its parameters. Moreover, the rigid-body fit before correction was already so good, given the e.s.d.'s of the vibrational parameters, that no further improvement was to be expected.
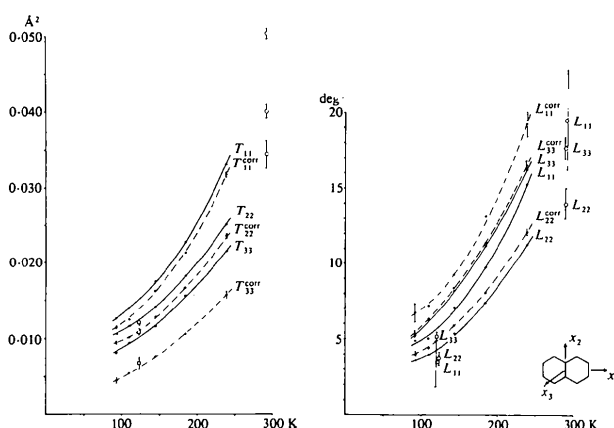
Discussion

Atomic vibrational parameters for naphthalene have been determined previously at 293 K (Cruickshank, 1957) and 123 K (PFA). PFA did not analyze their results in terms of the rigid-body model, but we have done so using Trueblood's (1978) program *THMB*. Whereas the overall fit is not too bad ($\langle\langle \Delta U^2 \rangle\rangle^{1/2} = 8 \times 10^{-4} Å^2$), the rigid-body test gives $\langle \Delta^2_{A,B} \rangle^{1/2} = 21 \times 10^{-4} Å^2$, a value that is twice as large as the upper limit of $10 \times 10^{-4} Å^2$ deemed acceptable by Hirshfeld (1976). The derived T and L tensors referred to the inertial axes are

$$
\mathbf{T} = \begin{pmatrix} 0{\cdot}0121\,(6) & 0{\cdot}0007\,(6) & 0{\cdot}0007\,(7) \\ & 0{\cdot}0108\,(8) & 0{\cdot}0008\,(8) \\ & & 0{\cdot}0067\,(16) \end{pmatrix} \text{Å}^2,
$$

$$
\text{and } \mathbf{L} = \begin{pmatrix} 3{\cdot}47\,(295) & 0{\cdot}67\,(60) & 1{\cdot}44\,(109) \\ & 3{\cdot}77\,(87) & 0{\cdot}18\,(64) \\ & & 5{\cdot}18\,(62) \end{pmatrix} \text{deg}^2.
$$

Compared with our results, their atomic vibrational parameters (Fig. 6) and rigid-body tensors (Fig. 9) seem to be uniformly too small, and we might suspect that they are contaminated by some sort of systematic error. On the other hand, Cruickshank's vibrational parameters lie on reasonable extrapolations of our curves although that may be a matter of good luck more than anything else since neither of the agreement indices obtained with his data for the rigid-body fit ($\langle \Delta U^2 \rangle^{1/2} = 22 \times 10^{-4}$ Å^2, $\langle \Delta^2_{A,B} \rangle^{1/2} = 50 \times 10^{-4}$ Å^2) is satisfactory by current standards. Cruickshank's $T^{ii}(i)$ and $L^{ii}(i)$ components (Fig. 9) are likewise compatible with our values before correction for internal motion, but his e.s.d.'s are about four times larger than ours.

Although the agreement indices for the rigid-body fit are much better for our results than for PFA's, we must also, reluctantly, admit the possibility that instead of PFA's vibrational amplitudes being systematically too low, ours (and Cruickshank's) are systematically too high. One factor that might point in this direction is the relatively low sin θ/λ limit of 0·65 Å^{-1} in our data and in the Cu-radiation data used by Cruickshank. The corresponding limit in PFA's work is not stated but is perhaps larger as they used an enormous (1 × 0·5 × 1·5 mm) crystal for data collection. While it is difficult to assess the cumulative effect of all the possible kinds of systematic errors which might be present, the experience of our laboratory is that vibrational amplitudes based on data extending out to *ca* 0·65–0·70 Å^{-1} may be systematically too large by up to 10–20% compared with those based on more extensive high-angle data of comparable quality. Such an error would raise **T** uniformly by about the same amount, but it would have a much smaller effect on **L**. Thus we need not feel immodest about giving preference at least to our librational tensors.

