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Intermolecular Forces and Vibrational Spectra of Crystalline Benzene and Naphthalene†‡

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Abstract—Theoretical calculations are presented for the splittings, caused by intermolecular forces, of vibrational spectroscopic transitions in crystalline benzene and naphthalene. Semi-empirical potential functions for the interactions between pairs of molecules are assumed. The interaction between two molecules is further assumed to be composed of central forces acting between pairs of atoms, one on each molecule.

Several semi-empirical potentials for hydrogen–hydrogen, hydrogen–carbon and carbon–carbon interactions are used in the computations. The infrared spectra of single crystals of naphthalene have been remeasured, and the observed splittings are compared with the theoretically calculated values; comparisons are also made for benzene.

It is concluded that short-range potentials similar to the ones assumed are primarily responsible for the observed splittings, that both hydrogen–hydrogen and hydrogen–carbon interactions are important, and that carbon–carbon interactions are only of marginal importance. Although one specific set of potential parameters gave the best results, it was not possible to refine the parameters significantly.

Introduction

A number of workers have studied the intermolecular force functions which are of importance in determining the physical properties of molecular crystals. For a number of crystals a potential function

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which depends on the interactions of pairs of atoms, one in each of two neighboring molecules, has proved rather successful,[1-4] and parameters for such potentials between hydrogen, carbon, etc., atoms have been given, derived from data on physical properties such as compressibility, intermolecular spacing, etc.

The changes in vibrational spectra which occur when a substance is condensed are also a consequence of intermolecular interaction,[5, 6] and efforts have been made to use observed splittings of vibrational transitions to obtain data on intermolecular forces. The postulate of atom–atom forces has met with some success in interpreting the spectra of methyl chloride, ethylene,[5, 6] and benzene,[7] among others. In these cases it has been assumed that intermolecular hydrogen–hydrogen atom contracts are of major importance.

It is the purpose of this work to use potential functions derived theoretically, or empirically from study of other physical properties, to predict the splittings of vibrational transitions in benzene and naphthalene, in order to determine the applicability of the functions, to study the compatibility of the various measurements as sources of information about intermolecular potentials, and to investigate the importance of various atom–atom interactions in these particular crystals.

Experimental

In order to compare the calculated frequencies with experimental spectra it is desirable to know not only the frequency splittings but also the polarizations of the transitions in the crystal. For benzene our present and previous calculations,[8] and those by Harada and Schimanouchi,[7] have had to be compared to spectra of polycrystalline samples, since the only single crystal study of benzene[9] was done at low resolution. We felt that improved instrumentation warranted repeating the work of Person, Pimentel and Schnepp[10] on the infrared spectrum of single crystal naphthalene.

Naphthalene single crystals of several square centimeters area and thicknesses in the range of 1 to 10 microns were grown by sublimation. All had the *ab* plane of the monoclinic ($P2_1/a$) structure developed. The known optical properties[11] allowed identification of the unique *b* axis by conoscopic observation. For the most strongly absorbing band (785 cm^{-1}) even the thinnest of these crystals were too thick, and a crystal about one half micron thick was grown from the melt between optically flat sodium chloride plates for determination on this band.

Infrared spectra were obtained at room temperature and at 80°K with a Perkin–Elmer 521 Spectrometer equipped with a wire-grid polarizer. The low temperature spectra of the single crystal samples were obtained using an Air Products Cryotip cell. The *b* axis of the crystal was placed perpendicular to the direction of light propagation in the spectrometer and at 45° to the direction of ruling of the grating. The polarizer was oriented at $\pm 45°$ to the ruling direction (parallel or perpendicular to the *b* axis) to minimize polarization effects from reflectance within the instrument. Room temperature spectra were also taken with the sample tilted at an angle of about 30° from perpendicular to the optical path in order to observe modes with transition moments nearly perpendicular to the *ab* plane. Spectra of polycrystalline samples were also obtained using a conventional cryostat and deposition from the vapor (with annealing). Our results do not indicate any significant departure from assignments based on previous experiments.[12–17]

THEORY

The calculations of crystal frequencies and splittings were made in the approximation common to molecular crystal theories, that intermolecular forces are weak compared to valence forces. The perturbation theory is well known, and will not be repeated here. The necessary results, as given by Dows,[6] are that crystal transition energies are

$$E^{\alpha} - E^{0} = \epsilon' - \epsilon^{0} + \mathbf{D} + \mathbf{M}^{\alpha}, \tag{1}$$

where α labels representations of the factor group and ϵ' and ϵ^0 are excited and ground state energies of the gaseous molecule. All results presented here are for vibrational excitons with wave vector $\boldsymbol{\varkappa} = 0$. The excitons are derived from internal molecular fundamental modes. It is assumed that external motions are separable as rigid-body motions of the molecules within the crystal (although this may not be a good approximation for the lowest frequency internal modes).

