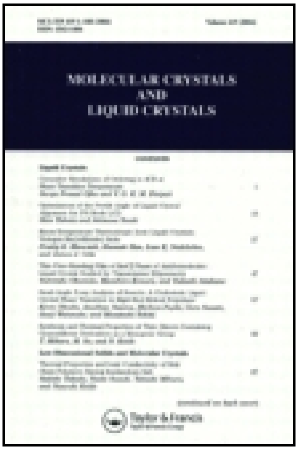

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Lattice Dynamics of Biphenyl

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Lattice Dynamics of Biphenyl

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Abstract—This paper presents calculations of the lattice dynamics of a biphenyl crystal, using the " 6-exp " potential function. It was noted that an " atom-atom " potential after Kitaigorodskii parameters describes properties of the crystal better than the potential after Poltev and Sukhorukov parameters. Calculations of librational frequencies at the $\mathbf{q} = 0$ point prove the misinterpretation of observed bands in Raman spectrum. It was shown that the ratio $\rho = \tilde{\nu}_H/\tilde{\nu}_D$ for the given librational frequencies cannot be treated as a correct criterion for assignment of the observed bands. Agreement between calculated elastic constants of a biphenyl crystal with experimental values is fairly good. T and L tensors of thermal vibrations could not be compared with experimental values because we lacked experimental data. Within the temperature range from 80 to 340 °K, the specific heat C_v for a biphenyl crystal is the following function of temperature:

$$C_v = 9.790 + 7.684 \times 10^{-2}\, T + 1.357 + 10^{-4}\, T^2 \,[\mathrm{cal} \cdot {}^\circ\mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}]$$

1. Introduction

Lattice dynamics of crystals is one of the important matters in solid state physics. Much interest has recently been devoted to molecular crystals especially to those of organic compounds. Many experimental papers have been published which describe measurements of elastic constants and of lattice vibrations in the centre of the Brillouin zone for that crystal type. An excellent review in this field was given by Venkataraman and Sahni.⁽¹⁾ All the quantities which are known from experiments can be obtained also from theory by solving the problem of lattice dynamics of a given crystal. Therefore, it seems to be of interest to carry out such calculations for crystals especially for those whose many physical properties are known from experimental works. One of those crystals is biphenyl, for which we know many physical properties which are necessary to compare calculations with experiment. That is why it was chosen for calculations.

The basic problem in calculations of lattice dynamics of an organic crystal, is the choice of a proper function of the potential energy. The problem will be discussed more fully in Sec. 3.

As for the method of calculations, it has already been mastered. Pawley's works(2,3) were the pioneer ones in the field. It seems, however, that the method of calculating force constants, used by Pawley, is not adequate. The problem may be solved in a better way. The details are given in Sec. 4.

The following sections describe the results for biphenyl crystal and comparison with the experiment.

A very important and sometimes even a helpful stage in solving the problem of lattice dynamics, is carrying out a full (if possible) group-theoretical analysis of lattice vibrations. The analysis should be carried out before starting the calculations. This is the reason for giving such an analysis for biphenyl crystal in the next section.

2. Group-Theoretical Analysis of Lattice Vibrations

The crystal structure of biphenyl ($C_{12}H_{10}$) is well known from X-ray investigations.(4–6) The crystal is monoclinic (space group $C_{2h}^5 - P2_1/a$) and the unit cell contains two exactly flat biphenyl molecules. Centres of gravity of the molecules occupy lattice sites with the C_i symmetry.

The $P2_1/a$ space group has the following elements of symmetry:

identity $\{E \mid \mathbf{t}\}$
two-fold screw axis $\{C_2^b \mid \mathbf{t}+\mathbf{R}\}$
glide plane $\{\sigma^{ac} \mid \mathbf{t}+\mathbf{R}\}$
inversion $\{I \mid \mathbf{t}\}$
with $\mathbf{t} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ (n_1, n_2, n_3—integers).

$\mathbf{R} = (a/2, b/2, 0)$ is the translation vector related to non-symmorphic elements of the space group.

Figure 1 shows a Brillouin zone for the C_{2h}^5 space group which is the type of a simple monoclinic lattice;(7) the figure also gives points and directions for which group-theoretical analysis will be carried out and dispersion curves will be calculated. In a biphenyl crystal there occur 12 lattice vibrations for each value of the wave vector $\mathbf{q}$.

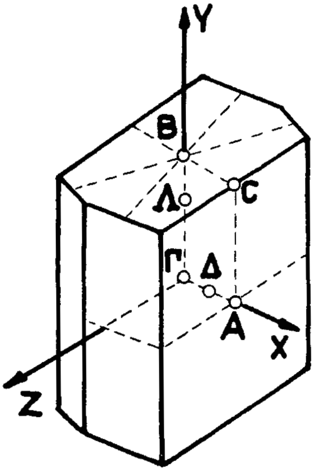

Figure 1. Brillouin zone for the $C_{2h}^5 - P2_1/a$ space group (according to Koster⁽⁷⁾).

Analysis of vibrations was made with the help of a well-known group-theoretical procedure⁽⁸⁾ and of the tables of irreducible representations of space groups in Kovalev's work.⁽⁹⁾

At the point $\mathbf{q} = 0$, wave vector group is isomorphous with a point group C_{2h} which has four irreducible representations (A_g, B_g, A_u, B_u). In the present work irreducible representations of the given wave vector group will be denoted by symbols originating from a symbol of the given point in the Brillouin zone. In the centre of the zone of biphenyl crystal there occur six librational and six translational vibrations. So, according to the symbol given in Fig. 1, librational vibrations possess the following symmetry:

$$3\Gamma_1(A_g) + 3\Gamma_3(B_g)$$

and translational vibrations possess

$$3\Gamma_2(A_u) + 3\Gamma_4(\mathrm{B}_u)$$

symmetry.

At $\Lambda(0, \xi \cdot \pi/b, 0)$ points, the symmetry is reduced and the factor group contains two elements of symmetry: $\{E|\mathbf{t}\}$ and $\{C_2{}^b|\mathbf{t}+\mathbf{R}\}$; it is isomorphous with the C_2 group. There are two vibration types possible in points Λ of the Brillouin zone: a symmetric (Λ_1) and an antisymmetric (Λ_2) with respect to the two-fold screw axis. The group-theory allows the dispersion curves with Λ_1 and Λ_2 symmetries to intersect at Λ points. However, the dispersion curves with the same symmetry would not intersect.

At the $B(0, \pi/2b, 0)$ point which lies on the surface of the Brillouin zone, there occur only double degenerated vibrations of B_1 type (Table 1).

At $\Delta(\xi \cdot \pi/a, 0, 0)$ points there again occur two vibration types: a symmetric (Δ_1) and an antisymmetric (Δ_2), with respect to the glide plane. In those points the factor group contains only two elements: $\{E \mid \mathbf{t}\}$ and $\{\sigma^{ac} \mid \mathbf{t}+\mathbf{R}\}$; it is isomorphous with the C_s group. On the surface of Brillouin zone in the $A(\pi/2a, 0, 0)$ point, six dispersion curves of the Δ_1 symmetry join six dispersion curves of the Δ_2 symmetry. Consequently, they give six double degenerated vibrations of the A_1 type (Table 2).

