# Lattice-Dynamical Evaluation of Temperature Factors in Non-Rigid Molecular Crystals: A First Application to Aromatic Hydrocarbons

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## Abstract

Evaluation of temperature factors from a harmonic lattice-dynamical theory of molecular crystals has been applied to some aromatic hydrocarbons in the non-rigid case: *i.e.* mixing of lattice vibrations with the lowest-frequency internal modes. The calculations start from known atomic coordinates, unit-cell parameters and symmetry operations, using Califano–Neto potentials for in-plane modes, Williams IVa potentials for inter-molecular interactions, and an overall value of 0·9 nN Å for any twisting around C–C bonds. Molecular motions inside the crystal are described on the basis of normal coordinates of the isolated molecule, by applying Gwinn's method. For some molecules (benzene and naphthalene) the rigid-body approximation is adequate for the carbon-atom framework, and practically no coupling occurs between the lattice vibrations and the internal motion. For anthracene and phenanthrene, there are differences between rigid-body and non-rigid estimates of temperature factors. Molecular vibration tensors **T**, **L**, and **S** can be calculated, and also a general molecular displacement matrix (tensor) including even the internal modes (**W**), which permits extension of the rigid-body analysis to non-rigid molecules.

## Introduction

The problem of calculating temperature factors in a harmonic approximation *via* the Born–von Kármán lattice-dynamical procedure has been the object of many papers. Such calculations, if feasible on a routine basis, would be particularly useful to crystallographers, not only as a theoretical check of experimental results, but as a practical tool to derive some information which is not accessible from Bragg-peak measurements.

For instance, a description of thermal motion in the crystal is essential for correcting bond lengths for thermal libration, especially when the molecules are not rigid (see especially Busing & Levy, 1964; Scheringer, 1972*b*). Even the so-called 'rigid bodies', *i.e.* the molecules which look as such from a least-squares fit of temperature factors, are not necessarily rigid: this applies especially to the motion of the external H atoms (Johnson, 1970*a*; Scheringer, 1972*a*; Gramaccioli, Filippini & Simonetta, 1982).

Another possible application of such calculations concerns determining the electron density in crystals. For instance, deriving significant information on such density within 0·3 Å from the atomic nuclei is often precluded, owing to the inaccuracy of most temperature factors which have been obtained from X-ray diffraction (Stewart, 1968). Moreover, in many cases the decomposition into 'internal' and 'lattice' vibrations can be quite useful for bridging the gap between the static electron density of molecules and the corresponding dynamic one, which is experimentally accessible. This decomposition cannot be deduced from any Bragg measurement (Hirshfeld, 1977).

Since the crystallographic estimates of temperature factors are affected by thermal diffuse scattering (see for instance Rouse & Cooper, 1969; Willis & Pryor, 1975; Helmholdt & Vos, 1977), application of lattice dynamics for correcting Bragg-peak measurements for this effect might be essential for accurate work. A good proof for the reliability of such calculations can be a consistent agreement with all kinds of available experimental data: these are, for instance, Raman- and infrared-active vibration frequencies, and also temperature factors, which implicitly include information throughout the whole Brillouin zone.

For the general case of a non-rigid molecule, the calculations can be very expensive, owing to the considerable size and number of dynamical matrices to be diagonalized. On the other hand, we expect that the molecular deformations which are coupled with lattice vibrations should correspond essentially to the internal modes with the lowest frequencies: these modes are often a minority with respect to the total. For these reasons, an extension of the rigid-body lattice-dynami-

cal procedure involving a few additional internal low-frequency modes might be a comparatively inexpensive and efficient routine.

## Method of calculation

In the harmonic lattice-dynamical theory of crystals the anisotropic temperature-factor coefficients $B_{ij}(\kappa)$ for a certain atom $\kappa$ are obtained from the so-called mean-square displacement matrix $\mathbf{U}(\kappa) = \langle \mathbf{u}(\kappa)[\mathbf{u}(\kappa)]^T \rangle$ through $\mathbf{B}(\kappa) = 2\pi^2 \mathbf{C}^T \mathbf{U}(\kappa) \mathbf{C}$. Here $\mathbf{B}(\kappa)$ is the matrix whose elements are the $B_{ij}(\kappa)$'s and $\mathbf{C}$ is the transformation matrix between the (reciprocal) crystal axes and the reference system (see, for instance, Willis & Pryor, 1975). In Cartesian co-ordinates, we have

$$U(\kappa) = (Nm_\kappa)^{-1} \sum_{\psi \mathbf{q}} E_\psi(\mathbf{q}) \, \omega_\psi(\mathbf{q})^{-2}$$

$$\times \, e(\kappa \mid \psi \mathbf{q}) \, [e^*(\kappa \mid \psi \mathbf{q})]^T, \qquad (1)$$

where $E_\psi(\mathbf{q})$, i.e. the average energy of the $\psi$ mode for a certain value of the wave vector $\mathbf{q}$, is evaluated as

$$E_\psi(\mathbf{q}) = h\omega_\psi(\mathbf{q}) \left(\tfrac{1}{2} + \{\exp [h\omega_\psi(\mathbf{q})/kT - 1]\}^{-1}\right). \quad (2)$$

Here $\omega_\psi(\mathbf{q})$ is the frequency of the mode, $m_\kappa$ is the mass of the atom, and $e(\kappa \mid \psi \mathbf{q})$ is the mass-adjusted polarization vector of the atom vibrating in such a mode. Both frequencies and polarization vectors are obtained from diagonalization of mass-adjusted dynamical matrices $\mathbf{D}(\mathbf{q})$, one for each value of $\mathbf{q}$ as derived from an appropriate Brillouin zone sampling. Elements of the dynamical matrices $\mathbf{D}(\mathbf{q})$ are given by

$$D_{\alpha\alpha'}(\kappa\kappa' \mid \mathbf{q}) = (m_\kappa \, m_{\kappa'})^{-1/2} \sum_{l'} \Phi_{\alpha\alpha'}(\kappa\kappa' \mid l')$$

$$\times \exp i\mathbf{q}\Delta r(\kappa\kappa' \mid l'), \qquad (3)$$

where the $\Phi_{\alpha\alpha'}$'s are the corresponding components of force constants relative to the coordinates $\alpha$ and $\alpha'$, $\Delta r(\kappa\kappa' \mid l')$ is the distance between the origins of asymmetric units. The summation index $l'$ refers to different unit cells [see Willis & Prior, 1975, expressions (3.10)].