The term **D** causes an energy shift, and for degenerate internal modes may cause loss of degeneracy:

$$\mathbf{D} = \sum_r (h/8\pi^2 c\nu_0)(\partial^2 V_{pr}/\partial Q_p^2)_0. \tag{2}$$

In this sum p labels a molecule at the origin while r ranges over all other molecules in the crystal. The second derivative is of the intermolecular potential, V_{pr}, with respect to the normal coordinate Q_p of the origin molecule. The term **M** gives the energy splitting of the crystal states; it expresses dynamic interactions of two oscillators.

$$\mathbf{M}^\alpha = t \sum_r B^*_{\alpha a} B_{\alpha b}(h/8\pi^2 c\nu_0)(\partial^2 V_{pr}/\partial Q_p\, \partial Q_r)_0. \tag{3}$$

B is a unitary matrix describing the transformations of the molecules within the unit cell by the factor group, and t is the number of equivalent sites in the unit cell. These results contain the usual assumption of harmonic intermolecular potentials.

If it is further assumed that the perturbing intermolecular forces may be expressed as pairwise interactions between atoms of the molecules, with the interatomic potential dependent only on the interatomic distance, then the second derivatives may be written

$$(\partial^2 V_{pr}/\partial Q_p\, \partial Q_r)_0 = \sum_{ij}\sum (\partial^2 V/\partial r_{ij}^2)_0 \left(\frac{\partial \mathbf{r}_{ij}}{\partial \mathbf{r}_i}\frac{\partial \mathbf{r}_i}{\partial Q_k}\right)\left(\frac{\partial \mathbf{r}_{ij}}{\partial \mathbf{r}_j}\frac{\partial \mathbf{r}_j}{\partial Q_k}\right). \tag{4}$$

Here r_{ij} is the distance between atom i of molecule k and atom j of molecule k'. $\mathbf{r}_i$ and $\mathbf{r}_j$ are the position vectors of the atoms. The first factor in (4) is computed at the equilibrium distance from an assumed potential function. The factors $(\partial \mathbf{r}_{ij}/\partial \mathbf{r}_i)$ are cosines of angles between interatomic vectors and position vectors, and are determined by the geometry of the crystal structure. The factor $(\partial \mathbf{r}_i/\partial Q_k)$ is the cartesian displacement of atom i in normal coordinate Q of molecule k.

All of the above formulae result from the assumption of first-order perturbation theory, that non-degenerate intramolecular modes do not interact in the crystal. This assumption is justified if the crystal splittings are small compared to the spacing of normal frequencies. Some calculations of inter-mode coupling have been made for benzene, and the results given below support the neglect of such coupling in most cases.

Benzene

The benzene crystal belongs to space group P_{bca}—D_{2h}^{15}. There are four molecules per unit cell on sites of symmetry $\bar{1}$. The structure determination[18] was carried out at -3°C; in order to compare our calculations with infrared data obtained at liquid nitrogen temperature it was assumed that the unit cell contracts according to the anisotropic temperature coefficients, with neither molecular reorientation nor molecular distortion. Kozhin[19] has determined the unit cell parameters at 77°K. Neutron diffraction studies[20] at -55 and -135°C show that as the temperature is lowered there is a small amount of reorientation such that there is closer packing along the c axis. Thus our assumption for the low temperature structure was not completely justified, but other approximations are probably more important. Carbon–hydrogen bond distances are all taken to be 1.08 Å.

Selection rules for $\mathbf{k}=0$ transitions have been given before.[6] Only the center of symmetry is retained in the site, so all *ungerade* modes are active in the infrared and there is no degeneracy. Non-degenerate molecular modes result in four crystal states; Raman transitions are allowed to all four if *gerade*, infrared transitions are allowed to three of the four if *ungerade*. Each of the three infrared transitions is polarized along one of the crystal axes, but the lack of well-resolved single crystal spectra precludes definite assignment of multiplet components on the basis of polarization data. Doubly degenerate molecular modes give eight crystal frequencies, six being infrared active if the mode is *ungerade*. Many of the predicted crystal transitions have been observed, and accurate frequency data have been reported by Hollenberg and Dows.[21]

Dr. James R. Scherer kindly provided us with numerical results for the Cartesian displacements for the in-plane modes of benzene corresponding to his published normal coordinate analysis.[22, 23] The single out-of-plane mode for which we did calculations is the only one of its species (A_{2u}) so that the normal coordinate is just the properly normalized symmetry coordinate.