At the $C(\pi/2a, \pi/2b, 0)$ point the wave vector group possesses four irreducible representations shown in Table 3. Analysis of

Table 1 Irreducible Representation of the Wave Vector Group in the Point B $(0, \pi/2b, 0)$

	$\{E \mid 0\}$	$\{C_2^b \mid \mathbf{R}\}$	$\{I \mid 0\}$	$\{\sigma^{ac} \mid \mathbf{R}\}$
B_1	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\-1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$

Table 2 Irreducible Representation of the Wave Vector Group in the Point A $(\pi/2a, 0, 0)$

	$\{E \mid 0\}$	$\{C_2^b \mid \mathbf{R}\}$	$\{I \mid 0\}$	$\{\sigma^{ac} \mid \mathbf{R}\}$
A_1	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$

Table 3 Irreducible Representations of the Wave Vector Group in the Point C $(\pi/2a, \pi/2b, 0)$

	$\{E \mid 0\}$	$\{C_2^b \mid \mathbf{R}\}$	$\{I \mid 0\}$	$\{\sigma^{ac} \mid \mathbf{R}\}$
C_1	1	1	1	-1
C_2	1	1	-1	1
C_3	1	-1	1	1
C_4	1	-1	-1	-1

vibrations for this point gives consequently the following types of symmetry of 12 lattice vibrations:

$$3C_1 + 3C_2 + 3C_3 + 3C_4.$$

Modes C_1 and C_3 are the vibrations of a purely librational type; those of the C_2 and C_4 types are the vibrations of a purely translational type. Polarization vectors of the librational vibrations in the C point of Brillouin zone will be discussed in Sec. 6.

3. Potential Function

It is generally assumed that a potential of a molecular crystal (in particular of organic crystals) can be expressed as the sum of atom-atom pair interactions of two different molecules:

$$V = \sum_{mn} V_{mn}, \tag{1}$$

where m and n are indices of two kinds of atoms. Potential V_{mn} is so-called " 6-exp " function:

$$V_{mn} = -A_{mn}\sum_{ps} r_{ps}^{-6} + B_{mn}\sum_{ps} \exp(-\alpha_{mn} \times r_{ps}) \tag{2}$$

in which the first term corresponds to attraction energy between atoms (dispersion energy) and the second one, the exponential one, corresponds to repulsion energy resulting from overlapping of electron shells of atoms which belong to two different molecules. A_{mn}, B_{mn} and α_{mn} parameters of the function (2) are usually determined in a semi-empirical way. The criterion of correctness of parameter assembly is the agreement between calculations of the unit cell dimensions and lattice energy of the crystal with experimental values. In such a way Kitaigorodskii(10) and Williams(11) found the parameters for the " 6-exp " function which determines atom-atom pair interactions and, indirectly, intermolecular interactions in hydrocarbon crystals. These parameters were used to calculate lattice dynamics of naphthalene and anthracene crystals.(2) It was proved then that best agreement with the experiment is obtained while using Kitaigorodskii parameters. Generally speaking, however, both parameter sets give a good enough correctness with the experiment on lattice vibrations frequencies in $\mathbf{q} = 0$ and with that on elasticity properties of crystal.

An interesting way of finding parameters of function (2) was introduced by Poltev and Sukhorukov.(12) They calculate parameters of " 6-exp " potential function as follows: A_{mn} constant of dispersion interaction is calculated from the approximate London formula:

$$A_{mn} = \frac{3}{2} \cdot \frac{a_m \cdot a_n \cdot U_m \cdot U_n}{U_m + U_n}, \tag{3}$$

where a_m and a_n are polarizabilities and U_m and U_n are ionization energies of atoms m and n, respectively. α_{mn} and α_{nn} parameters are found from the diagram of parameter dependence on the atomic number.(13) α_{mn} is found from the combination rule:(14)

$$\alpha_{mn} = \tfrac{1}{2}(\alpha_{mm} + \alpha_{nn}). \tag{4}$$

Using the following condition:

$$\left(\frac{\partial V}{\partial r_{ps}}\right)_{r_{ps} = R_{mn}} = 0, \tag{5}$$

where R_{mn} is usually the sum of van der Waals radii of m and n atoms, we can find the value of the third parameter: B_{mn}. Poltev and Sukhorukov's method, described in short, is of much importance because it allows us to find the parameters of potential functions between any atoms, while Kitaigorodskii or Williams parameters concern only interactions in hydrocarbon crystals, e.g. C...C, C...H, H...H.

The " 6-exp " potential function with the parameters calculated from Poltev and Sukhorukov's method, was used to calculate the lattice dynamics of adamantane crystal.(15) Consequently, it gives a good correctness with the experiment. It seemed useful, then, to calculate the lattice dynamics of biphenyl crystal with the help of

(1) Kitaigorodskii parameters—as those which determine best the properties of such crystals as naphthalene and anthracene,
(2) Poltev and Sukhorukov parameters—with the hope that this method of calculation may become useful in further works while calculating the lattice dynamics and properties of crystals whose molecules contain also heteroatoms.

Table 4 gives the parameters of the " 6-exp " potential function which were used while calculating the lattice dynamics of biphenyl.

TABLE 4 Parameters of the "6-exp" Potential Functions: A_{mn} are in erg × Å^6; B_{mn} in ergs; α_{mn} in Å^{-1}

mn	Parameter	after Kitaigorodskii(10)	after Poltev(12)
	$A\times10^{12}$	3.89	2.88
H . . . H	$B\times10^{12}$	2878.3	765.0
	α	4.86	4.54
	$A\times10^{12}$	10.46	8.85
C . . . H	$B\times10^{12}$	2878.3	7551.0
	α	4.12	4.56
	$A\times10^{12}$	24.44	27.20
C . . . C	$B\times10^{12}$	2878.3	90389.0
	α	3.58	4.58

4. Calculations

The $\phi_{ij}(lk, l'k')$ force constants of interactions between a kth molecule in a lth unit cell (lk) and a $(l'k')$ molecule are defined in terms of the energy V of crystal by

$$\phi_{ij}(lk, l'k') = \frac{\partial^2 V}{\partial u_i(lk)\,\partial u_j(l'k')}, \tag{6}$$

where u_i, u_j is one of six components $(u_x, u_y, u_z, u_\alpha, u_\beta, u_\gamma)$ of the displacement vector $\mathbf{u}(lk)$; u_x is the translational displacement of a molecule along the x-axis, u_α is rotational displacement about the x-axis.

Before starting the calculations it is necessary to choose an adequate coordinate system. This problem was discussed in detail by Venkataraman and Sahni.(1) In the case of biphenyl crystal (similarly, in the case of the majority of organic crystals), we will have two Cartesian coordinate systems to be chosen:

(1) coordinate system of the crystal axes: a, b, c^*,
(2) coordinate system of the molecular axes, which coincide with the axes of principal moments of inertia.

The crystal axes system is very convenient while calculating the $\phi(lk, l'k')$ tensor. The only inconvenience is that equations of motion assume very complicated forms (especially, there appear non-diagonal elements of the moment of inertia tensor). If the system of molecular axes is chosen, it gives very complicated formulae for elements of the tensor $\phi(lk, lk)$,⁽¹⁾ but equations of motion have a simple form because the molecular axes coincide with the axes of principal moments of inertia.

