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Calculation of Ground State Vibrational Structure and Phonons of the Isotopic Benzene Crystals*

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Using the "giant molecule" technique and existing intermolecular potentials, the normal modes, phonon and exciton structure, site shifts, site splitting, and orientational effect for the isotopic benzene crystals are calculated. The agreement between the calculations and the experimental observations is good for an H–H, C–H, and C–C potential set independently obtained by Williams from thermodynamic and structural properties of aromatic crystals. The calculation presented here serves to unify not only the thermodynamic and spectral properties, but also the diverse spectral properties themselves. This calculation emphasizes that *all* atom–atom interactions, not just H–H interactions, must be considered for best agreement between calculated and observed spectral data. This conclusion was also reached by Williams with respect to the thermodynamic and structural data. A discussion of the potentials, their form, and their relation to standard exciton theory integrals is presented. Future improvements in such calculations must be directed, not toward more extensive parametric data fitting of the atom–atom pair potential, but toward more general potential functions that include anharmonicities and multicenter terms. The use of actual site force constants rather than free molecule force constants is also indicated.

I. INTRODUCTION

Understanding the binding or cohesive forces in molecular aromatic crystals has been a long-sought-after goal for both theoreticians and experimentalists alike. Since anything approaching a complete calculation for all but the simplest systems is prohibitively difficult, the general problem has typically been approached by using a greatly simplified model, usually a reduced set of atom–atom interactions, to simulate the true intermolecular potential function. From this model one tries to calculate the thermodynamic and spectral properties of the crystal. For aromatic crystals for instance it has been popular to ignore all but nearby H–H contacts.[1,2] Unfortunately, such calculations accurately render only those properties for which they are designed. In many cases it has not even been possible to transfer the potentials from crystal to crystal for the calculation of identical properties.[1,3]

Parameteric potential calculations are useful only if they are able to reproduce data for many crystals, or if the potentials used to calculate successfully one type of crystal property can be transferred to obtain another.[4–6] Thus, it would be quite informative if the set of pairwise atom–atom potentials that have been successfully fit to a large number of thermodynamic or structural properties of many different crystals, could be employed in the calculation of crystal spectral data[7] such as phonons, site splittings, orientational effects, or exciton structure. Such a procedure would not only be satisfying from the point of view of getting more out of the calculation than was put into it, it would be informative in the sense that it would yield an accurate test of the model and its approximations. Furthermore, such a procedure would lead to a better understanding of the relationship between thermodynamic and spectral crystal properties.

Recent calculations by Kitaigorodskii[4] and by Williams[5] have been completed on the thermodynamic and structural properties of many aromatic crystals. Such a variety of data has been successfully fit that it is reasonable to assume that the atom–atom potentials employed in these calculations are near optimum at least for the properties discussed. In this paper these same potentials are tested on the spectral data.

The goals of this work, in the light of the foregoing discussion, are then, (a) to show that good intermolecular potentials are not only transferrable from crystal to crystal but are useful in the calculation and understanding of many diverse crystal properties, (b) to determine what parts, repulsion or attraction, of the intermolecular C–C, C–H, and H–H atom–atom potentials are important for the spectroscopic data, (c) to elucidate what changes in the potentials are to be made if the calculations of such properties are to be improved, and (d) to relate and unify the various spectroscopically observed phenomena such as isotopic mixed crystal spectra, neat crystal spectra, and phonons.

In Sec. II we shall discuss the theoretical considerations[8] leading to the calculation of the crystal normal modes and show that relationship between standard exciton theory[9,10] and the "giant molecule approach."[8] We shall further demonstrate how phonons,[1,8] exciton structure,[10–12] ideal mixed crystal energies,[7] site group splittings,[7] and the orientational effect[7] are interrelated. Section III will contain a description of the intermolecular potentials considered. This will be followed (Sec. IV) with a short description of crystal geometry with special emphasis on atom–atom contacts out to 4.0 Å. We shall then compare the calculated results for various potential sets (H–H; C–H; H–H and C–H; and H–H, C–H, and C–C) with the available experimental data (Sec. V).

II. THEORETICAL CONSIDERATIONS

The calculations of the normal modes of the benzene isotopic mixed and neat crystals were made employing the **GF** method of Wilson[13] as modified by Shimanouchi.[8] This is the so-called "giant molecule" technique in that the primitive unit cell of the crystal is treated as a single molecule whose motion is then assumed to be in phase with that of the rest of the crystal. The technique produces only the $\mathbf{k}=0$ or "optically active" modes.[8] Since it is most simple to determine the force constants in the normal coordinate system, the force field of the molecule[14] (often referred to in this paper as *the site*[7]) is expressed in molecular symmetry coordinates, and the intermolecular force field, obtained from the intermolecular potential, is expressed in the intermolecular symmetry coordinate system. Each force field, molecular and intermolecular, is therefore diagonal in its separate coordinate system. In order to add algebraically these two force constant matrices we must transform them to the same coordinate system, and it is most convenient for the present case of weak intermolecular coupling to chose the Cartesian coordinate system of the site. When such a transformation is applied to these matrices one obtains two groups or blocks, a "diagonal block" involving only the coordinates of one site and an "off-diagonal block" involving the coordinates of two sites. The resulting "one-site" force constant matrices ($\mathbf{F}_{\text{site}}+\mathbf{F}'$) yield the force constants of the *ideal mixed crystal*.[10] The neat crystal force constants are obtained from the two-site force constant matrices [$\mathbf{F}'(\mathrm{I, II})$, $\mathbf{F}'(\mathrm{I, III})$, and $\mathbf{F}'(\mathrm{I, IV})$] combined with the one-site matrices. These "super matrices," representing the force constants for the ideal mixed crystal or the neat crystal, are then mass weighted and numerically diagonalized, the eigenvalues and eigenvectors being found in the usual fashion. Since the mechanics of the above scheme have been amply represented in the literature,[1,8] we shall merely show here how it is related to the general Davydov formalism.[9,10]

In the Davydov scheme the energy, to first order in the crystal site wavefunctions, of the "optically active" transition is given by[10]

$$E^{f\alpha}(\mathbf{k}=0)=\bar{\varepsilon}^f+\Delta^f+L^{f\alpha}(\mathbf{k}=0), \tag{1}$$

where $\bar{\varepsilon}^f$ is the gas-phase transition energy, Δ^f is the site shift, and $L^{f\alpha}(\mathbf{k}=0)$, or simply $L^{f\alpha}(0)$, is the first-order Davydov energy associated with the fth excited molecular state and the αth representation of the interchange group. The site shift term Δ^f is composed of a site polarization term P and the usual Davydov D term. In the present vibrational problem P is probably caused by changes in the molecular force constants due to changes in the electronic eigenfunctions when the molecule is immersed in the crystal. The *ideal mixed crystal* energy[10] (no resonance interactions) is given by

$$E_{\mathrm{IMC}}{}^f=\bar{\varepsilon}^f+\Delta^f. \tag{2}$$

Approximately,

$$L^{f\alpha}(0)=2M_a+2M_b+2M_c+4a_{\mathrm{II}}{}^{\alpha}M_{\mathrm{III}}+4a_{\mathrm{III}}{}^{\alpha}M_{\mathrm{I\,III}}+4a_{\mathrm{IV}}{}^{\alpha}M_{\mathrm{I\,IV}}, \tag{3}$$

where M_t is the coupling constant for translationally equivalent molecules along the $t(=a, b, c)$ axis, M_{Iq} couples interchange equivalent molecules I and q (q = II, III, IV), and the $a_{\mathrm{q}}{}^{\alpha}$'s are coefficients determined from the interchange group character table.

We assume that the intramolecular force constant matrix $\mathbf{F}_{\text{site}}$ of the molecule at the site is the same as that of the free molecule, $\mathbf{F}_{\text{mol}}$. Within the framework of Eq. (1), such an approximation is equivalent to neglecting the site polarization energy P, thereby setting $\Delta=D$. This approximation is believed to be fairly reasonable because we are dealing with ground state vibrations where the gas-to-crystal shifts are small ($\lesssim 1\%$ of $E^{f\alpha}$).[7] The assumption can indeed be checked by the calculation itself as we do not vary the potentials to obtain final agreement. Any other approximations made in this calculation deal with the potential functions and force constants and will be discussed explicitly in the next section.

Hence, the force constant matrix for the neat crystal can be written as

$$\mathbf{F}_{\text{cryst}}{}^{\alpha}=\mathbf{F}_{\text{mol}}+\mathbf{F}'+\sum_{\mathrm{q=II}}^{\mathrm{IV}}a_{\mathrm{q}}{}^{\alpha}\mathbf{F}'(\mathrm{I, q}), \tag{4}$$

in exact analogy with Eq. (1). The ideal mixed crystal force constants are

$$\mathbf{F}_{\mathrm{IMC}}=\mathbf{F}_{\text{mol}}+\mathbf{F}', \tag{5}$$

$\mathbf{F}_{\text{mol}}$ and $\mathbf{F}'$ paralleling the $\bar{\varepsilon}^f$ and Δ^f terms of Eq. (2). Equation (5) is simply the "diagonal" or one-site component of the crystal force constant matrix for a unit cell. This force field gives, for the ideal mixed crystal, the orientational effect and the site splitting of degenerate molecular states since $\mathbf{F}'$ has the site symmetry $\mathbf{C}_i$.

