Site Effects in Isotopic Mixed Crystals—Site Shift, Site Splitting, Orientational Effect, and Intermolecular Fermi Resonance in the Vibrational Spectrum of Benzene

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phase delay at fixed scattering cell conditions was measured with 2.2-, 3.9-, and 7.5-MHz modulation frequencies. The single-sideband spectrum was not analyzed for rf harmonics at the 2.2- and 7.5-MHz frequencies, and for this or other unknown reason the lifetime obtained at 7.5 MHz was about 4% shorter. Choosing a compromise value, and allowing a 5% total uncertainty, our results are

$$\tau(\mathrm{Cs}\ ^2P_{3/2}) = 30.8 \pm 1.5 \times 10^{-9}\ \mathrm{sec},$$

$$\tau(\mathrm{Cs}\ ^2P_{1/2}) = 35.2 \pm 1.5 \times 10^{-9}\ \mathrm{sec}.$$

These are in good agreement with Link's phase-shift measurement[15] $\tau(\mathrm{Cs}\ ^2P_{3/2}) = 30.5 \pm 0.6$, our own Hanle-effect measurement[18] $\tau(^2P_{1/2}) = 34$, with Phelps and Chen's[19] index-of-refraction measurement $\tau(^2P_{3/2}) = 30 \pm 2$ and $\tau(^2P_{1/2}) = 35 \pm 2$ (based on Taylor–Langmuir Cs pressures), and with the Coulomb approximation values.[15,19] The agreement with Markova *et al.*,[16] $\tau(^2P_{3/2}) = 28 \pm 2$, is only marginal.

[18] A. Gallagher, Phys. Rev. **157**, 68 (1967).
[19] A. V. Phelps and C. L. Chen, ONR yearly report on contract NONR-4725(00) (to be published).

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Site Effects in Isotopic Mixed Crystals—Site Shift, Site Splitting, Orientational Effect, and Intermolecular Fermi Resonance in the Vibrational Spectrum of Benzene*, †

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A modification of the Davydov theory of energy levels in molecular crystals is applied to experimental observations on ground-state vibrations of various isotopic substituted benzene crystals. Three distinct and characteristic crystal-induced phenomena have been observed experimentally: (1) site group splitting—involving degenerate vibrations of the molecule that map into nondegenerate site modes; (2) orientational effects—concerning isotopic benzenes of symmetry D_{2h} or lower, and their relative positioning in two or more distinct orientations at crystal sites; and (3) intermolecular Fermi resonance—near-resonance interaction between two adjacent-site molecules of different isotopic compositions. The first two phenomena give rise to 10 cm^{-1} $\lesssim$splittings. A general mechanism is proposed to account for this, and the differences and similarities between these two effects are discussed. The importance of observed gas-to-crystal energy shifts is also discussed in the light of these experimental findings. In addition to intersite Fermi resonance, solid-enhanced intrasite Fermi resonance is reported and discussed qualitatively. Applying the Davydov theory for the case of no resonance interactions, one can obtain information concerning the shape of the molecule in the site field, the symmetry of the site field, and the general nature of the intermolecular interactions.

I. INTRODUCTION

Over the past 20 years, two complementary theoretical approaches have been taken to solve the problem of Frenkel excitons[1] in molecular crystals. The first one, which can be called the Halford–Hornig approach,[2] is almost purely group theoretical in nature. These authors have discussed such concepts as the relation of the site group and the factor group to the space group, and how, from these groups, selection rules for crystal transitions can be obtained. The second approach, called the Davydov theory,[3] is a technique for obtaining general crystal energy levels. In this paper a modified form of Davydov theory will be used for localized states in a molecular crystal, and the resulting simple theory will be applied to vibrational spectra of dilute isotopic mixed crystals of benzene. Because of the relationship between neat crystals and isotopic mixed crystals, useful information about neat crystal intermolecular interactions can be obtained by studying the mixed crystals.

II. THEORETICAL

In this discussion of the energy levels of molecular crystals, it will prove most convenient to begin within the general framework of the Davydov theory,[3] in

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|| Contribution No. 3300.
[1] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931).
[2] R. S. Halford and O. H. Schafer, J. Chem. Phys. **14**, 141 (1946); R. S. Halford, *ibid.* **14**, 8 (1946); H. Winston and R. S. Halford, *ibid.* **17**, 607 (1949); D. F. Hornig, *ibid.* **16**, 1063 (1948).
[3] A. S. Davydov, *Theory of Molecular Excitons* (McGraw-Hill Book Co., New York, 1962); Usp. Fiz. Nauk **82**, 393 (1964) [Sov. Phys.—Usp. **7**, 145 (1964)].

which a crystal transition from the ground to the fth excited state is given by[4]

$$E^{f\alpha}(\mathbf{k}) = \tilde{\epsilon}^f + \Delta^f + L^{f\alpha}(\mathbf{k}). \quad (1)$$

The left-hand side of Eq. (1) is the crystal transition energy; $\tilde{\epsilon}^f$ is the gas phase excitation energy for the $f \leftarrow 0$ transition; Δ^f is an energy shift term (site shift); and $L^{f\alpha}(\mathbf{k})$ incorporates the exciton terms.[4] The superscript α labels a particular irreducible representation of the interchange group.[4,5]

In this paper mixed-crystal effects will be of primary interest. In Ref. 4 the concept of the *ideal mixed crystal* was introduced. For vibrational states, except when there is Fermi resonance, the ideal mixed crystal is closely approximated by a $<1\%$ isotopic mixed crystal. Mathematically, the $L^{f\alpha}(\mathbf{k})$ terms of Eq. (1) disappear in first order if a localized excited site function is used in place of the one-site exciton wavefunction. Thus, in an isotopic mixed crystal, the energy levels of the guest are given to zero order in site functions and first order in energy by[4]

$$E^f = \tilde{\epsilon}^f + \Delta^f. \quad (2)$$

Within this same framework, site group splitting for a doubly degenerate molecular vibration can be defined as $(\Delta_+ - \Delta_-)$, namely the difference in shift terms for the two components of the degenerate vibration. In the benzene neat crystal, it is not possible to separate site group splittings from exciton effects.[4]

Orientational "splittings" can be similarly thought of as being caused by a dependence of Δ on orientation, relative to the crystallographic axes, of any one of the low symmetry ($<\mathbf{D}_{3h}$) isotopic modifications of benzene. More will be said about these effects later in the paper.