The argument shows consequently that the crystal axes system is convenient at the first stage of calculations and that equations of motion should be solved in the molecular axes system. While calculating biphenyl crystal, tensors of force constants were calculated in the crystal axes system: a, b, c^*. The way of calculating force constants was slightly different from that in Pawley's work.⁽²⁾

The program for a digital computer was taken down in the " ODRA-ALGOL " language with the following relations:

$$\frac{\partial^2 V}{\partial u_i(lk)\,\partial u_j(l'k')} = \sum_{mn,ps}\left[\left(\frac{\partial V}{\partial r_{ps}}\right)\left(\frac{\partial^2 r_{ps}}{\partial u_i(lk)\,\partial u_j(l'k')}\right)+\left(\frac{\partial^2 V}{\partial r_{ps}^2}\right)\left(\frac{\partial r_{ps}}{\partial u_i(lk)}\right)\left(\frac{\partial r_{ps}}{\partial u_j(l'k')}\right)\right] \quad (7)$$

Derivatives of distances between atoms in relation to molecular displacements for translational-translational force constants are as follows:

$$\left(\frac{\partial r_{ps}}{\partial u_i(lk)}\right)\left(\frac{\partial r_{ps}}{\partial u_j(l'k')}\right) = -\frac{1}{r^2}\cdot r_i\cdot r_j \quad (8)$$

$$\left(\frac{\partial^2 r_{ps}}{\partial u_i(lk)\,\partial u_j(l'k')}\right) = -\frac{1}{r^3}(\delta_{ij}\cdot r^2 - r_i r_j), \quad (9)$$

for $i, j = 1, 2, 3$. r_i, r_j are the components of the vector of distance between atoms, δ_{ij}—Kronecker delta.

While calculating librational-librational force constants, the formulae derived by Oliver and Walmsley⁽¹⁶⁾ were used:

$$\left(\frac{\partial r_{ps}}{\partial u_i(lk)}\right)\left(\frac{\partial r_{ps}}{\partial u_j(l'k')}\right) = -\frac{1}{r^2}\cdot r_a\cdot r_b\cdot P \quad (10)$$

$$\left(\frac{\partial^2 r_{ps}}{\partial u_i(lk)\,\partial u_j(l'k')}\right) = -\frac{1}{r^3}(\delta_{ab}\cdot r^2 - r_a\cdot r_b)\cdot P, \quad (11)$$

where

$$P = A_{ac}(lk)A_{bd}(l'k')\cdot\epsilon_{cie}\cdot\epsilon_{djf}\cdot\sigma_e(lk)\cdot\sigma_f(l'k') \quad (12)$$

for $a, b, c, d, e, f = 1, 2, 3$ and $i, j = 4, 5, 6$. Substituting A_{ac} by values of direction cosines between the a-axis of the crystal and the c-axis of the molecule, we can calculate librational-librational force constants in the molecular axes system. In our case the matrix of direction cosines was substituted by the unit matrix, which corresponded to rotation of the molecule about the crystal axes. In this way librational-librational force constants were calculated in the crystal axes system. $\sigma_e(lk)$ are the coordinates of the atoms of molecule (lk) in the molecular axes system. ϵ_{cie} is a Levi-Civit antisymmetric tensor.

The formulae of the translational-translational force constants and the librational-librational ones may be obtained by appropriate combination of the relations, given above.

Calculations[†] of the force constants tensor were made for the following pairs of molecules:

$(0, 0, 0) - (\frac{1}{2}, \frac{1}{2}, 0)$; $(0, 0, 0) - (0, 1, 0)$; $(0, 0, 0) - (1, 0, 0)$.

Force constants values for the last pair were about two orders lower than those for the former two so it did not seem important to calculate the tensor for the $(0, 0, 0) - (0, 0, 1)$ pair (as the lattice constant c is greater than a, b constants). Force constants for the remaining pairs of molecules were calculated on the basis of the symmetry relation:

$$\sigma^{ac} \cdot \phi(\tfrac{1}{2}, \tfrac{1}{2}, 0) \cdot \tilde{\sigma}^{ac} = \tilde{\phi}(-\tfrac{1}{2}, \tfrac{1}{2}, 0)$$

$$I \cdot \phi(\tfrac{1}{2}, \tfrac{1}{2}, 0) \cdot \tilde{I} = \phi(-\tfrac{1}{2}, -\tfrac{1}{2}, 0)$$

$$C_2{}^b \cdot \phi(\tfrac{1}{2}, \tfrac{1}{2}, 0) \cdot \tilde{C}_2{}^b = \tilde{\phi}(\tfrac{1}{2}, -\tfrac{1}{2}, 0)$$

Then the components of the tensor $\phi(0, 0, 0)$ were calculated according to the formulae given in (1). The symmetry of the tensor is determined only by the symmetry of lattice site which is C_i in biphenyl crystal. So the tensor contains only translational-translational and librational-librational force constants.

To obtain equations of motion in simple form all tensors of force constants which were calculated in the crystal axes system, $\phi^C(lk, l'k')$, were transformed to the molecular axes system, according to:

$$\phi^M(lk, l'k') = A(lk) \cdot \phi^C(lk, l'k') \cdot \tilde{A}(l'k') \qquad (13)$$

[†] Calculations were made on the ODRA-1204 digital computer in the Computation Centers of the Wrocław Technical University and of the Institute of Physics of the Jagiellonian University in Cracow.

$A(lk)$ is the matrix of direction cosines of the (lk) molecule. The equations of motion of the (lk) molecule with the use of force constants tensors in the molecular axes system will be as follows:

$$m\omega^2(\mathbf{q})U_x(k,\mathbf{q}) = \sum_{k',i} U_i(k',\mathbf{q})M_{xi}(k,k',\mathbf{q})$$

$$I_\alpha\omega^2(\mathbf{q})U_\alpha(k,\mathbf{q}) = \sum_{k',i} U_i(k',\mathbf{q})M_{\alpha i}(k,k',\mathbf{q}) \tag{14}$$

where m is molecular mass, I_α is the moment of inertia of the molecule, and

$$M_{ij}(k,k',\mathbf{q}) = \sum_{l'} \phi_{ij}^{M}(lk,l'k')\exp\{i\mathbf{q}[\mathbf{r}(l'k') - \mathbf{r}(lk)]\}$$

are the elements of the dynamical matrix.

Secular equations of the 12th order for each value of the wave vector $\mathbf{q}$ were solved similarly by Pawley.⁽²⁾ The result in each case was 12 values of lattice vibration frequencies and the corresponding polarization vectors expressed in the molecular axes system. This system of axes is particularly convenient while interpreting librational vibrations.

5. Lattice Vibrations in $\mathbf{q}=0$ point

It results from the group-theoretical analysis of lattice vibrations in $\mathbf{q} = 0$ that there occur six librational and six translational vibrations in the point. The fact that biphenyl molecules occupy the sites with the C_i symmetry in the crystal, causes librational vibrations to occur independently on translational vibrations. It points to a lack of translational–librational couplings, which consequently causes considerably simpler calculation of the lattice vibrations in the center of the Brillouin zone.

(A) LIBRATIONAL VIBRATIONS

In order to find the frequencies of six librational modes it is necessary to solve the 6×6 dynamical matrix which is real and contains only the elements dependent on librational-librational couplings. The calculations were made using two parameter sets of potential function for a biphenyl structure at 290 °K. We should, of course, be sure that the structure corresponds really to an equilibrium. For this purpose the lattice energy has been expressed in terms of a, b, c, β and Eulerian angles ψ, θ, η as parameters. The differences for parameter values for which V has a minimum and parameter values known from the X-ray structure amounted to about 0.2 Å for the length of axes and 2° for angles. Such discrepancies are comparable with standard deviations in positions of hydrogen atoms ($\sigma = 0.12$ Å(5)) and, therefore, it can be assumed that the crystal structure corresponds to a real equilibrium.

