Lattice-dynamical calculations on some rigid organic molecules

Giuseppe Filippini, Carlo M. Gramaccioli, Massimo Simonetta, and Giuseppe B. Suffritti

Istituto di Chimica Fisica e Centro C.N.R., Università di Milano, Via Saldini 50, 20133 Milano, Italy

(Received 30 May 1973)

Several physical–chemical properties in crystals formed by "rigid" organic molecules have been calculated by means of different semiempirical atom–atom potential functions. For nine different substances, vibration frequencies, dispersion curves, and "crystallographic" temperature factors have been evaluated, and as an example the density of states for two of them are also reported. Experimental data are in excellent to fair agreement with results obtained by use of "Williams IVa" functions; some of these results can be advantageously used for libration correction of bond lengths that are determined by x-ray or neutron diffraction. Among the examined substances, some anomalies are found for pyrene crystals, which confirm in this case a rather unusual way of packing.

I. INTRODUCTION

The problem of interpreting physical–chemical properties of molecular crystals from lattice-dynamical calculations involving use of approximate intermolecular potentials is becoming in recent years a reasonable one, which can be solved using modern computers even for molecules and crystals of some complexity.[1-6]

Owing to practical difficulties, the most feasible approach, at least at the present time, is based on the assumption that packing energy is a sum of several terms, each of them due to interaction between pairs of nonbonded atoms; the value of each term is supposed to be a function of distance and type of atoms. This procedure has been widely used for calculation of vibration frequencies, thermodynamic data, elastic constants, etc. by several authors.[1-6]

The recent literature contains several empirical functions for atom–atom potentials and many of them are considerably different from each other. A possible check of the general validity of these expressions would be the comparison of vibration frequencies, as obtained from Raman or infrared spectroscopy for a series of crystals, with results obtained through a lattice-dynamical treatment involving subsequent use of different empirical functions.

Since the experimental measurements of these frequencies are still surprisingly few, some more data can be obtained from results of crystal structure analysis by x-ray or neutron diffraction. In some well-refined structures, in fact, the so-called Debye–Waller factors, or better the "anisotropic temperature factors" (or "**B**"s, the latter being second rank tensors), which give the mean square amplitude of vibration for all the atoms, can be compared with lattice-dynamical results.

The aim of the present paper is a systematic

discussion of the fit to experimental values of results obtained for a series of different substances, using some of the empirical functions described in the literature which seem to be among the most reliable. Since these functions are particularly well known especially for hydrocarbons, as a first step our interest has been confined to hydrocarbons and—as an only exception—just one substance containing oxygen has also been taken into account. For the sake of relative simplicity, only "rigid" molecules have been considered; however, since the results seem to us to be particularly satisfactory, extension to nonrigid cases is being carried forward.

Because of our test for the general validity of a given function, obviously no effort has been made in changing the parameters even slightly in order to improve the fit for each separate substance; at the present stage of our research, we are therefore using a function as proposed by the authors who introduced it. In the future, however, an improvement of the over-all fit for a considerable number of these substances is planned.

The choice of the substances here examined was made on the following basis.

(1) The molecules can be expected to behave as "rigid bodies" on the basis of chemical and other experimental evidence (i.e., Schomaker–Trueblood's treatment of temperature factors).

(2) The crystal structures have been determined with considerable accuracy. A measurement of this accuracy is actually rather difficult to give; however, the number of reflections measured, how they have been measured, the so-called "*R*" index (percentage disagreement between observed and calculated structure factors), and the way of proceeding through structure refinement can give evidence for this. Naphthalene is an exception, but it was included in order to check the results obtained dynamically by other authors[2] and anyway

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experimental temperature factors are not being considered.

(3) At least for some of them, spectroscopic (Raman or infrared) measurements are given in the literature.

(4) The symmetry of crystals is lower or equal to orthorhombic, with one molecule or less per asymmetric unit. (This is because of the present limitations of our computer programs.) This limitation is however of rather little importance, because the great majority of organic substances forms crystals with symmetry equal to or lower than orthorhombic and even space groups with improper rotations or nonprimitive ones can be easily handled by our programs (see Table I). These substances are naphthalene (NAP), anthracene (ANT), phenanthrene (PHE), benzo(c)phenanthrene (BCP), pyrene (PYR), 1, 6 : 8, 13-propane-1, 3-diylidene [14] annulene (PAN), 1, 6 : 8, 13-butane-1, 4-diylidene [14] annulene (BUT), 3, 4 : 7, 8-dibenzotricyclo [4. 2. 0. $0^{2,5}$] octa-3, 7-diene (DTO), and bicyclo [2, 2, 2] octene-2, 3-$endo$-dicarboxylic anhydride (BIC). The crystallographic data about these substances together with reference indications are given in Table I.

II. THEORY

According to the treatment proposed by Born[16] and developed by various authors,[4,12] the angular and translational displacement of a rigid molecule can be expressed in the form

$$\mathbf{u}(lk) = \mathbf{U}(k\mathbf{q}) \exp i[\mathbf{q} \cdot \mathbf{r}(lk) - \omega(\mathbf{q})t], \qquad (1)$$

where $\mathbf{u}$ is a vector whose components are the rotational and translational displacements (referred preferably to the principal axes of inertia of each molecule), k is an index referring to the asymmetric unit in the cell to which each molecule belongs, l is another index referring to the cell, $\mathbf{q}$ is the so-called "wave vector" (expressed in fractions of the reciprocal unit cell), and $\mathbf{r}$ is the distance of the center of mass of each molecule from

the origin expressed in fractions of a unit cell.

The potential energy E of a molecule can be expressed as a function of its displacement from its equilibrium position:

$$E = E_0 + \frac{1}{2} \sum_{ij} (\partial^2 E / \partial u_i \partial u_j) u_i u_j$$

$$= E_0 + \frac{1}{2} \sum_{ij} \phi_{ij} u_i u_j, \qquad (2)$$

where ϕ_{ij} are force constants and E_0 is the energy at the equilibrium position.

For each molecule expressions of the following kind can be written:

$$m\ddot{u}_x(lk) = -\partial E / \partial u_x(lk) = -\sum_{l'k'i} \phi_{xi}(lk, l'k') u_i(l'k'),$$

$$I_\alpha \ddot{u}_\alpha(lk) = -\partial E / \partial u_\alpha(lk) = -\sum_{l'k'i} \phi_{\alpha i}(lk, l'k') u_i(l'k'), \qquad (3)$$

where u_x and u_α are the translational and rotational displacements, respectively, along a given axis, m and I_α are, respectively, the mass and the moment of inertia of the molecule with respect to that axis, and $\phi(lk, l'k')$ are force constants relative to the interaction between a molecule at $l'k'$ and a molecule at lk.

