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Vibrational calculations on the biphenyl crystal: The mixing between low frequency internal and lattice modes

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The low frequency optically active crystal vibrations of biphenyl have been calculated using atom–atom interaction potentials. The agreement with experimental data is good. It has been found that torsional and translational modes are very strongly coupled. The conformational change of the biphenyl molecule from gaseous to crystal state and the corresponding changes in the internal force field are discussed. Some assignments are reexamined taking into account the calculated results. The heat of sublimation is well reproduced from internal energy calculations.

INTRODUCTION

Molecular crystals are characterized by the occurrence of molecular species in the lattice. Usually, the forces acting among the atoms in a given molecule are much stronger than those among atoms of different molecules. As a consequence, molecules are almost negligibly distorted upon crystallization, and internal and external vibrations can be conveniently separated. The biphenyl crystal constitutes a very interesting exception to this general rule: although the above statements are true for each phenyl group, some of the forces relating them are of the same order as intermolecular ones. Gaseous biphenyl is nonplanar, and has D_2 symmetry; the two phenyl groups are rotated approximately 42° about their common bond.[1,2] The torsional barrier has been calculated by several methods, and its height estimated in about 2 kcal/mol.[2–7] On the other hand, crystalline biphenyl is monoclinic,[8,9] space group $C_{2h}^5\,(P2_1/a)$, and the molecules, located at C_i sites, are quasiplanar. This conformational change implies that intermolecular forces overcome the internal torsional field. Also, all vibrational normal modes resulting from the relative motion of the phenyl groups have to be essentially different from gaseous to solid state. It is therefore possible to expect an important frequency shift, and an appreciable mixture of at least some of these modes with crystal lattice normal modes. As each of the phenyl groups is only very slightly distorted in the crystal, normal modes associated with internal phenyl motions are to be expected to be almost unperturbed. The much higher frequency of these vibrations, on the other hand, indicates that they will be weakly coupled with interphenyl and external modes.

In the present work, we have applied the nonbonded atom–atom interaction model to the study of the low frequency vibration modes of biphenyl. This model has been applied with success to a large number of hydrocarbons, and is at the present time the most reliable semiempirical description of intermolecular forces in these systems. Our attention has been focused on the intermode mixing among internal and external vibrations, for which biphenyl is an ideal system. Also, our calculated results suggest possible modifications to some of the assignments, which are compatible with the experimental evidence.

LOW FREQUENCY NORMAL MODES

Description

The internal normal modes of biphenyl can be separated into two different types of vibrations. The intraphenyl modes, in the medium and high frequency region, are built up from in- and out-of-phase vibrations of the phenyl groups. The interphenyl modes stem from relative rotation and translation motions of the phenyl groups, and fall in the low frequency region. The separation is, of course, only approximate, and is mainly justified by the energy separation of the two groups of normal modes. In the crystal, the biphenyl molecules are almost planar, possessing D_{2h} pseudosymmetry.[10–14] Under that symmetry, each of the six interphenyl normal modes falls into a different symmetry species, and therefore normal and symmetry coordinates coincide in the rigid phenyl approximation. Zerbi and Sandroni[10] have performed a normal coordinate calculation for the in-plane modes, but no complete force field for biphenyl is available. In the present work we are interested in the low-lying interphenyl and lattice vibrations, for which a complete description is possible. It is to be noted that the Cartesian displacements obtained in the rigid phenyl approximation for in-plane modes are very close to those obtained by Zerbi and Sandroni, who allowed interaction with higher frequency modes, thus justifying our approach.

Table I summarizes the description of the six internal modes under consideration, their relation with rotation–translation coordinates of the phenyl groups, and the expected isotopic frequency ratio, ν_H/ν_D, for $C_{12}H_{10}$ and $C_{12}D_{10}$.

Table II shows the correlation between the six phenyl group rotation and translation coordinates, the 12 resulting molecular coordinates (including the six rigid molecule rotations and translations), and the 24 crystal normal modes.

Experimental data

The biphenyl crystal has been the object of several experimental investigations: Polarized Raman and infrared spectra at room temperature are available, and the low temperature behavior of the Raman bands has been investigated in polycrystalline samples.

TABLE I. Relation of the six interphenyl modes of planar biphenyl with phenyl rotation and translation coordinates, and corresponding isotopic ratios. M—molecular mass; I_k—molecular moment of inertia about the kth principal axis; D—distance from the phenyl center of mass to the center of the molecule; r_{kI}, r_{kII}, t_{kI}, t_{kII}: rotations and translations of phenyl groups I and II about the kth axis.