In evaluating the sums of equation (4) twenty intermolecular hydrogen–hydrogen contacts were included, five different distances with four symmetrically equivalent contacts each. The contact distances range from 2.4 to 2.7 Å, where there happens to be a break, so that the next contact distances are considerably larger. A repulsive potential was used:

$$V(\text{ergs}) = 1.2 \times 10^{-10} \exp(-3.54R), \tag{5}$$

where R (in Ångstrom units) is the interatomic distance; the parameters are taken from a theroetical calculation by deBoer,[24] and this potential has been discussed previously.[6] No interaction involving carbon atoms was considered in this exploratory study.

Results for the intense out-of-plane hydrogen bending mode (near 673 cm^{-1} in the gas phase spectrum) are shown in Fig. 1 and Table 1. In the figure, calculated frequencies (not intensities) are indicated by the markers superimposed on the experimental spectra from reference 21. The transition to the A_u crystal state is dipole-forbidden.

Figures 2 and 3 and Table 2 show the results for the in-plane degenerate vibrations (near 1036 and 1480 cm^{-1}). Here relative intensities were calculated to try to interpret the more complex structure. Intensities were based on the oriented gas approximation

$$I_\alpha \sim (C_1 \mu_\alpha^1 + C_2 \mu_\alpha^2)^2, \tag{6}$$

where C_1 and C_2 are mixing coefficients from the perturbation calculation. Superscripts label the two states degenerate in the

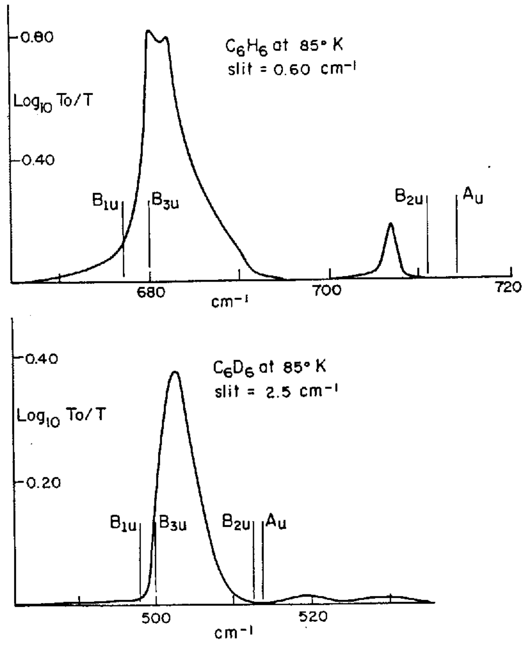

Figure 1. Infrared absorption spectrum of $\nu_{11}(a_{2u})$ in crystalline benzene and deuterobenzene. Vertical lines indicate calculated frequencies (but not intensities) of crystalline transitions.

TABLE 1 Experimental (Ref. 24) and Calculated Transition Frequencies for the "Umbrella" Mode of Benzene

	Calc. (cm^{-1})	Obs. (cm^{-1})	Direction
C_6H_6			
A_u	714	—	inactive
B_{1u}	677	680	*a*
B_{2u}	711	707	*b*
B_{3u}	680	681	*c*
C_6D_6			
A_u	514	—	inactive
B_{1u}	498	502[a]	*a*
B_{2u}	513	519	*b*
B_{3u}	500	502[a]	*c*

[a] Single broad band at 502 cm^{-1} contains both components.

free molecule; α designates the representation of the factor group, so that, e.g.,

$$\mu^1_{A_u} = \mu^1(1)+\mu^1(2)+\mu^1(3)+\mu^1(4). \tag{7}$$

This is the vector sum of the transition moments of the four molecules in the unit cell for a transition belonging to a state belonging

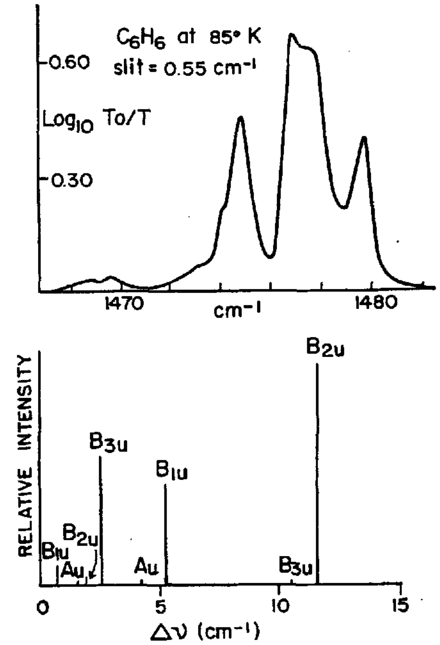

Figure 2. Infrared absorption spectrum of $\nu_{19}(e_{1u})$ in crystalline benzene. Vertical lines indicate calculated frequencies and intensities.

to the factor group representation A_u. These modes are of species E_{1u} in the free molecule—the degeneracy makes the computation more complex and the results correspondingly less reliable.