Developing Eqs. (1) and (3) leads to the eigenvalue equation

$$\omega^2(\mathbf{q})\xi(k, \mathbf{q}) = \mathfrak{M}(\mathbf{q})\xi(k, \mathbf{q}), \qquad (4)$$

where ω is the frequency of a normal mode, $\xi_i(k, \mathbf{q})$ is a normal coordinate (rotational or translational) of a molecule associated with the kth rotation matrix in the symmetry group, and $\mathfrak{M}(\mathbf{q})$ is the so-called "modified" dynamical matrix. The elements of $\mathfrak{M}(\mathbf{q})$ are defined as follows:

$$\mathfrak{M}(\mathbf{q})_{i+6(k-1); j+6(k'-1)} = \mathfrak{M}_{ij}(k, k', \mathbf{q})$$

$$= \sum_{l'} (1/m_i m_j)^{1/2} \phi_{ij}(lk, l'k') \exp i\mathbf{q} \cdot \mathbf{r}(l'k', lk), \qquad (5)$$

where $\mathbf{r}(l'k', lk)$ is the oriented distance between

TABLE I. Crystallographic data about the substances here considered.

| Compound | Cell dimensions (Å) | | | | Space group | Z | Crystall. molec. symmetry | R index | No. of reflections | Reference |
	a	b	c	β						
NAP	8.235	6.003	8.658	122.92°	$P 2_1/a$	2	$\bar{1}$	0.120	644	12
ANT	8.562	6.038	11.184	124.70°	$P 2_1/a$	2	$\bar{1}$	0.049	219	7
PHE	8.472	6.166	9.467	98.01°	$P 2_1$	2	1	0.060	947	14
BCP	14.666	14.157	5.785	(90°)	$P 2_1 2_1 2_1$	4	1	0.091	1392	8
PYR	13.649	9.256	8.470	100.28°	$P 2_1/a$	4	1	0.034	1008	15
PAN	19.455	36.358	6.572	(90°)	$Fdd2$	16	1	0.062	826	13
BUT	18.034	11.399	6.059	(90°)	$Fmm2$	4	$mm2$	0.045	407	10
DTO	10.716	7.706	6.719	98.37°	$P 2_1/c$	2	$\bar{1}$	0.069	925	11
BIC	6.534	10.480	12.184	96.37°	$P 2_1/c$	4	1	0.050	967	9

the center of mass of the molecule at $l'k'$ and the corresponding one at lk. The coordinates of each molecule refer to the corresponding principal axes of inertia; m_i and m_j are the masses (or the corresponding moments of inertia) of the molecules.

To perform our calculations, two computer programs have been written in Fortran IV language. An example of the input data for naphthalene is given in Table II. Starting from unit-cell parameters, experimental atomic coordinates, and assigned energy functions, the first of these programs shifts a molecule to its equilibrium position on the basis of the assigned potential functions, the amount of such rotational and translational shifts also giving an idea of the "goodness" of the functions used. For this stage, where the unit-cell

TABLE II. Input data for naphthalene.

Cell constants[12]:

$a = 8.235$, $b = 6.003$, $c = 8.658$ Å; $\beta = 122.91°$

Fractional atomic coordinates (asymmetric unit)[12]:

Atom	X	Y	Z
C_1	0.0856	0.0186	0.3251
C_2	0.0116	0.1869	−0.2541
C_3	0.1148	0.1588	0.2200
C_4	0.0749	0.2471	−0.0784
C_5	0.0472	0.1025	0.0351
H_1	0.1375	0.0657	0.4663
H_2	0.1888	0.3176	0.2752
H_3	0.1490	0.4056	−0.0233
H_4	0.0345	0.2999	−0.3394

Equivalent positions: $(Z = 2)$

1	$+X$	$+Y$	$+Z$ } 1st molecule
2	$-X$	$-Y$	$-Z$
3	$\frac{1}{2}-X$	$\frac{1}{2}+Y$	$-Z$ } 2nd molecule
4	$\frac{1}{2}+X$	$\frac{1}{2}-Y$	$+Z$

Primitive lattice

Maximum packing distance considered: 5.50 Å

Standardized C–H bonds: 1.09 Å

Parameters for atom-atom potential functions (Williams IVa, see text):

Contact	A	B	C
H···H	2654	3.74	27.3
C···H	8766	3.67	125.0
C···C	83630	3.60	568.0

Convergence tests for equilibrium position (see text): $\Delta u_i \leq 0.0003$ rad or ≤ 0.0001 Å; $\partial E/\partial u_i \leq 0.001$ kcal/mole·rad or kcal/mole·Å

Brillouin zone sampling: —for dispersion curves: regular intervals of 0.1 a^*, 0.1 b^*, 0.1 c^* Å^{-1}
—for temperature factors: three-dimensional grid made up with the points $q = 0.08$; 0.30; 0.70; 1.50; 3.14 on each reciprocal axis

Temperature: 300 °K

Channel width for density of states: 5.0 cm^{-1}

parameters are left unchanged, a Ralphson–Newton procedure is used, which involves a linear system of the following kind:

$$\mathbf{M}\Delta\mathbf{u} = \mathbf{d} \qquad (6)$$

where $M_{ij} = \partial^2 E/\partial u_i \partial u_j$, $\Delta\mathbf{u}$ is the vector whose components are shifts, and $d_i = -\partial E/\partial u_i$. Iteration is performed until no significant change is observed in coordinates and first derivatives of the energy are close to zero [$\Delta u_i \leq 0.0003$ rad or ≤ 0.0001 Å, respectively; $\partial E/\partial u_i \leq 0.001$ kcal/mole·Å (or kcal/mole·rad)].

In building the matrix $\mathbf{M}$, each derivative is obtained summing up contributions for all packing distances below an assigned value (usually 5.5 Å, in agreement with the results of other authors,[2,5] who—like us—find an extension of this limit practically useless). We have

$$\frac{\partial^2 E}{\partial u_i \partial u_j} = \frac{\partial r}{\partial u_j} \cdot \frac{\partial^2 E}{\partial r^2} \cdot \frac{\partial r}{\partial u_j} + \frac{\partial E}{\partial r} \cdot \frac{\partial^2 r}{\partial u_i \partial u_j} \quad . \qquad (7)$$

For each distance r, the program obtains analytically the first and second derivatives of r with respect to u_i and u_j.

The second computer program starts from the results given by the former and builds up force constants ϕ_{ij}; for these calculations, expressions like (7) are used and all derivatives are obtained analytically. In addition to the term $\phi_{ij}(lk, l'k')$, where derivatives relative to different molecules appear, the so-called "self-terms" $\phi_{ij}(lk, lk) = \partial^2 E/\partial u_i(lk)\partial u_j(lk)$, relative to the same molecule, are also obtained directly.

Once the force constants are at hand, the filling up of dynamical matrices is not particularly difficult. The procedure used in our program is similar to a practical way described by Pawley[17,18]; the diagonalization of these matrices is then accomplished by Householder's routine.