Cruickshank (1956c) used Raman-active rotational frequencies to calculate librational amplitudes and their temperature dependences. As was pointed out later (*e.g.* Pawley, 1967; VCD, 1978), this procedure is based on two incorrect assumptions, namely: (1) that the principal axes of **L** coincide with the inertial axes; and (2) that the librational frequencies, measured at $\mathbf{k} = 0$, are constant across the Brillouin zone. For naphthalene, the second assumption appears to have the more serious consequences in that it leads to systematic underestimation of the librational am-

plitudes (VCD, 1978). On the other hand, Cruickshank also showed how a vibrational amplitude measured at one temperature can be used to estimate a vibrational amplitude at any other temperature under the assumption that each L^{ii} is associated with a single effective frequency. This latter procedure has the advantage that the effect of any dispersion in the librations is implicitly taken up. In either case, the influence of the anharmonicity attributable to thermal expansion may be allowed for by introducing a temperature dependence of the experimental or effective frequencies. We might therefore ask whether the temperature dependence of the quantities v_i^{eff} determined from our data using the equation (Cruickshank, 1956c)

$$
L^{ii} = \frac{h}{8\pi^2 I_i v_i} \coth\left(\frac{hv_i}{2kT}\right) \tag{1}
$$

is reasonable. Again following Cruickshank, we may calculate an effective Debye temperature θ_M^{eff} (or related frequency $v_M^{\text{eff}} = k\theta_M/hc$) from each translational tensor using the equation

$$
\frac{1}{3}\text{Tr}(\mathbf{T}) = \frac{3h^2 T}{4\pi^2 mk\theta_M^2}\left[\varphi(x) + \frac{x}{4}\right], \tag{2}
$$

where

$$
x = \theta_M/T \quad \text{and} \quad \varphi(x) = \frac{1}{x}\int_0^x \frac{\xi d\xi}{e^\xi - 1}.
$$

In the temperature range covered by our measurements, a linear dependence of $\text{Tr}(\mathbf{T})$ or L^{ii} with temperature would correspond to a constant v_i^{eff}; for real, anharmonic crystals v_i^{eff} is expected to decrease as the temperature is raised.

The plots of the effective frequencies *versus* temperature (see Fig. 10) show that the experimental points, excluding those at 92 K, lie close to smooth curves. For the librations, the v_i^{eff} values turn out to be not too different from the experimental Raman frequencies (Suzuki, Yokoyama & Ito, 1968; see also Cruickshank, 1956c). Also, apart from the 92 K points, the general shapes of the curves are similar to the v_i^{exp} *versus* temperature curves; the slopes agree within a factor of two or three, and the curvatures have the same sign (Bellows & Prasad, 1979). Although the downturns of the v_1^{eff}, v_2^{eff}, and v_M^{eff} curves at 92 K are individually of dubious statistical significance, taken together they suggest that the corresponding translational and librational amplitudes measured at 92 K may be a little too high, perhaps because of the onset of some reorientation process in the crystal. Another possibility is that some of the approximations involved in the calculation become less valid at very low temperatures. (The internal-motion correction is not responsible, for it affects the shapes of these curves only slightly.)
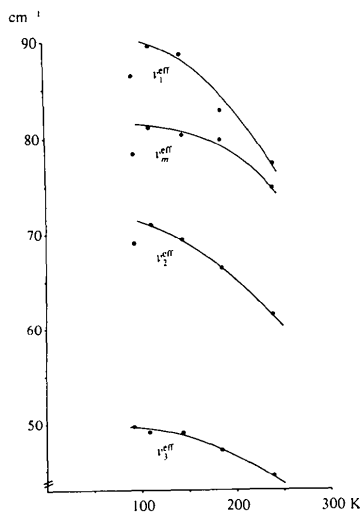
Fig. 10. Variation with temperature of effective frequencies v_i^{eff}, calculated from $L^{ii}(i)$, and v_M^{eff}, calculated from $\frac{1}{3}Tr(T)$, in both cases according to the procedure of Cruickshank (1956c).
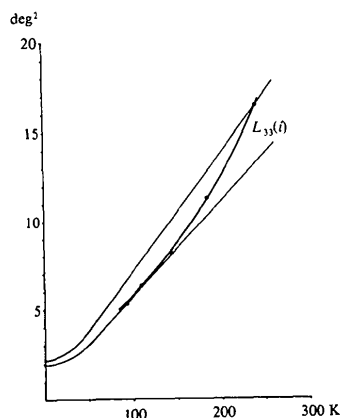

Fig. 12. Principal components of **T** and **L** in the inertial coordinate system as calculated by: Filippini, Gramaccioli & Simonetta (1981) (– – –); Vovelle, Chedin & Dumas (1978) (–·–·– and ⊙); and Pawley (1967) (●). Experimental values corrected for internal motion (bold lines) are shown for comparison. For all sets the relative order of the principal components is the same.

Fig. 11. Experimental values of $L^{33}(i)$ with corresponding curves calculated from $L^{33}(i)$ at 92 and 239 K using equation (1).

So far we have been using the Cruickshank model to test the physical significance of our derived translational and librational amplitudes. Having assured ourselves that these quantities are physically reasonable, we may now turn the argument around and say that the Cruickshank model provides a reasonably good description of the experimental facts. However, it may be used with confidence only if appropriate corrections for the anharmonicity due to thermal expansion can be made. Fig. 11 indicates the magnitude of the error that might ensue if such corrections were neglected.