It is usually assumed that the librations of molecules are executed about the axes of the principal moments of inertia. This assumption, however, is not always correct. For example, the calculations made for naphthalene(2,17) prove that antisymmetrical librational vibrations occur about the axes which differ from the axes of the moment of inertia even by 30°. This also occurs in a biphenyl crystal when proved by the polarization vectors which were normalized to one molecule in the axes system U, V, W. The U, V, W axes correspond respectively to the less, medium and the greatest moments of inertia of a biphenyl molecule. The vectors are given in Table 5 together with calculated values of librational vibration frequencies. The frequency values which were obtained by means of the two parameter sets are different. It is to be noted that Poltev and Sukhorukov parameters give worse results. That was the reason for carrying out the further calculations with Kitaigorodskii parameters only.

In particular, the frequencies for $\mathbf{q} = 0$ were calculated for biphenyl crystal at 77 °K, assuming that molecular orientation in the crystal does not change while the temperature is being lowered. The assumption makes a good approximation in hydrocarbon crystals. The investigations of structures at low temperatures(18,19) prove that when the temperature is lowered by about 200 °K molecular orientation changes only within the limit of 1–2°. The unit cell parameters at 77 °K are known(20): $a = 7.906$, $b = 5.601$, $c = 9.436$ Å, $\beta = 96.48° \pm 10'$. As the temperature is lowered, the unit cell dimensions do somewhat change but these changes do not exceed the experimental standard deviations concerning the positions of hydrogen atoms. Therefore, it is believed that at 77 °K the structure corresponds also to an equilibrium.

TABLE 5 Calculated Frequencies (in cm^{-1}) and Polarization Vectors of the Librational Vibrations in the Biphenyl Crystal at $\mathbf{q} = 0$

Type of vibration	Kitaigorodskii's parameters used								Poltev's parameters used			
	290°K				77°K				290°K			
	$\tilde{\nu}$	U	V	W	$\tilde{\nu}$	U	V	W	$\tilde{\nu}$	U	V	W
	18.5	−0.4088	0.7803	0.4731	21.5	−0.3618	0.8534	0.3749	12.0	−0.4426	0.7754	0.4501
$\Gamma_1(A_g)$	44.5	0.0072	−0.5134	0.8575	50.0	−0.0368	−0.4152	0.9090	41.0	0.0401	−0.4840	0.8738
	72.0	0.9131	0.3542	0.2044	79.5	0.9314	0.3149	0.1820	63.5	0.8959	0.4050	0.1831
	19.0	−0.0124	−0.5079	0.8616	19.5	−0.0357	0.4762	−0.8783	13.0	0.1380	−0.4913	0.8602
$\Gamma_3(B_g)$	49.0	−0.9906	−0.1104	−0.0800	62.0	−0.9686	−0.2329	−0.0865	34.0	−0.9865	−0.1424	0.0769
	70.0	0.1357	−0.8551	−0.5000	83.0	−0.2459	0.8478	0.4697	59.0	0.0848	−0.8593	−0.5042

TABLE 6 Comparison of Calculated (with Kitaigorodskii parameters used) and Experimental Frequencies (in cm^{-1}) of Librational Vibrations in the Biphenyl Crystal

290°K							Assignment of vibrations		77°K					
Experiment(25)			Calculations						Experiment(25)			Calculations		
$C_{12}H_{10}$	$C_{12}D_{10}$	ρ(a)	$C_{12}H_{10}$	$C_{12}D_{10}$	ρ(a)	$(I_D/I_H)^{1/2}$	This work	Ref. 25	$C_{12}H_{10}$	$C_{12}D_{10}$	ρ(a)	$C_{12}H_{10}$	$C_{12}D_{10}$	ρ(a)
	26.5		19.0	16.5	1.15	1.06	$\sim W^a\ B_g$	$W^s\ A_g$		31		19.5	18.0	1.08
41.6	39.5	1.05	18.5	19.0	1.00	1.05	$\sim V^s\ A_g$	$W^a\ B_g$	43.5	41	1.06	21.5	20.0	1.07
			44.5	41.5	1.07	1.06	$\sim W^s\ A_g$	$V^s\ A_g$	65(b)	62	1.05	50.0	47.0	1.06
53.5	51.5	1.04												
			49.0	44.5	1.10	1.10	$\sim U^a\ B_g$	$V^a\ B_g$	71(b)	66.5	1.07	62.0	56.5	1.10
88	79.5	1.10	72.0	65.0	1.11	1.10	$\sim U^s\ A_g$	$U^s\ A_g$	105	96.5	1.09	79.5	73.0	1.09
	84	1.05(c)	70.0	67.0	1.05	1.05	$\sim V^a\ B_g$	$U^a\ B_g$	115	108	1.06	83.0	79.0	1.05

Numerical values from Ref. 24 (c) Value obtained assuming $\tilde{\nu}_H = 88$ cm^{-1}.

It was possible to calculate librational frequencies at that temperature. The results shown in Table 5 prove that symmetrical librations (Γ_1) at a low temperature occur about the axes closer to the axes of the moments of inertia while antisymmetrical librations (Γ_3) are executed about the axes which are farther from the molecule axes. However, the differences are slight.

On the basis of value of polarization vectors it is to be noted in general that a strong mixing occurs of librational vibrations in a biphenyl crystal. Librational vibrations about an axis close to the long axis (U) of a molecule are, comparatively, the least " mixed ". The same is true in naphthalene(2,17) where the smallest " mixing " of vibrations occurs for the librations an axis close to the long axis of molecule with the lowest moment of inertia. Librational frequencies in a biphenyl crystal were investigated by Raman scattering experiments in Refs. 21–25. The following frequencies for 290 °K were obtained:

acc. (21): 42, 55, 85, 91 cm^{-1}
acc. (22): 24, 42.5, 55, 82, 91 cm^{-1}
acc. (23): 41, 53, 89 cm^{-1}
acc. (24): 42, 54, 88 cm^{-1}
acc. (25): 41.6, 53.5, 88 cm^{-1}.

The calculation results will be compared with experimental values which were obtained in the last two works as the papers also give the assignments of the observed frequencies. It is to be noted however, that the experiments were carried out starting at 25 cm^{-1} so that the 24 cm^{-1} frequency which was found in Ref. 22 might have passed unobserved in the remaining works. Table 6 shows that such a possibility exists.

It can be seen from Table 6 that the calculated highest and lowest frequencies are smaller than the experimental values. It seems that it can be caused by a strong coupling between librational vibrations and the intramolecular torsional vibrations whose frequencies occur within the range of lattice vibrations.(26,27) In particular, strong influence will be caused by the torsional vibrations with 63 and 74 m^{-1} frequencies.(25) The scheme of vibration is shown in Fig. 2. Torsional vibrations are supposed to have greatest influence on vibrational frequencies which are executed about an axis close to

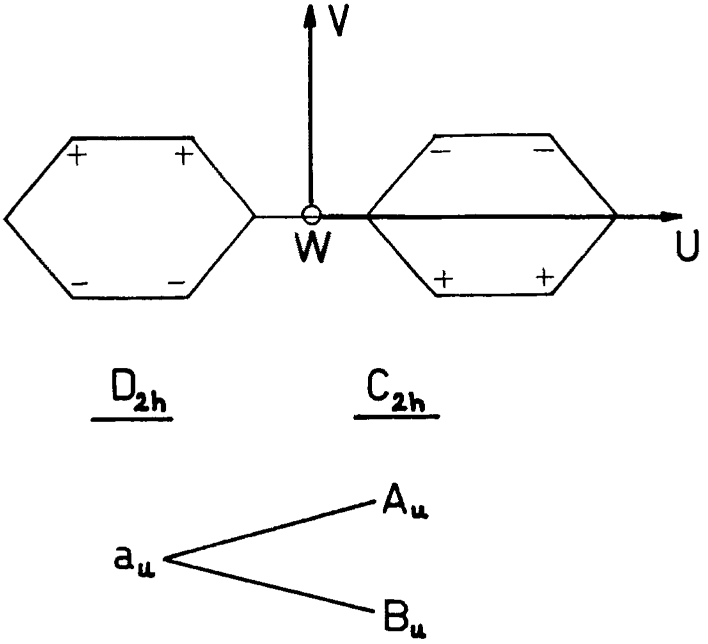

Figure 2. Torsional vibration of the biphenyl molecule in crystal and its symmetries.

the long axis of the molecule. This is a reason why the calculated frequencies for librations about the *U* axis are lower than experimental ones.