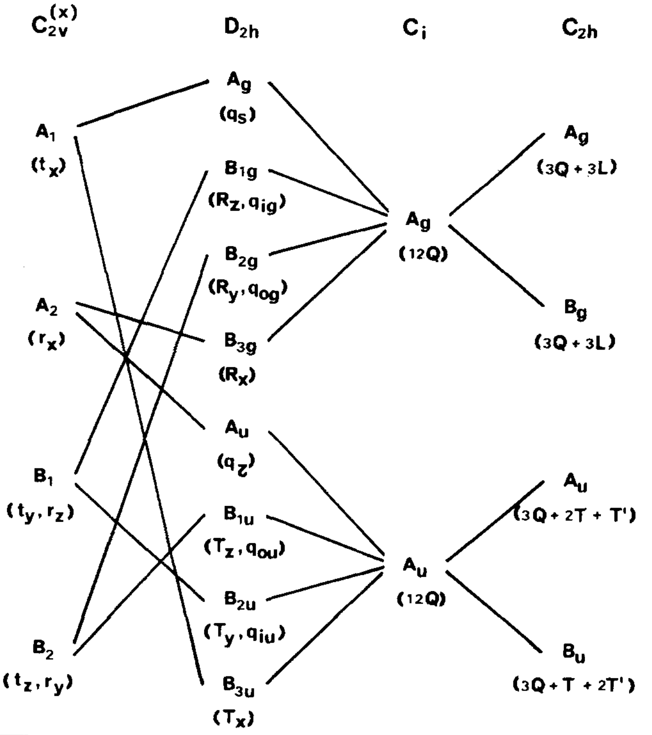
Molecular mode	Description	Relation with phenyl rotations and translations	Isotopic ratios
$\nu_{11}(A_g)$	q_s—phenyl–phenyl stretching	$\sqrt{M/4}\ (t_{xII}-t_{xI})$	$\sqrt{M_D/M_H}$
$\nu_{10}(B_{1g})$	q_{ig}—in-plane bending	$\sqrt{\frac{M(I_z-MD^2)}{4I_z}}\ [D(r_{zI}+r_{zII})+(t_{yI}-t_{yII})]$	$\sqrt{\frac{[M(I_z-MD^2)]_D(I_z)_H}{[M(I_z-MD^2)]_H(I_z)_D}}$
$\nu_6(B_{2g})$	q_{0g}—out-of-plane bending	$\sqrt{\frac{M(I_y-MD^2)}{4I_y}}\ [-D(r_{yI}+r_{yII})+(t_{zI}-t_{zII})]$	$\sqrt{\frac{[M(I_y-MD^2)]_D(I_y)_H}{[M(I_y-MD^2)]_H(I_y)_D}}$
$\nu_4(A_u)$	q_τ—phenyl–phenyl torsion	$\sqrt{I_x/4}\ (r_{xI}-r_{xII})$	$\sqrt{(I_x)_D/(I_x)_H}$
$\nu_6(B_{1u})$	q_{ou}—out-of-plane bending	$\sqrt{(I_y-MD^2)/4}\ (r_{yI}-r_{yII})$	$\sqrt{\frac{(I_y-MD^2)_D}{(I_y-MD^2)_H}}$
$\nu_{10}(B_{2u})$	q_{iu}—in-plane bending	$\sqrt{(I_z-MD^2)/4}\ (r_{zI}-r_{zII})$	$\sqrt{\frac{(I_z-MD^2)_D}{(I_z-MD^2)_H}}$

Figure 1 summarizes the results of the different ir and Raman spectra below 200 cm^{-1} at different temperatures. Friedman *et al.*[15] have suggested that at 15 °K the C_i site has been lost, thus allowing rotational modes to be ir active; for instance, they assign an ir band at 67 cm^{-1} to a libration. Ito *et al.*[16] and Bree *et al.*[11] find three librational bands in the room temperature polarized Raman spectrum, at 42, 54, and 88 cm^{-1}, which show main polarizations corresponding to B_g, A_g, and A_g characters, respectively. At low temperature, the highest band is split into two components, and a new band, attributed to the splitting of the 54 cm^{-1} band, also appears. In room temperature experiments performed in our laboratory,[17] we have found that the band at 88 cm^{-1} shows some intensity of B_g character, in agreement with Refs. 11 and 16, and therefore the weak component of the doublet at low temperature corresponds to a B_g band. However, we observed that the bands at 42 and 54 cm^{-1} show no appreciable intensity for A_g and B_g polarizations, respectively. It is possible that the weak intensities observed by Bree *et al.*[11] and Ito *et al.*[16] are remanences due to small imperfections in their samples. In that case, the experimental assignment of the band observed at low temperature at 71 cm^{-1} remains uncertain. We have observed no band in the 20–40 cm^{-1} region, which could correspond to that observed at 27 cm^{-1} for $C_{12}D_{10}$ by Pasquier.[14]

The observed splittings for the three low frequency internal g-bands are less than 2.5 cm^{-1}. The bands around 330 cm^{-1} are assigned to the $\nu_{11}(A_g)$ stretching mode, while those around 250 cm^{-1} correspond to the $\nu_6(B_{2g})$ out of plane vibration. The shifts from solution to crystal phase[14] are $(\nu_6)_{cryst}-(\nu_6)_{sol}=-19$ cm^{-1} and $(\nu_{11})_{cryst}-(\nu_{11})_{sol}=16$ cm^{-1}. The remaining mode has been assigned by Zerbi *et al.*[10] to the 407 cm^{-1} band, while Pasquier[14] assigns it to the bands around 364 cm^{-1}.