III. THE POTENTIALS AND FORCE CONSTANTS

As discussed in the last section, calculation of the ground electronic state vibrational frequencies of the crystal will be accomplished through the use of *intra*- and *inter*site force constants. It has been assumed the *intra*site force constants are the molecular ones. We then proceed with the determination of the *inter*site force constants and further divide these into "diagonal" (paralleling D) and "off-diagonal" (paralleling $L^{f\alpha}$) contributions to the unit cell vibrational energy.

The intermolecular force constants are found from the intermolecular potential by making the *harmonic approximation*, that is, by assuming that the force constant is the second derivative of the potential function $V(\mathrm{I})$. deBoer[15] has shown that nonspherical repulsion terms can be best represented in the form of a potential that decreases exponentially with distance. The attractive part of the interaction can be represented by an induced-dipole–induced-dipole term.[15,16] An over-all interatomic potential function is then represented at this level of approximation as

$$u(r)=B\exp(-\mathrm{C}r)-\mathrm{A}r^{-6}. \tag{6}$$

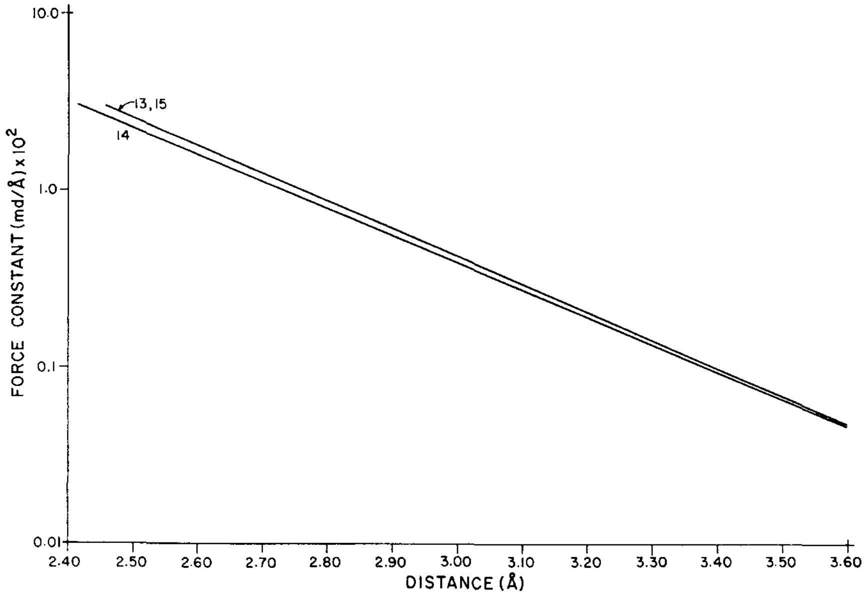

FIG. 1. A plot of force constant versus distance for the H–H potentials 13, 14, and 15 given in Table I. Potential 15 was derived to find the *A* constant necessary to fit potential 13 to the desired form.

We next assume that the molecular interaction potentials can be broken down into sums of pairwise atom–atom interactions (H–H, C–H, C–C). For example,

$$V(\mathrm{I},\mathrm{II})=\sum_{i,j}\{[B_{\mathrm{HH}}\exp(-C_{\mathrm{HH}}r_{ij})-A_{\mathrm{HH}}r_{ij}^{-6}]+[B_{\mathrm{CH}}\exp(-C_{\mathrm{CH}}r_{ij})-A_{\mathrm{CH}}r_{ij}^{-6}]+[B_{\mathrm{CC}}\exp(-C_{\mathrm{CC}}r_{ij})-A_{\mathrm{CC}}r_{ij}^{-6}]\}. \quad (7)$$

The sum in Eq. (7) goes over all atoms of each site ($12\times12=144$ unique terms for molecule I and each of its four type II neighbors). The other potentials V(I, III) and V(I, IV) are expressed in the same fashion. The r_{ij} are the intersite atom–atom distances and are thus *the symmetry coordinates in which the pairwise intermolecular force constant matrices are diagonal.* The second derivative of the potential function with respect to the r_{ij}'s gives the force constant for the atom–atom interactions,

$$F_{ij}'=\{[B_{\mathrm{HH}}C_{\mathrm{HH}}^{2}\exp(-C_{\mathrm{HH}}r_{ij})-42A_{\mathrm{HH}}^{2}r_{ij}^{-8}]+[B_{\mathrm{CH}}C_{\mathrm{CH}}^{2}\exp(-C_{\mathrm{CH}}r_{ij})-42A_{\mathrm{CH}}^{2}r_{ij}^{-8}]+[B_{\mathrm{CC}}C_{\mathrm{CC}}^{2}\exp(-C_{\mathrm{CC}}r_{ij})-42A_{\mathrm{CC}}^{2}r_{ij}^{-8}]\}. \quad (8)$$

The F_{ij}''s are the elements of a (144×144) diagonal matrix.

Before specifically discussing how the various *A*, *B*, and *C* parameters can be obtained, let us review the approximations that have been made. To begin with, the *P* term and any higher order contributions[10] were omitted. The pair-wise intersite interaction terms are represented by a pair-wise sum of two-center atom–

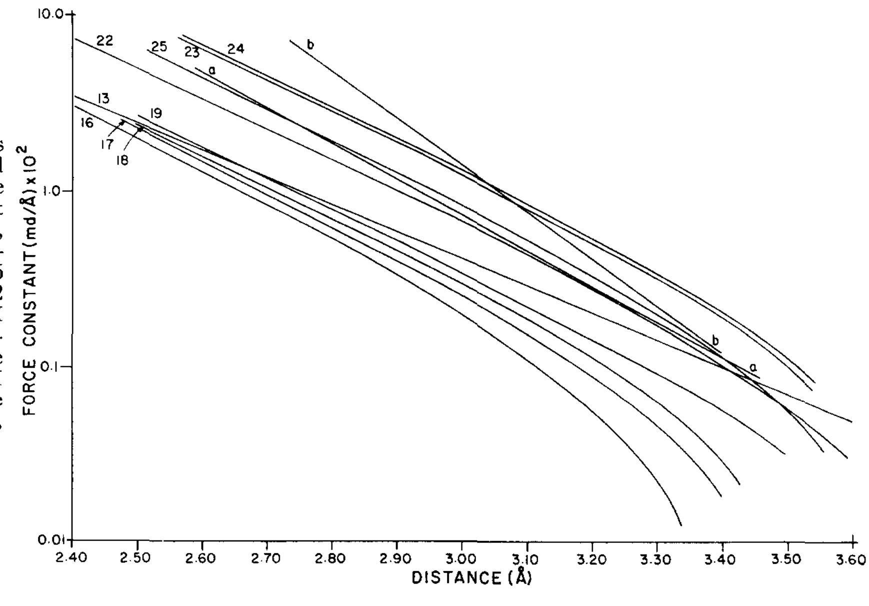

FIG. 2. A plot of the force constants versus distance for the potentials derived by Williams (Table I). Note that these potentials are determined in sets and that they pair (16, 22), (17, 23), (18, 24), and (19, 25). The best results are obtained from (16, 22). Potentials 16 through 19 represent H–H and 22 through 25 C–H interactions. The H–H potential 13 is also shown for a comparison. Lines *a* and *b* represent force constant curves for two separate C–H potentials (Ref. 1) used to describe the interaction in benzene and naphthalene, respectively.

TABLE I. Potentials for H–H, C–H, and C–C interactions in the form $V = Be^{-CR} - AR^{-6}$. Constants in atomic units.

Type of potential and set number		A	B	C	Ref.
H–H	1	3.397	13.207	2.434	a
	2	1.312	55.46	2.996	b
	3	5.886	10.892	2.257	c
	4	8.529	10.685	2.158	c
	5	3.573	29.14	2.636	d
	6	3.573	15.93	2.434	e
	7	3.573	21.66	2.497	e
	8	3.397	18.926	2.434	a
	9	3.573	10.51	2.160	f
	10	3.247	2.960	1.625	c
	11	4.496	100.9	2.645	g
	12	6.495	5.921	1.625	h
	13	···	4.02	1.92	i
	14	···	2.75	1.86	j
	15	−0.209	4.39	1.95	k
H–H I	16	5.12	6.35	1.98	l
II	17	4.19	6.35	1.98	l
III	18	3.59	6.35	1.98	l
IV	19	2.61	6.35	1.98	l
	20	3.10	47.9	2.645	m
C–H	21	10.30	47.9	2.210	m
I	22	6.21	10.77	1.94	l
II	23	11.55	20.09	1.94	l
III	24	12.02	21.10	1.94	l
IV	25	10.00	15.00	1.94	l
C–C I	26	43.47	142.15	1.904	l
II	27	31.76	66.17	1.904	l
III	28	31.27	69.98	1.904	l
IV	29	38.49	118.68	1.904	l

[a] D. H. R. Barton, J. Chem. Soc. **1948,** 340.

[b] T. L. Hill, J. Chem. Phys. **14,** 465 (1946); **16,** 399, 938 (1948).

[c] C. A. Coulson and C. W. Haigh, Tetrahedron **19,** 527 (1963).

[d] D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, J. Am. Chem. Soc. **83,** 2938 (1961).

[e] J. B. Hendrickson, J. Am. Chem. Soc. **83,** 4537 (1961).

[f] L. S. Bartell, J. Chem. Phys. **32,** 827 (1960).

[g] A. Müller, Proc. Roy. Soc. (London) **A154,** 624 (1936); **A178,** 227 (1941).

[h] E. A. Mason and M. M. Kreevoy, J. Am. Chem. Soc. **77,** 5808 (1955).

[i] Plotted from data of Ref. 1; see Fig. 1.

[j] D. A. Dows, J. Chem. Phys. **32,** 1342 (1960).