Table 2 also shows the result of taking into account the small perturbation caused by interaction of the 1036 and 1480 cm^{-1} states. This mixing of different modes does not appreciably alter the results; the fact that calculated splittings are only a few percent of the intermode separation indicated that this would be the case.

A mode of B_{1u} symmetry, inactive in the gas phase, near 1010 cm^{-1}, becomes allowed in the crystal. It is observed[21] as a sharp doublet of 0.5 cm^{-1} separation with a weak broad shoulder about 3 cm^{-1} lower. The computed frequency shifts are 0.60 (A_u), 0.22 (B_{1u}), 1.14 (B_{2u}) and 0.75 (B_{3u}).

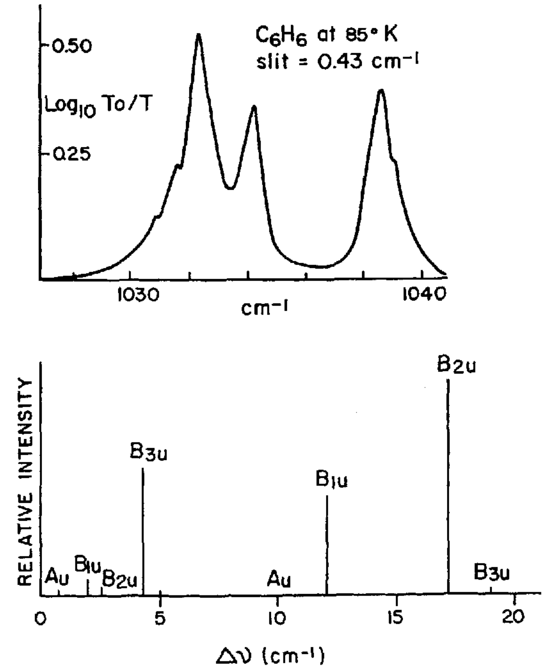

Figure 3. Infrared absorption spectrum of $\nu_{20}(e_{1u})$ in crystalline benzene. Vertical lines indicate calculated frequencies and intensities.

Calculations for the totally symmetric, Raman active mode at 992 cm^{-1} give frequency shifts of 0.70 (A_g), 0.01 (B_{1g}), 1.24 (B_{2g}) and 0.64 (B_{3g}). Mixing with other modes was not included. Raman experiments at 77°K,[25, 26] 4.2°K[27] and 2°K[26] have shown no observable splitting of this band.

One other mode of benzene was treated, the E_{2g} at 606 cm^{-1}. Ito and Ito and Shigeoka[25, 27] report no splitting from this band. Gee and Robinson[26] report four of the possible eight lines at 605.2, 606.3, 609.0 and 611.0 cm^{-1}. The calculated shifts are 1.09 and 0.03 (A_g), 0.41 and 0.15 (B_{1g}), 1.57 and 0.22 (B_{2g}) and 1.04 and 0.17 (B_{3g}).

TABLE 2 Calculated Results for the Doubly Degenerate (E_{1u} in D_{6h}) Modes of Benzene

	$\Delta\nu$, no mixing[a] (cm^{-1})	$\Delta\nu$, mixing (cm^{-1})
1036 cm^{-1} Mode species (D_{2h})		
A_u	1.1	0.75
	10.2	10.0
B_{1u}	2.2	2.0
	12.2	12.1
B_{2u}	17.4	17.2
	2.6	2.6
B_{3u}	19.1	19.0
	4.3	4.2
1480 cm^{-1} Mode species (D_{2h})		
A_u	1.3	1.6
	4.1	4.2
B_{1u}	0.5	0.73
	5.1	5.2
B_{2u}	11.7	11.6
	1.6	1.8
B_{3u}	10.5	10.6
	2.6	2.5

[a] "Mixing" and "no mixing" refer to interactions among the free molecule states with energies 1036 and 1480 cm^{-1}, i.e., for "no mixing" there are eight crystal states; with "mixing" sixteen which can interact.