Room temperature polarized ir spectra identify bands at ~70 cm^{-1}(B_u), 115 cm^{-1}(B_u), 90 cm^{-1}(A_u), and 118 cm^{-1}(A_u).[12] Of these, the 70 cm^{-1} band is split into two B_u components at 80 °K, which must correspond to torsion–translation modes. Two bands, which could be correlated to these, are observed in unpolarized $C_{12}D_{10}$ spectra at different temperatures.[14] Since there can be no other B_u mode in that region, the band observed at 38 cm^{-1} in unpolarized spectra of $C_{12}H_{10}$ by Pasquier,[14] must be assigned to the A_u species. Therefore, the bands at 115 and 118 cm^{-1} have been assigned to the

TABLE II. Correlation table between the symmetry groups of the phenyl groups (C_{2v}), planar biphenyl molecule (D_{2h}), and site (C_i) and factor (C_{2h}) groups in the crystal. r_k, t_k—phenyl group rotations and translations; R_k, T_k—molecular rotations and translations; q's indicate molecular normal coordinates; Q, L, T, and T' refer to crystal internal normal modes, librations, and optical and acoustical translations, respectively.



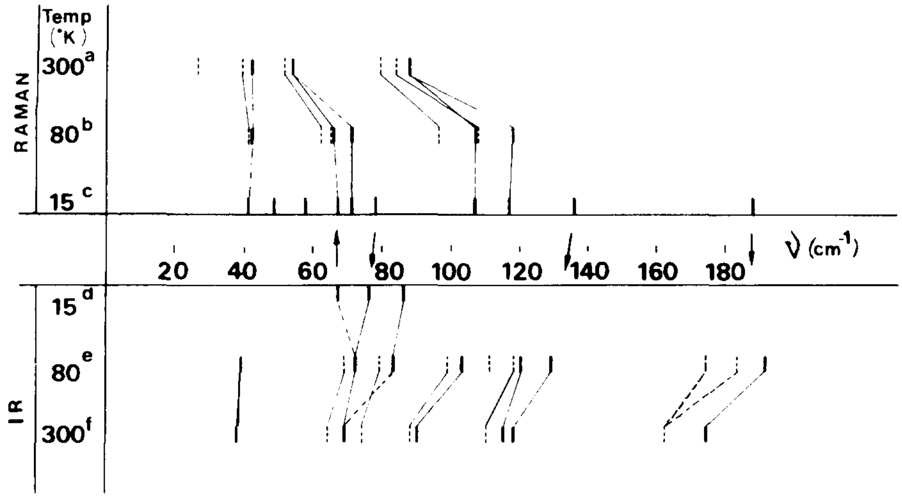


FIG. 1. Infrared and Raman observed frequencies for biphenyl in the 20–200 cm^{-1} region, at different temperatures. Full lines–$C_{12}H_{10}$. Dotted lines–$C_{12}D_{10}$. Correlations in thin lines; doubtful correlations in thin dotted lines. The arrows indicate possible correlations between *g* and *u* modes when the C_i site is lost at 15 °K. (a) References 11, 14, 16. (b) References 14, 16. (c) Reference 15. (d) Reference 12. (e) References 12, 14. (f) References 12, 14.

splitting of the $\nu_6(B_{1u})$ internal mode. One torsion-translation A_u mode is not observed. Unpolarized ir spectra show a single component for the band at 174 cm^{-1}, assigned to the $\nu_{10}(B_{2u})$ internal mode. For $C_{12}D_{10}$, this mode shows a 9 cm^{-1} splitting at 77 °K, while ν_6 shows a 6 cm^{-1} splitting at the same temperature. Zerbi and Sandroni[10] have interchanged the assignment of ν_6 and ν_{10}, in opposition to most authors.

CALCULATION METHOD

The calculation method used in the present work has been described in detail in Ref. 18 and has been applied to a series of crystals for which the molecule is only slightly distorted from the gaseous state equilibrium position.[19] The coordinate basis is formed from free-molecule normal coordinates and Eckart rotation and translation coordinates. The intramolecular potential, V_0, assumed to be that of the free molecule, is diagonal in these coordinates, and the matrix elements $\lambda_l = 4\pi^2\nu_l^2$ are the eigenvalues of the free molecule secular equation.

For $k=0$, i.e., optically active phonons, the crystal frequencies ν_c are obtained from the secular equation

$$|F_{\mu l}^{\nu m} - [\lambda_c - \lambda_l]\delta_{\mu\nu}\delta_{lm}| = 0 ,$$

with $\lambda_c = 4\pi^2\nu_c^2$ and

$$F_{\mu l}^{\nu m} = \sum_{\beta}{}' \left(\frac{\partial^2 V_e}{\partial Q_{1\mu l}\partial Q_{\beta\nu m}}\right) ,$$

where V_e is the intermolecular potential, β labels unit cells, μ and ν molecules in the unit cell, and l and m normal modes associated with normal coordinates $Q_{1\mu l}$ and $Q_{\beta\nu m}$. The atom–atom interaction potential is written as

$$V_e = \frac{1}{2}\sum_{\alpha\beta}\sum_{\mu\nu}\sum_{ij} V_{\alpha\mu i}^{\beta\nu j}(r_{ij}) \quad \alpha\neq\beta \text{ for } \mu=\nu ,$$

where $V_{\alpha\mu i}^{\beta\nu j}(r_{ij})$ (V_{ij} for shortness) depends on the interatomic distance r_{ij} between atoms i and j only. The second derivatives are