[k] From the data of Ref. 1 forced to fit the form used in this Table; see Fig. 1.

[l] D. E. Williams, J. Chem. Phys. **45,** 3770 (1966).

[m] A. I. Kitaigorodskii, Tetrahedron **14,** 230 (1961).

atom interactions. From these terms we extract only the harmonic contributions to the intermolecular force constants. The neglect of three- and four-center terms in the repulsion energy could be somewhat serious since such terms can account for as much as 5% of the lattice energy.[17] It is further assumed that the attractive terms in the interaction, those that hold the crystal together, are simply given by London dispersion terms. We completely ignore directional interactions such as "π-cloud interactions" or any other type of bond–bond coupling or polarization not already explicitly present in the atom–atom potential function. Of course, underlying all these approximations is the ubiquitous Born–Oppenheimer separation. Any improved calculation must address itself directly to these approximations. Certainly a fairly easy next step would be to include anharmonicities and to use actual site force constants rather than free molecule force constants in the calculation. The former is necessary to take care of the widespread occurrence of Fermi resonance in the crystal while the latter seems to be required to obtain better agreement between calculated and observed site shifts (*vide infra*). Three- and four-center terms in the potential functions must also be evantually considered. We now resort to the bulk crystal properties to find the best parameters for the potential model to be used in the present calculation.

The best information concerning the potentials is thermodynamic. Such considerations have been extensively discussed by Kitaigorodskii[4] and Williams.[5] One can characterize the equilibrium structure of a molecular crystal by a minimum in the free energy. In addition, the stress and strain tensors and the elastic constants can be represented, respectively, as derivatives of the entropy and free energy of the crystal.[18] Knowing the enthalpy of sublimation, the stress and strain tensors, and the elastic constants experimentally for a number of closely related crystals therefore enables one to evaluate the intermolecular potentials. The results of such calculations have recently been made available.[5] From these calculations it is found that the relative molecular orientation in the crystals is probably dominated by atom–atom repulsions of which H–H interactions have often been assumed the most important.[2] On the other hand, C–H and C–C interactions are the largest over-all contributors to the total energy and in contrast to the assumptions of Ref. 2 have been found to contribute substantially to the relative molecular orientations in the crystal.[5,19]

In Table I are found the A_{HH}, B_{HH}, and C_{HH} parameters for a number of potentials discussed in the literature, including those given by Williams.[5] The force constants derived from some of these potentials are plotted in Figs. 1–3. Williams' potentials seem clearly superior in view of the wide range of data they fit. They were obtained by simultaneously fitting the heat of sublimation, crystal structure, and elastic moduli of

TABLE II. Direction cosines of the molecular axes (x, y, z) with respect to the crystallographic axes (a, b, c) for molecule I at 77°K. Data obtained by using computer program described in Ref. 22.

	x	y	z
$T^{\mathrm{I}} = a$	0.6379	−0.3248	0.6814
b	0.1999	0.9456	0.2532
c	−0.7265	−0.0339	0.6867

$T^{\mathrm{II}} = C_2{}^a T^{\mathrm{I}}$, $T^{\mathrm{III}} = C_2{}^b T^{\mathrm{I}}$, and $T^{\mathrm{IV}} = C_2{}^c T^{\mathrm{I}}$

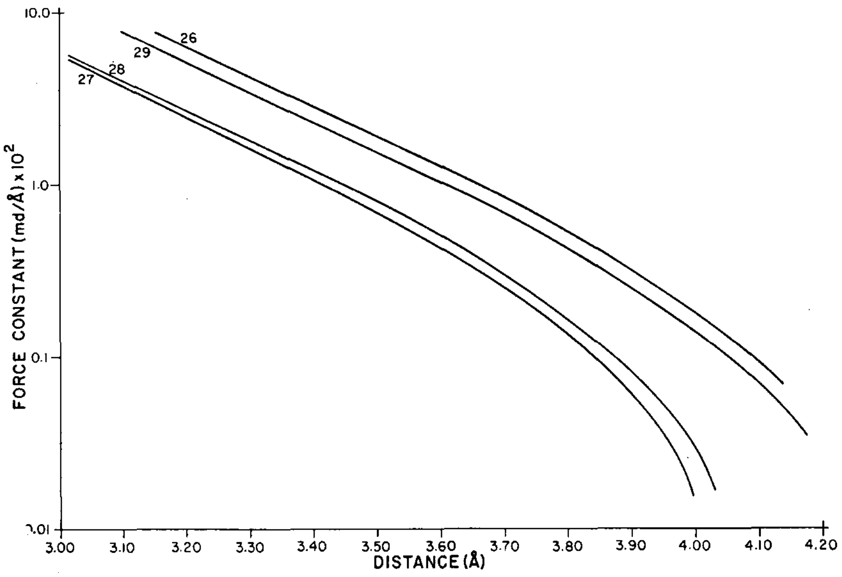

FIG. 3. Plot of the C–C force constants versus distance for the potentials derived by Williams (Table I). These C–C force constants pair with the C–H and H–H potentials of Fig. 2 such that the sets are (16, 22, 26), (17, 23, 27), (18, 24, 28), and (19, 25, 29).

TABLE III. Unique atom–atom contact distances to 4.0 Å between molecule I and molecules II, III, and IV.[a]

	II		III		IV	
Type of contact	Atom positions[b]	Distance Å	Atom positions[b]	Distance Å	Atom positions[b]	Distance Å
C–C	11–23	3.762	13–11	3.686	23–21	3.641
	12–23	3.965	21–12	3.902	22–21	3.752
			21–11	3.968	22–13	3.858
					22–22	3.860
					23–22	3.976
H–C	31–23	2.922	33–11	2.955	43–21	2.839
	32–23	3.374	41–12	3.120	42–23	3.062
	31–22	3.474	33–12	3.491	42–11	3.063
	31–11	3.519	33–23	3.504	42–22	3.075
	32–11	3.812	41–11	3.519	42–12	3.077
					42–21	3.079
					42–13	3.089
					43–22	3.325
					43–13	3.429
C–H	12–43	3.243	13–31	3.237	23–41	3.657
	11–43	3.303	21–32	3.487		
			21–31	3.589		
			13–32	3.987		
H–H	32–43	2.526	41–32	2.616	43–41	2.668
	31–43	2.652	33–31	2.694	43–42	3.517
	32–31	3.410	41–31	3.385	42–31	3.659
	31–42	3.630	33–32	3.697	42–43	3.669
	31–31	3.689	33–43	3.715	42–42	3.687
					43–33	3.690
					42–33	3.700
					42–32	3.702
					42–41	3.718

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[a] Data obtained by using computer program described in Ref. 22.

[b] See Fig 4 for numbering system. In the table the numbers on the right correspond to atom positions in molecule I.

TABLE IV. C_6H_6 phonons calculated and observed[a,b] (in cm^{-1}).

Phonon	A	B_1	B_2	B_3	Potential[c]
g	95.0	107.9	105.5	109.9	CH only
	91.7	123.9	127.2	126.0	HH only
	117.7	161.7	163.1	159.3	CH plus HH
	106.2	155.6	151.9	155.1	IV
	98.2	138.2	134.6	137.7	I
	...	132.2	...	132.2	Exptl
g	70.1	86.6	94.9	104.5	CH only
	67.4	79.0	72.5	116.0	HH only
	96.3	117.5	117.3	150.0	CH plus HH
	96.1	85.5	116.1	141.9	IV
	87.0	81.8	108.5	125.7	I
	83.1	83.1	93.7	...	Exptl
g	46.3	85.0	92.6	86.3	CH only
	35.0	50.2	66.2	55.3	HH only
	67.3	84.5	119.9	117.1	CH plus HH
	67.9	74.4	115.3	109.1	IV
	62.7	65.9	102.7	101.4	I
	61.0	66.5	83.1	98.1	Exptl
u	78.9	62.2	69.6	56.3	CH only
	68.1	60.5	50.8	55.3	HH only
	110.3	100.7	73.7	70.3	CH plus HH
	110.3	118.8	69.5	69.7	IV
	97.1	105.9	63.1	64.8	I
	...	102	72	...	Exptl
u	60.3	58.1	48.2	39.0	CH only
	59.4	43.3	38.5	33.8	HH only
	82.9	81.0	71.8	65.5	CH plus HH
	81.3	101.7	68.2	69.2	IV
	73.8	94.5	62.4	60.6	I
	...	90	...	...	Exptl
u	34.7	0	0	0	CH only
	27.9	0	0	0	HH only
	52.0	0	0	0	CH plus HH
	50.1	0	0	0	IV
	45.1	0	0	0	I
	..	...	...	...	Exptl

[a] Experimental g phonons from Ref. 25 using an ionized argon laser (4880-Å line) at 0.5 cm^{-1} resolution. Data were taken at 77°K. Polarizations were assigned employing Refs. 23 and 24. Only those lines observed are presented. Some authors (see Refs. 23, 24, and 26), on the basis of qualitative arguments, assume unobserved modes (A_g, B_{2g}, B_{3g}) to be degenerate with observed ones. This is not borne out by the present calculation. See text for fuller discussion.

[b] Observed u phonons from Ref. 26. The B_{2u} and B_{3u} phonons have been reassigned on the basis of this calculation.

[c] CH potential from Ref. 1; HH potential from Ref. 1; potentials IV and I from Ref. 5.

benzene, naphthalene, anthracene, phenanthrene, pyrene, chrysene, terphenylene, perylene, and ovalene.