Applying the above ideas to experiments, the effect of the crystal site on the ground-state vibrations of an isotopic guest molecule in the host crystal is investigated. In return, something can be learned about the site field. Using these site effects, it is possible to discuss semiquantitatively the magnitude of "static" interactions in molecular crystals, and to characterize the symmetry and nature of the site field in the benzene crystal. Specifically, the magnitudes of the site shift, the site splitting, and the orientational effect will be correlated. It will be seen that the effect of host or guest isotopic substitution on these interactions is negligible, showing that the potentials governing these interactions are not sensibly dependent upon isotopic substitution, a result that was suggested earlier by experiments on neat crystals.[6]

The simple expression given by Eq. (2) has not taken into account Fermi resonance, the occurrence of which is expected to complicate the energy level formulas. Induced intrasite Fermi resonance is observed for the individual guest molecules in some instances where, because of symmetry, Fermi resonance in the free molecule is not allowed. Intersite Fermi resonance is discussed for host–guest systems in which an infrared-active guest vibration is in resonance with an otherwise unobserved host vibration.

III. CRYSTAL STRUCTURE AND SITE SYMMETRY

Since we shall be interested in the effects of the crystal site on the molecular fundamentals of the benzene isotopes, it is very important to know the site symmetry and the exact shape of the molecule in the crystal site.

The benzene crystal structure, as given by Cox *et al.*,[7] is space group *Pbca* with four molecules per unit cell at sites of $\mathbf{C}_i$ symmetry. All sites are crystallographically and physically equivalent. Cox *et al.* conclude that the benzene molecule is both hexagonal and planar even though the molecules reside in an environment of no greater than $\mathbf{C}_i$ symmetry. The neutron-diffraction data of Bacon *et al.*,[8] extrapolated to 77°K, corroborate these conclusions. The thermally corrected C–C distance is 1.390 ± 0.002 Å, and the corrected H–H distance is 1.083 ± 0.004 Å. Small deviations among the bond length measurements are assumed to be within the experimental error. The carbon atoms are all out of the "carbon best plane" by ± 0.0015 Å, the hydrogen atoms are out of the "hydrogen best plane" by ± 0.0093 Å, and the maximum deviation of any atom out of the combined equally weighted "best plane" of the molecule is ± 0.0118 Å. As significant as these differences appear to be, because of thermal corrections and other uncertainties, both Cox and Bacon were forced to conclude that they lie within experimental error. Thus from crystallographic data alone the molecular shape reflects the $\mathbf{D}_{6h}$ symmetry of the free molecule.

Actually, it would be incorrect to assume that the site has an effective sixfold axis, as the crystal does not have one. Considering the arrangement and orientation of the molecules in the crystallographic lattice, the site is almost of $\mathbf{C}_{2h}$ symmetry, with an approximate plane passing through atoms 1 and 4 (Cox's notation). The observed deviations from the assumed planarity are most consistent with this effective site symmetry. The spectra of the benzene crystal can be used to learn more about the physical state of the molecule in the crystal and the nature of the distorting environment.

[4] For a more complete and detailed account of the form and implications of this development see E. R. Bernstein, S. D. Colson, R. Kopelman, and G. W. Robinson, J. Chem. Phys. **48**, 5596 (1968).

[5] See Ref. 4 for the full group-theoretical breakdown of the molecular exciton problem and also R. Kopelman, J. Chem. Phys. **47**, 2631 (1967).

[6] E. R. Bernstein and G. W. Robinson, J. Chem. Phys. **49**, 4962 (1968).

[7] E. G. Cox, Rev. Mod. Phys. **10**, 159 (1958); E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, Proc. Roy. Soc. (London) **A247**, 1 (1958).

[8] G. W. Bacon, N. A. Currey, and S. A. Wilson, Proc. Roy. Soc. (London) **A289**, 98 (1964).

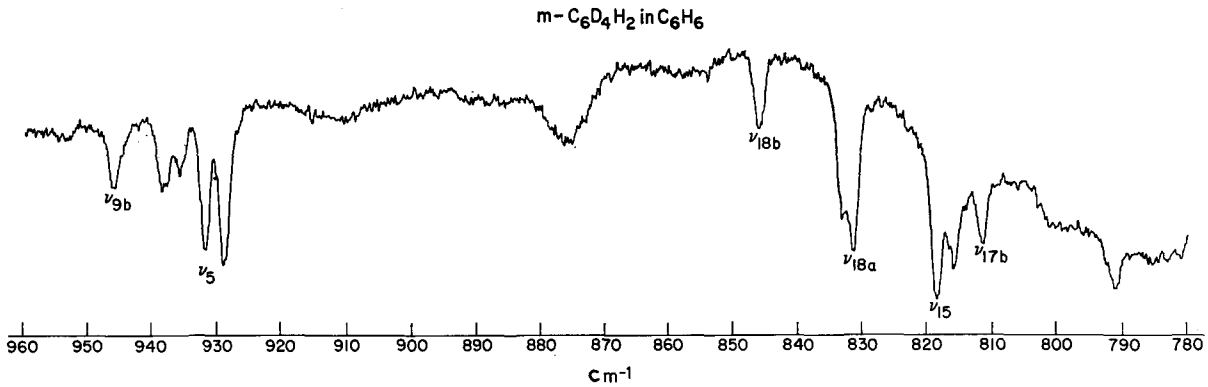


FIG. 1. A portion of the m-$C_6D_4H_2$ in C_6H_6 crystal spectra showing the increased interaction between fundamentals in the solid. Note orientation effects on most peaks, the presence of which further complicates the assignment of these transitions. Possible assignments for some of the observed lines are indicated on the figure. Major impurities are p-$C_6H_2D_4$ (990, 875 cm^{-1}) and C_6D_5H (935 cm^{-1}).

IV. EXPERIMENTAL

All isotopic substituted benzenes (C_6H_5D, p- and m-$C_6H_4D_2$, sym-$C_6H_3D_3$, m-$C_6H_2D_4$, C_6HD_5, C_6D_6) were purchased from Merck, Sharp & Dohme of Canada, Ltd. The C_6H_6 (Research Grade) was obtained from Phillips Petroleum Company. The isotopic guest concentration in either a C_6H_6 or a C_6D_6 host varied from 0.5% to 1.0%, and these mixed crystals were either 0.225 mm or 0.500 mm thick. For very intense bands (for example, the e_{1u} and a_{2u} bands of C_6H_6) a 0.5% guest solution was used in the holder with the 0.225-mm sample space.