$$\left.\frac{\partial^2 V_{ij}}{\partial Q_{1\mu l}\partial Q_{\beta\nu m}}\right) = \left.\frac{\partial^2 V_{ij}}{\partial r_{ij}^2}\right)\left[\frac{\partial r_i}{\partial Q_{1\mu l}}\frac{\partial r_{ij}}{\partial r_i}\right]\left[\frac{\partial r_j}{\partial Q_{\beta\nu m}}\frac{\partial r_{ij}}{\partial r_j}\right] + \left.\frac{\partial V_{ij}}{\partial r_{ij}}\right)\left[\frac{\partial r_i}{\partial Q_{1\mu l}}\frac{\partial}{\partial r_i}\right]\left[\frac{\partial r_j}{\partial Q_{\beta\nu m}}\frac{\partial r_{ij}}{\partial r_j}\right] .$$

Terms such as $\partial r_i/\partial Q_{1\mu l}$ are the Cartesian displacements of a molecule in the lth mode, which are obtained from an isolated molecule normal coordinate analysis (or in some cases from symmetry considerations) for the internal motions and from the Eckart relations for external modes.

Although the configuration of free biphenyl is severely distorted in the crystal, the method is applicable to this case with some additional remarks. In the rigid-phenyl approximation, and with a D_{2h} pseudosymmetry, the planar molecular configuration is at an extreme value—maximum or minimum—of its internal energy, with respect to five out of the six internal symmetry coordinates, as can be seen by straightforward symmetry considerations. With respect to the remaining coordinate, the phenyl–phenyl stretching, the energy can also be considered to be quadratic, since the frequency shift is less than 5%, and can be mainly attributed to the hardening of the intramolecular potential due to the shortening of the distance of the orthohydrogens belonging to different phenyl groups in the planar conformation. A rough calculation, based on nonbonded interactions between the phenyl groups using a Buckingham potential with parameters proposed by Williams,[20] yields a frequency shift of 9% in the observed sense, and a lengthening of the interphenyl distance of 0.04 Å, which is in rough accordance with the observed difference between gas and crystal interphenyl distance (~0.02–0.03 Å).

Even though frequency shifts from gaseous to solid state are not large, the values of the intramolecular energy matrix elements λ_l cannot be approximated by the free molecule data because of the conformational change. Instead, we have treated them as adjustable parameters. Their values will obviously change the band position, but its effect on the splittings will come only through the intermode mixing. In other words, for isolated modes the splitting is independent of λ_l, but the amount of mixing depends strongly on the closeness of the diagonal elements of the dynamical matrix. The observed crystal frequencies may give this way information on the intramolecular force field in the crystal.

The torsional mode is of particular interest. Al-

TABLE III. Atom–atom potential parameter sets for the Buckingham form: $V_{ij} = -A r_{ij}^{-6} + B \times \exp(-C\, r_{ij})$.

	Williams parameters (WP)			Kitaigorodskii parameters (KP)		
	C...C	C...H	H...H	C...C	C...H	H...H
B (kcal/mol)	83630	8766	2654	42000	42000	42000
C (Å^{-1})	3.60	3.67	3.74	3.58	4.12	4.86
A ((kcal/mol)Å^6)	568.0	125.0	27.3	358.0	154.0	57.0

though the frequencies associated with it in the gaseous and solid states lie both around 70 cm^{-1},[12] the internal force field is essentially different. The free molecule torsional potential barrier shows only one minimum for a torsional angle of 42°, and two symmetry required maxima for $\Theta = 0°$ and $\Theta = 90°$. Therefore, the planar configuration is unstable from the intramolecular point of view. This instability is overcome in the crystal by the intermolecular forces. The contribution of the internal force field to the total torsional barrier at $\Theta = 0°$ will therefore necessarily be negative (the associated imaginary frequencies are obviously physically meaningless) and will be also treated as an adjustable parameter.

The eigenvectors obtained from the solution of the secular equation directly indicate the composition of each crystal normal mode in terms of the basic coordinates, which have a clear physical meaning.

RESULTS

The calculations have been performed using a potential function of the Buckingham form with potential parameters proposed by Williams (WP)[20] and by Kitaigorodskii (KP)[21] for hydrocarbon crystals (see Table III). Most of the detailed calculations are reported using WP, which give slightly better agreement with experimental data, as is the case for other hydrocarbon crystals like benzene and naphtalene.[22]

The summation radius for all interactions was 6 Å, yielding a total of 1594 atom–atom contacts per molecule. The crystal structure at room temperature has been reported by Trotter[8] and Hargreaves and Rizvi[9] with very similar results; we have used the data of Ref. 9, which are based on more observed reflections and seem to be somewhat more accurate. The Cartesian displacements for the six internal modes under consideration were obtained through inversion of the 12×12 system formed by the relations between rotation–translation coordinates of the phenyl groups, and the six internal symmetry coordinates (Table I) plus the six molecular rotations and translations. As stated before, the site symmetry allows the separate calculation of *u* and *g* modes.

g modes

Table IV shows the results of the calculation for the *g* modes of $C_{12}H_{10}$ and $C_{12}D_{10}$, using WP and KP. We have also included experimental data, experimental and

TABLE IV. Calculated and observed interphenyl and lattice *g*-vibrations for $C_{12}H_{10}$ (ν_H) and $C_{12}D_{10}$ (ν_D) and corresponding isotopic ratios.