IV. THE CRYSTAL STRUCTURE, ATOM–ATOM DISTANCES, AND THE MOLECULAR GEOMETRY

The crystal structure of benzene has been determined to be $D_{2h}^{15}(Pbca)$ with four molecules per primitive unit cell all occupying equivalent sites of inversion symmetry.[20] The molecules are labeled I, II, III, and IV in accordance with the notation of Cox *et al.*[20] For molecule I, the carbon atoms are double indexed counterclockwise 11, 12, 13, 21, 22, 23, and the hydrogen atoms are labeled 31, 32, 33, 41, 42, 43, as given in Fig. 4. The molecular axis system is the right-handed system with the y axis through C_{11} and H_{31}, the x axis lies between C_{22}, H_{22}, and C_{23}, H_{43}, and the z axis is perpendicular to x and y. All the other molecules are generated from I using the operations of the $\mathbf{D}_2$ interchange group. This technique uniquely creates sites II, III, IV in such a fashion as to preserve the atomic numbering system and the right-handed coordinate system. It also specifies the phasing of the crystal site states.[10] Explicitly, $C_2^a\mathrm{I}=\mathrm{II}$, $C_2^b\mathrm{I}=\mathrm{III}$, and $C_2^c\mathrm{I}=\mathrm{IV}$, where $C_2^{a,b,c}$ in the full crystal represents twofold screw-axis operations about the a, b, or c crystal axes, respectively.

The detailed crystal structure parameters to be used in the calculations were obtained from the neutron diffraction data of Bacon *et al.*[21] H-atom positions are accurately determined, and the temperature of the neutron diffraction experiments (138°K) is close to the temperature at which the spectral data were obtained (77°K). The direction cosines between the crystal a, b, c axes and the site x, y, z axes obtained from the neutron diffraction data are given in Table II. Atom–atom contacts were computed from the reduced atomic positions and cell parameters of Bacon *et al.*[21] and extrapolated to 77°K using the CRYRM crystallographic program.[22] The results out to 4.0 Å for all unique contact distances are given in Table III. Since each molecule has 12 nearest neighbors (four of each of the

TABLE V. Phonons for C_6D_6 calculated employing potential set I[a] and observed[b] (in cm^{-1}).

Phonons	A	B_1	B_2	B_3
g	95.1	126.8	123.2	125.8 Calc
	...	123	...	123 Exptl
g	79.3	78.9	105.0	115.0 Calc
	77	77	90	... Exptl
g	60.5	60.0	93.7	97.9 Calc
	57	62	77	97 Exptl
u	88.8	96.7	60.2	62.5 Calc
	...	...	...	... Exptl
u	71.2	91.2	57.4	55.3 Calc
	...	...	...	... Exptl
u	44.1	0	0	0 Calc
	...	...	...	... Exptl

[a] Reference 5.

[b] References 23, 24, and 26. Only observed phonons have been tabulated. Estimated degeneracies of other g phonons have been omitted. See text. No u phonons have been observed for C_6D_6.

TABLE VI. Calculated[a] and experimental[b] data for C_6H_6 vibrations (in cm^{-1}).

Vibration and IMC value[c]	Δ IMC − gas[d]	δ_{ss}	Exciton components[e,f]				Potential
			A	B_1	B_2	B_3	
$\nu_1(a_{1g})$	+2.7		−0.8	+0.4	+0.9	−0.6	CH
CC	+0.7		+0.1	−0.1	+0.1	−0.2	HH
990.5	+2.4		−0.7	+0.3	+1.1	−0.6	CH plus HH
	+2.3		−0.8	+0.4	+1.1	−0.8	IV
	+1.7		−0.7	+0.4	+1.0	−0.7	I
	−1.3		···	···	···	−0.2	Exptl
$\nu_2(a_{1g})$	+7.4		+0.3	−0.1	−0.2	+0.2	CH
CH	+2.4		+0.2	−0.4	+0.1	0.0	HH
3063.3[g]	+9.4		+0.6	−0.3	−0.1	0.0	CH plus HH
	+7.7		+0.6	−0.4	−0.1	0.0	IV
	+6.0		+0.4	−0.4	−0.1	0.0	I
	+1.3		···	−0.6	···	···	Exptl
$\nu_3(a_{2g})$	+7.3		+0.7	+0.3	−0.4	−0.6	CH
$H^{\parallel}$	+10.7		−8.1	−5.9	+6.2	+7.8	HH
(1346)	+17.9		−7.5	−5.6	+5.9	+7.2	CH plus HH
	+14.6		−7.4	−5.3	+5.6	+7.1	IV
	+10.8		−5.2	−3.9	+4.1	+5.0	I
	···		···	···	···	···	Exptl
$\nu_4(b_{2g})$	+5.1		+2.3	−1.4	+0.7	−1.6	CH
$C^{\perp}$	+5.4		+3.2	−3.3	+2.6	−2.8	HH
704.9	+11.1		+5.6	−4.5	+3.0	−4.2	CH plus HH
	+9.0		+5.2	−4.8	+3.0	−3.4	IV
	+8.7		+3.6	−3.6	+2.5	−2.5	I
	−2.1		···	···	···	···	Exptl
$\nu_5(b_{2g})$	+5.4		−1.6	+0.9	−0.6	+1.1	CH
$H^{\perp}$	+16.2		+8.6	−8.3	+6.5	−6.9	HH
1004.9	+21.8		+7.1	−7.3	+6.1	−6.0	CH plus HH
	+20.6		+7.9	−10.1	+7.0	−4.8	IV
	+14.9		+5.7	−5.5	+5.1	−4.9	I
	+14.9		+7.6	···	···	···	Exptl
$\nu_6(e_{2g})$	+3.8	2.0	+1.4	+2.3	+2.2	−0.3	CH
			−0.8	−1.9	−1.5	−1.5	
$C^{\parallel}$	+2.1	0.6	+1.8	+0.7	+1.0	+0.8	HH
			−1.2	−1.2	−0.5	−1.3	
606.3	+5.9	1.7	+2.3	+2.2	+2.0	+0.1	CH plus HH
			−1.8	−2.3	−0.9	−2.5	
609.4	+5.6	0.8	+2.3	+1.6	+1.4	+1.2	IV
			−1.0	−2.4	−0.5	−2.8	
	+4.7	0.8	+2.1	+1.4	+1.2	+1.1	I
			−0.7	−2.2	−0.5	−2.3	
	+0.9	3.1	+3.1	···	+1.1	···	Exptl
			···	−1.5	···	−2.5	
$\nu_7(e_{2g})$	+7.2	3.5	+1.7	+1.8	+0.8	+1.7	CH
			−1.9	−1.8	−1.7	−1.9	
CH	+2.2	0.9	+0.5	+0.8	+0.5	+0.5	HH
			−0.7	−0.5	−0.5	−0.2	
3042.0[g]	+9.4	2.8	+1.5	+1.6	+2.0	+1.7	CH plus HH
			−1.4	−0.9	−1.6	−1.2	
3047.5	+7.6	2.9	+1.2	+1.5	+1.9	+1.1	IV
			−1.7	−1.3	−2.0	−1.2	
	+5.9	2.5	+1.0	+1.3	+1.6	+1.0	I
			−1.5	−1.2	−1.7	−1.1	
	+3.8	5.5	···	+2.2	+3.6	···	Exptl
			···	···	−2.6	···	

Table VI (*Continued*)

Vibration and IMC value^c	Δ IMC − gas^d	δ_{ss}	Exciton components^{e,f}				Potential
			A	B	B_2	B_3	
$\nu_8(e_{2g})$	+1.4	0.8	+0.4	−0.4	+0.7	+0.9	CH
			−0.5	−0.4	−0.6	−0.1	
CC	+1.1	0.2	+1.1	+0.8	+0.5	+0.4	HH
			−0.5	−0.5	−0.5	−0.8	
1584.2^g	+2.5	0.8	+1.4	+0.4	+0.8	+0.7	CH plus HH
			−1.0	−1.0	−0.6	−0.4	
	+1.3	0.4	+1.0	+0.6	+0.3	+0.5	IV
			−0.7	−0.8	−0.4	−0.5	
	+1.9	0.3	+0.6	+0.5	+0.2	+0.3	I
			−0.5	−0.6	−0.4	−0.4	
	−9.8	<0.3	···	···	···	···	Exptl
			···	···	···	···	
$\nu_9(e_{2g})$	+9.4	1.5	+1.3	+0.9	+0.4	+0.5	CH
			−1.2	−0.2	−1.4	−0.6	
$H^{\|}$	+13.5	2.4	+14.3	+15.2	+1.0	+0.5	HH
			−4.4	−6.0	−10.6	−9.9	
1174.3_4	+22.6	3.2	+13.1	+14.9	+1.3	+0.6	CH plus HH
			−3.2	−5.0	−11.4	−9.8	
1174.8_8	+18.4	4.1	+13.4	+14.9	+1.5	+0.1	IV
			−3.5	−6.0	−11.3	−9.0	
	+13.6	3.2	+8.9	+11.0	+1.2	−0.1	I
			−2.6	−4.8	−7.7	−6.6	
	−2.5	0.54	+6.8	···	+2.7	···	Exptl
			−0.9	···	···	−6.5	
$\nu_{10}(e_{1g})$	+6.5	3.2	+3.9	−0.1	+0.7	+1.2	CH
			−0.7	−2.5	−2.7	−2.0	
$H^{\perp}$	+19.3	9.9	−2.4	+15.3	+0.9	+12.8	HH
			−9.1	−5.0	−8.6	−3.9	
862.5	+25.7	11.7	+1.5	+14.5	+0.7	+11.2	CH plus HH
			−9.5	−6.6	−10.7	−2.3	
869.3	+24.4	10.5	+0.2	+15.0	−0.2	+12.0	IV
			−10.1	−6.0	−10.5	−2.2	
	+17.7	7.8	+0.7	+10.5	+0.5	+8.2	I
			−6.9	−4.3	−7.6	−1.4	
	+15.6	7.5	···	···	···	···	Exptl
			−9.8	−7.6	−11.8	−1.0	
$\nu_{11}(a_{2u})$	+8.9		−1.0	+1.6	−0.9	+0.4	CH
$H^{\perp}$	+28.2		+14.9	−14.5	+12.7	−13.0	HH
696.9	+36.8		+13.8	−13.1	+11.6	−12.3	CH plus HH
	+32.9		+15.4	−14.8	+12.7	−13.3	IV
	+25.4		+10.9	−10.3	+8.5	−9.3	I
	+23.9		+12.1	−15	+10.9	−7.7	Exptl
$\nu_{12}(b_{1u})$	+2.5		−0.4	+0.7	+0.6	−1.0	CH
$C^{\|}$	+1.2		+0.2	−1.1	0.0	+0.8	HH
1011.3	+2.8		+1.4	+1.2	−2.2	−0.6	CH plus HH
	+4.9		−0.7	+0.3	−0.7	+1.0	IV
	+2.9		+0.1	+1.0	+0.1	−1.3	I
	+1.3		+8.7	−1.5	−2.6	−4.6	Exptl
$\nu_{13}(b_{1u})$	+6.6		+0.1	−0.3	−0.2	+0.3	CH
CH	+2.2		+0.4	−0.2	0.0	−0.4	HH
(3048)^g	+9.0		+0.6	−0.4	−0.1	0.0	CH plus HH
	+7.1		+0.4	−0.3	+0.2	−0.3	IV
	+5.5		+0.3	−0.1	+0.2	−0.4	I
	···		···	···	···	···	Exptl

