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Lattice Dynamical Calculations of the Mean Square Amplitudes of Crystalline Biphenyl

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Abstract

The molecular mean-square-amplitude matrix of crystalline biphenyl, $C_{12}H_{10}$, is calculated with an intermolecular potential of the atom–atom type. The effect of the presence of the low-lying torsional mode, which interacts with translational modes, is discussed. The Born **S**-matrix method is used, and proves to be an excellent approximation, which takes about $\frac{1}{5}$ of the computer time of the exact calculation. The resulting amplitudes are in fair agreement with experiment, and show that the extremely high amplitude of libration about the long molecular axis may be satisfactorily explained without assuming a double-well shape for the torsional potential.

Introduction

The study of the thermal motions of the atoms in molecular crystals is of considerable interest for researchers in the field of X-ray and neutron diffraction and NQR spectroscopy, among others. Crystallographers have developed several models to interpret atomic displacements in terms of molecular motions, using diffraction data. Cruickshank (1956*a*,*b*) proposed his **TL** model of thermal motion, where the molecules are supposed to be rigid, and no interactions between translations and rotations are allowed; when this restriction is lifted, the widely used **TLS** model of Schomaker & Trueblood (1968) results.

A further complication arises when low-lying internal vibrations, which mix with the external modes, like the butterfly mode of naphthalene and the torsional mode of biphenyl, are present.

Although the usual crystallographic rigid-body model can be partially successful in accounting also for the mean square displacements relative to these internal modes, the treatment is nearly always incomplete: a practical demonstration of the limits of such a procedure is given here for biphenyl.

There are several difficulties associated with the correct interpretation of molecular thermal motions from diffraction data; in this sense, a lattice dynamical approach is particularly useful, since it allows correlation with other experimental data, like vibrational frequencies (see Filippini, Gramaccioli, Simonetta & Suffritti, 1974). A series of lattice dynamical calculations of the molecular mean-square-amplitude tensors **L**, **T** and **S** have been published (McKenzie & Pryor, 1971; Luty, 1972; Filippini, Gramacioli, Simonetta & Suffritti, 1973; Cerrini & Pawley, 1973; Pawley, 1972; for instance); the correct values of the **L** tensors are particularly important to obtain bond-length corrections.

In the present work we present a lattice dynamical calculation of the molecular mean-square-amplitude tensor of crystalline biphenyl at two temperatures, in the harmonic approximation. Although the semi-empirical atom–atom parameters due to Williams (1966) used in the calculations have not been adjusted

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for this substance, the results of a calculation on the optically active modes at room temperature are in good agreement with experiment (Burgos, Bonadeo & D'Alessio, 1976). However, anharmonicity and possible double-well effects have not been taken into account, and there are some uncertainties regarding the intramolecular field, which may affect the accuracy of the results. The presence of the torsional mode of biphenyl, on the other hand, provides an illustrative example of the effects of intermode mixing.

Theory

The general theory of lattice dynamics of molecular crystals, and its application to crystallographic problems is thoroughly discussed in the book by Willis & Pryor (1975). The method used in this work for the calculation of the dynamical matrix has been discussed in the literature (Taddei, Bonadeo, Marzocchi & Califano, 1973; Bonadeo & Taddei, 1973; Neto, Righini, Califano & Walmsley, 1978) and only the background for understanding the forthcoming discussion will be presented here.

The coordinate basis is formed by the isolated molecule normal coordinates, and mass-weighted translation and rotation coordinates; the intramolecular potential is diagonal in these coordinates, and the corresponding matrix elements $\lambda_1 = 4\pi^2 \nu_1^2$ are eigenvalues of the isolated molecule secular equation.

The dynamical matrix is written as

$$\mathbf{D}^{\nu m}_{\mu l}(\mathbf{k}) = \mathbf{F}^{\nu m}_{\mu l}(\mathbf{k}) + \lambda_l \delta_{lm} \delta_{\mu\nu} \qquad (1a)$$

with

$$\mathbf{F}^{\nu m}_{\mu l}(\mathbf{k}) = \sum_{\beta} \left(\frac{\partial^2 V_e}{\partial Q_{1\mu l} \partial Q_{\beta \nu m}} \right) \exp(i\mathbf{k}.\mathbf{r}_\beta), \qquad (1b)$$

where V_e is the intermolecular potential, β labels the unit cell, μ, ν the molecules within the unit cell; l, m are the molecular motions associated with coordinates $Q_{1\mu l}$, $Q_{\beta\nu m}$; and $\mathbf{r}_\beta$ is the radius vector joining the origin cell 1 and the cell β.