For calculation of temperature factors (B's), these are derived from "molecular" tensors, such as $\mathbf{T}$, $\mathbf{L}$ ($=\omega$), and $\mathbf{S}$. These are defined as $\mathbf{T} = \langle t^*t \rangle$, $\mathbf{L} = \langle \lambda^*\lambda \rangle$, $\mathbf{S} = \langle \lambda^*t \rangle$, where t and λ are translational and rotational displacements, respectively, of the whole molecule.[19,20]

Following Pawley,[2,21,22] we have for such tensors

$$T_{ij} = \sum_{6pN} \xi_i \xi_j \epsilon(\omega)/Nm\omega^2,$$

$$L_{kl} = \sum_{6pN} \xi_k \xi_l \epsilon(\omega)/N\sqrt{I_k I_l}\,\omega^2, \qquad (8)$$

$$S_{ik} = \sum_{6pN} \xi_i \xi_k \epsilon(\omega)/N\sqrt{mI_k}\,\omega^2,$$

where ξ_i or ξ_j are the real and imaginary coefficients of the translational components of the eigenvectors, ξ_k or ξ_l are the same coefficients for rotational com-

ponents, p is the number of molecules per unit cell, and $\epsilon(\omega)$ is given by

$$\epsilon(\omega) = \hbar \left[\tfrac{1}{2} + 1/\exp(\hbar\omega/kT - 1) \right].$$

The summation is extended to N points in a Brillouin zone: it is usually not necessary to refer to the whole Brillouin zone, but just to its symmetric unit, if one includes in (8) the ξ's relative to all different molecules in the cell.[2]

The procedure followed by our program is to accumulate contributions, each of them relative to a particular value of the wave vector q, scanning over the asymmetric unit of the Brillouin zone. In order to save computing time, a sort of unevenly spaced scanning, with the thickest intervals just around the origin (the summation being appropriately weighted), was found to be particularly advantageous.[17] The grid of such scanning (referring to the primitive unit cell) is 0.08, 0.30, 0.70, 1.50, and 3.14 along each reciprocal axis; it has been verified in several cases that results do not vary substantially even if one increases considerably the number of points in the zone.

III. EMPIRICAL FUNCTIONS

Of the various functions reported in the literature involving interaction between carbon and hydrogen atoms, many are of the following kind:

$$V(r) = A \exp(-Br) - Cr^{-6},$$

where r is the distance between nonbonded atoms. Some values for the parameters A, B, and C, according to various authors,[5,23,18] are reported in Table III; in addition to these Bartell's functions[24] were also taken into account. These are the following:

$$V(r)_{C-C} = 29\,9400r^{-12} - 325.3r^{-6} \quad (\text{kcal/mole}),$$

$$V(r)_{C-H} = 124.96r^{-6}[358 \exp(-r/0.49) - 1],$$

$$V(r)_{H-H} = 6590 \exp(-r/0.245) - 49.2r^{-6}.$$

For interactions involving oxygen, a formula proposed by Kitaigorodskii[26] was used:

$$V(r) = -0.14(r_0/r)^{-6} + 30000 \exp(-13.r/r_0)$$

$$(\text{kcal/mole}),$$

where r_0 is the sum of the van der Waals radii of the nonbonded atoms; here the following values were tentatively assigned to such radii: $r_C = 1.70$, $r_H = 1.50$, and $r_O = 1.50$ Å.

Since the interactions involving hydrogen are a major contribution to packing energy, it is particularly important to "standardize" C–H bond lengths, the ones found by x-ray diffraction being in general too short. In all the cases here examined, the coordinates of hydrogen atoms were shifted in order to bring C–H bonds to a conventional length of 1.09 Å, keeping experimental bond angles invariant.

Of the various functions examined, not all were found to be particularly suitable for our aims; for instance, Bartell's functions are exceedingly "soft" for naphthalene and anthracene (see Tables IV and V). Similarly, an adjustment of the coefficients of "Williams IVa" and "IVb" functions made by Taddei, Bonadeo, Marzocchi, and Califano[5] in order to improve the fit to experimental vibration frequencies in benzene has not given better results for anthracene and naphthalene than "original" Williams functions.

For these reasons, the comparison of our re-

TABLE III. Parameters for atom–atom potential functions.

Potential	Contact	A (kcal/mole)	B (Å^{-1})	C (kcal·Å^6/mole)
Williams IVa[23]	H···H	2654.0	3.74	27.3
	H···C	8766.0	3.67	125.0
	C···C	83630.0	3.60	568.0
Williams IVb[24]	H···H	4000.0	3.74	36.0
	H···C	9411.0	3.67	139.0
	C···C	74460.0	3.60	535.0
Kitaigorodskii[18]	H···H	42000.0	4.86	57.0
	H···C	42000.0	4.12	154.0
	C···C	42000.0	3.58	358.0
Taddei α[5]	H···H	2260.3	3.74	26.5
	H···C	8810.0	3.67	128.0
	C···C	78659.0	3.61	567.0
Taddei β[5]	H···H	3429.8	3.79	44.1
	H···C	9772.8	3.67	150.0
	C···C	65821.0	3.61	443.0

TABLE IV. Evaluation of agreement between crystallographic data and results derived from use of various empirical potential functions.

Substances and functions[a]		Function of merit	R_B	ΔB
NAP	(1)	0.04		
	(2)	0.03		
	(3)	0.07		
	(4)	0.06		
ANT	(1)	0.06	13.3	−10.1
	(2)	0.08	11.2	−3.9
	(3)	0.11	13.8	−4.4
	(4)	0.16	71.4	−69.1
	(5)	0.08	24.6	−21.7
	(6)	0.07	22.5	−19.8
PHE	(1)	0.12	23.9	−17.0
	(2)	0.19	45.1	−39.6
	(3)	0.50	34.6	−27.5
BCP	(1)	1.23	12.8	12.8
	(2)	1.85	17.7	10.7
	(3)	1.18	16.3	6.9
PYR	(1)	3.96	21.5	11.5
	(2)	4.56	24.3	14.8
	(3)	6.29	24.3	15.9
PAN	(1)	0.19	12.5	−3.4
	(2)	0.26	15.2	8.3
	(3)	0.15	19.7	14.1
BUT	(1)	0.00[b]	13.4	9.7
	(2)	0.00[b]	24.9	20.4
	(3)	0.00[b]	27.8	23.2
DTO	(1)	0.43	14.2	4.6
	(2)	0.42	20.2	17.8
	(3)	0.42	28.3	25.4
BIC	(1)	0.41	20.1	−14.9
	(2)	0.48	19.0	−3.8
	(3)	0.47	18.7	−5.9

[a]For each substance, the numbers (1), (2), (3), (4), (5), and (6) refer to results obtained by use of Williams IVa, Williams IVb, Kitaigorodskii's, Bartell's, and Taddei, Bonadeo, Marzocchi, and Califano's α and β functions, respectively. The same convention is maintained in Table V.

[b]The position of BUT in the unit cell is fixed because of symmetry requirements.

sults with experimental data for all substances is limited to Kitaigorodskii's and Williams IVa and IVb functions, the others having not been considered for further calculations.