The holder consists of two copper rings with grooves for 0.050-in.-diam indium wire upon which CsI windows are placed. The indium serves to apply firm, uniform pressure to the soft windows and aids in the thermal contact between the CsI and the copper. When the two halves of the holder are screwed together, the windows are spaced by either a 0.050- or 0.026-in. indium wire gasket, not made into a closed circle. The holder gives, rather reproducibly, the above quoted sample thick-

TABLE I. One% C_6H_6 in 99.0% C_6D_6 (u vibrations only).[a]

Vibration number and type	Symmetry (D_{6h})	Gas phase[b] (cm^{-1})	Energy (cm^{-1})	Comment	Site splitting [cm^{-1} (δ_{ss})]
C-C nonplanar ν_{16}	e_{2u}	398.1	404.8 413.0	W, Equal I	8.2
C-H nonplanar ν_{11}	a_{2u}	673	694.1 696.9	$W^{13}CC_5H_6$ Sh	
C-H nonplanar ν_{17}	e_{2u}	967	978.3	Both lines are blue shaded	5.6
			983.9	Equal I	
C-C planar ν_{12}	b_{1u}	1010	1011.3	Sh	
C-H planar ν_{18}	e_{1u}	1037	1034.8 1038.6	Sh, equal I	3.8
C-H planar ν_{15}	b_{2u}	1146	1146.9	Sh	
C-H planar ν_{14}	b_{2u}	1309	1308.0 1312.6	$^{13}CC_5H_6$	
C-C planar ν_{19}	b_{1u}	1482	1460–78	B and flat, FR	
C-H planar ν_{20}	e_{1u}	3043	3012.5[c]		
ν_{13}	e_{1u}	3057	3033.9		
$\nu_{19}+\nu_8$	e_{1u}	3083	3038.9		
$\nu_1+\nu_6+\nu_{19}$	e_{1u}	3100	3046.2		
plus other combinations			3060.3 3072.5 3078.5 3082.5 3087.5 3094.1	FR	?

[a] Key: W, weak; B, broad; I, more intense component of a doublet; FR, Fermi resonance; Sh, sharp.

[b] See Ref. 13 and J. H. Callomon, T. M. Dunn, and I. M. Mills, Phil. Trans. Roy. Soc. London **259**, 499 (1966).

[c] Some of these lines have been assigned erroneously as factor group components of C_6H_6 $\nu_{20}(e_{1u})$ band and $\nu_{13}(b_{1u})$ band; see Ref. 18.

nesses. After assembly of the holder, the benzene mixture is injected through the gap left in the indium spacer, and this gap is then sealed with the remaining tails of the indium spacer. Such a technique usually produces a cell that is vacuum tight, i.e., the holder can be evacuated from the outside without loss of liquid benzene in the cell. The sample holder is then attached to the cold finger of a helium Dewar and brought to liquid-nitrogen temperature in about 10 min. The sample thus produced is decidedly polycrystalline but not opaque. Samples were studied at both 4.2° and 77°K with no essential differences observable in the spectra. Most of the data reported here were taken at 77°K for convenience.

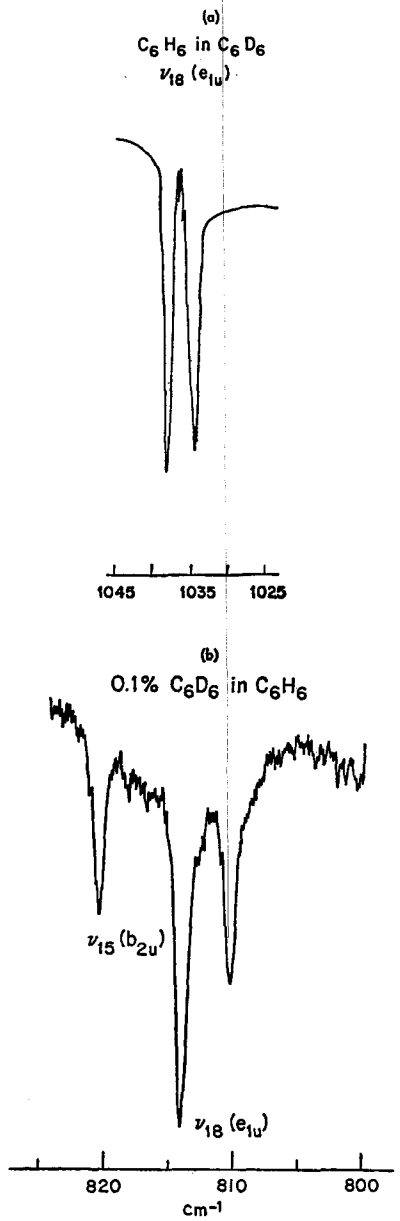


FIG. 2. (a) Three-fourths % C_6H_6 in C_6D_6 to show 3.8 cm^{-1} site group splitting on the ν_{18} (e_{1u}) degenerate fundamental; (b) 0.1% C_6D_6 in C_6H_6 showing ν_{18} (e_{1u}) and ν_{15}(b_{2u}).

All spectra were recorded on a Beckman IR-12. The typical resolution in the region of greatest interest (350–1500 cm^{-1}) was about 0.75 cm^{-1} and in some cases was as good as 0.50 cm^{-1}. The linewidths of the best samples are believed to be instrument limited, but are generally dependent on the quality of the crystal and on the concentration of the guest. Thick, well-prepared, low-concentration (~0.1% guest) mixed crystals gave rise to lines whose measured half-width was <0.5 cm^{-1}. The data obtained are reported in Tables I–VI, and some representative spectra are displayed in Figs. 1–12.

V. RESULTS AND DISCUSSION

A. General Ground-State Vibrational Structure of the Isotopes

Of the 20 benzene normal modes ($2a_{1g}$, $1a_{2g}$, $2b_{2g}$, $4e_{2g}$, $1e_{1g}$, $1a_{2u}$, $2b_{1u}$, $2b_{2u}$, $2e_{2u}$, $3e_{1u}$) only a_{1g}, e_{1g}, e_{2g} (Raman), and e_{1u}, a_{2u} (infrared) fundamentals have been observed directly in the gas phase because of the $\mathbf{D}_{6h}$ group theoretical selection rules. All other gas phase frequencies are known from combinations and overtones. These selection rules apply exactly only to the isotopic species C_6H_6 and C_6D_6, which possess the full $\mathbf{D}_{6h}$ symmetry. In the isotopes of lower symmetry, *sym*-$C_6H_3D_3$, *p*-$C_6H_4D_2$, C_6H_5D, the gas phase activity of vibrations is given as a first approximation not by the group character table selection rules but by correlation to active modes in C_6H_6 or C_6D_6. Only modes that correlate to or mix with a_{1g}, e_{1g}, e_{2g}, e_{1u}, or a_{2u} have an appreciable intensity in the gas phase Raman or infrared spectra. Thus, for the gaseous molecule, the substitution of a deuterium atom for a hydrogen atom in benzene is not a large perturbation upon the selection rules. See Table VII.