The main advantage of this coordinate basis is that the dynamical matrix can be factorized *a priori* according to the values of the different λ_l. In particular, only those modes which have a low λ_l, and therefore interact with the external motions, are taken into account in the lattice-mode calculation, thus keeping the dynamical matrix within a manageable size.

Since the mean square displacements are independent of β, μ, ν, these subscripts will be dropped in what follows.

The mean square atomic displacement matrix for atom i is

$$\mathbf{B}^{\text{atom}}(i) = \langle \mathbf{u}_i \mathbf{u}_i^{+} \rangle. \qquad (2)$$

The atomic displacements can be written in terms of our basis coordinates as

$$\mathbf{u}_i = \sum_l \boldsymbol{\xi}_{i,l} Q_l + \tfrac{1}{2} \sum_{lm} \boldsymbol{\zeta}_{i,lm} Q_l Q_m \qquad (3a)$$

with

$$\boldsymbol{\xi}_{i,l} = \frac{\partial \mathbf{r}_i}{\partial Q_l};$$

$$\boldsymbol{\zeta}_{i,lm} = \frac{\partial^2 \mathbf{r}_i}{\partial Q_l \partial Q_m}. \qquad (3b)$$

From (3*a*),

$$\langle \mathbf{u}_i \rangle = \tfrac{1}{2} \sum_{lm} \boldsymbol{\zeta}_{i,lm} \langle Q_l Q_m \rangle \qquad (4)$$

and, neglecting terms in Q^4,

$$\langle \mathbf{u}_i \mathbf{u}_i^{+} \rangle = \sum_{lm} \boldsymbol{\xi}_{i,l} \boldsymbol{\xi}^{+}_{i,m} \langle Q_l Q_m \rangle. \qquad (5)$$

The coefficients $\boldsymbol{\xi}_{i,l}$ are the usual Cartesian displacements, obtained from the isolated molecule secular equation for the internal modes and the Eckart relations for the rotations and translations. The $\boldsymbol{\zeta}_{i,lm}$'s are non-vanishing only if both Q_l and Q_m involve angular deformations or rotations. The particular form of the coefficients depends on the type of coordinate involved; for the case of molecular rotations, see Neto *et al.* (1978). It can be seen that in principle all angular motions may contribute to the apparent shift of an atom.

We may define a generalized molecular mean square displacement tensor as

$$\mathbf{B}^{\text{mol}}_{lm} = \langle Q_l Q_m \rangle. \qquad (6)$$

When Q_l and Q_m are rotation and translation coordinates the matrix elements $\mathbf{B}^{\text{mol}}_{lm}$ are proportional to the elements of the usual **T**, **L** and **S** matrices. When internal modes interact with these motions, this fact has to be taken into account in order to obtain an accurate description of $\mathbf{B}^{\text{atom}}$ in (5).

$\mathbf{B}^{\text{mol}}$ may be calculated as

$$\mathbf{B}^{\text{mol}}_{lm} = \frac{1}{N} \sum_{bk} \mathbf{e}(l, b\mathbf{k}) \mathbf{e}^{+}(m, b\mathbf{k}) \frac{h}{8\pi^2 \nu_b(\mathbf{k})} \coth\left(\frac{h\nu_b(\mathbf{k})}{2k_B T} \right), \qquad (7)$$

where b labels branches, and $\mathbf{e}(l,b\mathbf{k})$ is the eigenvector connecting the basis coordinate l with the crystal normal mode having eigenvalue $\lambda_b(\mathbf{k}) = 4\pi^2 \nu_b^2(\mathbf{k})$. This procedure requires the diagonalization of the dynamical matrix $\mathbf{D}^m_l(\mathbf{k})$ for a large number N of values of $\mathbf{k}$. Born (1942) has shown that, expanding $x \coth x$ in series it is possible to write