IV. RESULTS AND DISCUSSION

A. Spectroscopic and Crystallographic Data

Table IV reports some results of our calculations. For each substance, we have (a) a "function of merit," defined as $\sum (\Delta x_i)^2$, where Δx_i are shifts of coordinates of each atom (in angstroms) between the experimental position in the unit cell and the position corresponding to a minimum of packing energy, (b) a percentage disagreement between calculated and observed temperature factors "R_B" $= 100 \sum |B_{ij(\text{obs})} - B_{ij(\text{cal})}| / \sum |B_{ij(\text{obs})}|$, and (c) a function "$\Delta B$" $= 100 \sum (B_{ij(\text{obs})} - B_{ij(\text{cal})}) / \sum B_{ij(\text{obs})}$,

which shows whether the calculated temperature factors are on the whole systematically smaller or greater than the observed values. It can be seen that results obtained from functions (1), (2), and (3) are very reasonable for all substances; this is in line with the agreement between observed and calculated vibration frequencies, reported in Table V and with various results reported in the literature.

Strangely enough, the function of merit for pyrene attains considerably higher values than for all the other substances examined here. As a matter of fact, the shifts (translational and angular) between actual position of the molecule in the unit cell and the potential-energy minimum amount to 0.26– 0.34 Å (depending on the potential functions used) and 4°–6.3°, respectively. The minimum obtained for all potential functions lies approximately in the same direction with respect to experimental position; it seems indeed that this structure has some peculiar characteristics and this may depend on a particular way of packing, which may give rise to some degree of π-electron interaction between molecules.[22] As a matter of fact, an inspection of packing shows that we have couples of parallel molecules.[31]

From the point of view of interpreting temperature factors (B's), Williams IVa functions seem to be definitely the best, the average discrepancy from experimental data being often the same as between two independent crystallographic measurements of these B's for the same structure. As an example, when data obtained by Mason and Sparks for anthracene[7b] are compared, the percentage disagreement R_B is 16%; the disagreement between B's obtained for phenanthrene by x-ray or neutron diffraction[14] is 18%. This is usually 2–3 times as great as the alleged standard deviations of B_{ij}'s, but it is well known that crystallographic B's are very liable to be affected by various systematic errors. Because neglecting thermal diffuse scattering (TDS) tends to decrease the experimental values of B's,[32] a slightly negative value of ΔB is to be considered as preferable; also in this respect Williams IVa functions seem on the whole to give the best results. One might also be tempted to take the positive values of ΔB as evidence for some degree of nonrigid behavior of the molecules, but we feel that inferring too much from these results might prove to be rather hazardous.

From the point of view of interpreting vibration spectra, the situation is similar. The agreement of Williams IVa results with experimental data is indeed very good for anthracene, D-anthracene, and naphthalene, as reported by Suzuki et al.,[28] and substantially good for phenanthrene. This is

TABLE V. Calculated lattice vibration frequencies (cm^{-1}) according to various potential functions (see Table IV). Experimental values are also reported when available. T indicates a translational mode.

NAP

Exp. (I)[27]		(II)[28]		(1)		(2)		(3)		(4)	
(146)	A	109	A	114.2	A	122.2	A	138.4	A	118.1	A
(124)	B	125	B	114.4	B	121.7	B	128.3	B	106.2	B
(90)	A	74	A	80.9	A	91.9	A	90.9	A	76.0	A
				89.1	AT	90.7	AT	88.0	AT	67.2	AT
(86)	B	71	B	68.7	B	78.9	B	76.0	B	63.9	B
(71)	A	51	A	52.1	A	57.5	A	60.5	A	52.3	A
				53.2	BT	56.9	BT	56.0	BT	46.5	BT
(59)	B	46	B	44.7	B	47.4	B	47.9	B	42.1	B
				41.8	AT	45.2	AT	46.3	AT	37.7	AT

ANT

Exp.				(1)		(2)		(3)		(4)	
121	A[28]	131	[27]	128.2	A	140.0	A	160.0	A	139.2	A
125	B	125		122.5	B	131.4	B	141.7	B	116.5	B
				94.2	AT	95.9	AT	94.5	AT	74.5	AT
70	A	74		72.2	A	78.4	A	80.2	A	64.0	A
65	B	66		60.6	B	67.0	B	62.7	B	50.1	B
				53.0	BT	56.7	BT	55.7	BT	47.4	BT
45	B	48		46.4	B	50.8	B	48.2	B	41.9	B
39	A	42		39.5	A	45.2	A	42.5	A	38.2	A
				35.9	AT	38.6	AT	39.3	AT	31.8	AT

D-ANT

Exp. Raman[28]	INS[29]	(1)		(2)		(3)	
		118.1	A	126.8	A	147.3	A
		112.6	B	119.5	B	130.3	B
		91.6	AT	92.7	AT	92.0	AT
66.0	68 ± 4	68.8	A	74.6	A	76.5	A
		57.8	B	63.6	B	59.8	B
		51.6	BT	55.0	BT	54.2	BT
	45 ± 2	44.0	B	48.3	B	45.8	B
36.5	35 ± 2	37.5	A	42.7	A	40.3	A
		35.0	AT	37.3	AT	38.2	AT

PHE

Exp. Raman[30]		ir[30]		(1)		(2)		(3)	
127	A	108	A	109.8	A	114.4	A	133.2	A
109	B	(99?)	B	96.8	B	100.1	B	113.4	B
89	A			81.9	A	83.6	A	84.9	A
				76.7	B	81.3	B	83.8	B
		62	A	59.8	A	68.1	A	72.4	A
				49.1	AT	54.9	AT	54.5	AT
60	B	60	B	50.2	B	53.1	B	51.0	B
		33	A	34.4	A	35.8	A	35.9	A
		31	B	26.5	B	25.5	B	27.2	B

BCP

(1)		(2)		(3)	
96.3	B_1	99.6	B_1	94.9	B_1
91.9	A_1	94.6	A_1	93.4	B_2
84.8	B_2	89.0	B_2	90.2	B_1
80.5	B_2	85.3	B_2	89.2	A_1
80.0	B_1	84.1	B_1	80.3	B_2
77.9	B_3	80.0	B_3	76.6	B_3
72.0	A_1	75.6	A_1	73.9	A_1

TABLE V. (Continued)

BCP

(1)		(2)		(3)		(4)
65.4	B_3	71.5	B_3	69.8	B_1	
63.6	B_1	68.2	B_1	68.4	B_2	
55.7	A_1	62.2	A_1	64.5	A_1	
54.2	B_1	58.0	B_1	61.0	B_2T	
53.4	B_2T	58.0	B_2T	57.4	B_1	
48.3	B_3	52.7	B_2	54.9	B_2	
47.8	B_2	50.2	B_3	54.5	B_3	
45.3	B_1	49.1	B_1	50.0	B_1	
42.3	B_3	45.1	B_3	46.9	B_3	
36.2	B_2T	37.0	B_2T	33.3	B_2T	
30.2	A_1	32.1	A_1	32.6	A_1	
26.2	A_1	28.6	A_1	27.1	A_1	
24.4	A_1	25.2	B_3	27.0	B_3	
23.5	B_3	24.3	A_1	22.1	A_1	