The crystal environment changes the selection rules more dramatically, even though the energy perturbations are not large. The molecular symmetry of benzene in the crystal is reduced at least in theory to $\mathbf{C}_i$, and thus all vibrations having *u* symmetry at least in principle are active in the infrared and all vibrations having *g* symmetry are active in the Raman. Indeed, all *u* vibrations are observed in the infrared spectrum of the crystal. The gas phase ($\mathbf{D}_{6h}$) active vibrations are still the most intense in the Raman and infrared, as would be expected for weak intermolecular interactions. It should be pointed out, however, that from considerations of selection rules alone, the site symmetry cannot be fixed uniquely. See Table VIII.

A remark should also be made concerning the symmetry assignments and numbering of the vibrational transitions of the non-$\mathbf{D}_{6h}$ isotopes. In most cases there is strong mixing between vibrations of the same sym-

TABLE II. 1% C_6H_5D in 99.0% C_6H_6 and C_6D_6.[a]

Vibration number and type		Symmetry (D_{6h})	Symmetry (C_{2v})	Gas phase[b] (cm^{-1})	Energy (C_6H_6 cm^{-1})	Energy (C_6D_6 cm^{-1})	Comment	Orientational effect [cm^{-1} (δ_{oe})]
C–C nonplanar	ν_{16}	e_{2u}	b_2	381	385.9 390.2	387.8 392.4	W I, B	~4.5
			a_2	403		~410	VW, B	
C–H nonplanar	ν_{11}	a_{2u}	b_2	607	621.4 623.5	621.4 623.6	I, B (621.0 S) induces ν_6 (e_{2g}) in C_6H_6 606.0, 608.8	2.2
C–C nonplanar	ν_4	b_{2g}	b_2	698		703.9		
C–H planar	ν_{18}	e_{1u}	b_1	857	854.1 858.8	856.9 859.0		~3.4
C–H nonplanar	ν_{17}	e_{2u}	b_2	924	935.9	936.4		
C–C planar	ν_1	a_{1g}	a_1	983		980.0	B, W	
C–H nonplanar	ν_{17}	e_{2u}	a_2	967		986.2	B, W (FR)	
C–H nonplanar	ν_5	b_{2g}	b_2	984	997.7	996.9	Blue shaded and B, W (FR)	
C–C planar	ν_{12}	b_{1u}	a_1	1007		1003.2	Red shaded (FR)	
C–H planar	ν_{18}	e_{1u}	a_1	1034		1032.7 1035.5	B	2.8
C–H planar	ν_{15}	b_{2u}	b_1	1077	1078.1	1078.3	Red shaded	
C–H planar	ν_9	e_{2g}	b_1	1158	1157.5	1157.4		
C–H planar	ν_9	e_{2g}	a_1	1174		1175–1193	($\nu_{11}+\nu_{10}$) of C_6D_6 near by	
C–C planar	ν_{19}	e_{1u}	a_1	1446		1435.7 1444.8	($\nu_{17}+\nu_{10}$) of C_6D_6 near by	
C–C planar	ν_8	e_{2j}	b_1	1576		1576.2 1580.0	S ($\nu_6+\nu_1$)	
			a_1	1593		1592.5	W, B	

[a] Key: VW, very weak; W, weak; B, broad; I, more intense component of a doublet; FR, Fermi resonance; S, shoulder.

[b] S. Brodersen and A. Langseth, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Skrifter 1, No. 7 (1959).

TABLE III. 1% p-$C_6H_4D_2$ in 99% C_6H_6 and C_6D_6.[a]

Vibration number and type	Symmetry (D_{6h})	Symmetry (D_{2h})	Gas phase[b] (cm^{-1})	Energy (C_6H_6 cm^{-1})	Energy (C_6D_6 cm^{-1})	Comment	Orientational effect [cm^{-1} (δ_{oe})]
C–C nonplanar ν_{16}	e_{2u}	b_{1u}		367.6 372.3			4.7
C–H nonplanar ν_{11}	a_{2u}	b_{1u}	596	613.7 613.9	613.7	Possible splitting, shaded symmetrically in C_6D_6, induces ν_6 (e_{2g}) 605.5 607.7 in C_6H_6, 579.5, 580.4 in C_6D_6	<1.0
C–H planar ν_{18}	e_{1u}	b_{3u}	817	817.6 821.3		Sh I	3.7
C–H nonplanar ν_{17}	e_{2u}	b_{1u}	871	882.9 885.8	882.3 885.3 885.9		3.0, 0.6
C–H nonplanar ν_{17}	e_{2u}	a_u	967		977.8 979.8	I	2.0
C–C planar ν_{12}	b_{1u}	b_{2u}	997		990.6 993.7	I	3.1
C–H planar ν_{18}	e_{1u}	b_{2u}	1032		1031.0 1034.1	I	3.1
C–H planar ν_{15}	b_{2u}	b_{3u}	1104		1104.3 1106.4	B, ~equal I	2
C–H planar ν_{14}	b_{2u}	b_{3u}	1291	1297.6	1294.5 1295.3	Blue shaded, VW	<1.0

[a] Key: VW, very weak; B, broad; I, more intense component of a doublet; Sh, sharp. [b] Table II, Footnote b.