For molecular crystals, the most appropriate basis is given by the normal coordinates of the isolated molecule, including the mass-adjusted translational and rotational coordinates (Taddei, Bonadeo, Marzocchi & Califano, 1973; Bonadeo & Taddei, 1973; Neto, Righini, Califano & Walmsley, 1978; Bonadeo & Burgos, 1982). The procedure of the calculations which are performed on such a basis is essentially the same as for the rigid body, which is a well known particular case (see, for instance, Cochran & Pawley, 1964; Pawley, 1967, 1968, 1972a,b; Willis & Pryor, 1975). For calculating normal coordinates, the method proposed by Gwinn (1971) has proven to be the most

practical, as we have already shown (Gramaccioli, Filippini & Simonetta, 1982).

Force constants $\Phi$ can be assumed to be a sum of contributions ($\Phi_{int}$) internal to the molecule and external ($\Phi_{ext}$). Since the $\Phi_{ext}$'s are obtained more easily in a Cartesian reference system (preferably the principal axes of inertia), transformation to normal coordinates is obtained from $\Phi_\chi = \mathbf{V}^T \Phi_x \mathbf{V}$, where the symbols $x$ and $\chi$ indicate the mass-weighted Cartesian, or the normal coordinate system, respectively. Here $\mathbf{V}$ is a matrix whose columns are the eigenvectors $\mathbf{q}_\xi$ of the (mass-adjusted) dynamical matrix $\mathbf{M}$ of the isolated molecule.* Since the intramolecular potential is diagonal in a normal-coordinate basis, and $\omega_\xi^2 \, \mathbf{q}_\xi = \mathbf{M}\mathbf{q}_\xi$, the contributions $\Phi_{int}$ are equal to the squares of the internal frequencies $\omega_\xi$; such contributions involve the 'self-matrices' $\Phi(\kappa\kappa' \, 0)$ only (see Bonadeo & Burgos, 1982).

The major advantage of a normal-coordinate basis derives from the possibility of having a drastic reduction in size of the dynamical matrices: this happens because these matrices, if referred to such a basis, can be easily factorized. In other words, in line with the approximation that only the low-frequency internal modes can interact with the lattice motion, the normal coordinate basis necessary for lattice-dynamical calculations can be restricted only to those normal modes (of the molecule) which correspond to the frequencies which are inferior to a pre-assigned limit $\omega_L$. This reduction in size will correspond to a satisfactory approximation if the calculated values of temperature factors remain stationary on raising $\omega_L$. As is shown in Table 2, such a convergence takes place very early for the molecules which are considered here, and the matrix $\mathbf{V}$ can be accordingly reduced to a mere 'strip' of a few columns; if the number of such columns is six (five for a linear molecule) the calculations become the same as for the rigid body.

The contribution of the highest-frequency modes to the displacement matrices $\mathbf{U}(\kappa)$ are supposed to be constant throughout the whole Brillouin zone, and to remain the same as for the isolated molecule. This contribution is given by the various terms in (4):

$$U(\kappa) = m_\kappa^{-1} \sum_\xi E_\xi \, \omega_\xi^{-2} \, e(\kappa \mid \xi) \, [e^*(\kappa \mid \xi)]^T, \qquad (4)$$

which corresponds to (1). Here the polarization vectors $e(\kappa \mid \xi)$ correspond to blocks of those $\mathbf{q}_\xi$'s which are excluded from the matrix $\mathbf{V}$, and $E_\xi$ is the average energy of an internal mode, which can be obtained from (2).

This approximation is justified also by observing the behaviour of the highest branches of the dispersion

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* Here also the eigenvectors corresponding to zero frequency should be included, and in this way the normal-coordinate basis includes molecular translation and rotation.

curves. A small increase (of a few cm$^{-1}$) is observed to take place for the higher frequencies, on passing from the free molecule to the crystal; however, the effect upon temperature factors is negligible, because of weighting by $\omega_i^{-2}$.

From diagonalization of the dynamical matrices in normal coordinates, the best way to obtain temperature factors does not involve immediate transformation to Cartesian coordinates.

A mean-square displacement matrix (**W**) relative to all the molecule can be obtained as for **U**($\kappa$) in (1):

$$\mathbf{W} = \langle \mathbf{vv}^T \rangle = N^{-1} \sum_{\psi\mathbf{q}} E_\psi(\mathbf{q}) \, \omega_\psi(\mathbf{q})^{-2} \, \mathbf{p}(\psi\mathbf{q}) \, [\mathbf{p}^*(\psi\mathbf{q})]^T,$$

(5)

where $E_\psi(\mathbf{q})$ is given by (2), $\mathbf{p}(\psi\mathbf{q})$ are the eigenvectors of the dynamical matrix $\mathbf{D}(\mathbf{q})$, and **v** indicates the displacement in terms of internal normal translational and rotational (mass-weighted) coordinates. Transformation of **W** to a mean-square displacement matrix $\mathbf{\Omega}$ relative to Cartesian coordinates can be obtained as $\mathbf{\Omega} = \mathbf{Vm}^{-1/2} \, \mathbf{Wm}^{-1/2} \, \mathbf{V}^T$. Here **m** is the so-called 'mass matrix', which is formed by repeating each of the atomic masses three times along the diagonal and by putting all other elements as zero.