PYR

Exp.[30]		(1)		(2)		(3)	
		108.7	A_u	120.2	A_u	117.6	A_u
		108.7	B_u	120.1	B_u	115.4	B_u
126	B_g	106.1	B_g	118.8	B_g	114.8	B_g
126	A_g	103.4	A_g	115.8	A_g	111.9	A_g
93	B_g	91.4	B_g	96.0	B_g	93.9	B_g
92	A_g	90.3	A_g	96.0	A_g	94.1	A_g
		81.7	B_u	83.9	B_u	79.8	B_u
		79.0	A_u	83.5	A_u	77.1	A_u
76	A_g	70.1	A_g	65.1	A_g	69.9	A_g
67	B_g	67.2	B_g	73.4	B_g	74.4	B_g
		52.2	B_u	54.2	B_u	55.0	A_u
		50.6	A_uT	54.1	A_u	53.9	A_u
		47.9	A_u	51.9	A_uT	52.9	B_u
56	A_g	44.8	A_g	50.2	A_g	51.5	A_g
56	B_g	43.6	B_g	48.8	B_g	52.4	B_g
46	A_g	39.2	A_g	40.8	A_gT	41.9	A_g
41	B_g	38.0	B_g	39.5	B_gT	40.7	B_g
		34.6	B_u	37.7	B_u	36.1	B_u
30	B_g	27.8	B_g	28.7	B_g	29.5	B_g
		24.0	A_uT	23.0	A_uT	23.7	A_uT
30	A_g	22.1	A_g	23.8	A_g	23.6	A_g

PAN

(1)		(2)		(3)	
104.0	B_2	119.6	B_2	120.8	B_2
102.5	B_1	117.4	B_1	117.5	B_1
91.2	A_2	106.5	A_2	109.0	A_2
88.2	A_1	102.4	A_1	103.5	A_1
79.3	A_1T	84.8	A_1T	92.9	A_1T
68.2	B_2	73.9	B_2	81.8	B_2
64.2	B_1	69.1	B_1	74.8	B_1
57.5	A_2T	61.2	A_2T	65.9	A_2
53.6	B_1	57.0	B_1	65.7	B_1
49.3	A_2	55.6	A_2	61.0	A_2
47.9	A_2	48.5	A_2	59.2	A_2
45.2	B_2	48.4	B_2	53.5	A_1
43.0	A_1	47.2	A_1	52.0	B_2
40.6	A_1	41.8	A_1	48.8	A_1
38.9	B_2	41.1	B_2	44.0	B_2
37.9	B_1	39.2	B_1	43.0	B_1
34.9	B_1	37.8	B_1	41.4	B_1
27.3	A_2	30.0	A_2	29.2	A_2
23.7	A_1T	25.8	A_1T	27.6	A_1

TABLE V. (*Continued*)

PAN

(1)		(2)		(3)		(4)
23.6	B_2T	23.8	B_2T	25.4	B_2T	
21.0	A_2T	21.6	A_2T	19.0	A_2T	

BUT

(1)	(2)	(3)
89.6	101.2	94.4
74.9	75.8	83.4
42.0	50.7	53.1

DTO

(1)		(2)		(3)	
176.9	A	187.1	A	203.7	A
151.9	B	172.6	B	166.8	B
86.0	BT	90.6	BT	99.4	BT
76.9	B	84.0	B	91.5	B
73.0	AT	75.9	AT	87.2	AT
68.2	A	75.8	A	82.6	A
61.0	AT	70.8	AT	73.1	AT
33.8	A	38.2	A	39.6	A
30.4	B	33.9	B	33.8	B

BIC

(1)		(2)		(3)	
82.5	A_g	93.4	A_g	94.2	A_g
79.6	B_g	89.5	B_g	89.6	B_g
66.7	A_u	70.4	B_g	74.5	B_gT
66.5	B_gT	69.5	A_u	74.2	A_u
64.7	B_u	66.9	B_u	71.1	B_u
56.3	A_g	61.0	A_g	59.3	A_g
55.2	B_g	59.4	B_g	57.3	B_g
54.6	B_g	57.3	A_g	54.8	A_g
53.6	A_g	56.7	B_g	54.4	B_g
48.0	B_u	50.9	A_u	50.1	A_g
47.9	A_u	48.0	B_g	48.4	B_u
44.9	A_u	45.4	A_u	47.0	A_u
44.1	A_g	44.9	A_g	46.5	A_g
40.8	B_g	43.5	B_g	43.6	B_g
40.4	A_u	42.0	A_u	41.3	A_u
40.3	A_g	40.8	A_g	40.5	A_g
36.4	B_u	35.5	B_u	37.4	B_u
32.7	B_u	34.5	B_g	34.1	B_u
31.9	B_g	33.6	B_u	33.3	B_g
30.8	A_g	32.2	A_g	29.7	A_g
20.7	A_uT	21.4	A_uT	22.3	A_uT

in line with the results reported for crystalline benzene[5] and is to be considered as a very strong evidence for rigid-body behavior of these molecules. To this purpose, it is also interesting to consider that the maximum frequency of internal modes for benzene, naphthalene, anthracene, and phenanthrene is 403.5, 390, 243, and 240 cm^{-1}, respectively[5,28,30]; the maximum experimental frequency for external modes is almost the same for all these compounds and lies just below 130 cm^{-1}. This confirms a good separation of modes for these molecules.

The measurements reported in Pawley[2] for naphthalene are considerably different form Suzuki *et al.*'s[28] results; it seems, however, that the former data are not correct, the frequencies as reported being in general too high compared with accepted values. In Table V, these frequencies are shown side by side with Suzuki *et al.*'s data

TABLE VI. **T**, **L**, **S** tensors, (1) from Schomaker and Trueblood's treatment (2) from our calculations (Williams IVa functions). Cartesian reference system with axes on **a***, **b**, **a***×**b**.