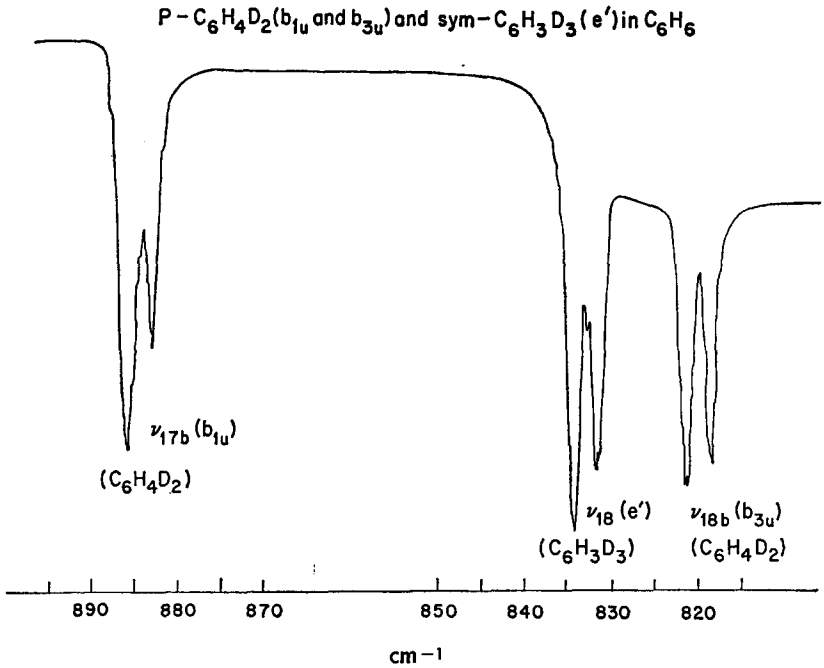


FIG. 3. Three-fourths % p-$C_6H_4D_2$ and 0.75% sym-$C_6H_3D_3$ in C_6H_6; this shows the apparent similarity between site group splitting and the orientational effect. The two transitions of p-$C_6H_4D_2$ show the orientational effect while the $e'(\nu_{18})$ mode of sym-$C_6H_3D_3$ is site group split.

metry. This becomes even further complicated for degenerate vibrations for which, due to this mixing, assignment to the **a** or **b** split component is at best tenuous. The assignments made in this paper, where conflicts or ambiguities exist, are chosen to agree with the electronic emission work of Bernstein, Colson, Tinti, and Robinson.[9] This approach is taken since in some cases the symmetry assignments can be made unambiguously from vibronic intensity arguments. Throughout this paper, as a convenience only, we shall retain the use of the molecular point group symbols to characterize the crystal site vibrations.

Tables I–VI and Figs. 1–12 present data on the isotopic mixed-crystal spectra of C_6H_6, C_6D_6, sym-$C_6H_3D_3$, p-$C_6H_4D_2$, C_6H_5D and C_6D_5H. Vibrations have been observed for all these isotopic derivatives but the

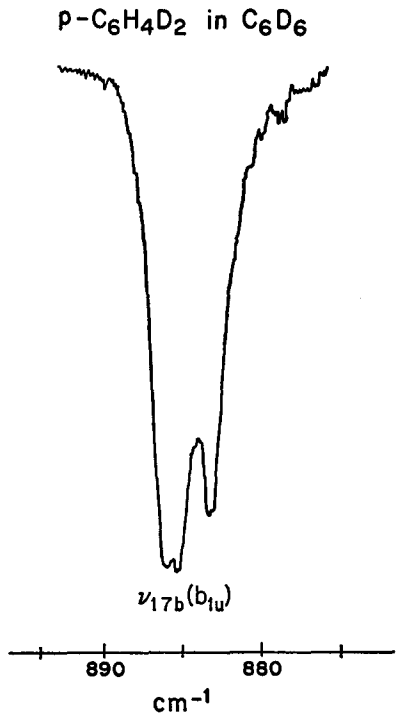


FIG. 4. High-resolution trace of ν_{17b} showing the triplet orientational structure.

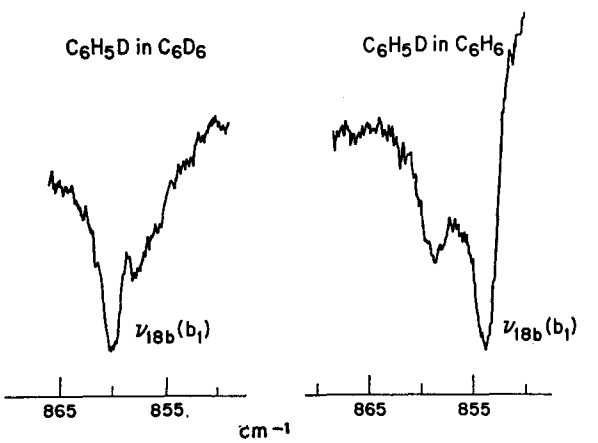


FIG. 5. The ν_{18b} transition of 1% C_6H_5D guest in C_6H_6 and C_6D_6 hosts. Note the intensity and energy differences for the two solvents. This is most likely caused by a third unresolved line.

[9] E. R. Bernstein, S. D. Colson, D. S. Tinti, and G. W. Robinson, J. Chem. Phys. **48**, 4632 (1968).

TABLE IV. One% *sym*-1, 3, 5-$C_6H_3D_3$ in 99.0% C_6H_6 and C_6D_6.[a]

Vibration number and type		Symmetry (D_{6h})	Symmetry (D_{3h})	Gas phase[b] (cm^{-1})	H_6 energy (cm^{-1})	D_6 energy (cm^{-1})	Comment	Site splitting [cm^{-1} (δ_{ss})]
C–C nonplanar	ν_{16}	e_{2u}	e''	368	377.5 385.0			7.5
C–H nonplanar	ν_{11}	a_{2u}	a_2''	531	538.8 539.2 545.3	538.9 539.3 545.6	$^{13}CC_5H_3D_3$ (or *m*-$C_6H_2D_4$ ν_{11}) Induces ν_6 (e_{2g}) (580.0, 582.5) in C_6D_6	
C–C nonplanar	ν_4	b_{2g}	a_2''	697		703.8		
C–H planar	ν_{18}	e_{1u}	e'	833	831.6	831.7	ν_{15} and ν_{18} of C_6D_6	3.1
					834.4	835.0	nearby and C_6D_5H ν_{18}	
C–H planar	ν_{15}	b_{2u}	a_2'	912	908.1	908.0	FR	
C–H nonplanar	ν_5	b_{2g}	a_2''	917	927.4	928.5		
C–H nonplanar	ν_{17}	e_{2u}	e''	924	935.7 939.4	936.0 938.8	C_6D_6 combination near, and C_6D_5H in C_6D_6	3.3
C–H planar	ν_9	e_{2g}	e'	1101		1102.5 1104.9	B I	2.4

[a] Key: B, broad; I, more intense component of a doublet; FR, Fermi resonance. [b] See Ref. 13.