The 3 × 3 blocks along the main diagonal of $\mathbf{\Omega}$ are the atomic mean-square displacement matrices **U**($\kappa$), and they are identical with the results which can be obtained from (1). The off-diagonal blocks are identical with the so-called 'coupling tensors' **U**($\kappa\kappa'$) = $\langle \mathbf{u}(\kappa) \, [\mathbf{u}(\kappa')] \rangle^T$ between the displacements of the atoms $\kappa$ and $\kappa'$; these tensors are essential for bond-length correction in the general case (Johnson, 1970$b$; Scheringer, 1972$b$), and cannot be obtained from the usual diffraction data.

When a limited number of internal degrees of freedom is included in the lattice-dynamical calculations, **W** is a relatively small matrix, if compared to $\mathbf{\Omega}$. When the latter is obtained from **W** with a restricted basis, the contributions of the highest internal frequency modes should be added (see for instance Gramaccioli, Filippini & Simonetta, 1982).

It might be interesting to check which are the relationships between **W** and the tensors **T**, **L**, and **S** of Schomaker & Trueblood (1968). For this purpose, **W** can be partitioned as follows:

$$\mathbf{W} = \begin{pmatrix} \mathbf{W}_{ext} & \mathbf{W}_{cor} \\ (\mathbf{W}_{cor})^T & \mathbf{W}_{int} \end{pmatrix},$$

(6)

where $\mathbf{W}_{ext}$, $\mathbf{W}_{int}$ and $\mathbf{W}_{cor}$ refer to external (translational–librational), internal and correlation between external and internal motions, respectively.

By defining $\mathbf{U}^{mol}(\kappa|\psi\mathbf{q})$ and $\mathbf{B}^{mol}(\kappa)$ as a displacement vector and matrix of the *molecule* $\kappa$ [see equation (6.3) of Willis & Pryor (1975)], we have

$$\mathbf{B}^{mol}(\kappa) = \sum_{\psi\mathbf{q}} \mathbf{U}^{mol}(\kappa|\psi\mathbf{q}) \, (\mathbf{U}^{*mol}(\kappa|\psi\mathbf{q}))^T$$

$$= \langle \mathbf{u}^{mol}(\kappa) \, [\mathbf{u}^{mol}(\kappa)]^T \rangle,$$

(7)

where $\mathbf{u}^{mol}(\kappa)$ corresponds to its atomic counterpart $\mathbf{u}(\kappa)$, and $\langle \ldots \rangle$ indicates the time average (see Willis & Pryor). Since $\mathbf{u}^{mol}(\kappa) = \mathbf{D}^{-1/2} \, \mathbf{v}$, we have

$$\mathbf{B}^{mol}(\kappa) = \langle \mathbf{u}^{mol}(\kappa) \, [\mathbf{u}^{mol}(\kappa)]^T \rangle$$

$$= \mathbf{D}^{-1/2} \langle \mathbf{vv}^T \rangle \, \mathbf{D}^{-1/2}$$

$$= \mathbf{D}^{-1/2} \, \mathbf{W}_{ext} \, \mathbf{D}^{-1/2},$$

(8)

where **D** is a matrix which is formed by repeating the molecular mass three times and the principal moments of the inertia of the molecule along the diagonal and by putting all other elements to zero. The above written equations, of course, hold only if $\mathbf{B}^{mol}(\kappa)$, $\mathbf{u}^{mol}(\kappa)$, *etc.* are referred to the principal axes of inertia.

Since [see Willis & Pryor, equation (6.4)]

$$\mathbf{B}^{mol}(\kappa) = \begin{pmatrix} \mathbf{T} & \mathbf{S} \\ (\mathbf{S}^*)^T & \mathbf{L} \end{pmatrix} = \mathbf{D}^{-1/2} \, \mathbf{W}_{ext} \, \mathbf{D}^{-1/2},$$

(9)

the relationships between all these tensors is clear. Whereas for a rigid-body transformation to $\mathbf{B}^{mol}(\kappa)$ according to (8) may be preferable, for the general case, *i.e.* when internal motions are also included, it is difficult to define a matrix corresponding to **D** and involving all degrees of freedom. For this purpose, in this work we are directly referring to **W** in showing the results of our analysis (see Table 5).

## Applications and discussion

As a first application of these calculations, a series of aromatic hydrocarbons such as benzene, naphthalene-$d_8$, anthracene, phenanthrene and pyrene has been considered. These substances are the same which have been treated in a previous work by Gramaccioli, Filippini & Simonetta (1982; here onwards GFS), where the contributions of internal and external modes to the temperature factors were considered separately.

The potentials which have been used here are the same as in GFS: that is, for in-plane vibrations, the force field of Neto, Scrocco & Califano (1966) has been used and, for out-of-plane vibrations, a force constant of 0·9 nN Å† has been assigned to all twistings around C—C bonds, irrespective of the $\pi$-bond order. This treatment of out-of-plane vibrations gives a substantially good agreement with experimental data for all these hydrocarbons (see GFS and Table 1). Such twisting force constants could be further improved, particularly if a better fit to vibrational frequencies as

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† In our last work (GFS) this value was erroneously indicated as 0·9 nN Å$^{-1}$.

they are observed in the crystal is considered. The search for an improved set of out-of-plane potentials will be the argument of another paper centered on this subject (Filippini, Simonetta & Gramaccioli, 1983): here we are only concerned in showing examples of such temperature-factor calculations. On the other hand, no substantial changes involving refinement of the internal potential are expected to occur, since the greatest contributions to temperature factors are given by lattice modes.

For van der Waals interactions we used the Williams IVa functions (Williams, 1967), with a maximum packing distance of $5.5 \text{ Å}$ and a C—H distance standardized to $1.09 \text{ Å}$, just as in GFS: the use of semiempirical potentials of this kind has proved to be particularly valuable for reproducing the experimental dispersion curves for naphthalene (Natkaniec et al., 1980; Pawley et al., 1980), and of anthracene-$d_{10}$ (Dorner et al., 1982).