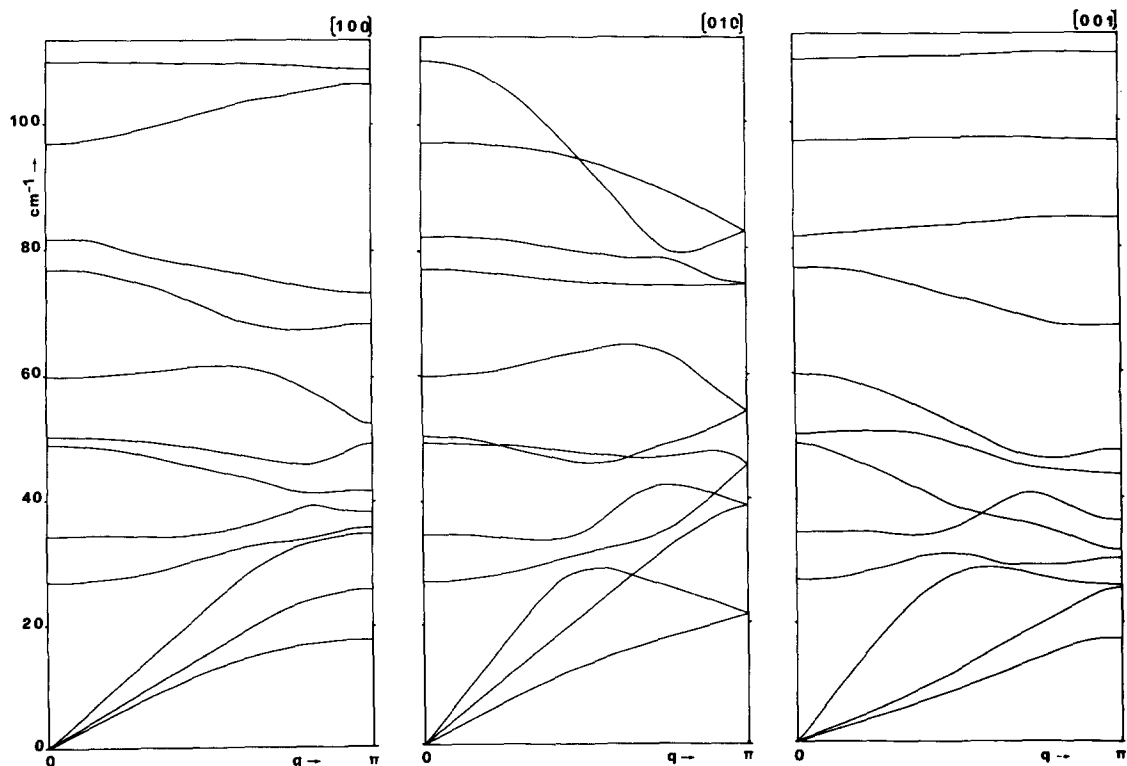|	**T** ($\text{Å}^2 \times 10^4$)			**L** ($\text{rad}^2 \times 10^4$)			**S** ($\text{Å} \cdot \text{rad} \times 10^4$)			Eigenvalues of **L** (degree^2)
NAP										
(2)	522	32	−51	70	−2	−8				28.4
		527	−8		66	−15				23.2
			564			73				17.0
ANT										
(1)	391	27	−93	23	0	1				10.0
		423	−25		24	0				8.0
			500			18				3.3
(2)	444	15	−101	33	0	−5				19.2
		442	−15		26	−12				10.6
			514			53				6.9
PHE										
(1)	444	46	72	55	−5	0	−11	−10	21	21.4
		560	−19		38	6	−3	18	−9	18.4
			566			64	6	4	−7	11.7
(2)	560	53	18	75	−11	−13	−35	−28	5	29.1
		611	19		44	6	22	30	5	19.3
			589			69	17	1	8	13.4
PYR										
(1)	413	47	189	53	−18	4	10	10	−3	23.0
		354	33		47	14	9	0	9	17.8
			618			49	−7	−6	−10	8.1
(2)	490	77	1	38	−12	4	2	−4	5	18.1
		452	−12		45	7	−5	−2	−8	14.8
			729			43	−5	0	−11	8.5

FIG. 1. Dispersion curves for phenanthrene.

TABLE VII. Experimental (obs.) and dynamical (cal.) values of anisotropic temperature factors $B_{ij}(\times 10^4)$. Accurate experimental data for Naphthalene are lacking. The temperature factors are in the form:

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

NAP (cal.)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C 1	367	513	229	28	158	−8
C 2	356	467	285	36	195	70
C 3	300	382	237	−15	125	−52
C 4	288	333	294	−7	162	27
C 5	215	293	222	4	109	−9

	B_{11}		B_{22}		B_{33}		B_{12}		B_{13}		B_{23}	
	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.
ANT												
C 1	271	291	444	482	136	136	6	34	112	111	−22	1
C 2	197	254	317	364	116	131	−10	4	73	90	−23	−29
C 3	150	174	242	270	124	123	−2	2	73	70	−1	−11
C 4	158	183	241	249	130	134	−5	−15	77	74	−31	−12
C 5	144	168	241	267	126	129	−11	0	72	74	21	4
C 6	189	227	332	351	146	157	15	−5	85	104	−31	33
C 7	260	271	468	473	144	155	16	27	114	122	61	46
PHE												
C 1	233	229	510	571	135	139	1	3	44	16	47	47
C 2	237	252	604	735	132	148	−17	−40	12	−3	−15	−37
C 3	211	248	521	601	162	199	−47	−101	1	19	−55	−89
C 4	186	215	348	393	153	187	−25	−60	37	44	−13	−28
C 5	190	277	362	477	158	162	27	82	47	66	29	75
C 6	265	363	597	770	123	151	92	168	45	56	70	100
C 7	227	340	669	943	140	135	50	165	9	0	−56	−14
C 8	198	259	561	730	169	164	68	71	−26	−14	−106	−98
C 9	176	209	378	374	200	216	−35	−28	42	22	−29	−47
C10	202	210	310	339	195	201	−9	−20	55	37	28	27
C11	149	172	330	361	155	140	28	0	33	22	8	27
C12	134	163	283	321	130	137	−17	1	34	29	24	6
C13	134	182	317	363	133	133	32	45	38	30	−15	14
C14	141	188	397	440	154	153	27	35	25	8	−34	−43
PYR												
C 1	91	84	177	200	234	278	10	12	23	−12	−38	−60
C 2	65	72	149	163	287	322	−13	−8	36	10	−59	−51
C 3	63	63	104	123	228	266	−4	−1	57	27	−16	−17
C 4	86	82	123	138	283	307	−8	−9	89	55	26	8
C 5	98	94	151	146	242	257	15	9	93	56	47	26
C 6	72	75	132	130	164	209	27	20	47	28	20	5
C 7	86	97	210	176	176	210	45	32	22	11	−1	−8
C 8	75	89	223	188	244	256	24	21	18	−14	−43	−42
C 9	58	70	171	157	318	294	−9	−1	37	0	−57	−34
C10	56	59	106	121	252	247	−1	3	54	−19	−5	−7
C11	81	73	132	140	318	281	−13	−6	90	40	26	18
C12	97	84	142	153	243	240	13	8	86	40	54	29
C13	74	69	115	137	172	207	17	17	53	21	17	1
C14	102	89	181	188	153	218	34	26	29	4	−6	−19
C15	55	55	83	109	170	212	5	11	46	22	0	−7
C16	53	56	90	107	170	207	8	13	43	21	1	−3

(the first two columns), the latter being much more in agreement with Williams IVa results.