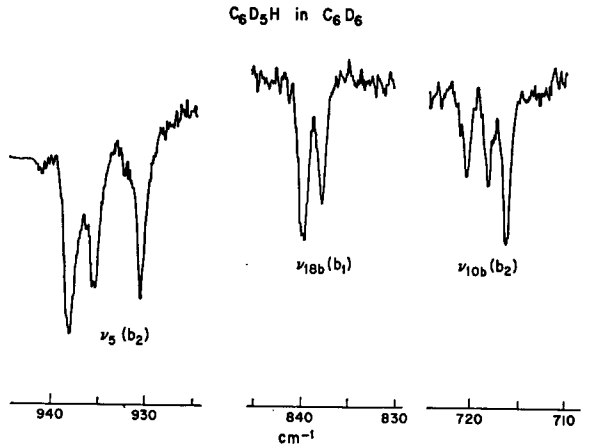


FIG. 6. Approximately 2% C_6D_5H impurity in C_6D_6. This figure illustrates the difference between the "out-of-plane" and "in-plane" orientational effect for the benzene isotopes. $\nu_5(b_2)$ and ν_{10b} (b_2) are out-of-plane vibrations and show three orientational components, while ν_{18b} (b_1), an "in-plane" vibration, shows only two components with an approximate 2:1 intensity ratio.

only data reported are those for which the assignments are certain. Data for two of the isotopes, *m*-$C_6H_4D_2$ and *m*-$C_6H_2D_4$ (Fig. 1), are not given in the tables since complications due to orientational effects, poor gas phase data, mixing of vibrations, and inherent isotopic impurity make many assignments almost impossible.

B. Solid-Enhanced Fermi Resonance

Solid-enhanced Fermi resonance has been discussed by Strizhevsky[10] in the case for which an accidental resonance occurs between a fundamental and an overtone or combination level. Such resonances are

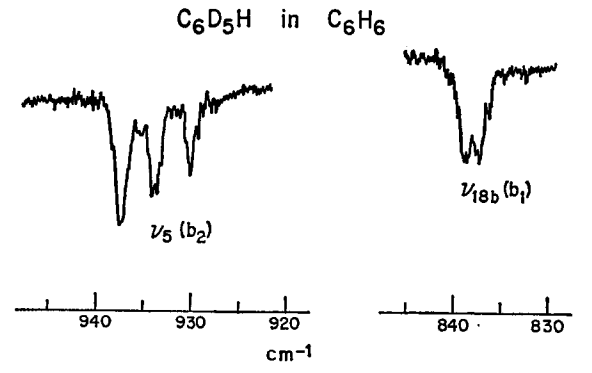


FIG. 7. Approximately 2% C_6D_5H in C_6H_6 showing two of the transitions in Fig. 6. The shoulder on the low-energy side of ν_{18b} is not believed to be real. If it is, it represents the only case of an in-plane vibration experiencing the effect of the full site symmetry (C_i).

[10] V. L. Strizhevsky, Opt. Spektrosk. 8, 165 (1960) [Opt. Spectrosc. 8, 86 (1960)].

TABLE V. C_6D_5H in C_6H_6 and C_6D_6.

Vibration number and type		Symmetry (D_{6h})	Symmetry (C_{2v})	Gas phase[a] (cm^{-1})	Energy (C_6D_6 cm^{-1})	Energy (C_6H_6 cm^{-1})	Comment	Orientational effect [cm^{-1} (δ_{oe})]
C–H nonplanar	ν_{11}	a_{2u}	b_2	512	527.3	527.3		
C–H nonplanar	ν_{10}	e_{1g}	b_2	706	715.9 717.8 720.6			1.9, 2.8
C–H planar	ν_{13}	e_{1u}	b_1	838	837.6 839.8	837.4 838.9		2.4
C–H nonplanar	ν_5	b_{2g}	b_2	922	930.7 935.6 938.6	930.4 934.5 938.1		4.5, 3.3
					1278.2		Combination	

[a] Table II, Footnote b.

present in both gaseous and solid benzene and are, for the most part, well known.[11–13]

In an isotopic mixed crystal of benzene, there is a chance of further Fermi resonance. Fundamentals that were orthogonal in $\mathbf{D}_{6h}$ symmetry can now mix in the "$\mathbf{C}_i$-distorted" molecule of the crystal. The isotopic modifications C_6H_5D, *sym*-$C_6H_3D_3$, *m*-$C_6H_4D_2$, and *m*-$C_6H_2D_4$ best illustrate this effect. However, the latter two molecules have so many accidental degeneracies in the crystal that the spectra are very difficult to interpret and thus cannot be given as clear examples of this phenomenon even though it is extensively present. The 925-cm^{-1} region of *sym*-$C_6H_3D_3$, the 980-cm^{-1} region of C_6H_5D, the 3000-cm^{-1} region of C_6H_6, and the 2250-cm^{-1} region of C_6D_6, however, all represent rather clear-cut examples of crystal-induced intrasite mixing. Looking at Table IV, it is obvious that ν_5, ν_{15}, and ν_{17} of *sym*-$C_6H_3D_3$ are interacting with one another since the site shifts are much larger and of different sign than those for the same vibrations in the other isotopes. Table II shows the same phenomenon for ν_1, ν_{17}, ν_5, and ν_{12} of C_6H_5D. One of the most striking shifts appears for ν_{13} ($\sim$20 cm^{-1}) of C_6D_6. See Table VI. In C_6H_6 (Table I) the mixing between ν_{13}, ν_{20}, $(\nu_{19}+\nu_8)$, $(\nu_1+\nu_6+\nu_{14})$ and others is so extensive that it becomes impossible to assign the absorptions to specific vibrations. In Fig. 1 also we see that due to intrasite Fermi resonance the spectrum of *m*-$C_6D_4H_2$ is almost impossible to assign uniquely. While this spectrum may further be complicated by the presence of other isotopes, a possible partial assignment of the absorptions is presented on the figure.

C. Site Shifts

The experimental site shifts Δ can be determined from the tables of data. A few pertinent and representative cases shall be discussed as examples of the various types of typical vibrations: $\nu_{11}(a_{2u})$—an intense, gas-phase allowed transition, $\nu_{16}(e_{2u})$—weak intensity, crystal induced, $\nu_{18}(e_{1u})$—medium intensity, gas phase allowed, and $\nu_{12}(b_{1u})$ and $\nu_{15}(b_{2u})$—weak intensity, crystal induced. Of particular interest are whether or not such shifts are present, what trends in the shifts can be determined as a function of vibrational state, and what are the host or guest isotope effects on these shifts. Fermi resonance in the crystal and the inaccuracy of the gas phase data (caused not only by the presence of rotational structure but also by the less direct methods of measuring symmetry forbidden transitions in the gas phase) gives rise to uncertainties in the site shift measurements (approximately 4 cm^{-1}). Only those vibrations for which it is believed these complications are minimized will be discussed explicitly in the text.