The normal coordinates corresponding to the internal low-frequency modes which have been taken as a basis for our calculations (together with translational and rotational coordinates) for all these substances are characterized in Table 1(a)*

An example of calculated frequencies at $\mathbf{q} = 0$ for naphthalene-$d_8$ is reported in Table 1, and for anthracene in Table 2(a).* Here the agreement with the experimental data is satisfactory; the splitting and the shifts due to packing in the crystals are of the same order of magnitude as in similar calculations which have been performed with a complete basis of all internal modes (Taddei, Bonadeo, Marzocchi & Califano, 1973; Pawley & Cyvin, 1970). We also clearly see that on introducing additional internal modes the frequencies of the others are perturbed only very slightly.

Examples of temperature factors (B's) relative to these hydrocarbon crystals are reported in Table 2; the complete set of results is reported in Table 3(a).* For a certain atom, the different lines refer to: (1) calculations with a rigid-body model, where the contributions of lattice modes only are considered; (2) calculations with another rigid-body model, where the internal mode contributions are added to the results on the first line, and no mixing is assumed to take place between the lattice modes and the internal modes; (3) (4) (5) an increasing number ($n_L$) of the internal vibration modes is assumed to mix with the lattice modes. These internal modes correspond to all the calculated internal frequencies which are below a threshold $\omega_L$ (which is specified in the last-but-one

Table 1. *Calculated values of vibration frequencies at* $\mathbf{q} = 0$ *in the crystal* $(cm^{-1})$ *for various values of the limiting frequency* $\omega_L$, *and comparison with experimental data. 'Out-of-plane' modes are marked by an asterisk*

Naphthalene-$d_8$ at room temperature.

| | Experimental | Calculated $\omega_L = 0$ (rigid) | $\omega_L = 400$ | $\omega_L = 600$ | $\omega_L = 1000$ |
|---|---|---|---|---|---|
| $a_u$ | | 42 | 39 | 39 | 39 |
| $b_g$ | 43 | 42 | 42 | 42 | 42 |
| $a_g$ | 49 | 49 | 49 | 49 | 49 |
| $b_u$ | 63 | 53 | 52 | 52 | 52 |
| $b_g$ | 70 | 66 | 66 | 66 | 65 |
| $a_g$ | 70 | 78 | 78 | 77 | 76 |
| $a_u$ | 100 | 86 | 86 | 85 | 85 |
| $b_g$ | 107 | 105 | 104 | 104 | 103 |
| $a_g$ | 102 | 106 | 106 | 105 | 104 |
| $B_{3u}*$ | 166 | 174 | 182–190 | 182–190 | 182–190 |
| $A_u*$ | 193 | 191 | 213–213 | 213–213 | 212–213 |
| $B_{2g}*$ | 348 | 338 | 347–351 | 347–351 | 347–351 |
| $B_{2u}$ | 328 | 343 | 346–349 | 346–349 | 346–349 |
| $B_{3u}*$ | 402 | 387 | 394–400 | 394–400 | 394–400 |
| $B_{1g}*$ | 410 | 417 | | 422–425 | 422–425 |
| $A_g$ | 494 | 488 | | 491–491 | 491–491 |
| $B_{3g}$ | 494 | 493 | | 495–497 | 495–497 |
| $B_{2g}*$ | 547 | 504 | | 517–518 | 516–518 |
| $A_u$ | | 506 | | 513–516 | 513–516 |
| $B_{3u}*$ | 628 | 579 | | 584–585 | 584–585 |
| $B_{1u}$ | 590 | 618 | | 623–624 | 621–622 |
| $B_{1g}*$ | 649 | 626 | | | 637–638 |
| $A_u*$ | | 638 | | | 648–649 |
| $A_g$ | 697 | 688 | | | 693–694 |
| $B_{2u}$ | 738 | 748 | | | 751–752 |
| $B_{2g}*$ | 761 | 748 | | | 756–756 |
| $B_{1g}*$ | (760) | 759 | | | 764–764 |
| $B_{3u}*$ | 791 | 800 | | | 805–806 |
| $B_{1u}$ | 828 | 802 | | | 804–805 |
| $A_u*$ | | 814 | | | 820–820 |
| $B_{3g}$ | 831 | 818 | | | 822–824 |
| $A_g$ | 838 | 832 | | | 836–838 |
| $B_{1u}$ | (880) | 836 | | | 838–840 |
| $B_{2u}$ | 879 | 838 | | | 840–844 |
| $B_{1g}*$ | (829) | 846 | | | 851–851 |
| $A_g$ | 862 | 850 | | | 852–853 |

*Note:* The experimental values are taken from Bree & Kydd (1970). Labelling is given for the lattice modes and internal modes according to the symmetry of the crystal, or the isolated molecule, respectively.

column). The last line reports the corresponding experimental data: these have been derived from the literature (benzene: Bacon, Curry & Wilson, 1964; naphthalene-$d_8$: Pawley & Yeats, 1969; anthracene: Lonsdale & Milledge, 1961; Mason, 1964; phenanthrene: Kay, Okaya & Cox, 1971; pyrene: Hazell, Larsen & Lehmann, 1972; anthracene-$d_{10}$: Lehmann & Pawley, 1972; Chaplot, Lehner & Pawley, 1982). Additional calculated temperature factors for the hydrogen atoms in anthracene and naphthalene are reported in Table 4(a).*

* See deposit footnote.

### Table 2. *Calculated temperature factors* ($\times 10^4$)

Temperature factors are in the form

$$T_i = \exp\left|-B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)\right|$$

For each temperature factor, the various lines refer to different models, starting with the rigid body (see text); the last line reports the experimental values, taken from the literature.