TABLE VI (*Continued*)

Vibration and IMC value[c]	Δ IMC − gas[d]	δ_{ss}	Exciton components[e,f]				Potential
			A	*B*	B_2	B_3	
$\nu_{14}(b_{2u})$	+2.0		+0.1	−0.3	+0.3	0.0	CH
CC	+2.6		−1.8	−1.4	+1.4	+1.7	HH
1312.6	+4.9		−1.8	−1.8	+1.9	+1.9	CH plus HH
	+4.1		−1.8	−1.5	+1.5	+1.7	IV
	+3.1		−1.3	−1.1	+1.0	+1.2	I
	+3.6		−3.1	−0.4	+1.8	+2.7	Exptl
$\nu_{15}(b_{2u})$	+8.9		0.0	+0.3	−0.3	0.0	CH
$H^{\|}$	+13.0		−8.2	−6.2	+6.8	+7.9	HH
1146.9	+21.2		−7.9	−5.5	+6.0	+7.5	CH plus HH
	+17.5		−8.2	−5.6	+5.9	+7.9	IV
	+13.0		−6.3	−4.2	+4.6	+6.0	I
	+0.9		−0.7	+1.7	+3.4	−4.4	Exptl
$\nu_{16}(e_{2u})$	+9.6	3.5	−0.4	+7.2	−0.6	+3.3	CH
			−2.1	−3.4	−2.6	−2.9	
$C^{\perp}$	+14.7	7.7	−0.7	+11.7	+0.9	+9.8	HH
			−5.3	−2.9	−5.6	−2.2	
404.8	+24.7	10.6	−2.2	+16.7	−1.4	+11.6	CH plus HH
			−7.9	−6.7	−7.9	−4.6	
413.0	+23.5	8.8	−1.3	+14.7	−2.0	+10.9	IV
			−8.2	−5.7	−7.5	−3.0	
	+18.2	7.0	−1.0	+11.6	−1.5	+8.5	I
			−6.3	−4.5	−5.6	−2.4	
	+10.7	8.2	···	+10.1	···	···	Exptl
			···	−4.2	−6.4	···	
$\nu_{17}(e_{2u})$	+5.2	2.4	+1.0	+0.5	+2.1	+0.6	CH
			−1.3	−2.2	−1.4	−1.4	
$H^{\perp}$	+14.3	6.7	−2.3	+10.1	−2.9	+7.6	HH
			−5.7	−4.5	−7.4	−3.8	
978.3	+20.1	9.3	−1.7	+7.5	+3.7	+7.0	CH plus HH
			−6.9	−4.5	−7.7	−4.1	
983.9	+17.8	6.0	−0.6	+10.3	−1.0	+3.0	IV
			−6.0	−2.8	−6.3	−3.0	
	+13.6	5.7	−1.0	+5.5	−0.6	+6.3	I
			−5.5	−2.6	−5.6	−2.9	
	+14.2	5.5	···	+7.0	+0.8	+7.6	Exptl
			···	−2.1	−8.5	−5.8	
$\nu_{18}(e_{1u})$	+7.1	3.4	+2.5	+0.6	+2.7	+1.7	CH
			−1.2	−1.6	−2.0	−2.0	
$H^{\|}$	+9.1	2.0	+8.8	+8.1	+5.5	+2.6	HH
			−3.3	−4.4	−5.3	−6.4	
1034.8	+25.9	4.6	+10.5	+7.6	+3.7	+1.3	CH plus HH
			−3.7	−5.1	−3.8	−5.7	
1038.6	+13.1	3.6	+10.0	+7.7	+4.9	+1.3	IV
			−3.8	−4.9	−3.7	−5.2	
	+10.0	2.9	+7.7	+5.9	+3.1	+1.0	I
			−3.0	−3.7	−2.5	−4.1	
	+0.8	3.8	···	+4.2	+4.1	−0.1	Exptl
			···	−2.4	−1.4	−4.7	

Table VI (*Continued*)

Vibration and IMC value[c]	Δ IMC − gas[d]	δ_{ss}	Exciton components[e,f] *A*	*B*	B_2	B_3	Potential
$\nu_{19}(e_{1u})$	+4.3	1.3	+0.5	+0.8	+0.7	+1.0	CH
			−2.3	−0.6	−0.8	−0.7	
CC	+5.7	2.3	+6.3	+7.0	+0.1	+0.3	HH
			−2.0	−3.4	−4.8	−4.1	
1470[g,h]	10.1	1.2	+5.1	+6.5	+1.5	+0.7	CH plus HH
			−1.5	−2.6	−5.2	−4.2	
	+8.2	1.7	+5.5	+6.6	+1.4	+0.2	IV
			−1.8	−2.7	−4.5	−3.7	
	+6.1	1.4	+4.0	+5.1	+1.1	+0.4	I
			−1.5	−1.6	−2.8	−2.4	
	···	···	···	+3.3	+2.0	+0.8	Exptl
			···	−1.3	−3.4	−2.0	
$\nu_{20}(e_{1u})$	+7.5	2.7	+1.3	+1.3	+1.3	+1.4	CH
			−1.5	−1.1	−1.3	−1.7	
CH	+2.3	0.9	+0.2	+0.5	+0.5	+0.5	HH
			−0.8	−0.5	−0.7	−0.3	
(3036)[g]	+9.6	2.5	+1.1	+1.1	+1.4	+1.3	CH plus HH
			−1.6	−0.7	−1.4	−1.3	
	+7.8	3.1	+1.5	+1.2	+1.6	+1.7	IV
			−2.4	−1.2	−1.9	−1.4	
	+6.0	2.7	+1.4	+1.1	+1.4	+1.5	I
			−1.7	−1.1	−1.6	−1.2	
	···	···	···	···	···	···	Exptl
			···	···	···	···	

[a] CH and HH potentials from Ref. 1; potentials I, IV from Ref. 5.

[b] Taken from Refs. 7 and 10–12.

[c] Ideal mixed crystal energy of Ref. 7 is given (±0.5 cm^{-1}). When IMC value is not known liquid phase estimates appear in parentheses.

[d] Experimental Δ is determined to ±4 cm^{-1} due to the uncertainty in the gas-phase values. As discussed in Ref. 7, when the gas and liquid values differ by more than the experimental error, the liquid value is the one to use.

[e] References 11 and 12. Measured from the center of gravity of the exciton components except for the degenerate *u* vibrations for which only the 6 B_u components are used to determine the center of gravity. All experi-components except for the degenerate *u* vibrations for which only the 6 B_u components are used to determine the center of gravity. All experimental numbers are ±0.5 cm^{-1}.

[f] For vibrational bands for which only some of the 8 or 4 components are experimentally observed (e.g., the *g* vibrations), we refer the components to the IMC value (±0.5 cm^{-1}).

[g] Shifts and splittings due in part to Fermi resonance.

[h] Very broad (∼20 cm^{-1}) in mixed crystal.

other three translationally inequivalent molecules), each unique contact generates three others, related to it by the crystal symmetry. It can be seen from the distribution of atom–atom contacts in the table that seriously misleading conclusions might be reached if just one type of contact were employed in the calculation.

From an examination of the potentials and the force constants as a function of distance (Sec. III and tables and figures), the contacts for C–H and H–H interaction were cut off at 3.4 Å and the C–C interaction at 4.0 Å. At greater distances the intermolecular atom–atom force constants are less than 10^{-3} mdyn/Å and no longer significantly contribute to the crystal vibrational energy. It should be noted that these cutoffs eliminate any interaction between translationally equivalent molecules since such interaction distances are at least 5 Å. Thus, the translational shift $L^f(0)=0$, and the ideal mixed crystal frequency is the center of the neat crystal exciton band for nondegenerate states. This had been assumed in earlier work[11] in order to interpret the vibrational exciton data.