An extensive comparison of site shifts is possible for

[11] E. B. Wilson, Phys. Rev. **46**, 146 (1934).
[12] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1950), p. 362.
[13] S. Brodersen and A. Langseth, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Skrifter **1**, No. 1 (1956).

the out-of-plane $\nu_{11}(a_{2u})$ vibration. The site shifts $\Delta^{\nu_{11}}$ (host) are

	C_6H_6	C_6H_5D	p-$C_6H_4D_2$	s-$C_6H_3D_3$	m-$C_6H_2D_4$	C_6D_5H	C_6D_6
$\Delta^{\nu_{11}}(C_6H_6)=$	···	15.4	17.8	14.4	15.0	15.3	15.3 cm^{-1},
$\Delta^{\nu_{11}}(C_6D_6)=$	23.9	15.4	17.8	14.6	15.0	15.3	··· cm^{-1},

measured in both C_6H_6 and C_6D_6 hosts where applicable. Aside from the large value for C_6H_6 in the C_6D_6 host, which probably arises from an accidental resonance, there appears to be no isotopic effect on Δ related either to the host or the guest.

For the out-of-plane $\nu_{16}(e_{2u})$ vibration, the mean shifts $\bar{\Delta}$ obtained by averaging the two site-split components are as follows:

	C_6H_6	s-$C_6H_3D_3$	C_6D_6
$\bar{\Delta}^{\nu_{16}}(C_6H_6)=$	···	13.8	11.9 cm^{-1},
$\bar{\Delta}^{\nu_{16}}(C_6D_6)=$	10.9	···	··· cm^{-1}.

The site shift for this vibration appears to be sensibly isotope independent.

The mean shifts for the planar $\nu_{18}(e_{1u})$ vibration appear to be less than 2 cm^{-1}:

	C_6H_6	s-$C_6H_3D_3$	C_6D_6
$\bar{\Delta}^{\nu_{18}}(C_6H_6)=$	···	0.5	−2.0 cm^{-1},
$\bar{\Delta}^{\nu_{18}}(C_6D_6)=$	∼1.0	0.5	··· cm^{-1}.

For the planar $\nu_{15}(b_{2u})$ and $\nu_{12}(b_{1u})$ vibrations, the shifts are

	C_6H_6	C_6H_5D	p-$C_6H_4D_2$	s-$C_6H_3D_3$	C_6D_6
$\Delta^{\nu_{15}}(C_6H_6)=$	···	0.5	∼2	−4.0	3.4 cm^{-1},
$\Delta^{\nu_{15}}(C_6D_6)=$	0.9	0.6	∼1	−4.0	··· cm^{-1},

	C_6H_6	C_6H_5D	p-$C_6H_4D_2$	s-$C_6H_3D_3$	C_6D_6
$\Delta^{\nu_{12}}(C_6H_6)=$	···	···	···	···	1.0 cm^{-1},
$\Delta^{\nu_{12}}(C_6D_6)=$	1.3	−3.8	−5	···	··· cm^{-1}.

The latter three sets of shifts for planar vibrations are somewhat erratic, and the large shifts can all be correlated with the presence of other vibrations close by. Thus a Fermi interaction is quite likely.

All the available data have not been covered in the text and the tables should be consulted for a more complete picture. In summary, there are two cases that are generally found, $\Delta\sim1$ cm^{-1} for planar vibrations and $\Delta\sim10$ cm^{-1} for nonplanar vibrations. Exceptions to this trend for a given state occur but can be explained by solid-enhanced Fermi resonance between nearly degenerate gas phase fundamentals. It is thus concluded that there is no significant isotope (host or guest) effect on the Δ term for the ground vibrational states.

D. Site Group Splitting

It is interesting to look at the site group splitting as a function of guest and host for the various isotopes having degenerate vibrations. For comparison the reader is referred to Sec. V.C where the site shifts are listed for these vibrations. Again it is emphasized that the vibrations discussed in the text are representative of the general case, and are chosen because they remain relatively unmixed from isotope to isotope and are experimentally well determined. The tables should be consulted for the remainder of the data.

For the in-plane e_{1u} vibration ν_{18} with a mean Δ of ~0.0 cm^{-1} in all the isotopes, the site group splitting as a function of the host, $\delta_{ss}^{\nu_{18}}$ (host), is

	C_6H_6	$C_6H_3D_3$	C_6D_6
$\delta_{ss}^{\nu_{18}}(C_6H_6)=$	···	2.8	(4.1) cm^{-1},
$\delta_{ss}^{\nu_{18}}(C_6D_6)=$	3.8	3.3	··· cm^{-1}.

The C_6D_6 value of 4.1 cm^{-1} may partly be affected by Fermi resonance between ν_{18} and ν_{15} [see Fig. 2(b)]. The apparent difference between the site splittings for *sym*-$C_6H_3D_3$ in C_6H_6 and C_6D_6 is interesting and, if not