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{33}$ | $\omega_L$ (cm$^{-1}$) | $n_L$ |
|---|---|---|---|---|---|---|---|---|
| **Benzene at 138 K** | | | | | | | | |
| C(1) | 153 | 68 | 177 | −1 | −7 | −3 | | |
| | 158 | 70 | 183 | −2 | −7 | −4 | | |
| | 159 | 70 | 184 | −1 | −7 | −2 | 400 | 2 |
| | 83 | 49 | 111 | 3 | −12 | 0 | (observed) | |
| H(1) | 236 | 72 | 274 | 17 | 5 | 2 | | |
| | 280 | 106 | 326 | 10 | 27 | −4 | | |
| | 282 | 105 | 328 | 14 | 28 | 0 | 400 | 2 |
| | 184 | 69 | 204 | 0 | 20 | 6 | (observed) | |
| **Naphthalene-$d_8$ at 298 K** | | | | | | | | |
| C(A) | 346 | 492 | 205 | 35 | 145 | −4 | | |
| | 353 | 501 | 218 | 34 | 149 | −1 | | |
| | 367 | 504 | 215 | 30 | 151 | −4 | 300 | 2 |
| | 370 | 508 | 217 | 30 | 153 | −4 | 400 | 5 |
| | 262 | 357 | 181 | −12 | 115 | 3 | (observed) | |
| C(B) | 278 | 358 | 213 | −11 | 112 | −51 | | |
| | 285 | 367 | 226 | −11 | 115 | −47 | | |
| | 300 | 370 | 225 | −15 | 118 | −51 | 300 | 2 |
| | 305 | 372 | 224 | −17 | 120 | −52 | 400 | 5 |
| | 202 | 250 | 187 | −50 | 87 | −31 | (observed) | |
| D(A) | 520 | 724 | 221 | 44 | 193 | −33 | | |
| | 541 | 793 | 289 | 49 | 203 | −11 | | |
| | 585 | 797 | 267 | 31 | 214 | −31 | 300 | 2 |
| | 589 | 803 | 265 | 30 | 215 | −32 | 400 | 5 |
| | 432 | 561 | 197 | −42 | 163 | −17 | (observed) | |
| **Phenanthrene at 295 K** | | | | | | | | |
| C(2) | 255 | 732 | 141 | −35 | −9 | −42 | | |
| | 260 | 768 | 151 | −35 | −10 | −54 | | |
| | 286 | 793 | 148 | −55 | −12 | −40 | 220 | 3 |
| | 293 | 802 | 149 | −59 | −11 | −39 | 300 | 5 |
| | 294 | 808 | 151 | −60 | −11 | −38 | 450 | 9 |
| | 237 | 604 | 132 | −17 | 12 | −15 | (observed) | |
| C(7) | 351 | 942 | 126 | 165 | −6 | −11 | | |
| | 358 | 977 | 136 | 166 | −6 | −23 | | |
| | 393 | 993 | 136 | 173 | −11 | −10 | 220 | 3 |
| | 397 | 1001 | 137 | 170 | −12 | −6 | 300 | 5 |
| | 401 | 1008 | 139 | 173 | −12 | −6 | 450 | 9 |
| | 227 | 669 | 140 | 50 | 9 | −56 | (observed) | |
| **Anthracene at 290 K** | | | | | | | | |
| C(1) | 267 | 448 | 125 | 36 | 101 | 2 | | |
| | 287 | 458 | 148 | 39 | 120 | 5 | | |
| | 308 | 475 | 136 | 30 | 114 | 0 | 200 | 2 |
| | 314 | 479 | 136 | 28 | 115 | 0 | 300 | 5 |
| | 313 | 480 | 137 | 28 | 115 | −1 | 405 | 8 |
| | 271 | 444 | 136 | 6 | 112 | −22 | (observed) | |
| C(7) | 247 | 439 | 143 | 29 | 111 | 46 | | |
| | 266 | 450 | 166 | 32 | 130 | 50 | | |
| | 282 | 469 | 156 | 20 | 126 | 44 | 200 | 2 |
| | 286 | 473 | 156 | 19 | 126 | 45 | 300 | 5 |
| | 286 | 474 | 158 | 20 | 127 | 44 | 405 | 8 |
| | 260 | 468 | 144 | 16 | 114 | 61 | (observed) | |
| **Pyrene at 298 K** | | | | | | | | |
| C(1) | 85 | 201 | 274 | 15 | −18 | −65 | | |
| | 90 | 216 | 279 | 21 | −16 | −63 | | |
| | 91 | 214 | 289 | 13 | −21 | −62 | 200 | 2 |
| | 92 | 215 | 292 | 12 | −22 | −63 | 300 | 5 |
| | 91 | 177 | 234 | 10 | 23 | −38 | (observed) | |
| C(4) | 81 | 135 | 302 | −8 | 53 | 7 | | |
| | 85 | 146 | 309 | −4 | 54 | 8 | | |
| | 89 | 149 | 317 | −11 | 57 | 5 | 200 | 2 |
| | 91 | 150 | 320 | −14 | 58 | 4 | 300 | 5 |
| | 86 | 123 | 283 | −8 | 89 | 26 | (observed) | |

### Table 2 (*cont.*)

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{33}$ | $\omega_L$ (cm$^{-1}$) | $n_L$ |
|---|---|---|---|---|---|---|---|---|
| C(5) | 94 | 144 | 248 | 10 | 54 | 24 | | |
| | 98 | 155 | 254 | 14 | 55 | 26 | | |
| | 103 | 157 | 261 | 8 | 57 | 24 | 200 | 2 |
| | 104 | 158 | 264 | 5 | 58 | 23 | 300 | 5 |
| | 98 | 151 | 242 | 15 | 93 | 47 | (observed) | |
| C(16) | 55 | 103 | 199 | 13 | 18 | −6 | | |
| | 59 | 113 | 203 | 16 | 20 | −4 | | |
| | 61 | 115 | 208 | 14 | 20 | −6 | 200 | 2 |
| | 61 | 115 | 211 | 10 | 19 | −6 | 300 | 5 |
| | 53 | 90 | 170 | 8 | 43 | 1 | (observed) | |
| H(1) | 109 | 269 | 325 | 19 | −46 | −104 | | |
| | 132 | 340 | 366 | 47 | −42 | −91 | | |
| | 133 | 330 | 378 | 25 | −51 | −90 | 200 | 2 |
| | 134 | 327 | 383 | 18 | −55 | −91 | 300 | 5 |
| | 119 | 279 | 343 | 9 | −1 | −86 | (observed) | |
| H(2) | 82 | 193 | 436 | −30 | 10 | −74 | | |
| | 107 | 257 | 457 | −15 | 15 | −66 | | |
| | 108 | 252 | 471 | −29 | 11 | −67 | 200 | 2 |
| | 109 | 251 | 478 | −35 | 9 | −66 | 300 | 5 |
| | 100 | 226 | 437 | −60 | 63 | −77 | (observed) | |
| H(14) | 127 | 251 | 202 | 45 | 3 | −4 | | |
| | 149 | 313 | 239 | 63 | 16 | −4 | | |
| | 151 | 313 | 246 | 49 | 11 | −3 | 200 | 2 |
| | 152 | 315 | 248 | 44 | 10 | −3 | 300 | 5 |
| | 158 | 287 | 217 | 36 | 56 | 49 | (observed) | |