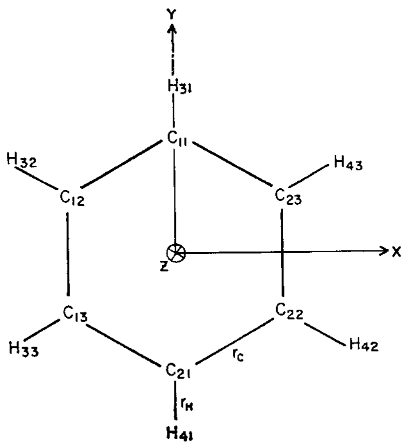

Fig. 4. The structure and numbering of the benzene molecule I at 77°K, with $r_C=1.390$ Å and $r_H=1.083$ Å (see Ref. 22).

TABLE VII. Calculated (potential set I)[a] and experimental data for C_6D_6 vibrations (in cm^{-1}).

Vibration and IMC value[b]	Δ IMC − gas[c]	δ_{ss}	Exciton components[d,e,f]				
			A	B_1	B_2	B_3	
$\nu_1(a_{1g})$, CC	+3.1		−0.7	+0.5	+0.9	−0.7	Calc
(945.6)	···		···	···	···	···	Exptl
$\nu_2(a_{1g})$, CH	+3.6		+0.4	−0.3	−0.2	+0.2	Calc
(2293)[g]	···		···	···	···	···	Exptl
$\nu_3(a_{2g})$, $\mathrm{H}^{\|}$	+5.9		−2.6	−2.0	+2.1	+2.5	Calc
(1059)	···		···	···	···	···	Exptl
$\nu_4(b_{2g})$, $\mathrm{C}^{\perp}$	+12.4		+6.6	−6.0	+4.1	−4.9	Calc
(599)	···		···	···	···	···	Exptl
$\nu_5(b_{2g})$, $\mathrm{H}^{\perp}$	+5.2		+0.7	−0.9	+1.1	−1.0	Calc
(829)[g]	···		···	···	···	···	Exptl
$\nu_6(e_{2g})$, $\mathrm{C}^{\|}$	+5.4	1.1	−0.8	−2.5	−0.2	−2.7	Calc
			+2.2	+1.9	+1.0	+1.0	
(580.2)	···	···	···	···	···	···	Exptl
			···	···	···	···	
$\nu_7(e_{2g})$, CH	+2.5	1.5	−0.7	−0.7	−0.7	−0.5	Calc
			+0.4	+0.9	+0.8	+0.4	
(2266)[g]	···	···	···	···	···	···	Exptl
			···	···	···	···	
$\nu_8(e_{2g})$, CC	+1.2	0.2	−0.2	−0.3	−0.2	0.0	Calc
			0.0	+0.1	+0.1	+0.3	
(1553)[g]	···	···	···	··	···	···	Exptl
			···	···	···	···	
$\nu_9(e_{2g})$, $\mathrm{H}^{\|}$	+9.2	1.9	−1.4	−3.0	−5.6	−4.2	Calc
			+6.4	+7.3	+0.5	0.0	
(869)[g]	···	···	···	···	···	···	Exptl
			···	···	···	···	
$\nu_{10}(e_{1g})$, $\mathrm{H}^{\perp}$	+10.5	4.3	−3.3	−3.0	−4.2	−0.3	Calc
			+0.8	+5.5	+0.1	+4.1	
(660)	···	···	···	···	···	···	Exptl
			···	···	···	···	
$\nu_{11}(a_{2u})$, $\mathrm{H}^{\perp}$	+16.7		+6.9	−6.4	+5.1	−5.6	Calc
511.3	+15.1		+6.7	−9.2	+7.7	−5.3	Exptl
$\nu_{12}(b_{1u})$, $\mathrm{C}^{\|}$	+3.2		+0.1	+0.1	−0.1	−0.3	Calc
971.0	+1.0		+7.1	−0.6	−1.4	−4.2	Exptl
$\nu_{13}(b_{1u})$, CH	+3.2		+0.2	−0.1	+0.1	−0.1	Calc
2268.1[g]	−6.9		···	···	···	···	Exptl
$\nu_{14}(b_{2g})$, CC	+0.7		−0.1	0.0	0.0	+0.1	Calc
1285.1	+3.1		−7.1	+3.6	+2.4	+1.1	Exptl
$\nu_{15}(b_{2u})$, $\mathrm{H}^{\|}$	+11.0		−5.9	−4.0	+4.5	+5.5	Calc
820.6[g]	−3.4		−12.6	+3.5	+6.3	+2.8	Exptl
$\nu_{16}(e_{2u})$, $\mathrm{C}^{\perp}$	+17.6	6.9	−6.4	−4.2	−5.7	−2.2	Calc
354.8			−0.7	+11.6	−1.0	+8.7	
364.6	+12.0	9.8	···	−7.9	−10.3	−5.6	Exptl
			···	+11.6	+5.7	+8.5	

TABLE VII (*Continued*)

Vibration and IMC value[b]	Δ IMC − gas[c]	δ_{ss}	Exciton components[d,e,f]				
			A	B	B_2	B_3	
$\nu_{17}(e_{2u})$, $H^{\perp}$	+9.3	2.9	−1.6	−2.7	−1.8	−3.3	Calc
791.3[g]			+5.1	+6.1	+0.4	+1.1	
797.8[g]	+7.6	6.5	⋯	−4.6	+0.1	−5.5	Exptl
			⋯	+6.3	+0.5	+2.9	
$\nu_{18}(e_{1u})$, $H^{\parallel}$	+6.8	2.7	−1.1	−1.6	−2.6	−2.4	Calc
810.5[g]			+0.8	+3.0	+1.5	+2.2	
814.6[g]	−1.5	4.1	⋯	−0.7	−3.7	−2.6	Exptl
			⋯	+3.6	+0.6	+3.0	
$\nu_{19}(e_{1u})$, CC	+2.2	0.2	−0.4	−0.1	−0.6	−0.5	Calc
1329.2[g]			+0.6	+0.9	+0.3	−0.2	
	0	<1	⋯	+0.3	−0.8	⋯	Exptl
			⋯	+6.8	+5.9	+1.1	
$\nu_{20}(e_{1u})$, CH	+3.6	1.6	−1.0	−1.5	−0.9	−0.8	Calc
2278.9[g]			+0.9	+0.7	+0.8	+1.0	
2282.5[g]	+4.7	+4.5	⋯	⋯	⋯	⋯	Exptl
			⋯	⋯	··	·	

[a] Reference 5.

[b] Taken from Ref. 7(a).

[c] Experimental Δ is determined to ±4 cm^{-1} due to the uncertainty in the gas-phase values. As discussed in Ref. 7, when the gas and liquid values differ by more than the experimental error, the liquid value is the one to use.

[d] References 11 and 12. Measured from the center of gravity of the exciton components except for the degenerate *u* vibrations for which only the 6 B_u components are used to determine the center of gravity. All experimental numbers are ±0.5 cm^{-1}.

[e] For vibrational bands for which only some of the 8 or 4 components are experimentally observed (e.g., the *g* vibrations), we refer the components to the IMC value (±0.5 cm^{-1}).

[f] Although excellent Raman data exist for the neat crystal *g* modes (Ref. 12), since neither all of the 8 or 4 exciton components are observed for any of the 10 *g* vibrations nor are the IMC values available, there is no method by which it is possible to compare calculation and experiment (see Refs. 10 and 11).

[g] Shifts and splittings due in part to Fermi resonance. Note especially ν_{15}, ν_{17}, and ν_{18}, which interact strongly.

TABLE VIII. Calculated (potential set I) and observed site effects for sym-$C_6H_3D_3$.[a]

Vibration	Experimental IMC value (cm^{-1})[b]	Δ (cm^{-1})[c]		δ_{ss} (cm^{-1})	
		Calc	Obs	Calc	Obs
$\nu_1(a_1')$	954.6	+3.1	0		
$\nu_2(a_1')$	3046.3	+6.2	−16		
$\nu_3(a_2')$	(1252)	+5.0	⋯		
$\nu_4(a_2'')$	703.9	+11.8	+7		
$\nu_5(a_2'')$[d]	927.8	+9.9	+10		
$\nu_6(e')$	591.8 593.5	+5.2	−1	1.0	1.7
$\nu_7(e')$[d]	2269.0 2274	3.3	−2	1.3	5
$\nu_8(e')$[d]	1571.2 1572.2	+1.7	−3	0.2	1.0
$\nu_9(e')$[d]	1102.5 1104.9	+10.6	+2	2.6	2.4
$\nu_{10}(e'')$	718.2 722.7	+10.7	+10	4.3	4.5
$\nu_{11}(a_2'')$	545.5	+16.8	+15		
$\nu_{12}(a_1')$	1002.9	+2.9	0		
$\nu_{13}(a_1')$[d]	2281.4	+3.8	−1		
$\nu_{14}(a_2')$	(1322)	+7.1	⋯		
$\nu_{15}(a_2')$[d]	908.0	+12.0	−3		
$\nu_{16}(e')$	377.5 385.0	+17.9	+12	7.0	7.5
$\nu_{17}(e')$	935.7 939.4	+14.2	+14	5.1	3.7
$\nu_{18}(e')$	831.5 834.6	+9.1	0	2.4	3.1
$\nu_{19}(e')$[d]	1410.8	+5.3	−1	1.1	<1
$\nu_{20}(e')$[d]	3060.6	+5.6	−2	2.4	<3

[a] Potential set I from Ref. 5. Experimental quantities from Ref. 7.