Solution[a]		Crystal											
			Experimental[b]			Williams parameters (WP)				Kitaigorodskii parameters (KP)			
Sym.	ν_H	Sym.	ν_H	ν_D	ν_H/ν_D	ν_l	ν_H	ν_D	ν_H/ν_D	ν_l	ν_H	ν_D	ν_H/ν_D
		B_g	42	39.5	1.06		42.7	40.4	1.057		44.1	41.6	1.060
		A_g	(54)				51.5	48.6	1.059		52.4	49.4	1.060
		A_g	54	51.5	1.05		56.2	53.2	1.056		58.2	54.7	1.064
		B_g	(54)				65.2	59.6	1.094		57.9	52.8	1.096
		A_g	88	80	1.10		80.7	73.8	1.093		91.0	83.8	1.086
		B_g	88	84	1.05		82.0	77.5	1.058		82.9	78.5	1.056
ν_6		A_g					250.4	239.0	1.048		252.2	241.0	1.046
(B_{2g})	268		251	232	1.08	242.0				242.0			
		B_g					250.6	239.3	1.047		250.9	239.7	1.047
ν_{11}		B_g					328.9	318.7	1.032		329.1	318.9	1.032
(A_g)	314		330	319	1.03	328.0				328.0			
		A_g					330.9	320.7	1.032		331.8	321.7	1.031
		B_g					362.7	343.0	1.057		363.4	343.7	1.057
			364			360.0				360.0			
		A_g					364.5	344.6	1.058		366.4	346.4	1.058

[a] References 10, 13, 14.

[b] References 11, 13, 14, 16.

TABLE V. Composition of crystal g-modes in terms of molecular rotations (R_k) and interphenyl motions (q) for WP. $I_z > I_y > I_x$.

ν_{calc} (cm^{-1})	R_z	R_y	R_x	q_{og}	q_s	q_{ig}
42.7	−0.92	0.40	−0.02	−0.02	0.00	0.00
51.5	0.59	−0.74	−0.32	0.00	0.00	−0.01
56.2	0.69	0.67	−0.26	−0.02	0.00	0.01
65.2	0.14	0.38	0.91	0.01	0.00	−0.01
80.7	0.41	−0.06	0.91	0.00	0.01	0.00
82.0	0.37	0.84	−0.41	−0.01	0.00	−0.01
250.4	0.02	0.01	0.00	0.99	−0.01	0.02
250.6	0.01	−0.01	0.01	−0.99	−0.01	−0.02
328.9	0.00	0.00	0.00	0.01	−0.99	0.01
330.9	0.00	0.00	−0.01	0.01	0.99	−0.01
362.7	0.00	−0.01	0.00	0.02	−0.01	−0.99
364.5	−0.01	−0.01	0.00	−0.02	0.01	0.99

calculated isotopic ratios, and the values of ν_l for inplane bending (ν_{ig}), out-of-plane bending (ν_{og}), and stretching (ν_s) modes, which have been adjusted to fit $C_{12}H_{10}$ observed frequencies. The corresponding values for $C_{12}D_{10}$ were obtained through the isotopic ratios (Table I). The eigenvectors, which give the normal mode compositions, are reported for WP in Table V. They are only slightly changed by deuteration. The eigenvectors obtained with KP are very similar.

It can be seen that the coupling between internal and external modes, and among different internal modes is negligible. This fact allows an independent adjustment of the ν_l's. On the other hand, most external modes are associated with more than one principal axis rotation. It can be seen that for $\nu_6(B_{2g})$, the difference between the frequency in CCl_4 solution and ν_{og} is -26 cm^{-1}, which indicates a weakening of the internal force field, while the intermolecular force field causes a $+8$ cm^{-1} shift. For the stretching frequency the internal force field is strengthened, the difference being 14 cm^{-1}, in accordance with our rough calculation. The splittings are less than 2 cm^{-1} in agreement with experiment.

The lowest lying librational frequency for both parameters sets is B_g; also, two A_g bands are calculated around 54 cm^{-1}. For the two higher frequency librational modes, WP predict a quasidegeneration for $C_{12}H_{10}$ and splitting for $C_{12}D_{10}$. The frequency ordering for WP is in complete agreement with experimental assignments at low temperature.