Generally our results, which also extended to calculation of lattice frequencies, agree well to those of Harada and Shimanouchi,[7] so that when their work appeared it seemed more worthwhile to shift our attention to a more extensive calculation on naphthalene rather than to continue with other modes of benzene.

NAPHTHALENE

Naphthalene belongs to the space group $P2_1/a—C^5_{2h}$, with two molecules per unit cell on sites of symmetry $\bar{1}$. Cruickshank's refinement[28] of the original room temperature data of Abrahams, Robertson and White[29] was used. The structure has also been determined at 77°K,[30] but the accuracy of our calculations does not warrant a meaningful comparison of differences in results for the two temperatures. The factor group is isomorphous with $2/m$ (C_{2h}); consequently each *ungerade* molecular mode is split into two components in the crystal. One of these components will have its transition moment parallel to the *b* axis, and the other will lie in the *ac* plane. The out-of-plane modes belonging to A_u in the free molecule become infrared active in the crystal. All the *gerade* modes are Raman active in the free molecule, and in the crystal each is split into two components by the correlation of the dynamics of the two molecules in the unit cell.

Although several normal coordinate analyses of naphthalene have been published, the numerical values of the Cartesian displacements were not available to us. We therefore repeated the molecular analysis to compute them. For the out-of-plane modes we attempted to reproduce the results of Scully and Whiffen,[12] using their potential constants. Because of possible ambiguities in the definition of their force field and differences in definitions of coordinates in related papers of theirs,[13–15] we did not succeed in reproducing exactly their frequencies. We did eventually arrive at a set of frequencies with at least as good agreement with accepted assignments as theirs, and computed Cartesian displacements. For in-plane vibrations we used the force field of Neto, Scrocco and Califano.[16] We made the simplifying assumption that the molecular geometry involved two adjacent regular hexagons with carbon–carbon bond lengths of 1.40 Å, and calculated frequencies in close agreement with theirs. The computed Cartesian displacements for the in-plane modes are in very satisfactory agreement with Scherer's graphical results,[17] especially since Scherer used a Urey-Bradley force field and our calculations used the valence force field. Our numerical results are available.[31]

The summation of equation (4) was extended over all non-bonded contacts less than 5 Å. These total nearly 700, comprising 156 H—H, 348 H—C and 192 C—C interactions. A computer program effected the evaluation of the crystal energies. Input data included atomic coordinates in the crystal, Cartesian displacements, and parameters for the interatomic potential functions. The program transforms the Cartesian vectors from molecular to crystal coordinates, including factor group transformations; processes the sequence of contacts, sorting the interactions into C—C, C—H and H—H types and also sorting the interactions between molecules equivalent or not under primitive translations; evaluates derivatives of the potentials; computes the geometrical factors; combines the factors into products; and finally computes the lattice sums.

The potentials used were all of the form

$$V = -AR^{-6} + B\exp(-CR), \tag{8}$$

where R is the interatomic distance. There are three sets of each of the parameters A, B, and C to account for H—H, H—C and C—C potentials. Pawley[4] has recently calculated a number of properties involving the lattice dynamics of naphthalene and anthracene using these potentials with the parameters of Kitaigorodskii,[2] who himself has for some time used these potentials for crystal packing calculations. We have used Kitaigorodskii's parameters, the deBoer potential mentioned above in the calculation on benzene, and also two sets of parameters given by Williams,[3] who has obtained several sets by fitting seventy-seven experimentally determined properties of fourteen aromatic hydrocarbon crystals. The numerical values of each of our sets of parameters are given in Table 3. Our objective is to determine whether these potentials, empirically fit to properties such as elastic constants, expansion coefficients, heats of sublimation, etc., can also account for the vibrational splittings.

Tables 4–7 give the splittings and polarization behaviour as observed (where available) and as calculated with the parameters of Table 3 for naphthalene at room temperature. The approximate frequencies are for identification only. For the out-of-plane modes

TABLE 3 Parameters for the Potential Function $V = -AR^{-6} + B\exp(-CR)$

	DEBOER[a]	KITAIGORODSKII[b]	WILLIAMS (I)[c]	WILLIAMS (III)[c]
$A_{\mathrm{H-H}}$ (erg Å × 10^{12})	0	3.96	4.93	3.47
$B_{\mathrm{H-H}}$ (erg × 10^{10})	1.20	29.2	2.78	2.78
$C_{\mathrm{H-H}}$ (Å^{-1})	3.54	4.86	3.74	3.74
$A_{\mathrm{C-H}}$ (erg Å^{6} × 10^{12})	0	10.7	5.98	11.7
$B_{\mathrm{C-H}}$ (erg × 10^{10})	0	29.2	4.70	9.22
$C_{\mathrm{C-H}}$ (Å^{-1})	0	4.12	3.67	3.67
$A_{\mathrm{C-C}}$ (erg Å^{6} × 10^{12})	0	24.9	41.8	30.4
$B_{\mathrm{C-C}}$ (erg × 10^{10})	0	29.2	62.0	30.6
$C_{\mathrm{C-C}}$ (Å^{-1})	0	3.58	3.60	3.60

[a] Reference 24.
[b] Reference 2.
[c] Reference 3.