It is a very complicated matter to take into consideration the intramolecular torsional vibrations while calculating the lattice dynamics of biphenyl. It would require the knowledge of the potential function, which includes both interaction between hydrogen atoms in the ortho position and π-electronic interaction as well. As a matter of fact, such a function for a free biphenyl molecule was suggested(28); however, its application in crystal calculations would be a difficult matter. On the other hand the free state of the molecule is not flat and it would be very difficult, if not impossible, to introduce the internal modes of such a molecule into the calculation using the method of Pawley and Cyvin,(30) for example.

In Table 6 assignment of librational vibrations are designated by the types of symmetry which are characteristic for the C_{2h} point group, and by the symbols which determine the types of vibrations (antisymmetrical—*a*, symmetrical—*s*) executed about axes close to one of *U*, *V*, *W* axes of the molecule.

As for the interpretation of individual bands, it seems to be slightly incorrect. The fact that in the major part of the experiments one band is observed at 88 cm^{-1} at 290 °K does not result from the fact of a small splitting of symmetrical and antisymmetrical vibrations about the same *U* axis as was suggested by Ito and his coworkers,⁽²⁴⁾ but from the fact that the frequencies of $\sim U^s$ and $\sim V^a$ vibrations are very near. The experimental resolution usually amounts to 2–3 cm^{-1}, so it is possible to observe only a single slightly broadened band.⁽²⁴⁾ Therefore, it cannot be interpreted as two vibrations about the same axis. This is supported by comparison of the experimental and the calculated values of the ratio $\rho = \tilde{\nu}_H/\tilde{\nu}_D$, both for 290 °K and 77 °K temperatures.

Librational vibration frequencies for a deuterated biphenyl were calculated in the following way: the dynamical matrix was constructed with the use of force constant tensors for $C_{12}H_{10}$, substituting values of moments of inertia for $C_{12}D_{10}$. Then diagonalization of the dynamical matrix was carried out. In this case it was proved that librational vibrations do not occur about the molecular axes. That is the reason why the frequency ratio $\rho = \tilde{\nu}_H/\tilde{\nu}_D$ is not equal to the factor $(I_D/I_H)^{1/2}$. Differences between the factors are greater the more the axis, about which the libration occurs, differs from the axis of the inertia moment. That is why the ratio $\rho = \tilde{\nu}_H/\tilde{\nu}_D$ should not be regarded as a criterion of assignments of librational vibrations, as is usually assumed in experimental works.

(B) OPTICAL TRANSLATIONAL VIBRATIONS

For optical translational vibrations the group theory provides the following types of symmetry: $2A_u + B_u$. As for the polarization vectors of those vibrations, the group theory provides direction of the B_u type vibration only (parallel, to the *b* axis of a crystal); polarization vectors of two A_u vibrations should lie in the (010) plane. Vector directions of these vibrations are not determined from group-theoretical analysis. Table 7 gives frequencies of optical translational vibrations which were calculated using two parameter sets. It also gives polarization vectors which were calculated in the *a*, *b*, *c** axes system. It is to be noted that calculations carried out

TABLE 7 Calculated Frequencies (in cm^{-1}) and Polarization Vectors of the Optical Translational Vibrations in the Biphenyl Crystal

Type of vibrations	Kitaigorodskii parameters								Poltev parameters			
	290°K				77°K				290°K			
	$\tilde{\nu}$	a	b	c^*	$\tilde{\nu}$	a	b	c^*	$\tilde{\nu}$	a	b	c^*
$\Gamma_2(A_u)$	26.0	0.3171	0	0.9480	23.0	0.3102	0	0.9470	25.0	0.3449	0	0.9385
$\Gamma_4(B_u)$	61.0	0	1	0	68.5	0	1	0	58.5	0	1	0
$\Gamma_2(A_u)$	96.5	0.9480	0	−0.3171	110.0	0.9470	0	−0.3202	88.5	0.9385	0	−0.3449

TABLE 8 Comparison of Calculated (with Kitaigorodskii parameters used) and Experimental Frequencies (in cm^{-1}) of Optical Translational Vibrations in the Biphenyl Crystal

Type of vibrations	290°K					77°K			
	Experiment			Calculations		Experiment		Calculations	
	$C_{12}H_{10}$[25]	$C_{12}H_{10}$[29]	$C_{12}D_{10}$[25]	$C_{12}H_{10}$	$C_{12}D_{10}$	$C_{12}H_{10}$[25]	$C_{12}D_{10}$[25]	$C_{12}H_{10}$	$C_{12}D_{10}$
A_u	38	31 37		26.0	25.0	39		29.0	28.0
B_u				61.0	60.0			68.5	66.5
A_u	91	90 94	88	96.5	94.0	103	99	110.0	106.0

with Poltev and Sukhorukov method, result in frequencies which are similar to those obtained with Kitaigorodskii parameters. Table 8 gives the comparison of calculation and experimental frequencies. Besides, polarization vectors calculated with various parameters, differ slightly. Measurements of the absorption spectrum of biphenyl crystal in the far infrared region were published in Refs. 25, 29. In Ref. 29 there were observed four absorption bands from which only two (probably 37 and 90 cm^{-1}) originate from optical translational vibrations. Within the range of 30–100 cm^{-1} frequencies we can also observe one absorption band for $C_{12}H_{10}$ and two bands for $C_{12}D_{10}$ which originate from the A_u and B_u components of the torsional vibration of biphenyl molecule (Davydov splitting, Fig. 2). The vibrations can be found within the range of 60–70 cm^{-1}, which causes the lack of a separate band originating from translational vibration B_u for which the theory provides frequency about 60 cm^{-1} (Table 8).

It is possible to state that within the range of optical translational vibrations the theory agrees with the experiment fairly well. This happens for both parameter sets of the potential function of crystal, which are used while calculating. Agreement with the experiment should probably be interpreted in the following way: intramolecular torsional vibration of biphenyl molecule of a type schematically shown in Fig. 2, does not couple with optical translational vibrations. That means that assumption of biphenyl molecule rigidity, which was assumed for calculating, is satisfied within the range of translational vibrations.

6. The Dispersion Curves

Calculations of the dispersion curves were made with the help of Kitaigorodskii parameters for three directions: [010], [100] and [110]. The results for 290 °K are shown in Figs. 3, 4 and 5. The figures also show types of symmetry anticipated from group-theoretical analysis. For all three directions of the **q** vector, there occurs strong mixing of translational and librational vibrations and the dispersion curves change their character as the wave vector **q** increases.