In a previous paper[23] we have reported the calculated intensities of the Raman active lattice modes of biphenyl using the oriented gas model. If, as suggested by our calculation, there are two non resolved A_g bands around 54 cm^{-1}, the agreement with experiment is fair, within the roughness of the model. However, these results have to be taken with caution, since we have shown that the oriented gas model is not very reliable for a large number of molecular crystals.

u modes

The results for the u modes are shown in Table VI and Table VII. It can be seen that while $\nu_6(B_{1u})$ and $\nu_{10}(B_{2u})$ are only weakly coupled to each other and to lattice modes, there is a very strong coupling between torsion and translation coordinates. Therefore, only the internal force field frequencies for the out-of-plane (ν_{ou}) and the in-plane (ν_{iu}) bending modes have been adjusted independently for agreement with the $C_{12}H_{10}$ spectrum; again, the ν_l's for $C_{12}D_{10}$ have been obtained from the isotopic ratios. The tentative assignment $\nu_{iu} > \nu_{ou}$, is based on the calculated splittings and expected internal field modifications. Although the splitting for the higher mode has not been observed in $C_{12}H_{10}$, spectra of $C_{12}D_{10}$ at 77 °K show a larger splitting for this mode. There are no solution data for the higher mode, but the solution frequency for the crystal doublet at 115–118 cm^{-1} is 109 cm^{-1}. The shift caused by intermolecular forces would be about 10 cm^{-1} for ν_{iu} and 18 cm^{-1} for ν_{ou}, and therefore in either case there would be a weakening of the internal field. It is clear, however, that this field is strengthened for the in-plane mode when the molecule becomes planar. This tends to confirm the assignment of the lower frequency bands to the out-of-plane mode, yielding a weakening of the internal field of about 11 cm^{-1}, which is comparable to those estimated for ν_{og} and ν_s.

In any case, the assignment of ν_{ou} and ν_{iu} does not affect the calculation of the remaining five modes. Since

TABLE VI. Calculated and observed interphenyl and lattice u vibrations for $C_{12}H_{10}$ (ν_H) and $C_{12}D_{10}$ (ν_D) and corresponding isotopic ratios.

Solution[a]		Crystal											
		Experimental[b]				Williams parameters (WP)[c]				Kitaigorodskii parameters (KP)[d]			
Sym.	ν_H	Sym.	ν_H	ν_D	ν_H/ν_D	ν_l	ν_H	ν_D	ν_H/ν_D	ν_l	ν_H	ν_D	ν_H/ν_D
ν_4 (A_u)	(70)	A_u	38				40.3	38.5	1.049		37.5	35.2	1.065
		B_u	68	64	1.06		63.9	59.9	1.066		67.6	63.1	1.072
		A_u					70.7	65.4	1.081		71.4	67.1	1.064
		B_u		74			74.1	69.6	1.064		81.5	77.0	1.058
		A_u	91	88	1.03		85.8	82.5	1.040		95.1	90.9	1.046
ν_6 (B_{1u})	109	B_u	115			98.0	113.6	106.4	1.068	95.0	110.3	103.1	1.070
		A_u	118	110	1.07		119.6	112.7	1.061		122.6	116.0	1.057
		B_u				160.7	166.0	152.9	1.085	153.5	160.6	148.1	1.085
		A_u	174	162	1.07		174.0	160.3	1.085		174.1	160.6	1.084

[a] References 12, 13, 14.
[b] References 12, 14.
[c] $\nu_\tau = 20$ cm^{-1}.
[d] $\nu_\tau = 10$ cm^{-1}.

TABLE VII. Composition of crystal u modes in terms of molecular translations (T_k) and interphenyl motions (q) for WP. $I_z > I_y > I_x$. $\nu_\tau = 20$ cm^{-1}.

ν_{calc} (cm^{-1})	T_z	T_y	T_x	C_τ	q_{1u}	q_{ou}
40.3	0.02	−0.04	−0.88	0.47	−0.03	−0.02
63.9	0.43	0.62	−0.02	−0.64	−0.02	−0.15
70.7	0.16	−0.10	0.47	0.85	0.00	−0.11
74.1	0.37	0.54	−0.01	0.74	0.04	0.17
85.8	0.79	−0.55	−0.05	−0.16	−0.05	0.21
113.6	0.00	0.00	0.00	0.22	0.05	−0.97
119.6	0.16	−0.11	−0.05	−0.14	0.13	−0.96
166.0	−0.01	−0.01	0.00	−0.05	0.99	0.04
174.0	0.02	−0.01	−0.02	0.02	0.99	0.14

the torsion is strongly coupled to the translational modes, the corresponding value of λ_τ cannot be adjusted independently. As stated before, since the planar configuration corresponds to a maximum of the internal configuration energy, the values of λ_τ must be negative. We have calculated its values from different torsional barrier estimations. Taking the values of the conjugation energy given by Franchini *et al.*[6] or those of Dewar *et al.*,[7] and adding nonbonded interactions with WP gives a value of about 70 cm^{-1} for $\nu_\tau = \sqrt{-\lambda_\tau/4\pi^2}$, and 60 cm^{-1} for the torsional oscillations of the free molecule around its equilibrium angle of ~42°. This estimation is an upper limit for ν_τ, since the phenyl geometry has been kept fixed, and therefore ortho-hydrogens are probably too close in the planar molecule. Similar results are obtained from the standard series development of the barrier in terms of its height and position of the minimum.