TABLE 4 *Ungerade* Out-of-plane Modes of Naphthalene

Molecular species	Approximate frequency (cm^{-1})	OBSERVED		DEBOER		KITAIGORODSKII		WILLIAMS (I)		WILLIAMS (III)	
		Splitting (cm^{-1})	Higher[a]	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher
A_u	970	~0	B_u[b]	4.4	B_u	1.2	B_u	2.7	B_u	3.2	B_u
A_u	841	3	B_u	1.1	B_u	1.0	B_u	1.0	B_u	1.5	B_u
A_u	581[c]	?	?	2.2	B_u	2.4	B_u	2.6	B_u	3.5	B_u
A_u	210	3[d]	?	2.7	B_u	0.7	A_u	2.3	B_u	2.2	B_u
B_{3u}	957	3	A_u	0.3	B_u	0.9	A_u	0.2	A_u	0.7	A_u
B_{3u}	782	10	A_u	8.4	A_u	2.3	A_u	4.1	A_u	6.3	A_u
B_{3u}	475	11	B_u	0.2	B_u	12.6	B_u	7.1	B_u	10.9	B_u
B_{3u}	176	16[d]	?	6.5	A_u	9.3	A_u	9.1	A_u	12.1	A_u

[a] The polarization of the higher frequency component of the doublet is given; A_u is parallel to b, B_u perpendicular.

[b] Observed polarization in low temperature spectra.

[c] No absorption was observed here in our spectra.

[d] Our interpretation of unpolarized spectra of reference 7.

TABLE 5 *Gerade* Out-of-plane Modes of Naphthalene

Molecular species	Approximate frequency (cm^{-1})	DEBOER		KITAIGORODSKII		WILLIAMS (I)		WILLIAMS (III)	
		Splitting (cm^{-1})	Higher[a]	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher
B_{1g}	941	1.4	B_g	1.9	A_g	0.06	B_g	0.6	A_g
B_{1g}	715	6.0	B_g	2.6	B_g	4.4	B_g	4.8	B_g
B_{1g}	385	1.2	B_g	6.0	B_g	4.2	B_g	6.3	B_g
B_{2g}	982	3.8	A_g	2.5	A_g	2.9	A_g	3.5	A_g
B_{2g}	878	1.8	A_g	0.06	B_g	0.6	A_g	1.8	A_g
B_{2g}	774	0.06	A_g	0.9	A_g	0.06	A_g	4.1	A_g
B_{2g}	*c*. 500?	3.1	A_g	2.6	A_g	3.0	A_g	0.6	A_g

[a] The species of the higher frequency component of the doublet is given.

TABLE 6 *Ungerade* In-plane Modes of Naphthalene

Molecular species	Approximate frequency (cm^{-1})	OBSERVED		DEBOER		KITAIGORODSKII		WILLIAMS (I)		WILLIAMS (III)	
		Splitting (cm^{-1})	Higher[a]	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher
B_{1u}	3065[b]	?	?	2.8	A_u	5.0	A_u	3.2	A_u	3.9	A_u
	3029[b]	?	?	3.2	B_u	4.4	B_u	3.1	B_u	3.6	B_u
	1595	1	B_u	0.3	B_u	0.4	B_u	0.2	B_u	0.3	B_u
	1389	1	A_u	0.6	A_u	1.3	A_u	0.8	A_u	0.8	A_u
	1265	3	B_u	0.4	A_u	0.4	A_u	0.3	A_u	0.1	A_u
	1125[d]	5?	?	0.9	B_u	2.2	B_u	1.1	B_u	1.1	B_u
	810[c]	2?	B_u?	0.5	B_u	0.8	B_u	0.7	B_u	0.7	B_u
	362	3	A_u	4.2	A_u	7.0	A_u	4.5	A_u	5.1	A_u
B_{2u}	3056[b]	?	?	3.2	A_u	4.6	A_u	3.2	A_u	3.8	A_u
	3029[b]	?	?	3.5	B_u	4.3	B_u	3.2	B_u	3.7	B_u
	1509	<1	A_u	0.5	A_u	0.5	A_u	0.2	A_u	0.4	A_u
	1361	?	?	3.0	A_u	0.1	B_u	3.2	A_u	0.2	B_u
	1209	2	B_u	0.3	B_u	0.8	A_u	0.1	A_u	0.4	B_u
	1144[d]	<1	?	1.7	B_u	3.7	B_u	2.3	B_u	3.3	B_u
	1008	<1	A_u	1.2	A_u	1.0	A_u	0.9	A_u	0.8	A_u
	618	2	A_u	0.5	B_u	1.3	B_u	0.8	B_u	1.2	B_u