Tables 2 and 3($a$)* show that convergence is readily obtained, even by including a very limited number of internal modes in the lattice-dynamical calculations. The rigid-body behaviour of benzene and naphthalene is also evident, since the assumption of mixing internal and lattice modes does not involve any substantial variation in the calculated temperature factors. A substantial rigid-body behaviour can be claimed for pyrene on these grounds: for phenanthrene and anthracene, however, there are small, but definite deviations from rigid-body behaviour. For instance, for many atoms in these structures, the variations which can be observed between the calculated values which are reported in lines 1 and 2 are about the same as between lines 2 and 5. This implies that the differences in calculated temperature factors due to mixing internal and external modes (lines 1 and 2) are comparable with the separate contribution of the internal modes (lines 2 and 1). These indications have a counterpart in the lowest vibrational frequencies of the isolated molecule: for anthracene and phenanthrene, such frequencies are of the same order of magnitude as the highest lattice frequencies of the crystal, a situation which certainly does not happen for benzene and naphthalene. For anthracene, similar indications about a non-rigid motion of the molecule have been obtained also by Lehmann & Pawley (1972) and Chaplot, Lehner & Pawley (1982), from neutron-diffraction data.

The movement of hydrogen atoms in most cases seems to be uncorrelated with lattice vibrations, since the differences in the calculated temperature factors which are due to mixing internal and lattice modes are usually negligible. This is in agreement with the

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* See deposit footnote.

Table 3. *A comparison between various estimations of the tensors* **T**, **L**, **S** $(\times 10^4)$ *(in* $\text{Å}^2$, $\text{rad}^2$, *or* $\text{Å rad}$, *respectively*

(a) Schomaker–Trueblood from experimental data
(b) Lattice-dynamical rigid body
(c) Lattice-dynamical non-rigid

The reference system is a set of Cartesian axes oriented along $\mathbf{a^*}$, $\mathbf{b}$, $\mathbf{a^*} \times \mathbf{b}$, with the origin at the centre of mass of the molecule.

(1) Benzene at 138 K

| | T | | | L | | | $\lambda(\mathbf{L})$ as $(°)^2$ |
|---|---|---|---|---|---|---|---|
| (a) | 117 | −62 | −67 | 57 | −23 | −9 | 45·4 |
| | | 219 | −29 | | 123 | −27 | 24·4 |
| | | | 177 | | | 73 | 13·0 |
| (b) | 318 | −34 | −31 | 53 | −2 | −5 | 27·9 |
| | | 296 | −15 | | 81 | −11 | 19·5 |
| | | | 314 | | | 59 | 15·8 |
| (c) | 320 | −35 | −32 | 53 | −2 | −5 | 28·0 |
| | | 298 | −15 | | 81 | −11 | 19·5 |
| | | | 314 | | | 59 | 15·8 |

(2) Naphthalene-$d_8$ at 298 K

| | T | | | L | | | $\lambda(\mathbf{L})$ as $(°)^2$ |
|---|---|---|---|---|---|---|---|
| (a)† | 340 | 102 | −119 | 70 | 13 | −32 | 33·6 |
| | | 343 | −25 | | 63 | −14 | 17·9 |
| | | | 445 | | | 52 | 9·0 |
| (b) | 479 | 37 | −48 | 70 | −3 | −8 | 28·4 |
| | | 476 | −5 | | 65 | −15 | 23·5 |
| | | | 501 | | | 73 | 16·6 |
| (c) | 494 | 38 | −52 | 71 | −3 | −8 | 29·0 |
| | | 382 | −3 | | 67 | −15 | 23·8 |
| | | | 516 | | | 75 | 17·0 |

(3) Anthracene-$d_{10}$ at 290 K

| | T | | | L | | | $\lambda(\mathbf{L})$ as $(°)^2$ |
|---|---|---|---|---|---|---|---|
| (a)† | 313 | 163 | −235 | 50 | 13 | −34 | 31·0 |
| | | 309 | 15 | | 36 | 4 | 14·3 |
| | | | 355 | | | 67 | 5·1 |
| (b) | 387 | 18 | −96 | 31 | 0 | −5 | 18·1 |
| | | 379 | −14 | | 24 | −12 | 9·9 |
| | | | 456 | | | 50 | 6·3 |
| (c) | 420 | 23 | 104 | 32 | 0 | −5 | 18·8 |
| | | 395 | 12 | | 26 | −12 | 10·3 |
| | | | 484 | | | 52 | 6·8 |

(4) Phenanthrene at 295 K

| | T | | | L | | | $\lambda(\mathbf{L})$ as $(°)^2$ | S | | |
|---|---|---|---|---|---|---|---|---|---|---|
| (a) | 444 | 46 | 72 | 55 | 5 | 0 | 21·4 | (−11) | −10 | 21 |
| | | 560 | −19 | | 38 | 6 | 18·4 | −3 | (18) | −9 |
| | | | 566 | | | 64 | 11·7 | 6 | 4 | (−7) |
| (b) | 558 | 58 | 6 | 76 | −11 | −13 | 29·6 | −34 | −29 | 2 |
| | | 594 | 20 | | 47 | 7 | 19·9 | 24 | 29 | 5 |
| | | | 548 | | | 70 | 14·2 | 16 | 1 | 11 |
| (c) | 593 | 61 | 8 | 81 | −12 | −14 | 31·6 | −36 | −29 | 3 |
| | | 617 | 24 | | 51 | 7 | 20·8 | 26 | 29 | 3 |
| | | | 578 | | | 74 | 15·2 | 16 | 1 | 12 |