With the development of lattice-dynamical calculations based on atom–atom potentials, rigid-body **T** and **L** tensors for naphthalene have been calculated by Pawley (1967), VCD (1978), and Filippini, Gramaccioli & Simonetta (1981) (hereafter, FGS), the latest calculation being based on our new atomic positions
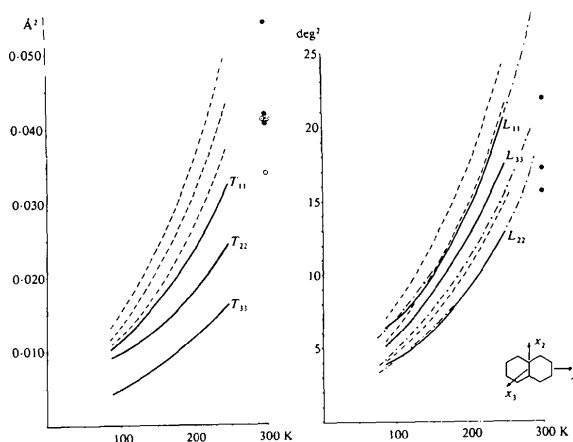
and cell constants. Both VCD and FGS give temperature-dependent values for the $L^{ii}(i)$, and FGS have also provided them for the $T^{ii}(i)$ (see Fig. 12). The differences among the three sets of calculated results are partly due to differences in the potential functions; Pawley used Kitaigorodskii potentials while the other two groups used the somewhat softer Williams potentials [details of FGS's calculations are the same as given in Filippini, Gramaccioli, Simonetta & Suffritti (1973) except that the summation limit was increased from 5·5 to 15 Å, and the potentials were Williams's (1967) set IV]. Unfortunately, VCD do not make it clear which of the two sets of Williams IV potentials (Williams, 1966, 1967) they used.*

As a result of his harder potential functions, Pawley calculates lower $T^{ii}(i)$ and $L^{ii}(i)$ values than do the others. Relative to our experimental values, his $L^{ii}(i)$ are all too low, and his **T** tensor is too isotropic. On the other hand, the values of FGS are uniformly too high. The best fit is for the calculations of VCD. (The agreement noted by VCD between Pawley's results and Cruickshank's **T** and **L** tensors is not to be taken too seriously considering that the experimental values have very large standard deviations. In any case, if the experimental values are corrected for internal motion,

* Professor Simonetta has informed us that very recent calculations by FGS using Williams's (1967) set IV potentials but reducing the summation limit from 15 to 5·5 Å give results essentially identical to those of VCD. It is interesting that the agreement with experiment worsens as the cut-off limit is increased, presumably because in this parametrization the effects of the long-range, electrostatic interactions are not included explicitly but are absorbed into the other parameters. At any rate, the worsened agreement underlines the importance of using parametrized potential functions only under the exact conditions for which the parametrization was made.
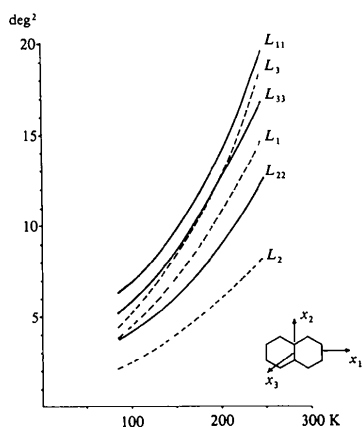
Fig. 13. Rotational amplitudes L^i (– – –) around the principal axes of the inertia tensor calculated according to the procedure of Shmueli & Goldberg (1973) and corresponding to the quantity $\langle \varphi^2 \rangle$ described by Shmueli & Kroon (1974). Experimental $L^{ii}(i)$ values (bold lines) are shown for comparison.

the agreement becomes much worse.) One gets the impression that, on the whole, the agreement between theory and experiment is better for the L's than for the T's.

Lattice-dynamical calculations are complicated because they involve the correlated motions of all the molecules in the crystal. In contrast, calculations based on the Einstein approximation (a single molecule moving within a rigid framework) are conceptually and computationally much simpler. Vibration amplitudes calculated by this method are systematically too small, so one knows at least in which direction they err. We have used the program *PACKRB* (Shmueli & Goldberg, 1973) with Williams IV (1967) potential functions (but with C—H distances of 1·09 Å to match the practice of FGS) to calculate librational amplitudes from the atomic positions and cell dimensions found at each temperature. For simplicity, we assumed that the libration axes coincide with the molecular inertial axes; the quantities calculated (L^i) are thus nearly but not exactly comparable to the experimental quantities $L^{ii}(i)$. All atom–atom interactions were included out to a limit of 8 Å. The results are shown in Fig. 13 together with the experimental values. The agreement is not too good $(L^3 > L^{33}$ at high temperatures; order of L^1 and L^3 reversed), but it is not so very much worse than that obtained with the lattice-dynamical calculations referred to above. Considering the effort involved and the uncertainties in the atom–atom potential functions, calculations based on the simple model should not be disregarded for making rough predictions about librational amplitudes and their temperature dependences.

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