$$\mathbf{B}^{\text{mol}}_{lm} = \sum_k \mathbf{S}_{lm}(\mathbf{k}) \qquad (8a)$$

with the Born **S** matrix defined as

$$\mathbf{S}_{lm}(\mathbf{k}) = \frac{k_B T}{N} \left\{ [\mathbf{D}_l^m]^{-1}(\mathbf{k}) + \frac{1}{12}\left[\frac{h}{k_B T}\right]^2 \mathbf{I} - \frac{1}{720}\left[\frac{h}{k_B T}\right]^4 \mathbf{D}_l^m(\mathbf{k}) + \dots \right\}. \quad (8b)$$

It can be seen that in this case it is sufficient to invert the dynamical matrix, a simpler and much faster procedure than diagonalization.

Crystalline biphenyl

The crystal structure of biphenyl has been determined at 300 K (Hargreaves & Rizvi, 1962; Charbonneau & Delugeard, 1977) and 110 K (Charbonneau & Delugeard, 1976). The unit cell is monoclinic, space group $P2_1/a$ (C_{2h}^5) with two molecules located at inversion sites. In the gaseous state, the two phenyl groups are at 42° (Bastiansen, 1949), a compromise between the opposite effects of atomic repulsion and electronic conjugation. In the crystal, the intermolecular forces overcome the internal forces, and the molecule is quasi-planar. There is strong spectroscopic evidence for phase transitions at 40 and 17 K (38 and 24 K for $C_{12}D_{10}$); the 40 K transition has been interpreted in terms of a Brillouin zone (BZ) boundary soft mode in the (110) plane, leading to a permanent torsional deformation (Friedman, Kopelman & Prasad, 1974; Bree & Edelson, 1977, 1978). On the other hand, the spectroscopic evidence of the loss of the inversion center at low temperature, and the extremely large librational amplitude found by Charbonneau & Delugeard (1976, 1977), has led them to a different interpretation: there would be a torsional double well at all temperatures; at high temperatures the average position would be that determined by X-ray diffraction, and at low temperatures the molecule would be frozen in one of the distorted positions.

Luty (1972) has calculated the lattice dynamical properties of biphenyl including the **L** and **T** tensors, without taking into account the torsional motion; the results do not agree well with experiment. Later on, Burgos *et al.* (1976) studied the low-frequency optically active vibrations of biphenyl at room temperature. In their calculation, they used intermolecular potentials of the atom–atom type, with parameters due to Williams (1966) and included intermode mixing between lattice modes and the six interphenyl motions; these internal modes enter the calculation *via* their Cartesian displacements and the values of λ_l of (1*a*). The former may be obtained, at least approximately, from symmetry considerations, but the values of λ_l cannot be transferred from the gaseous state since the geometry is very different, and therefore they were treated as adjustable parameters. The calculation showed good agreement with experiment; it was found that only the torsion mixes with the external modes, to such an extent that most *u* normal modes cannot be labeled translational or torsional. The intramolecular potential associated with this motion, λ_τ, is negative, since the planar configuration is a maximum of the internal energy. For values of $\nu_\tau = [-\lambda_\tau/4\pi^2]^{1/2}$ between 0 and 30 cm^{-1}, the agreement was best, and for $\nu_\tau = 62$ cm^{-1}, the torsional modes become unstable.

Taking into account the results of the previous calculations, we have considered only the mixing of the lattice modes with the torsional motion. Since there is an inversion center, the 7 × 7 $\mathbf{B}^{\text{mol}}$ matrix will be factorized in two blocks: one 3 × 3 libration tensor and one 4 × 4 translation–torsion tensor. For these modes, the Cartesian displacements are

$$\xi_{R_l,i} = \frac{\hat{\mathbf{l}} \times \mathbf{r}_i}{\sqrt{I_l}}, \quad l = x,y,z \text{ (libration)};$$

$$\xi_{T_l,i} = \frac{\hat{\mathbf{l}}}{\sqrt{M}}, \quad l = x,y,z \text{ (translation)};$$

$$\xi_{\tau,i} = \pm \frac{\hat{\mathbf{x}} \times \mathbf{r}_i}{\sqrt{I_x}}, \quad \text{torsion};$$

where the molecular axes are defined to make $I_x < I_y < I_z$; $\mathbf{r}_i$ is the coordinate of atom *i* in the principal inertial molecular axes; *M* is the molecular mass, and the plus or minus sign for $\xi_{\tau,i}$ refers to atoms belonging to different phenyl groups.