(5) Anthracene at 290 K

| | T | | | L | | | $\lambda(\mathbf{L})$ as $(°)^2$ |
|---|---|---|---|---|---|---|---|
| (a) | 391 | 27 | −93 | 23 | 0 | 1 | 10·0 |
| | | 423 | −25 | | 24 | 0 | 8·0 |
| | | | 500 | | | 18 | 3·3 |
| (b) | 400 | 17 | −102 | 32 | 0 | −5 | 18·6 |
| | | 391 | −13 | | 25 | −12 | 10·2 |
| | | | 470 | | | 51 | 6·4 |
| (c) | 431 | 22 | −110 | 33 | 0 | −5 | 19·2 |
| | | 406 | −11 | | 26 | −12 | 10·6 |
| | | | 495 | | | 53 | 7·0 |

Table 3 (*cont.*)

(6) Pyrene at 298 K

| | T | | | L | | | $\lambda(\mathbf{L})$ as $(°)^2$ | S | | |
|---|---|---|---|---|---|---|---|---|---|---|
| (a) | 413 | 47 | 189 | 53 | −18 | 4 | 23·0 | (10) | 10 | −3 |
| | | 354 | 33 | | 47 | 14 | 17·8 | 9 | (0) | 9 |
| | | | 618 | | | 49 | 8·1 | −7 | −6 | (−10) |
| (b) | 486 | 78 | −9 | 39 | −13 | 5 | 19·1 | 1 | −6 | 3 |
| | | 439 | −21 | | 48 | 7 | 14·9 | −5 | 0 | −8 |
| | | | 697 | | | 42 | 8·5 | −4 | 1 | −10 |
| (c) | 504 | 81 | −12 | 41 | −14 | 5 | 20·0 | 2 | −5 | 3 |
| | | 454 | −23 | | 50 | 8 | 15·6 | −6 | −1 | −10 |
| | | | 727 | | | 44 | 8·8 | −4 | 1 | −11 |

† Including hydrogen (deuterium) atoms.

conclusions of other authors, for example Pawley & Yeats (1969) and Johnson (1970a) on naphthalene and benzene. Some exceptions can, however, be noticed, especially for anthracene or phenanthrene, which are in line with the partial non-rigidity of these molecules.

For all the hydrocarbons here treated, there is no essential difference between the lattice-dynamical estimates of the molecular vibration tensors **T**, **L**, **S**, which are obtained from a rigid-body and non-rigid lattice-dynamical model (see Table 3). There is often, however, a non-negligible difference with respect to the Schomaker–Trueblood interpretation of crystallographic data: this difference is not great for **T** and **L**, whereas no agreement at all is obtained for **S**. Such a situation has already been noticed and discussed (Filippini, Gramaccioli, Simonetta & Suffritti, 1974): most of such differences probably derive from neglecting corrections for thermal diffuse scattering (TDS), since the observed temperature factors are nearly always systematically lower than the corresponding calculated values. An overall prospect of such agreement (or disagreement) in temperature factors is given in Table 4. Here, for each compound, the disagreement indices are given as:

$$R = 100 \sum |B_{ij(\text{obs})} - B_{ij(\text{calc})}| / \sum |B_{ij(\text{obs})}|$$

and

$$\Delta B = 100 \sum (B_{ij(\text{obs})} - B_{ij/\text{calc}}) / \sum B_{ij(\text{obs})}$$

and separate results are shown for different lattice-dynamical models.

From Tables 2, 4 and 3(a)‡ we see that the agreement between observed and calculated temperature factors differs from case to case: a maximum difference is found for benzene, and a substantially very good agreement for anthracene and pyrene. Most of the differences are systematic, and involve values of the experimental temperature factors which are too small: this is exactly in line with the effect of TDS. For pyrene, however, no systematic disagreement is ob-

‡ See deposit footnote.

served, in spite of having crystallographic data not corrected for TDS. Such a situation had already been noticed by us (GFS) when dealing with the rigid-body motion of these molecules, and we had argued that the different behaviour of pyrene could be ascribed to non-rigid-body motion. This is, however, not the case. Probably here the strategy in collecting and utilizing the crystallographic data is important, as for any example in which accurate experimental values of temperature factors are obtained (cutoff of low-angle reflexions, scanning range and estimation of the background, etc.). It is probably significant that the neutron diffraction data for pyrene have been obtained in a particular way, taking also care of the limit of the peak 'so that $\sigma(I)/I$ is as small as possible' (Hazell, Larsen & Lehmann, 1972). For anthracene-$d_{10}$ at 16 K, most of the observed disagreement is probably due to anharmonicity.

A slight, but definite increase of the calculated temperature factors can be noticed on passing from the rigid-body to the non-rigid model. This effect is due to

**Table 4. Overall agreement between observed and calculated temperature factors**

|  | R (%) | ΔB (%) |
|---|---|---|
| Benzene lattice only | 32.9 | −18.9 |
| rigid | 49.9 | −34.8 |
| non-rigid | 49.8 | −37.1 |
| Napththalene-$d_8$ lattice only | 34.5 | −30.0 |
| rigid | 43.7 | −39.9 |
| non-rigid | 46.9 | −41.2 |
| Anthracene lattice only | 9.8 | −1.0 |
| rigid | 12.5 | −9.3 |
| non-rigid | 14.6 | −11.4 |
| Phenanthrene lattice only | 23.1 | −10.1 |
| rigid | 26.7 | −13.8 |
| non-rigid | 32.7 | −24.5 |
| Pyrene lattice only | 21.8 | 12.8 |
| rigid | 19.9 | 2.4 |
| non-rigid | 20.2 | 2.4 |
| Anthracene-$d_{10}$ at 290 K lattice only | 23.5 | −15.6 |
| rigid | 32.8 | −26.2 |
| non-rigid | 37.3 | −32.8 |
| Anthracene-$d_{10}$ at 17 K lattice only | 64.3 | 45.7 |
| rigid | 54.2 | 40.6 |
| non-rigid | 44.6 | 33.3 |

'softening' of the lattice modes, when mixing with internal moles is accounted for (see Table 1). Since the observed temperature factors are too low, this leads to the curious situation that the agreement with the experimental data becomes worse and worse, on improving the lattice-dynamical model (see Table 4). On the other hand, such lattice-dynamical results could be more significant than their experimental counterparts, in view of the considerable errors in evaluating such data from X-ray or neutron diffraction; this point of view can be supported by the good agreement of our calculations with all the available spectroscopic data.