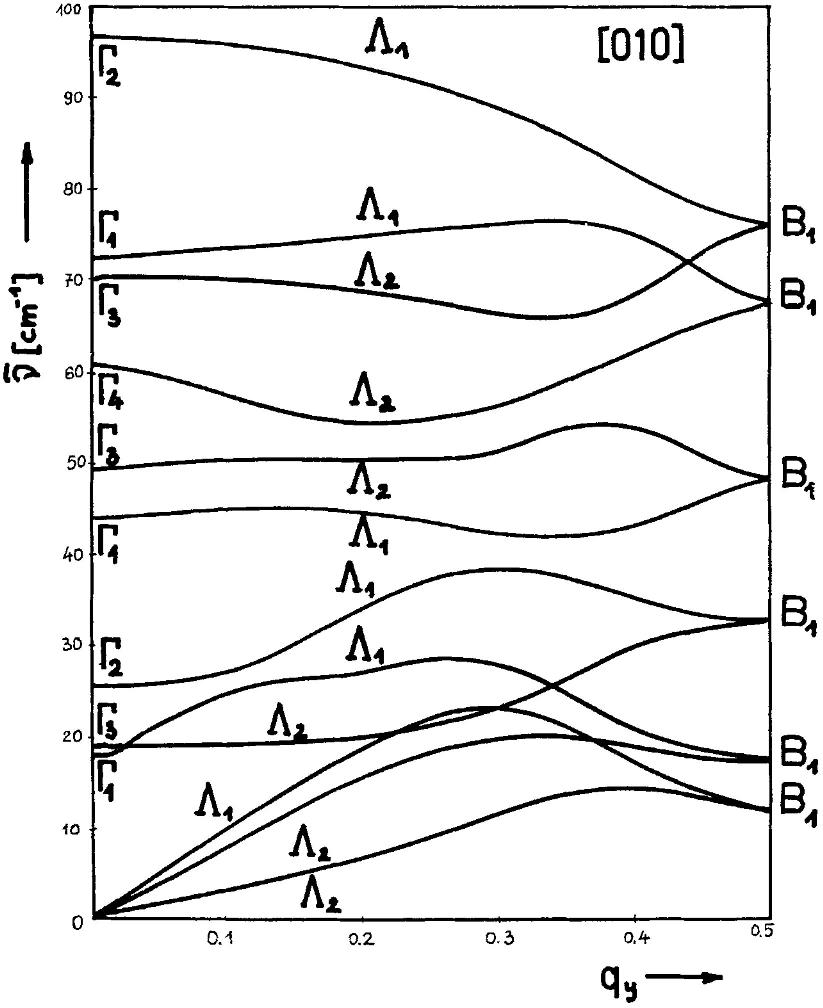

Figure 3. Calculated dispersion curves for biphenyl in the [010] direction.

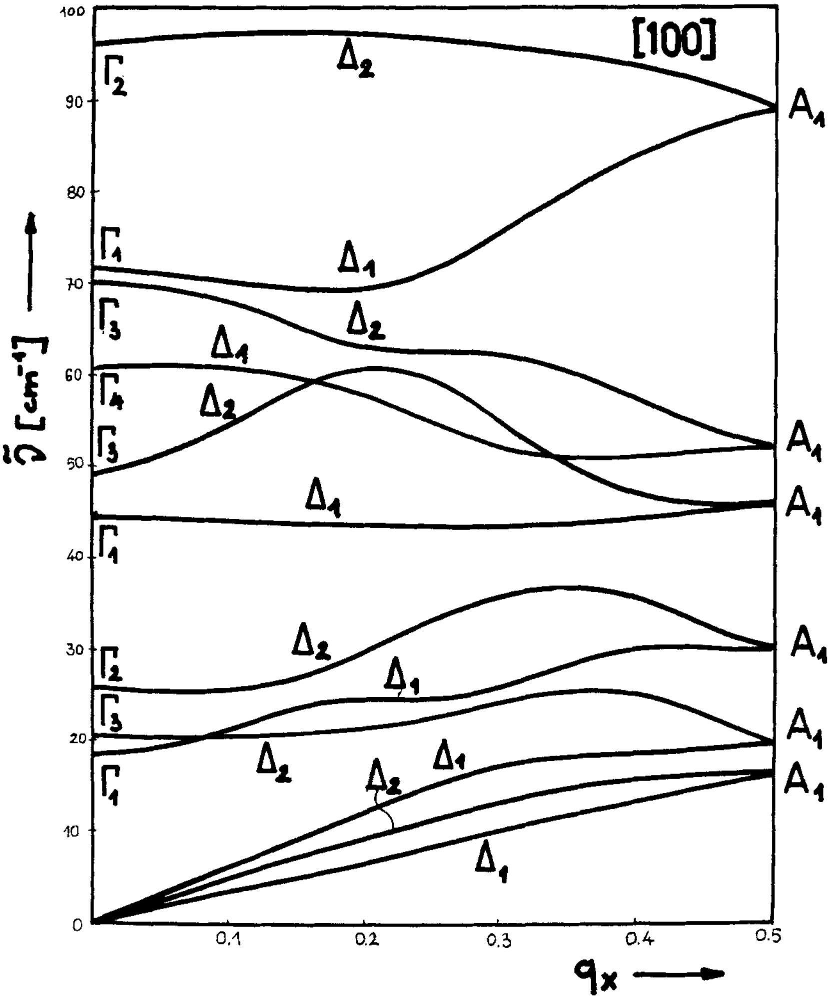

Figure 4. Calculated dispersion curves for biphenyl in the [100] direction.

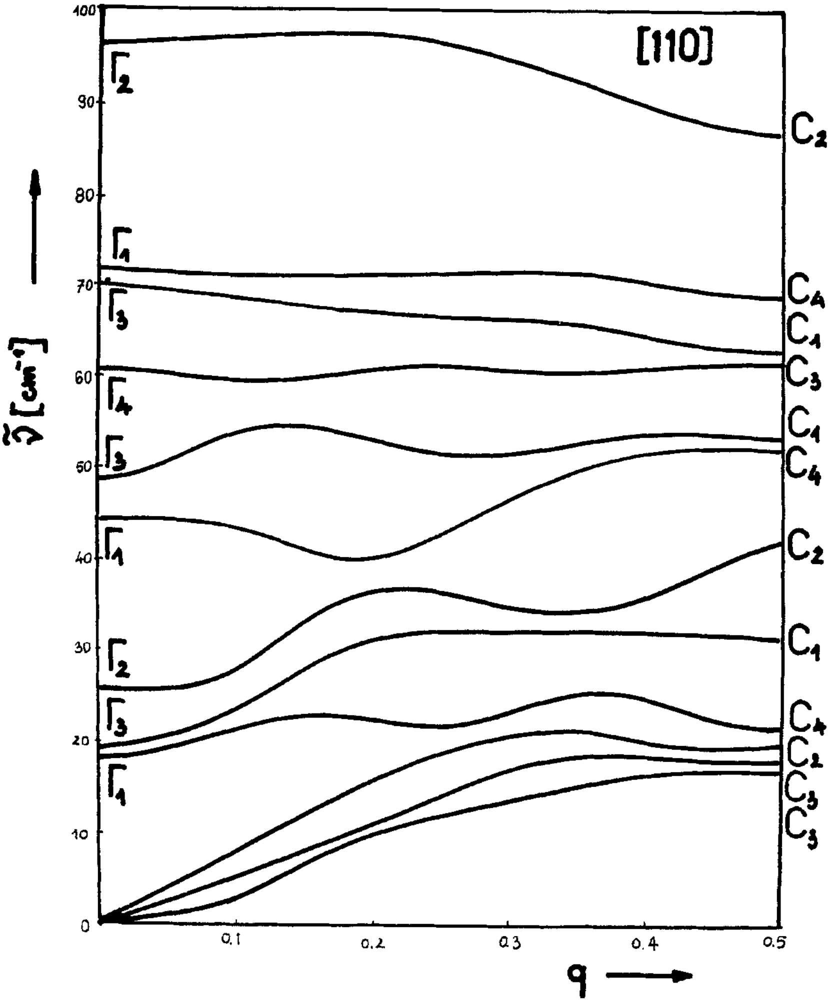

Figure 5. Calculated dispersion curves for biphenyl in the [110] direction.