[b] From Ref. 7. When IMC value is unknown, liquid phase value appears in parentheses.

[c] Experimental Δ is determined to ±4 cm^{-1} due to the uncertainty in the gas phase values. The mean is used for site-split lines in crystal. As discussed in Ref. 7, when the gas and liquid values differ by more than the experimental error the liquid value is used.

[d] Shifts and splittings due in part to Fermi resonance.

TABLE IX. Calculated (potential set I) and observed orientational effect for C_6H_5D.

Vibration No.	Gas	Sites[a] (in cm^{-1}) 1	2	3	Orientational effect[b] (in cm^{-1}) Calculated	Observed
1	979.0	982.2	982.2	982.3	0.1(*L*)	0.4(*H*)
2	3078.6	3085.7	3085.4	3083.3	+0.3 −2.1	···
3	1296.4	1299.9	1299.6	1299.6	0.3(*L*)	1.0
4	692.7	704.4	704.3	704.5	+0.1 −0.1	0.1
5	1001.2	1016.3	1015.2	1016.3	1.1(*H*)	+~0.2 −1.0
6*a*	604.2	608.8	609.1	609.1	0.3(*H*)	
6*b*	604.9	609.8	609.8	609.9	0.1(*L*)	
7*a*	2282.7	2285.0	2285.9	2287.5	+1.6 −0.9	
7*b*	3043.7	3050.4	3049.5	3048.3	+0.9 −1.2	
8*a*	1595.6	1597.2	1597.3	1597.3	0.1(*H*)	0.2[d]
8*b*	1591.8	1593.8	1593.6	1593.6	0.2(*L*)	0[d]
9*a*	1172.0	1187.1	1184.9	1184.6	+2.2 −0.3	d
9*b*	1157.1	1169.3	1170.4	1170.5	+0.1 −1.1	0.1
10*a*	853.6	869.8	875.2	868.4	+5.4 −1.4	
10*b*	784.3	800.5	797.8	800.5	2.7(*H*)	
11	606.9	624.3	624.2	625.2	+0.9 −0.1	2.2(*L*)[d]
12	1006.0	1008.8	1008.8	1009.1	0.3(*L*)	
13	3053.7	3059.1	3059.7	3060.0	+0.3 −0.6	
14	1327.5	1337.9	1336.8	1336.5	+1.1 −0.3	2.2(*L*)
15	1080.6	1091.2	1091.4	1091.4	0.2(*H*)	1.7(*H*)
16*a*	400.0	416.4	421.6	417.2	+4.4 −0.8	
16*b*	377.7	397.4	391.5	397.2	+0.2 −5.7	4.5(*H*)
17*a*	994.2	1006.5	1010.8	1006.0	+4.3 −0.5	
17*b*	944.3	957.8	958.5	957.6	+0.7 −0.2	0.7
18*a*	1031.9	1042.9	1040.8	1040.2	+2.1 −0.6	2.8(*L*)
18*b*	858.6	865.8	868.8	869.8	+1.0 −3.0	+1.1 −2.9 (~3.5)[c,d]
19*a*	1474.1	1481.2	1480.2	1480.1	+1.0 −0.1	
19*b*	1451.4	1456.9	1457.4	1457.3	+0.1 −0.4	0.2[d]
20*a*	3069.6	3076.0	3075.3	3074.6	+0.7 −0.7	
20*b*	3075.2	3080.8	3080.7	3081.5	+0.7 −0.1	

[a] The meaning of "Sites" is discussed in the text.

[b] Signs for both calculated and experimental values [Refs. 7(a) and 7(b)] are relative to the component of intermediate frequency when all three components are resolved. This convention, which is different from that used in our earlier papers, was adopted for convenience of comparing calculated and observed splittings since the assignment of the observed components is not known. For the theoretical data the notation *H* or *L* is used to indicate that an accidental degeneracy occurs in the high (*H*) or low (*L*) frequency pair of components. The most intense experimental line is labeled *H* or *L* depending upon whether it is the high or low frequency member of the pair. When two lines of an experimental triplet are unresolved, it is expected that the unresolved pair has the greater intensity (see Ref. 7). The experimental data corresponding to ν_{11}, ν_{14}, ν_{16b}, and ν_{18a}, for example, provide good examples of the theoretically expected intensity relationship. As discussed in Ref. 7, for the experimental values with no *H* or *L* next to them, it was not possible to determine which line is degenerate.

[c] Infrared and ultraviolet data differ. The infrared shows a doublet with splitting $\sim 3.4\pm0.5$ cm^{-1}. See Refs. 7(a) and 7(b). Note that ν_{10a} and ν_{18b} are nearly degenerate.

[d] Splitting may be due in part to Fermi resonance. See Ref. 7.

V. RESULTS OF THE CALCULATION AND DISCUSSION

Tables IV and V contain the calculated optical phonons for C_6H_6 and C_6D_6. For C_6H_6 (Table IV), phonons obtained employing five different potentials are presented: CH, HH, and CH plus HH from Ref. 1, and sets IV and I of Williams.[5] The experimentally observed phonons,[23,24] including new high resolution Raman data taken at 77°K,[25] are also presented there for comparison. In Table V the C_6D_6 phonons calculated from potential set I[5] and the experimental values[23,24] are given. Gas-to-crystal (site) shifts Δ, site splittings δ_{ss}, and exciton structure for these isotopic benzenes are presented in Tables VI (C_6H_6) and VII (C_6D_6). Again, along with the experimental data,[7,11,12] all five potentials are given for C_6H_6 while only the set I calculated values are tabulated for C_6D_6. The ideal mixed crystal site effects of *sym*-$C_6H_3D_3$, C_6H_5D, and *p*-$C_6H_4D_2$, calculated (set I) and observed values,[7] can be found in Tables VIII, IX, and X, respectively.

From Tables IV and VI, it is clear that much of the experimental spectroscopic data are moderately well reproduced using the H–H, C–H, and C–C potential set I of Williams.[5] The result is quite satisfying, as set I of all the potentials we have considered is also the one that best fits the thermodynamic and structural data for many aromatic crystals. *It appears that for*

TABLE X. Calculated (potential set I) and observed orientational effect for p-$C_6H_4D_2$.[a]

Vibration No.	Gas	Sites (in cm^{-1})			Orientational effect (in cm^{-1})	
		1	2	3	Calculated	Observed
1	975.6	978.6	978.5	978.5	0.1(L)	
2	3063.2	3070.2	3069.5	3067.9	+0.7 −1.6	
3	1308.6	1320.7	1318.8	1318.4	+1.9 −0.4	+1.3 −3.4
4	629.2	641.1	637.0	642.5	+1.4 −4.1	+2.4 −3.3
5	988.9	1006.8	1010.7	1006.2	+3.9 −0.6	
6*a*	598.8	603.4	603.2	603.2	0.2(L)	
6*b*	598.9	603.8	604.4	604.5	+0.1 −0.6	
7*a*	2278.5	2280.8	2281.7	2283.3	+1.6 −0.9	
7*b*	3043.7	3050.5	3049.6	3048.3	+0.9 −1.3	
8*a*	1588.2	1589.6	1589.6	1589.6	0.0	
8*b*	1581.4	1583.6	1583.4	1583.4	0.2(L)	
9*a*	1169.5	1184.6	1182.4	1182.1	+2.2 −0.3	+1.1 −0.4
9*b*	912.6	919.7	922.1	922.5	+0.4 −2.4	+0.7 −1.9
10*a*	853.6	869.7	875.2	868.9	+5.5 −0.8	
10*b*	738.6	748.2	747.4	747.3	+0.8 −0.1	+1.4 −0.5
11	598.9	617.9	618.2	617.1	+0.3 −0.8	<1(L)
12	994.2	992.3	992.6	993.0	+0.4 −0.3	3.1(L)[b]
13	2287.0	2289.4	2290.3	2291.9	+1.6 −0.9	
14	1291.5	1292.5	1292.6	1292.6	0.1(H)	<1.0
15	1103.6	1116.3	1114.8	1114.6	+1.5 −0.2	~2.0
16*a*	357.3	376.8	370.4	377.2	+0.4 −6.4	4.7(H)
16*b*	400.0	416.2	421.6	416.9	+4.7 −0.7	
17*a*	971.2	984.7	988.5	984.2	+3.8 −0.5	2.0(H)[b]
17*b*	897.3	908.8	910.6	908.3	+1.8 −0.5	+0.6 −3.0
18*a*	1029.5	1040.0	1037.9	1037.2	+2.1 −0.7	3.1(L)
18*b*	819.1	826.4	829.8	830.4	+0.6 −3.4	3.7(H)
19*a*	1468.5	1475.7	1474.6	1474.6	1.1(L)	
19*b*	1412.0	1417.4	1416.7	1416.4	+0.7 −0.3	
20*a*	3071.2	3077.8	3076.6	3075.7	+1.2 −0.9	
20*b*	3078.5	3085.7	3085.2	3083.3	+0.5 −1.9	

[a] See footnotes for Table IX.

[b] Splitting may be due in part to Fermi resonance.

these crystals a potential may be found that is not only transferrable from crystal to crystal for the thermodynamic and structural properties, but can be used with moderate success for the spectroscopic properties as well.