For translations and rotations, the relation between $\mathbf{B}^{\text{mol}}$ and the usual $\mathbf{B}^{\text{mol}}$ is simply

$$\mathbf{B}^{\text{mol}}_{T_l T_n} = \frac{\mathbf{B}^{\text{mol}}_{T_l T_n}}{M} = \mathbf{T}_{ln} \quad (9a)$$

$$\mathbf{B}^{\text{mol}}_{R_l R_n} = \frac{\mathbf{B}^{\text{mol}}_{R_l R_n}}{\sqrt{I_l I_n}} = \mathbf{L}_{ln}. \quad (9b)$$

For elements involving the torsion

$$\mathbf{B}^{\text{mol}}_{\tau\tau} = \frac{\mathbf{B}^{\text{mol}}_{\tau\tau}}{I_x} = \mathbf{\Theta}_{\tau\tau} \quad (9c)$$

$$\mathbf{B}^{\text{mol}}_{T_l \tau} = \frac{\mathbf{B}^{\text{mol}}_{T_l \tau}}{\sqrt{M I_x}} = \mathbf{\Theta}_{l\tau}. \quad (9d)$$

It is to be noted that such simple expressions are possible because of the particular form of $\xi_{\tau,l}$, but that for general internal coordinates the mass effects cannot be written out explicitly; this is, of course, the reason for defining $\mathbf{B}^{\text{mol}}$ as in (6).

If, for the sake of simplicity, the molecule of biphenyl is taken to be perfectly planar, with $\mathbf{r}_i = x_i\hat{\mathbf{x}} + y_i\hat{\mathbf{y}}$, the atomic displacement matrix $\mathbf{B}_i^{\text{atom}}$ in (5) may be written explicitly as

$$\mathbf{B}_i^{\text{atom}} = \begin{pmatrix} \mathbf{T}_{xx} + y_i^2\mathbf{L}_{zz} & \mathbf{T}_{xy} - x_iy_i\mathbf{L}_{zz} & \mathbf{T}_{xz} - y_i^2\mathbf{L}_{xz} + x_iy_i\mathbf{L}_{yz} \pm y_i\mathbf{\Theta}_{x\tau} \\ \text{symmetric} & \mathbf{T}_{yy} + x_i^2\mathbf{L}_{zz} & \mathbf{T}_{yz} - x_i^2\mathbf{L}_{yz} + x_iy_i\mathbf{L}_{xz} \pm y_i\mathbf{\Theta}_{y\tau} \\ \text{symmetric} & \text{symmetric} & \mathbf{T}_{zz} + x_i^2\mathbf{L}_{yy} + y_i^2(\mathbf{L}_{xx} + \mathbf{\Theta}_{\tau\tau}) - 2x_iy_i\mathbf{L}_{xy} \pm 2y_i\mathbf{\Theta}_{z\tau} \end{pmatrix}. \tag{10}$$

It is clear from (10) that since $\mathbf{L}_{xx}$ and $\mathbf{\Theta}_{\tau\tau}$ show the same dependence on the atomic coordinates it is impossible to separate their effects experimentally, and that in fact the rigid-body model allows implicitly for this torsional effect, with $\mathbf{L}_{xx}^{\text{eff}} = \mathbf{L}_{xx} + \mathbf{\Theta}_{\tau\tau}$. The effect of the $\mathbf{\Theta}_{l\tau}$ elements, however, is neglected in such a picture.

It should be pointed out that in our case the bond-length correction (equation 4) is correctly performed, taking an $\mathbf{L}_{xx}^{\text{eff}}$ as before; the off-diagonal elements do not contribute in our case because $\zeta_{i,T_l\tau} = 0$ and the torsion–rotation elements of $\mathbf{B}^{\text{mol}}$ are also zero.