The degenerate vibrations of the A_1 and B_1 type on the surface of Brillouin zone are also of a mixed translational–librational type. As for the $(\pi/2a, \pi/2b, 0)$ point, the vibrations which occur there are purely translational and librational ones. Purely librational vibrations in that point are different from those in the center of the Brillouin zone as for the behaviour of both molecules in the unit cell of a biphenyl crystal. It is clearly shown in Table 9 which shows the examples of chosen polarization vectors of vibrations $\Gamma_1(A_g)$ and $\Gamma_3(B_g)$ in $\mathbf{q} = 0$ as well as C_1 and C_3 in the $(\pi/2a, \pi/2b, 0)$ point.

TABLE 9 Comparison of Polarization Vectors of the Librational Vibrations in $=\mathbf{q}\,(0, 0, 0)$ and $\mathbf{q} = (\pi/2a, \pi/2b, 0)$ Points

Molecule	Axis	$\mathbf{q} = (0, 0, 0)$		$\mathbf{q} = (\pi/2a, \pi/2b, 0)$	
		$\Gamma_1(A_g)$	$\Gamma_3(B_g)$	C_1	C_3
1	U	0.6452	-0.7005	0.1292	-0.7725
	V	0.2505	-0.0781	0.0307	0.2966
	W	0.1445	-0.0566	0.5425	0.0580
2	U	0.6452	0.7005	0.7725	0.1293
	V	0.2505	0.0781	-0.2966	0.0305
	W	0.1445	0.0566	-0.0582	0.5425

The best way of checking the calculated dispersion curves would be that of carrying out measurements of inelastic neutron scattering on a deuterated biphenyl single crystal. Carrying out the experiment, however, would cause some difficulties at present and for that reason we must concentrate on the spectrum of inelastic incoherent neutron scattering on a biphenyl polycrystalline sample. Such an experiment was carried out by Krebs and Sandroni(27) who presented the result as the dependence of the number of neutrons per channel, on frequency. Such a spectrum is a complicated function of the spectrum of the frequency distribution $g(\omega)$ because it contains two-phonon transitions and it depends on polarization vectors. Polarization vectors influence the spectrum intensity.(31) In this respect the comparison of calculated $g(\omega)$ function to the spectrum obtained from experiments may concern only the peak positions.(31) Frequency distribution function was calculated on the basis of the dispersion curves from 300 points in the Brillouin zone. Figure 6 shows the $g(\omega)$ function as a histogram; the arrows point out the maximum positions in the experimental spectrum. Agreement between maximum positions is satisfactory enough.

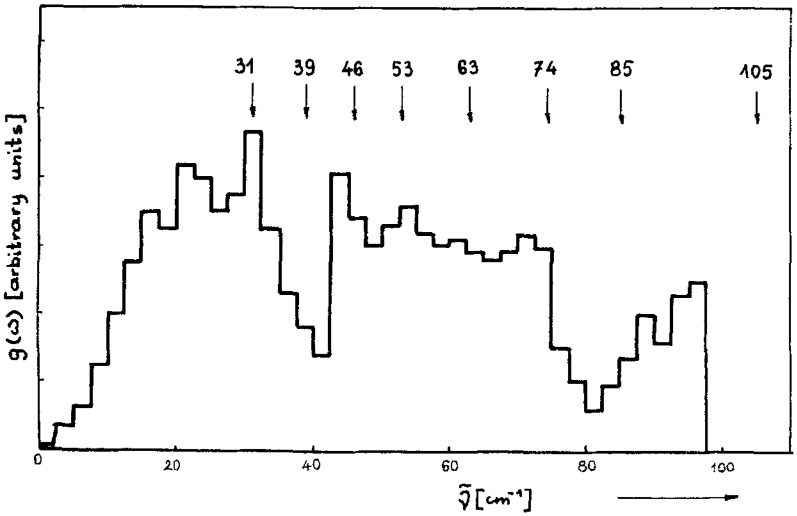

Figure 6. Calculated frequency distribution function in the histogram form. The arrows indicate the position of peaks in the experimental function $g(\omega)$.(27)

If we know the polarization vectors of lattice vibrations, it is possible to calculate mean square amplitudes of translational (T_{ij}) and librational (L_{ij}) vibrations, according to the formulae given by Pawley(2):

$$T_{ij} = \sum_{\substack{12N \\ \text{modes}}} \frac{\xi_i \xi_j + \xi_{i+6}\xi_{j+S}}{2Nm\omega^2} \cdot \epsilon(\omega) \tag{16}$$

$$L_{ij} = \sum_{\substack{12N \\ \text{modes}}} \frac{\xi_{i+3}\xi_{j+3} + \xi_{i+9}\xi_{j+9}}{2N\sqrt{I_i \cdot I_j}\,\omega^2} \cdot \epsilon(\omega) \tag{17}$$

ξ_i is the ith component of polarization vector in the molecule axes system. The vector corresponds to the lattice frequency ω and $\epsilon(\omega)$ is the mean energy of normal vibration:

$$\epsilon(\omega) = \hbar\omega\left[\frac{1}{2} + \left(\exp\left\{\frac{\hbar\omega}{kT}\right\} - 1\right)^{-1}\right] \tag{18}$$

Tensor values in the molecule axes system, which were obtained from calculations are as follows:

$$T = \begin{bmatrix} 4.28 & 0.02 & 0.06 \\ & 3.86 & -0.32 \\ & & 3.16 \end{bmatrix} \times 10^{-2}\,\text{Å}^2$$

$$L = \begin{bmatrix} 30.6 & 3.2 & 1.4 \\ & 12.5 & 5.3 \\ & & 21.3 \end{bmatrix} \text{deg}^2$$

Comparatively great values of the off-diagonal elements L_{12} and L_{23} result from the fact that librational vibrations do not occur exactly about the principal axes of the moments of inertia. Unfortunately, there are no data concerning the values of the amplitudes of thermal vibrations which are usually obtained from X-ray methods. Then the values T and L cannot be compared to experimental values.

With the knowledge of the values of librational vibration frequencies (ν_1—a symmetrical one and ν_2—an antisymmetrical one) in $\mathbf{q} = 0$, it is possible to calculate the L_{ii} elements according to the formula:

$$L_{ii} = \frac{h}{8\pi^2 I_i}\left\{\frac{1}{2\nu_1}\coth\left(\frac{h\nu_1}{2kT}\right) + \frac{1}{2\nu_2}\coth\left(\frac{h\nu_2}{2kT}\right)\right\} \tag{19}$$

Such calculations were carried out by Ito and his coworkers(24) and the results were as follows: $L_{11} = 20$, $L_{22} = 9$, $L_{33} = 13$ deg^2 (the results were taken from diagram(24)). However, these values can hardly be compared to the values in the present paper for the following reason. Formula (19) is right only when librational vibrations occur about the axes of the moment of inertia and when the librational modes are flat. These conditions are not fulfilled in a biphenyl crystal.