[a] Polarization of the higher frequency component of the doublet; A_u is parallel to *b*, B_u perpendicular.

[b] Results for C—H stretching modes are not clear.

[c] This band disappears at low temperatures; it may be a difference band or mode mixing may be different at low temperatures.

[d] These two modes appear to be strongly mixed in the crystal—the results are dubious.

TABLE 7 *Gerade* In-plane Modes of Naphthalene

Molecular species	Approximate frequency (cm^{-1})	DEBOER Splitting (cm^{-1})	DEBOER Higher[a]	KITAIGORODSKII Splitting (cm^{-1})	KITAIGORODSKII Higher	WILLIAMS (I) Splitting (cm^{-1})	WILLIAMS (I) Higher	WILLIAMS (III) Splitting (cm^{-1})	WILLIAMS (III) Higher
A_g	3055	2.9	B_g	5.0	B_g	3.3	B_g	3.8	B_g
	3025	3.4	A_g	4.3	A_g	3.2	A_g	3.7	A_g
	1579	1.0	A_g	0.7	A_g	0.7	A_g	0.6	A_g
	1460	2.9	B_g	4.1	B_g	2.9	B_g	3.6	B_g
	1379	0.1	B_g	0.3	B_g	0.2	B_g	0.3	B_g
	1144	5.9	A_g	6.2	A_g	5.1	A_g	6.5	A_g
	1025	1.3	B_g	1.3	B_g	1.0	B_g	0.8	B_g
	763	3.0	B_g	2.0	B_g	1.5	B_g	1.8	B_g
	512	1.3	A_g	2.1	A_g	1.4	A_g	1.7	A_g
B_{3g}	3055	3.0	B_g	5.0	B_g	3.3	B_g	3.8	B_g
	2980	3.3	A_g	4.5	A_g	3.1	A_g	3.6	A_g
	1624	0.03	A_g	0.3	B_g	0.1	B_g	0.3	B_g
	1436	0.3	A_g	0.6	A_g	0.3	A_g	0.5	A_g
	1240	2.3	B_g	2.7	B_g	1.9	B_g	1.9	B_g
	1099	2.2	A_g	3.8	A_g	2.2	Ag	2.6	A_g
	936	0.3	Ag	1.5	A_g	0.9	A_g	1.5	A_g
	506	2.5	B_g	4.0	B_g	2.6	B_g	3.2	B_g

[a] The species of the higher frequency component of the doublet is given.

in Tables 4 and 5 they are the "assigned" values given by Scully and Whiffen.[12] For the low frequency modes see also reference 15. In Tables 6 and 7 they are the "observed" values for in-plane frequencies as given by Neto, Scrocco and Califano.[16] The vibrational species of the molecular vibrations from which the crystal states are derived are given for a molecular coordinate system in which $x(B_{3u})$ is out of plane, $y(B_{2u})$ is the long-axis, and $z(B_{1u})$ is the short-axis. All of these calculations include contributions from every contact shorter than 5 Å.

Table 8 gives the results of some calculations which were done to determine the sensitivity to changes in the potential model. The *ungerade* out-of-plane modes are used for example. The tabulation shows the effects of decreasing the limit on contact distances included in the lattice sums to 4 Å, and of neglecting carbon–carbon interactions. Comparison of the deBoer potential results with the others of Tables 4–7 shows the consequences of disregarding carbon–hydrogen forces.

Inspection of the various tables suggests the following conclusions. First, the slight sensitivity of decreasing the radius of interaction from 5 to 4 Å illustrates the short-range nature of the forces involved. Second, carbon–carbon interactions have relatively little effect on the calculated splittings. Third, the carbon–hydrogen forces may not reasonably be neglected. The last confirms the conclusions of others.[1, 7]

These tables show only the computed splittings, not the frequency shifts. The computed shifts (available in reference 31) are probably not directly comparable to observed shifts because of neglect of dielectric effects. They are all to higher frequencies, generally small, but larger for out-of-plane than for in-plane modes.