Considering anthracene, we can see that in spite of the relatively high disagreement between frequencies calculated by using different functions, the values of B's in several cases are about the same (as it can be seen for instance from the values
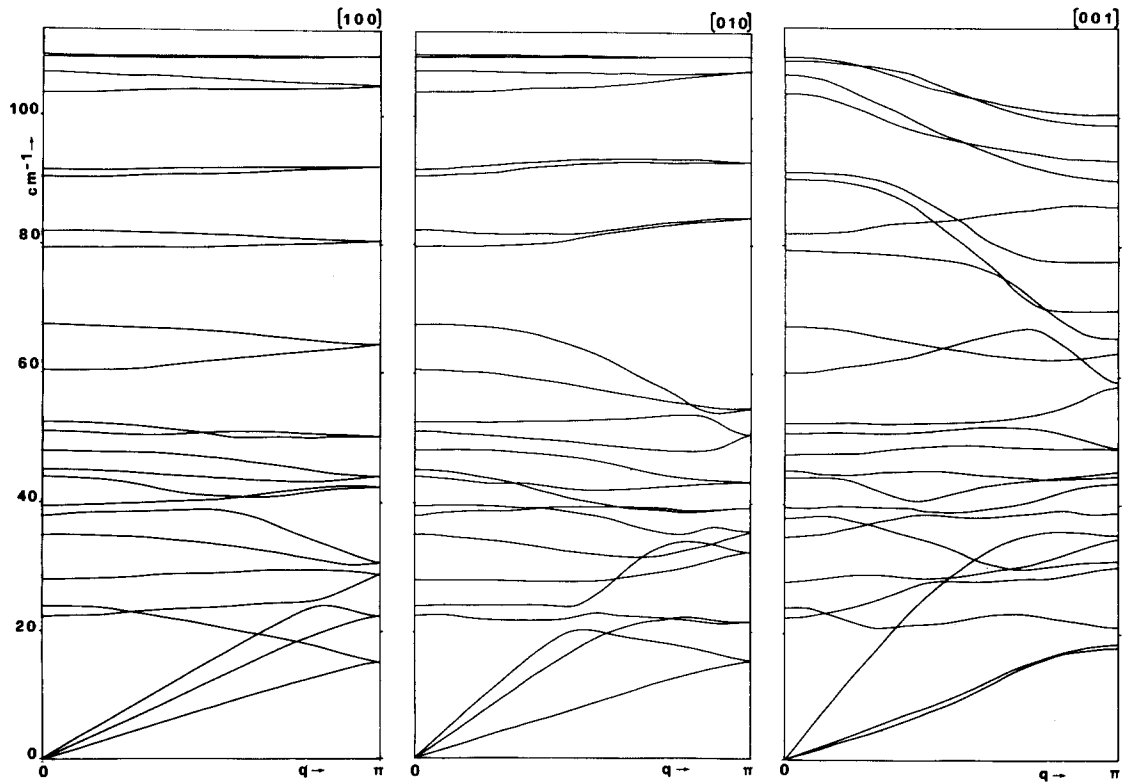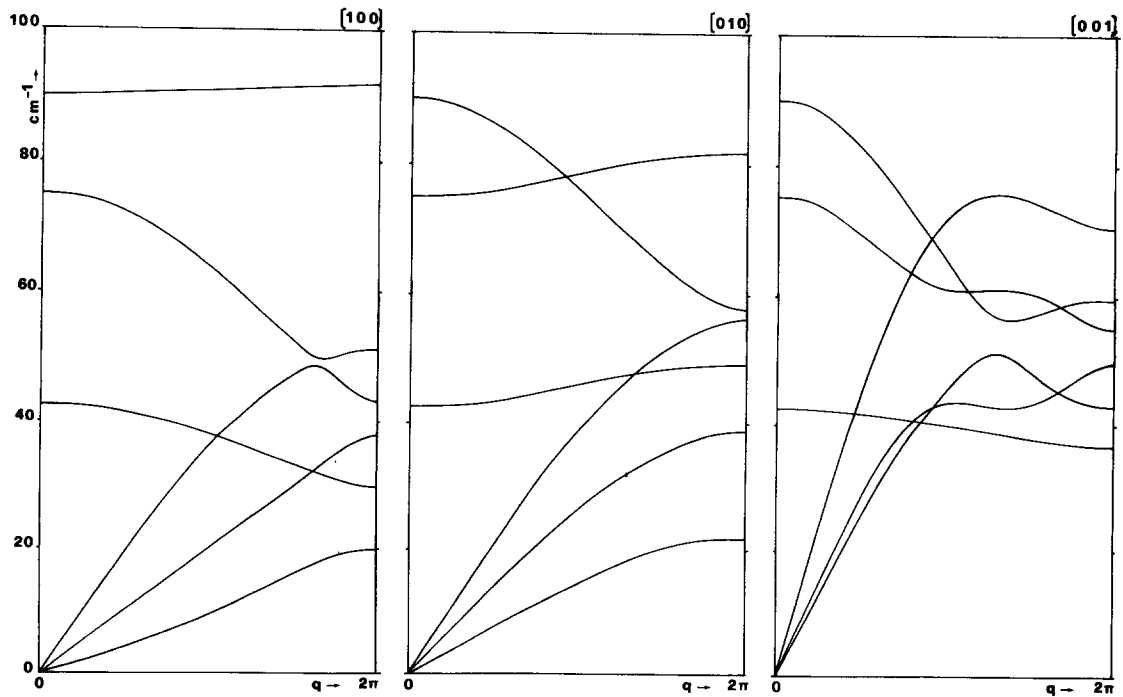
FIG. 2. Dispersion curves for pyrene.

FIG. 3. Dispersion curves for BUT.

of R_B and ΔB). This happens because at ordinary temperature the greatest number of molecules vibrates in low-energy modes, whose frequencies may not vary greatly when potential functions are changed. For similar reasons, we think that even in case some of the molecules considered here should show a nonstrictly rigid behavior, this would not be particularly important in affecting values of B's and/or thermodynamic functions, since the modes involving considerable distortion must correspond only to the highest frequencies.