Although set I of Williams is found to give the best agreement with all the combined data, some calculated properties for certain of the vibrations simply do not agree with measured values. It is believed that these discrepancies could be caused by the neglect of three- and four-center terms or of anharmonic contributions to the potentials. For example, crystal-induced Fermi resonance brought about by these anharmonicities was not taken into account, even though it is known to be of importance in certain instances. The occasionally poor agreement in the site shift Δ, in particular the trend towards negative shifts in the experimental values (*vide infra*), may simply be caused by the neglect in our calculation of such crystal-induced Fermi resonance as has been discussed in Refs. 7, 10, and 11. Moreover, we have assumed at the beginning that the force constants $\mathbf{F}_{\mathrm{site}}$ and $\mathbf{F}_{\mathrm{mol}}$ are identical, or conversely that the P term in the Davydov representation was zero, while in actuality the $\mathbf{F}_{\mathrm{site}}$ force constants may be somewhat smaller because of electron delocalization in the crystalline state. (See Sec. V.C. for further comments on this approximation.)

A. Phonons

It can be seen from the calculated C_6H_6 data for the various potentials (Table IV) that the phonons are most sensitive to the form and size of the intermolecular force constants. The calculated values using potential set I for both C_6H_6 and C_6D_6 (Table V) lattice modes are good; the only significant differences between observed and calculated frequencies are two B_{2g} phonons of both C_6H_6 and C_6D_6 and one B_{2u} phonon of C_6H_6.

Three g lattice modes of A_g, B_{2g}, and B_{3g} symmetry are inactive and cannot be experimentally observed directly.[23,24] Qualitative arguments have predicted them to be degenerate with certain observed ones.[24] Since the other phonons are so well calculated we must reject these arguments and place the unobserved B_{2g} phonons at 135 cm^{-1} (C_6H_6) and 125 cm^{-1} (C_6D_6) and the unobserved B_{3g} phonons at 125 cm^{-1} (C_6H_6)

and 115 cm^{-1} (C_6D_6), while the unobserved A_g mode in both cases should lie at ~100 cm^{-1}. These modes may be sensitive to intermolecular anharmonicities or many-center interactions. Recently C_6H_6 lattice modes of *u* symmetry have been observed[26] and again rough estimates have been used to assign their polarization properties. Our calculations however require that the phonons be reassigned as given in Table IV. The sensitivity of the phonon assignments to potential function indicates the necessity of using good potentials and of considering *all* types of atom–atom interactions in crystal calculations. Improved calculations should in the future cause such theoretically based assignments to be even more reliable than those presented here.

B. Exciton Structure (C_6H_6 and C_6D_6)

While the potential set that gave the best agreement between the calculated and experimental results for the phonons is also the best potential here, the exciton structure of C_6H_6 and C_6D_6 seems less accurately described by our model (see Tables VI and VII). With few exceptions, however, the general trends are reproduced. It is clear that the experimental data are far from complete as not all components of the bands are observed. Polarization data[27] are scanty and those available are from low resolution spectra. Furthermore, the existing data on *g* vibrations of C_6D_6 cannot be interpreted,[10–12] and, especially for the ν_{17}, ν_{18}, and ν_{15} modes and the ν_5 and ν_9 modes of C_6D_6, there is strong interaction between some of the vibrations. These difficulties make a straightforward comparison between the calculated and observed exciton structure not always possible. Bands for which this is the case are indicated in the tables. However, there are cases of real disagreement (ν_{15} and ν_{12} of C_6H_6 in particular). All that can be said here is that although the potential model does with few exceptions predict the over-all magnitude of the splitting and order of the exciton components, the detailed structure of the bands is not always obtained. Again this indicates the possibility that anharmonic or multicenter terms are important, especially for such a complex phenomenon as exciton structure. The exciton structure of many C_6H_6 bands, notably ν_1, ν_2, ν_6, ν_9, ν_{10}, ν_{11}, ν_{14}, ν_{16}, ν_{17}, ν_{18}, and ν_{19} are, however, quite well characterized by our model. No comment can be made about ν_3, ν_4, ν_{13}, and ν_{20} due to lack of good experimental data for these vibrations, while for C_6D_6 only ν_{11}, ν_{12}, ν_{14}, and ν_{16} can be compared for agreement.

C. Gas-to-Crystal (Site) Shift

Site shifts have been calculated for all the isotopes and are tabulated here for C_6H_6, C_6D_6 and *sym*-$C_6H_3D_3$ (Tables VI, VII, and VIII). Data are presented for these isotopes alone since the experimental data are most reliable for them. Agreement between theory and experiment is a direct check on the approximation in which the site distortion energy is assumed small ($P\equiv 0$ in this calculation), and would indicate that the entire shift is due to the D term or the "diagonal" contribution of the intermolecular force field to the force field of the site. Disagreement between theory and experiment would throw doubt on this approximation.

Site shifts have been discussed extensively recently[7] and the problems involved with accurately measuring them have been enumerated (increased Fermi resonance in the condensed phase, gas-phase experimental error for unresolved bands, to mention two). Nevertheless, the data presented in Tables VI, VII, and VIII indicate the agreement between the theoretical model (employing potential set I) and the observed values is generally pretty good. Three bands however show complete variance between the calculations and the experimental findings in all the isotopes: ν_9, ν_{15}, and ν_{18}. The calculated shifts are all much too large for these vibrations. For ν_{15} the calculated exciton structure was also found to be incorrect, while the exciton splittings for ν_9 and ν_{18} were represented well by the theoretical model. It is interesting to note that these three vibrations are $H^{||}$ modes in which both the carbon and the hydrogen atoms move parallel to one another in the molecular plane, but in opposite directions.

D. Site Group Splitting

The splitting of a degenerate vibration into two crystal site states has previously been discussed for benzene.[7,10] Only C_6H_6, C_6D_6, and *sym*-$C_6H_3D_3$ have degenerate molecular fundamentals and thus show this effect. In the present approach it is the force constants of the ideal mixed crystal ($\mathbf{F}_{\mathrm{mol}}+\mathbf{F}'=\mathbf{F}_{\mathrm{IMC}}$) that give rise to the experimental site splitting δ_{ss}. Tables VI, VII, and VIII contain both the calculated and observed values of δ_{ss} for these isotopes. Agreement is again very good using potential set I. (In C_6D_6 ν_{18} and ν_{17} are in Fermi resonance and the experimental splittings of ν_7 and ν_{20} are also perturbed by Fermi resonance in all the isotopes.)

It is necessary to comment on ν_6, ν_8, and ν_9 of C_6H_6 and *sym*-$C_6H_3D_3$. The calculations predict that $\delta_{ss}^{\nu_6}(C_6H_6)=0.7$, $\delta_{ss}^{\nu_6}(C_6H_3D_3)=2.0$, and $\delta_{ss}^{\nu_6}(C_6D_6)=1.1$ cm^{-1}, while the observed values are 3.1, 1.7, and 1.2 cm^{-1}, respectively. The experimental value for C_6H_6 appears to be out of line with *both* the calculated and the observed $\delta_{ss}^{\nu_6}$ for the other isotopes. For the C_6H_6 band $(\nu_6+\nu_1)$, in Fermi resonance with ν_8, $\delta_{ss}=1.2$ cm^{-1}. It is difficult to understand why for a given vibration of one isotopic modification the atom–atom potential would appear to give correct results while it does not for another. Likewise the site splitting in the ν_8 band of C_6H_6 and *sym*-$C_6H_3D_3$ [also in Fermi resonance with $(\nu_6+\nu_1)$] is difficult to understand. The same problem arises in ν_9 where the calculated and experimental values agree for *sym*-$C_6H_3D_3$ but not at all for C_6H_6.

E. Orientational Effect

The orientational effect,[7] calculated by changing the relative numbering of the mass matrix with respect to the site force constant matrix, has been obtained for all isotopes of lower than $\mathbf{D}_{3h}$ symmetry. From symmetry arguments[7a,28] it is expected and has been verified by direct calculation that C_6H_6, C_6D_6, and *sym*-$C_6H_3D_3$ do not show an orientational effect in the $\mathbf{C}_i$ crystal site. The experimental data and calculated results for C_6H_5D and *p*-$C_6H_4D_2$ using potential set I are given in Tables IX and X. The agreement in most cases is good. It should be pointed out that while the calculated splittings are always known in an absolute sense ("sites" 1, 2, 3 referring to a deuterium substitution position), the experimental ones are arbitrarily determined(i.e., the specific orientation of the molecule in the site, relative to the crystal axes, is unknown). Thus the calculated sign of the orientational effect is of little significance when we compare these numbers with the experimental results; the quantity that is of concern is the "splitting" pattern or the relative positions of the lines with respect to one of them. Again interactions between vibrations that are orthogonal in the gas phase but not orthogonal under the reduced symmetry of the site make comparison between experimental and calculated numbers not meaningful in some cases.

V. CONCLUSIONS

The most important conclusion of this work is that the model of pairwise, atom–atom, interaction potentials is a quantitatively reasonable one for the calculation of intermolecular interactions (exciton structure, phonons, site shifts and splittings, and the orientational effect) and that such potentials are not only transferable from crystal to crystal for the thermodynamic and structural data but to spectroscopic properties as well. To improve the calculation of such crystal properties and site effects, attention must be directed to the approximations upon which this model is grounded. Therefore, general potentials that take into account three- and four-center interactions, and force constants that include anharmonic contributions should be considered if one is to fit the experimental results more faithfully. Some way of evaluating, and including if necessary, the effect of site polarization on the electronic structure and force constants should be found. Further, this calculation graphically demonstrates the need to consider all atom–atom interactions and not just H–H terms. Indeed, grossly misleading results and conclusions can be obtained by assuming only one set of interactions is important. In conclusion we remark that no isotopic effects are obvious in the calculations, that is, the same potentials work equally well for H–H, H–D, D–D, C–H, and C–D interactions.

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