7. The Elastic Constants

Propagation velocities of an acoustic wave were calculated on the basis of the course of the dispersion curves for acoustic vibrations in the proximity of $\mathbf{q} = 0$. The calculated values were compared to corresponding experimental values(32) in Table 10. The comparison was drawn only for nine values as calculations for the dispersion curves were carried out for three directions of a wave vector. This

TABLE 10 Acoustic Mode Velocities (in 10^5 cm/s)

Wave vector direction	[010]			[100]			[110]		
Calculations	3.04	1.18	2.36	2.68	1.95	1.57	2.49	0.85	1.53
Experiment(32)	2.50	1.28	1.90	2.32	1.91	1.40	2.90	1.04	1.32

was the reason for calculating the next nine out of thirteen independent components of the elasticity tensor, by means of solving the secular equation(33):

$$\begin{vmatrix} M_{11}-\rho\nu^2 & M_{12} & M_{13} \\ M_{21} & M_{22}-\rho\nu^2 & M_{23} \\ M_{31} & M_{32} & M_{33}-\rho\nu^2 \end{vmatrix} = 0 \qquad (20)$$

where ρ is the crystal density. Because the component $q_3 = 0$, for all the directions of the wave vector which have been considered in the present work, the elements of Eq. (20) are as follows:

$$\begin{aligned} M_{11} &= c_{11}q_1^2 + c_{66}q_2^2 \\ M_{12} &= (c_{66}+c_{12})q_1q_2 = M_{21} \\ M_{13} &= c_{15}q_1^2 + c_{46}q_2^2 = M_{31} \\ M_{22} &= c_{66}q_1^2 + c_{22}q_2^2 \\ M_{23} &= (c_{25}+c_{46})q_1q_2 = M_{32} \\ M_{33} &= c_{55}q_1^2 + c_{44}q_2^2. \end{aligned}$$

Table 11 gives the comparison of the calculated and experimental(32) values of elastic constants. Taking into consideration a good agreement between experimental and calculated velocities it can be stated that the proposed model anticipates elastic properties of biphenyl crystal well enough.

TABLE 11 Elastic Stiffness Constants (in 10^{10} dyn cm^2)

c_{ij}	c_{11}	c_{22}	c_{44}	c_{55}	c_{66}	c_{12}	c_{25}	c_{15}	c_{46}
Calculations	7.42	10.2	3.06	5.05	4.18	3.12	1.80	1.56	0.54
Experiment(32)	5.95	6.97	1.83	2.26	4.11	4.05	0.94	0.40	−0.89

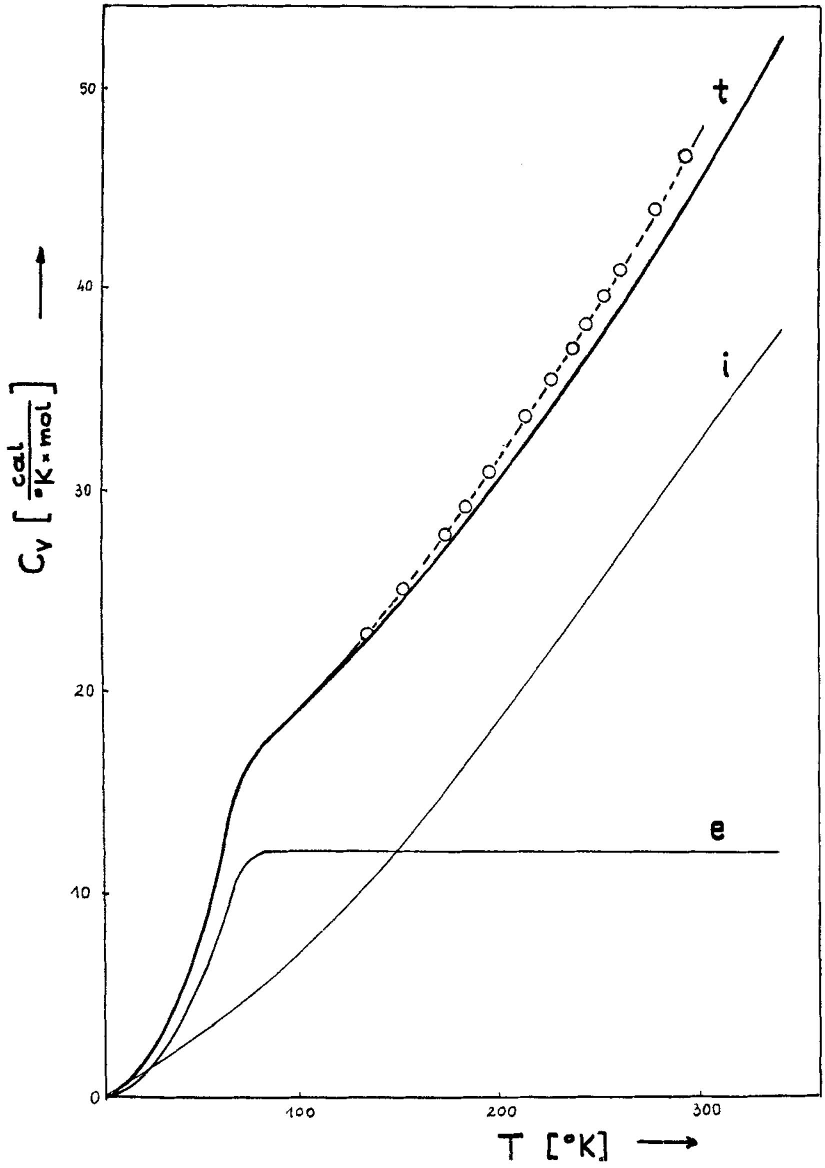

Figure 7. A set of specific heat–temperature curves for a biphenyl crystal illustrating the contribution of various vibrations to C_v. Curve *e*: lattice modes only, curve *i*: internal modes only, *t*: total. – – ○ – – dashed curve indicate experimental function of C_p, according to Ref. 35.

8. The Specific Heat of Biphenyl Crystal

The specific heat of a biphenyl crystal, C_v, was calculated according to:

$$C_v = \sum_{i=1}^{60} \frac{\hbar^2\omega_i^2}{kT^2} \cdot \frac{\exp(-\hbar\omega_i/kT)}{[\exp(-\hbar\omega_i/kT)-1]^2} + \frac{1}{kT^2}\int_0^\infty \frac{\hbar^2\omega^2 \exp(-\hbar\omega/kT)}{[\exp(-\hbar\omega/kT)-1]^2} \cdot g(\omega)\,\mathrm{d}\omega. \tag{21}$$

The first term expresses the contribution of intramolecular vibrations which were treated as Einstein oscillators to a total C_v; the second one—lattice vibrations contribution to a total C_v. The frequencies were taken from Ref. 34. Figure 7 shows the temperature dependence of C_v and experimental results of C_p.(35) Within the temperature range from 80 to 340 °K, calculated C_v for a biphenyl crystal is a function of temperature:

$$C_v = 9.790 + 7.684 \times 10^{-2}\,T + 1.357 \times 10^{-4}\,T^2 [\mathrm{cal} \cdot {}^\circ\mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}].$$

Values of the specific heat at a constant pressure, C_p, may be calculated in two ways:

(i) from the solid state equation:

$$C_p - C_v = \frac{\alpha^2 \cdot V_0}{\beta} \cdot T \tag{22}$$

(ii) or from an empirical relation given by Lord *et al.*(36):

$$C_p - C_v = a \cdot T \cdot C_v^2 \tag{23}$$

Equation (22) cannot be used here because β is temperature dependent but the exact form of this dependence is not known for biphenyl. However, an excellent agreement with experimental values can be achieved in the whole temperature range (90 to 300 °K) using Eq. (23) with $a = 3.71 \times 10^{-6}$ [mol · cal^{-1}].

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