For pyrene, the agreement is less good. This is probably due to a combination of several effects, among which can be included a certain nonrigidity of the molecule, as would be expected from the low value of separation between internal and external modes (169 and 126 cm^{-1}, respectively[31]) and from its relatively large dimensions. However, the highest calculated frequency might be expected to be higher than the experimental one instead of being lower; this fact is probably connected with the particular packing observed for this substance and the possible presence of π bonding between different molecules.
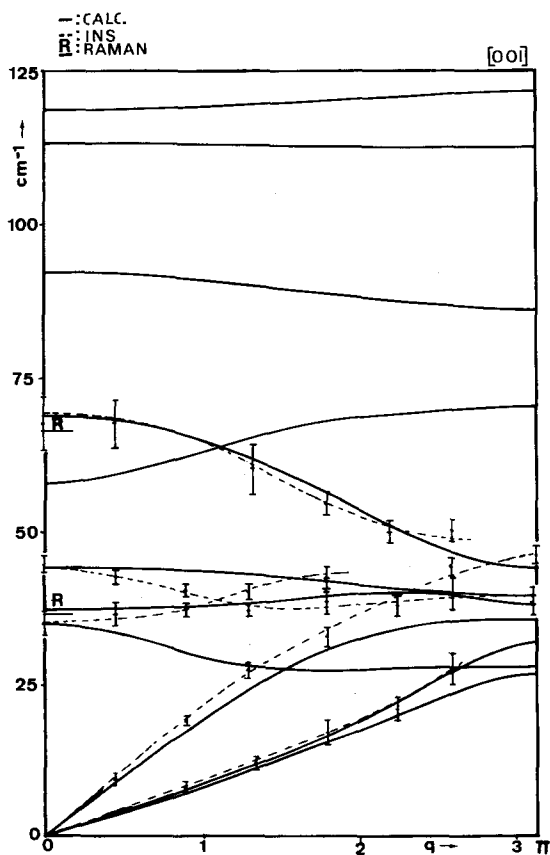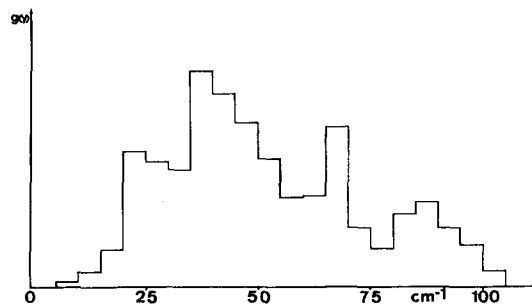

FIG. 5. Density of states for PAN.

The values of **T**, **L**, **S** tensors and of the B's have been calculated by Williams IVa functions for all the substances here examined; for the sake of simplicity in Table VI and VII only the results for NAP, ANT, PHE, and PYR have been reported.

In general, for the reason mentioned above, the values are not subject to extensive variation when Williams IVb or Kitaigorodskii's expressions are used instead of Williams IVa functions. In most cases, the agreement with values obtained from Schomaker–Trueblood's treatment[19] of crystallographic data is fair; the differences, however, are not quite negligible and in some cases, in spite of the excellent agreement between experimental and dynamical B's, they are surprisingly large. For instance, the value of L_{33} for anthracene is 0.0053 rad^2, to be compared with an "experimental" value of 0.0018 rad^2. This points to a certain degree of ill conditioning in the normal equation matrix of Schomaker–Trueblood's treatment, because small differences in the B's, such as those existing between experimental and calculated values, give rise to quite different interpretations of this rigid-body motion. Such ill conditioning is not surprising; see for instance a discussion of singular cases reported by Johnson.[20] As a matter of fact, especially when the agreement with spectroscopic data is excellent, as for anthracene, we feel that the dynamical treatment is indeed more reliable than the results obtained from crystallographic data and this may provide an effective way for appropriate correction of bond lengths, as an alternative to the usual crystallographic routine.[19,33,34] Moreover, this alternative may eventually prove to be the only way available when the normal-equation matrix of Schomaker–Trueblood's technique is singular or even ill conditioned (apart from the indeterminacy of the trace of **S**), the regression on principal components as proposed by Johnson[20] being very questionable for most cases on physical-mathematical grounds.

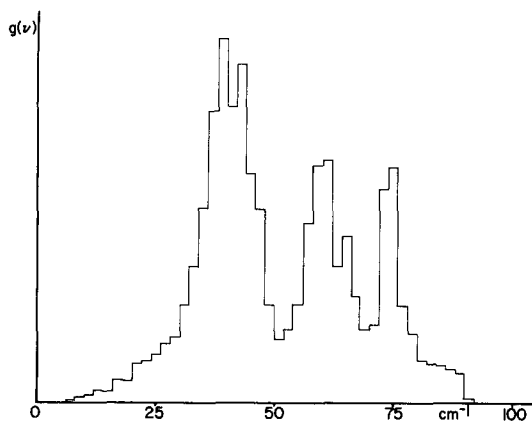Further work in this field is in progress; comparing bond length corrections obtained by a

FIG. 4. Comparison between experimental and calculated dispersion curves for deutero-anthracene along |001|.

FIG. 6. Density of states for BUT.

functions, however, as well as the **B**'s, are mostly connected with the region of lower frequencies (see above).

As an example, the density of states for PAN and BUT are reported in Figures 5 and 6. As for the evaluation of **B**'s, this density is evaluated by accumulating for each energy interval all frequencies resulting from sampling the Brillouin zone with a given number of points; if scanning intervals are uneven, a weight proportional to the extension of the zone between adjacent points is assigned.

For PAN, the sampling points throughout the Brillouin zone are the same (500) used for calculation of **B**'s and the plot reported in Figure 5 came out indeed as a "by product" of these calculations. For BUT, a "thicker" sampling was tried, using an evenly spaced grid of $\pi/10$ along each reciprocal axis of the primitive cell, so that 4000 points have been considered.

Since these calculations may become very cumbersome and time consuming, the number of sampling points is to be considered with particular care, in view of the applications one intends to develop. This point is particularly evident for larger dynamical matrices, such as the one of PAN, whose order is 24, to be compared with the corresponding matrices in BUT, whose order is 6 and where the problem is of course less critical. Further work is in progress to set up a practical way for obtaining significant values of thermodynamic functions without involving huge amounts of calculation, a goal we accomplished for the evaluation of temperature factors[17]; it might well be that the same scanning could be just as good. Also an extension of this method to semirigid molecules is being presently considered.

Schomaker–Trueblood treatment or through a lattice dynamical analysis shows differences amounting to a maximum of 0.004 Å; this is surely not a very important effect, but it may be of importance in particularly accurate work and anyway already gives an idea about the problems which are still to be solved before claiming accuracy below 0.005 Å in "crystallographic" bond lengths.

B. Dispersion Relations and Frequency Distribution

The programs as written afford several other possibilities, such as easy calculation of dispersion curves along any direction and density of states. As is well known, such calculations on rather complex molecules, although scarce at present, can provide further possibilities of testing the goodness of empirical atom–atom potential functions.

The dispersion curves have been calculated along principal directions (reciprocal crystallographic axes) for all the substances here examined, using Williams IVa functions: Figures 1–3 show, as an example, the ones for PHE, PYR, and BUT (the others are available from the authors at request); Fig. 4 shows dispersion curves relative to deuterated anthracene (D-ANT) along [001], the only case for which comparison with experimental data is available at present.[29] It can be seen that the agreement is fairly good.

Concerning the density of states, for which no direct experimental data are yet available for these substances, some indirect (and partial) evidence for its essential correctness can be given by the values of **B**'s, whose agreement with experimental results, as we have seen, is good. Further indirect evidence can be obtained by evaluation of thermodynamic functions, a method which at the present time is being considered with particular attentiveness in our laboratory; the values of these

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