Results and discussion

We have calculated $\mathbf{B}^{\text{mol}}$ for crystalline biphenyl with the Born **S**-matrix method, (8). For the frequencies and temperatures involved, this approximation is better than 0·1%, compared with the results of (7). On the other hand, the computing time is about a fifth of the exact calculation, certainly an important difference.

The BZ sampling, in the context of the calculation of mean square amplitudes, has been discussed by Filippini, Gramaccioli, Simonetta & Suffritti (1976). They conclude that an uneven sampling, with more points near $\mathbf{k} = 0$, is more efficient than the usual regular mesh over the irreducible part of the BZ. Chadi & Cohen (1973), on the other hand, give a general criterion for choosing special points, which depend on symmetry considerations alone, to achieve rapid convergence of averages of general functions of $\mathbf{k}$ over the BZ. We have performed calculations with the sampling methods indicated as A and C in Fig. 3 of the paper by Filippini *et al.* (1976), which correspond to their worst and best converging cases, respectively, with five points in each direction of reciprocal space; the sampling, in our case, has to be extended over positive values of k_x, k_y and k_z, and negative values of k_x or k_y, to cover the irreducible part of the BZ with 250 points. The special points defined by Chadi & Cohen (1973) for our symmetry may be chosen as those for which k_x, k_y and k_z take the values $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$ and $\frac{7}{8}$, *i.e.* 128 points, with equal weight. For case A of Filippini *et al.* (1976), the values of the elements **T** were appreciably underestimated; the results for case C and the special points method are practically identical, and are those reported in the tables.

Table 1 shows the calculated values of $\mathbf{B}^{\text{mol}}$ of crystalline biphenyl at 110 and 300 K; we have included calculations for two values of the torsional force parameter ν_τ. It should be noted that, although the torsion–rotation elements of $\mathbf{B}^{\text{mol}}$ are zero, the values of these elements in the dynamical matrix for general values of $\mathbf{k}$ are non-zero: they vanish when the average over the BZ is performed. Therefore the value of ν_τ affects the libration tensor **L**, because the torsion–libration elements are taken into account in the diagonalization process of (7) or the matrix inversion of (8).

In Table 2 we show the values of $\mathbf{B}^{\text{atom}}$ for a hydrogen atom in the *ortho* position with respect to the interphenyl bond, obtained from (5) with the data of Table 1 for $T = 300$ K and $\nu_\tau = 30$ cm^{-1}. Although the value $\mathbf{B}_{zz}^{\text{atom}}$ is only slightly affected by the inclusion of the elements $\Theta_{l\tau}$, these are dominating in the off-diagonal elements B_{xz}^{atom} and B_{yz}^{atom}. This shows that, in our case, the values obtained for $\mathbf{L}_{xz}$, $\mathbf{L}_{yz}$, $\mathbf{T}_{xz}$ and $\mathbf{T}_{yz}$ in a rigid-body treatment of diffraction data will be subject to large errors.

Table 1. *Calculated molecular thermal-motion tensors*

$I_x < I_y < I_z$.

	Temperature (K)	110		300	
Units	ν_τ (cm^{-1})	0	30	0	30
Å^2	$\mathbf{T}_{xx}$	0·0166	0·0169	0·0703	0·0728
	$\mathbf{T}_{xy}$	0·0008	0·0009	−0·0099	−0·0096
	$\mathbf{T}_{xz}$	0·0000	−0·0001	−0·0023	−0·0024
	$\mathbf{T}_{yy}$	0·0113	0·0114	0·0534	0·0544
	$\mathbf{T}_{yz}$	−0·0017	−0·0018	0·0126	0·0128
	$\mathbf{T}_{zz}$	0·0122	0·0124	0·0573	0·0576
Å (°)	$\mathbf{\Theta}_{x\tau}$	−0·106	−0·106	0·420	0·586
	$\mathbf{\Theta}_{y\tau}$	0·028	0·028	0·118	0·178
	$\mathbf{\Theta}_{z\tau}$	−0·022	−0·022	0·060	0·083
	$\mathbf{\Theta}_{\tau\tau}$	9·38	11·08	40·72	57·70
(°)^2	$\mathbf{L}_{xx}$	11·44	11·59	53·61	54·50
	$\mathbf{L}_{xy}$	−0·12	−0·14	1·73	2·14
	$\mathbf{L}_{xz}$	−0·64	−0·68	−3·97	−4·37
	$\mathbf{L}_{yy}$	2·80	2·87	11·31	11·84
	$\mathbf{L}_{yz}$	0·71	0·71	−2·93	−3·02
	$\mathbf{L}_{zz}$	3·21	3·28	12·58	13·38