For the *gerade* vibrations the only experimental information available is the statement[32] of Gee and Hanson that "the factor group splittings are generally less than 1 cm^{-1}". Our calculations give several splittings larger than this, but qualitatively give splittings for *gerade* modes smaller than for *ungerade* modes.

The experimental data show a definite tendency to larger splittings for out-of-plane than for in-plane modes. The calculations

TABLE 8 Some Results with Variations on the Use of the Kitaigorodskii Potential

Molecular species	Approximate frequency (cm^{-1})	5 Å limit		4 Å limit		5 Å limit Without C—C terms	
		Splitting (cm^{-1})	Higher[a]	Splitting (cm^{-1})	Higher	Splitting (cm^{-1})	Higher
A_u	980	1.2	B_u	1.0	B_u	1.2	B_u
	845	1.0	B_u	0.8	B_u	1.0	B_u
	581	2.4	B_u	2.2	B_u	2.2	B_u
	210	0.8	A_u	0.8	A_u	1.2	A_u
B_{3u}	960	1.0	A_u	1.0	A_u	1.0	A_u
	785	2.4	A_u	2.6	A_u	2.4	A_u
	480	12.6	B_u	12.4	B_u	11.8	B_u
	175	9.2	A_u	9.8	A_u	8.2	A_u

[a] The species of the higher frequency component of the doublet is given.

are correct in reproducing this tendency. A significant success is that nearly all of the predicted polarizations of the infrared transitions are correct. The general features of the data are represented semi-quantitatively by these computations based on the atom–atom model. A measure of the quality of the results was taken to be

$$M = \frac{\sum|S_{\text{obs}} - S_{\text{calc}}|}{\sum|S_{\text{obs}}|} \tag{9}$$

where S is the frequency splitting between band components and the sum was calculated for the fourteen infrared bands for which experimental splittings were reasonably well determined (if doubt existed as to polarization the sign of the calculated splitting was taken to be the same for observed and calculated S). The values of M are 0.68, 0.57, 0.57 and 0.41 for the deBoer, Kitaigorodskii, Williams (I) and Williams (III) potentials, respectively. In most cases the calculations tended to predict smaller splittings than were observed.

Conclusions

The calculations presented in the paper have proved moderately successful in explaining the splittings of benzene and naphthalene infrared transitions in the crystals. The minimum which can be said is that the magnitudes of the splittings are approximately correct, the signs (polarizations) are properly predicted in general and that large (10 cm^{-1}) splittings are predicted to be large, small (3 cm^{-1}) to be small. One way to evaluate the results a bit further is to consider some of the approximations, and at the same time what improvements might be made in a more refined calculation aimed at obtaining improved potential parameters.

The first assumption is that perturbation theory based on molecular normal coordinates is applicable. This is almost certainly a correct assumption for these crystals, but it contains what may be a serious limitation, the quality of the solution for the isolated molecule. Vibrational analysis for molecules of this size has improved a great deal in the past few years with extensive application of computers, least squares refinements and consideration of numerical problems of accuracy. However, it is still difficult to know the quality of the results. The crystal calculations require not only the energies, but also the wave functions which give the atomic displacements in the various normal modes. Neglect of anharmonicities and other approximations in the intramolecular force field are among the most important factors limiting the results.

In the crystal calculation itself a possible serious problem is the neglect of mixing between modes separable in the isolated molecule but not in the crystal. This has been shown here not to be serious for some of the benzene modes. However, many pairs of internal frequencies are separated by energies which are not too much larger than the possible splittings, and perturbations between such motions, and between low-frequency internal motions and lattice vibrations, could be extensive. The principles of correcting for such interactions are well known, but the complexity of the problem is considerable.

The structures of benzene and naphthalene are among the best known of molecular crystals. Still there is an often incompletely understood temperature dependence and a greater uncertainty about hydrogen positions. These factors are probably not of the importance of normal coordinate or mode mixing uncertainties; some calculations concerning temperature effects are discussed in reference 31.

Obviously the intermolecular potential functions are of the greatest interest in this work. A series expansion is used which ignores terms of higher order than the second in coordinates, and ignores any possible angle dependence of the potentials. Parameters for the atom–atom contributions might be refined, but other contributions must be considered before such refinement would be meaningful. For instance, for intense transitions the interaction of molecular dipoles (transition dipole moments), may become important.[6]

In the crystals treated here the results counteract the pessimism which might be indicated from the above discussion of approximations. Certainly, refinements of parameters at this stage would be dangerous, but it seems to be true that the intermolecular forces which control other physical properties of benzene and naphthalene can also account for the vibrational splittings in the crystals.

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