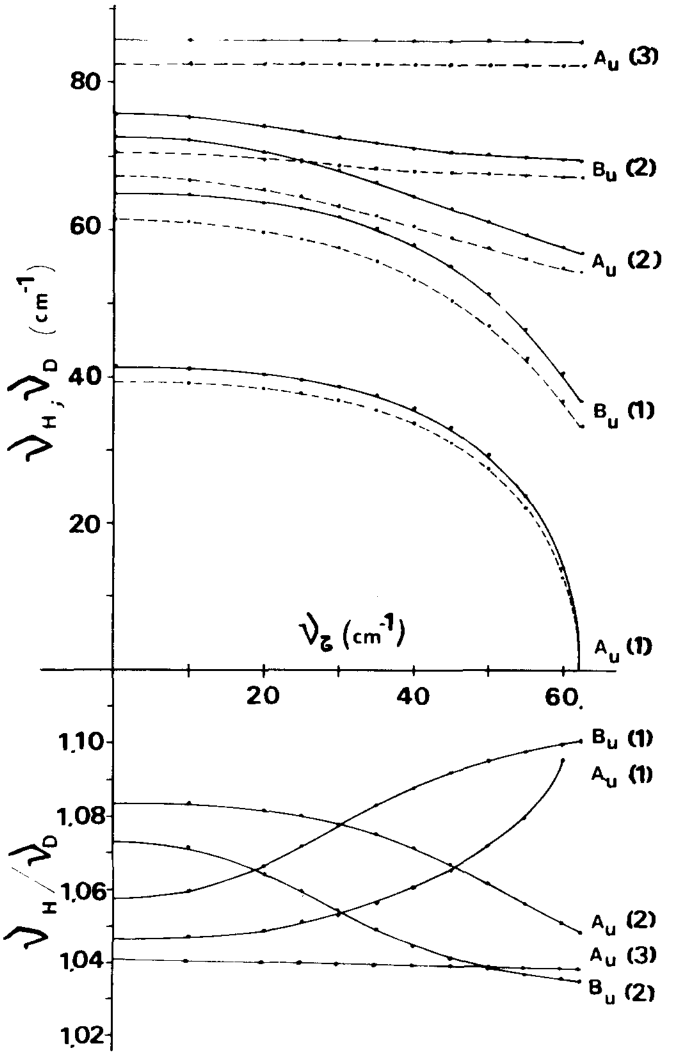


FIG. 2. Calculated u frequencies for $C_{12}H_{10}$ and $C_{12}D_{10}$, and isotopic ratios ν_H/ν_D as a function of ν_τ (see text). The modes have been numbered within each symmetry species.

The calculated frequencies for WP of the five translation–torsion modes are shown in Fig. 2 as a function of ν_τ, together with the corresponding isotopic ratios. Figure 3 shows the percentage mixing of the torsional coordinates in the crystal mode composition, as a function of ν_τ; it can be seen that, as expected, the general pattern is similar to that of the isotopic ratios.

The best agreement with experimental values corresponds to ν_τ between 0 and 30 cm^{-1}, a region for which the pattern is not very sensitive to ν_τ. Tables VI and VII show the calculated results for $\nu_\tau = 20$ cm^{-1} (WP) and $\nu_\tau = 10$ cm^{-1} (KP). The upper limit to ν_τ is 62.5 cm^{-1} for WP (see Fig. 2) and 50 cm^{-1} for KP; above these values, the planar structure becomes unstable, and one frequency imaginary. The results of Table VI show that the agreement with experiment is good for both potentials. It is also observed (Table VII) that the torsion is significantly mixed with all lattice modes except one, and that any calculation not taking this coupling into account cannot be realistic.

Heat of sublimation

The internal energy of a molecular crystal can be equated to its heat of sublimation, if entropic effects are neglected. The energy falls off with the atom–atom distance much slower than the force constants: at a cutoff distance of 6 Å, where the frequencies are completely stabilized, the intermolecular energy calculated with WP is − 16.6 kcal/mol, and at 10 Å, for instance, it is − 20.6 kcal/mol. We have found that a simple extrapolation method is very accurate: If one assumes that after a certain atom–atom distance the atoms present a uniform radial distribution in the crystal, it is straightforward to calculate E_∞ from E_r, if r is sufficiently large. For biphenyl, the value of E_∞ ex-

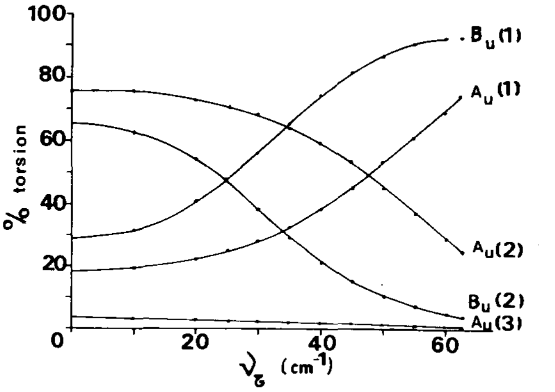


FIG. 3. Percentage mixing of the torsional coordinate in the torsion–translation modes as a function of ν_τ (see text).

trapolated from $E_{4Å}$, $E_{5Å}$, and $E_{6Å}$ differ by less than 0.1 kcal/mol, and the value of E_∞ is found to be − 21.7 kcal/mol for WP and − 20.8 kcal/mol for KP. Since there is a conformational change from the solid to the gas with an estimated barrier height of 2 kcal/mol, the final values for E_∞ are − 19.7 (WP) and − 18.8 (KP) kcal/mol, which correlate very well with the heats of sublimation reported by different authors, 19.5[24] and 18.1[25] kcal/mol.