Table 2. *Thermal motion tensor of a hydrogen atom in the ortho position with respect to the interphenyl bond, calculated including and excluding elements* $\mathbf{\Theta}_{l\tau}$

Units 10^4 Å^2. T = 300 K; $\nu_\tau = 30$ cm^{-1}. $I_x < I_y < I_z$.

	$\mathbf{\Theta}_{l\tau} = 0$	$\mathbf{\Theta}_{l\tau} \neq 0$
$\mathbf{B}_{xx}$	922	922
$\mathbf{B}_{xy}$	−185	−185
$\mathbf{B}_{xz}$	−107	116
$\mathbf{B}_{yy}$	585	585
$\mathbf{B}_{yz}$	108	176
$\mathbf{B}_{zz}$	2211	2274

Table 3. *Observed and calculated effective molecular thermal-motion tensors*

Units **T** in 10^4 Å^2; **L** in $(°)^2$. $\nu_\tau = 30$ cm^{-1}. $I_x < I_y < I_z$.

	110 K		300 K		
	Observed	Calculated	Observed		Calculated
	(*A*), (*B*)		(*A*)	(*B*)	
$\mathbf{T}_{xx}$	281	169	593	560	728
$\mathbf{T}_{xy}$	15	9	−12	−50	−96
$\mathbf{T}_{xz}$	7	−1	18	50	−24
$\mathbf{T}_{yy}$	216	114	453	320	544
$\mathbf{T}_{yz}$	20	−18	0	−30	128
$\mathbf{T}_{zz}$	133	124	403	470	576
$\mathbf{L}^{\text{eff}}_{xx}$	45·70	22·67	109·17	105·9	112·20
$\mathbf{L}_{xy}$	—	−0·14	—	—	2·14
$\mathbf{L}_{xz}$	—	−0·68	—	—	−4·37
$\mathbf{L}_{yy}$	2·46	2·87	8·39	11·1	11·84
$\mathbf{L}_{yz}$	—	0·71	—	—	−3·02
$\mathbf{L}_{zz}$	3·45	3·28	11·47	8·0	11·38

References: (*A*) Charbonneau & Delugeard (1977); (*B*) Charbonneau & Delugeard (1976).

Under these conditions, a comparison between our calculations on the off-diagonal elements of **L** and **T** and the effective amplitude tensors obtained by Charbonneau & Delugeard (1976, 1977) is not meaningful since they refer to essentially different things. It is possible, however, to make such a comparison for the diagonal elements of $\mathbf{L}^{\text{eff}}$ and **T** consistently.

Table 3 shows that the calculated values for $T = 300$ K are somewhat overestimated, and those for $T = 110$ K somewhat underestimated, a fact that can be attributed to the roughness of the model. However, the overall agreement is fair, and the correct order of the different tensor elements is obtained. The most important result refers to the motion about the long molecular axis x. It is clear that the extremely high values of $\mathbf{L}^{\text{eff}}_{xx}$ obtained by Charbonneau & Delugeard (1976, 1977) can be perfectly well explained within the limits of our harmonic calculation. Although this does not prove that there is no torsional double well, it invalidates the only argument supporting its existence at the temperatures considered.

We have performed frequency calculations for several relevant values of **k**. The important results may be summarized as follows: whereas for most points the lowest frequencies are associated with molecular translations, we find low frequencies, associated with the torsional motion, for the points $(0\frac{1}{2}0)$ and $(\frac{1}{2}\frac{1}{2}0)$. This fact is in agreement with the ideas presented by Bree & Edelson (1977, 1978), and further discussed by Cailleau and co-workers (Cailleau, Girard, Moussa & Zeyen, 1979; Cailleau, Moussa & Mons, 1979), interpreting the phase transition at low temperatures in terms of a BZ boundary soft mode which doubles or quadruples the unit cell in just these directions.

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