Examples of the mean-square displacement tensors (**W**) are given in Table 5 (anthracene) and 5(a) (phenanthrene, pyrene).* These examples show how the Schomaker–Trueblood interpretation of temperature factors can be extended to all molecular crystals. Owing to the symmetrical nature of **W**, the upper triangular part only is represented. Reference of the various rows (and columns) is made, in sequence: (1) to translational motions along the principal axes of the molecule; (2) to rotational motions around these axes; (3) to the internal degrees of freedom, in order of increasing frequency (up to $\omega_L$). The relationship to **T**, **L**, and **S** has already been discussed (see above, formulae 8 and 9): here the first $3 \times 3$ block along the main diagonal corresponds to **T**, and second to **L** and the first 'off-diagonal' block to **S**. Another advantage of **W** is that of representing the mean-square displacements along any degree of freedom on the same scale (here atomic mass units × Å²).

On examining **W**, we can notice the strong prevalence of the diagonal translational and rotational elements. Then we have the off-diagonal translational and rotational elements, or the translational–rotational elements (when they are non-zero). In all these molecules, which are not far from the rigid body, the diagonal elements corresponding to the lowest-frequency internal modes are often of the same order of magnitude as the off-diagonal translational and rota-

* See deposit footnote.

**Table 5. The tensor W for anthracene (atomic mass units × Å²; referred to the principal axes of inertia)**

The rows and columns refer, in sequence, to translational, rotational and internal coordinates in order of increasing frequency (see text).

| 10·2790 | 0·1512 | −0·4830 | 0·0000 | 0·0000 | 0·0000 | −0·0102 | −0·1350 | −0·0044 | 0·0000 | 0·0000 | −0·0116 | 0·0000 | 0·0000 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | 7·1656 | 0·2268 | 0·0000 | 0·0000 | 0·0000 | 0·0690 | −0·1026 | 0·0004 | 0·0000 | 0·0000 | 0·0182 | 0·0000 | 0·0000 |
|  |  | 6·2804 | 0·0000 | 0·0000 | 0·0000 | 0·0372 | 0·0656 | −0·0056 | 0·0000 | 0·0000 | 0·0026 | 0·0000 | 0·0000 |
|  |  |  | 1·2886 | 0·1644 | 0·5114 | 0·0000 | 0·0000 | 0·0000 | 0·0132 | −0·0142 | 0·0000 | 0·0022 | 0·0036 |
|  |  |  |  | 2·4114 | −0·0190 | 0·0000 | 0·0000 | 0·0000 | −0·0112 | −0·0078 | 0·0000 | 0·0040 | −0·0024 |
|  |  |  |  |  | 4·8482 | 0·0000 | 0·0000 | 0·0000 | 0·0172 | −0·0142 | 0·0000 | 0·0016 | 0·0082 |
|  |  |  |  |  |  | 0·5132 | −0·0016 | −0·0002 | 0·0000 | 0·0000 | −0·0036 | 0·0000 | 0·0000 |
|  |  |  |  |  |  |  | 0·2652 | −0·0018 | 0·0000 | 0·0000 | 0·0026 | 0·0000 | 0·0000 |
|  |  |  |  |  |  |  |  | 0·1294 | 0·0000 | 0·0000 | −0·0008 | 0·0000 | 0·0000 |
|  |  |  |  |  |  |  |  |  | 0·1160 | −0·0008 | 0·0000 | 0·0002 | 0·0002 |
|  |  |  |  |  |  |  |  |  |  | 0·0880 | 0·0000 | −0·0002 | 0·0000 |
|  |  |  |  |  |  |  |  |  |  |  | 0·0620 | 0·0000 | 0·0000 |
|  |  |  |  |  |  |  |  |  |  |  |  | 0·0566 | 0·0000 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 0·0538 |

tional elements, but their value rapidly becomes smaller, on going toward the higher frequencies. The off-diagonal elements of **W** involving internal motions coupled with translations and rotations are still smaller (by about one order of magnitude); finally, the elements corresponding to coupling between internal vibrational modes are generally so small not to be even noticeable.

All this supports our approximation which excludes coupling of high-frequency internal modes. These examples also show the importance of **W**, which gives the amount of coupling between any normal co-ordinates *through the whole Brillouin zone*, to go beyond its possible applications to crystallography.

In conclusion, we have shown that a complete lattice-dynamical derivation of temperature factors for any molecular crystal is no longer prohibitive, and can give useful information to crystallographers. Further application of this method to other groups of crystalline substances, with more non-rigid character, is in progress. We hope that such application might eventually become a routine procedure, especially if semi-empirical potentials which are as good as for hydrocarbons can be applied to other molecular crystals. For instance, in the absence of Coulombic interactions, such as here, a complete set of calculations of this kind can be obtained in a CPU time which ranges from about 5 to 15 min on a UNIVAC 1100/80 computer; therefore, we are not far from the cost of a least-squares refinement of a crystal structure. At the same time, a careful redetermination of temperature factors on some of these substances, after correction for TDS and peak-shape analysis by either neutron or X-ray diffraction, might be quite interesting, in order to have a good comparison for lattice-dynamical calculations. For non-rigid molecules, in particular, it will be interesting to see how much bond-length corrections could be improved; another possible application might be checking how much electron density maps can be improved by substituting these temperature factors in their experimental counterparts, and, moreover, if corrections for TDS are considered.

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