CONCLUSIONS

In the present work we have examined the dynamical behavior of the biphenyl crystal in terms of the atom–atom interaction potential. The agreement of the calculation with experimental data is good, allowing a reexamination of existing assignments. It is to be noted that previous calculations on this crystal[26,27] have led to unsatisfactory results.

According to our calculations, it is extremely important to consider the intermode mixing between the torsional and the translational coordinates. Although for naphthalene, for instance, the mixing of external vibrations and low-lying internal modes has been shown to be appreciable,[28] this is, to our knowledge, the first case which has been analyzed that shows that an internal mode, the torsion, and external modes, the translations, completely lose their identity in the crystal vibration: In view of our calculated eigenvectors, it is impossible to refer to any of these modes (except the higher frequency translational mode) as "translational" or "torsional."

It is clear that this effect will appear in any molecular crystal for which there is a large conformational change of the molecule upon crystallization: In those cases, intermolecular and some intramolecular forces will be comparable, thus violating the basic assumptions of the usual perturbative approach. The conformational change will indirectly affect other modes, even though these may be relatively uncoupled to external vibrations: For these too, our calculation method may give valuable information on the internal field of the molecule within the crystal.

The coordinate basis used in our calculation is particularly appropriate for these cases, since it allows a very direct interpretation of the results, even lacking a complete information on the intramolecular force field, and saves a considerable amount of computing time by allowing *a priori* separation of the dynamical matrix. It is should be noted, however, that the biphenyl crystal constitutes a fortunate case, since the planar configuration is an extremum—in our case a maximum—of the internal torsional field. Much more severe modifications on our approach would have been necessary if this had not been the case, since a separate quadratic form for internal and intramolecular energies is no longer possible.

The present calculation confirms the validity of the atom–atom model for the calculation of dynamical properties of hydrocarbon crystals. Likewise, statical properties such as heats of sublimation are in good agreement with experiment.

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[1] O. Bastiansen, Acta Chem. Scand. 3, 408 (1949).
[2] A. Gamba, G. F. Tantardini, and M. Simonetta, Spectrochim. Acta, Part A 28 10, 1877 (1972).
[3] J. E. Katon and E. R. Lippincott, Spectrochim. Acta 19, 627 (1959).
[4] D. Perahia and A. Pullman, Chem. Phys. Lett. 19, 73 (1973).
[5] A. Tajiri, S. Tagaki, and M. Hatano, Bull. Chem. Soc. Jpn. 46, 1067 (1973).
[6] P. Franchini and G. Sbrana, Trans. Faraday Soc. 66, 572 (1970).
[7] M. Dewar and A. Herget, Proc. R. Soc. London A 315, 443 (1970).
[8] J. Trotter, Acta Crystallogr. 14, 1135 (1961).
[9] A. Hargreaves and H. Rizvi, Acta Crystallogr. 15, 365 (1962).
[10] G. Zerbi and S. Sandroni, Spectrochim. Acta, Part A 24, 483, 511 (1968).
[11] A. Bree, C. Y. Pang, and L. Rabeneck, Spectrochim. Acta, Part A 27, 1293 (1971).
[12] G. V. Lecolier, B. Wyncke, and A. Hadni, J. Chim. Phys. Phys.-Chim. Biol. 68, 1606 (1971).
[13] B. Pasquier and D. M. Lebas, J. Chim. Phys. Phys.-Chim. Biol. 64, 765 (1967).
[14] B. Pasquier, Mol. Cryst. Liq. Cryst. 11, 35 (1970).
[15] P. Friedman, R. Kopelman, and P. Prasad, Chem. Phys. Lett. 24, 15 (1974).
[16] M. Ito, M. Suzuki, and T. Yokoyama, "Excitons, Magnons, and Phonons," *Proceedings of the International Symposium on Molecular Crystals* (Cambridge University, London, 1968), p. 1.
[17] E. Burgos, Tesis de Doctorado, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Buenos Aires (1975).
[18] G. Taddei, H. Bonadeo, M. P. Marzocchi, and S. Califano, J. Chem. Phys. 58, 966 (1973).
[19] H. Bonadeo and E. D'Alessio, Rend. Sci. Int. Fis. Enrico Fermi 55 (1972).
[20] D. E. Williams, J. Chem. Phys. 45, 3770 (1966).
[21] A. I. Kitaigorodskii, J. Chim. Phys. Phys.-Chim. Biol. 63, 6 (1966).
[22] G. Taddei, H. Bonadeo, and S. Califano, Chem. Phys. Lett. 13, 136 (1972).
[23] E. Burgos, H. Bonadeo, and E. D'Alessio, J. Chem. Phys. 63, 38 (1975).
[24] R. S. Bradley and T. G. Cleasby, J. Chem. Soc. **1953** 1690.
[25] R. C. Weast, *Handbook of Chemistry and Physics* (Chemical Rubber, Cleveland, 51st ed., 1970–1971), p. C716.
[26] T. Luty, Mol. Cryst. Liq. Cryst. 17, 327 (1972).
[27] A. I. Kitaigorodskii and E. I. Mukhtarov, Opt. Spektrosk. 31, 706 (1971).
[28] G. S. Pawley and S. J. Cyvin, J. Chem. Phys. 52, 4073 (1970).