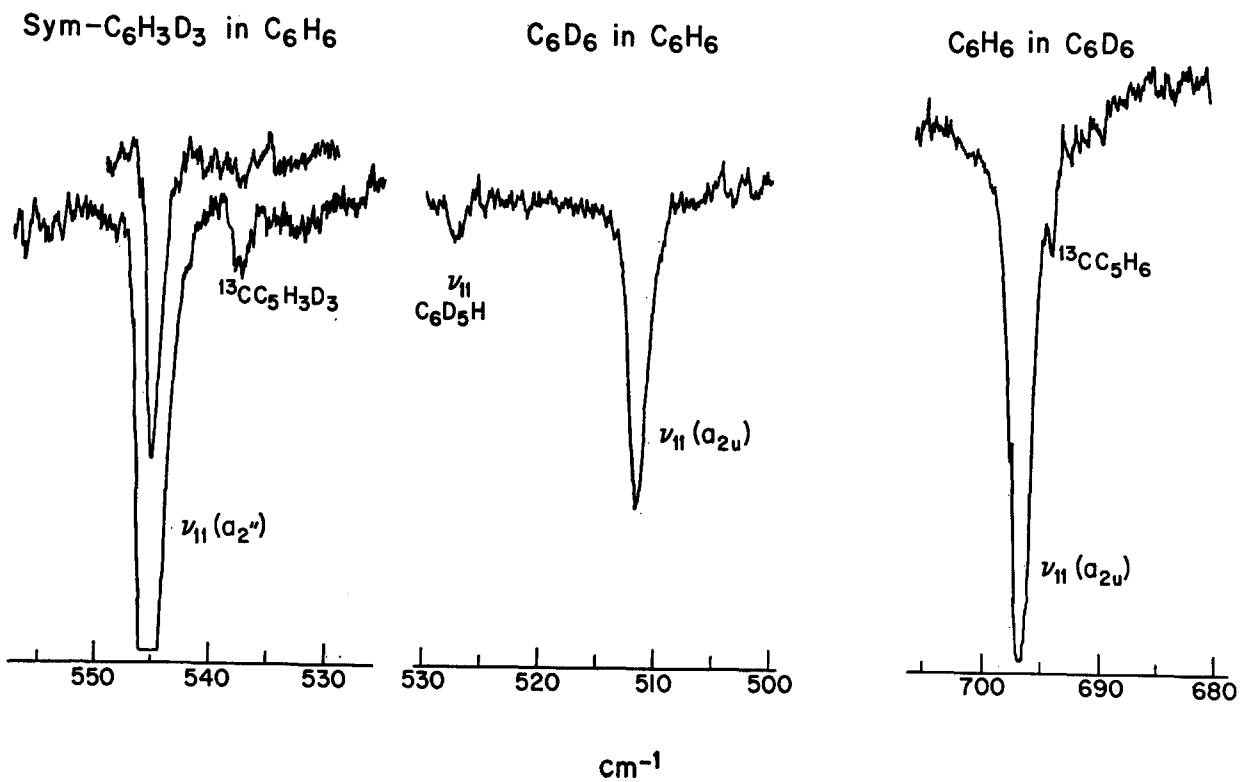


FIG. 8. The ν_{11} band of the three isotopes having D_{3h} or higher symmetry, which are not expected to show orientational effects. Linewidths are of the order of 0.75 cm^{-1} and are probably instrument limited. It is possible, but unlikely, that the line assigned to $^{13}CC_5H_3D_3$ is really ν_{11} of the impurity *m*-$C_6H_4D_2$.

TABLE VI. One% C_6D_6 in 99.0% C_6H_6.[a]

Vibration number and type	Symmetry (D_{6h})	Gas phase[b] (cm^{-1})	Energy (cm^{-1})	Comment	Site splitting [cm^{-1} (δ_{ss})]
C–C nonplanar ν_{16}	e_{2u}	347.8	354.8 364.6	W W	9.8
C–H nonplanar ν_{11}	a_{2u}	496	511.3 527.4[c]	 C_6D_5H	
C–H nonplanar ν_{17}	e_{2u}	787	791.3 797.8	I 	6.5
C–H planar ν_{18}	e_{1u}	814	810.5 814.6	Sh FR I	4.1
C–H planar ν_{15}	b_{2u}	824	820.6		
C–C planar ν_{12}	b_{1u}	970	971.0		
C–H planar ν_{14}	b_{2u}	1282	1285.1	($\nu_{16}+\nu_{10}$) nearby	
C–C planar ν_{19}	e_{1u}	 1333	1321.3 1326.0 1329.2	$^{13}CC_5D_6$ C_6D_5H (?), VW II	 <1.0
C–H planar ν_{13}	b_{1u}	2285	2268.1	FR	
C–H planar ν_{20}	e_{1u}	2288	2278.0 2282.5	FR	4.5
$\nu_1+\nu_{19}$ plus other combinations					

[a] Key: VW, very weak; W, weak; I, more intense component of a doublet; FR, Fermi resonance; Sh, sharp.

[b] See Ref. 13 and J. H. Callomon, T. M. Dunn, and I. M. Mills, Phil. Trans. Roy. Soc. London **259**, 499 (1966).

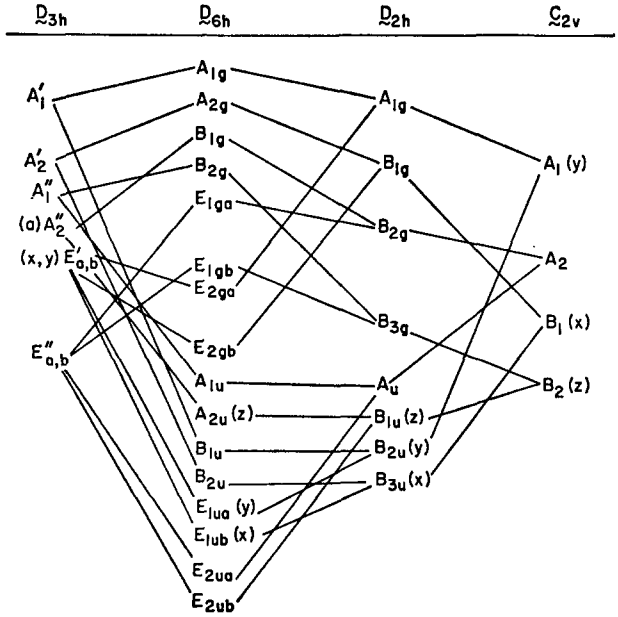
[c] This band has been erroneously assigned as an interchange group component of the C_6D_6 a_{2u}; see Ref. 18.

caused by guest–host Fermi resonance between $\nu_{18}(C_6H_3D_3)$ and ν_{15}, $\nu_{18}(C_6D_6)$, may be caused by a crystal zero-point effect; that is, the C_6D_6 crystal is more compact, allowing the nonbonded C–D and C–C interactions to become stronger. However, see below.

For the out-of-plane e_{2u} vibrations ν_{16} and ν_{17} the site splittings are

	C_6H_6	*sym*-$C_6H_3D_3$	C_6D_6
$\delta_{ss}^{\nu_{16}}(C_6H_6) =$	···	8.5	10.8 cm^{-1},
$\delta_{ss}^{\nu_{16}}(C_6D_6) =$	8.2	···	··· cm^{-1},
$\delta_{ss}^{\nu_{17}}(C_6H_6) =$	···	3.7	6.5 cm^{-1},
$\delta_{ss}^{\nu_{17}}(C_6D_6) =$	5.6	2.8	··· cm^{-1}.

TABLE VII. Correlation tables for the benzene isotopes (y axis through C_1, x axis between C_5 and C_6, z axis perpendicular to molecular plane; y axis preserved).

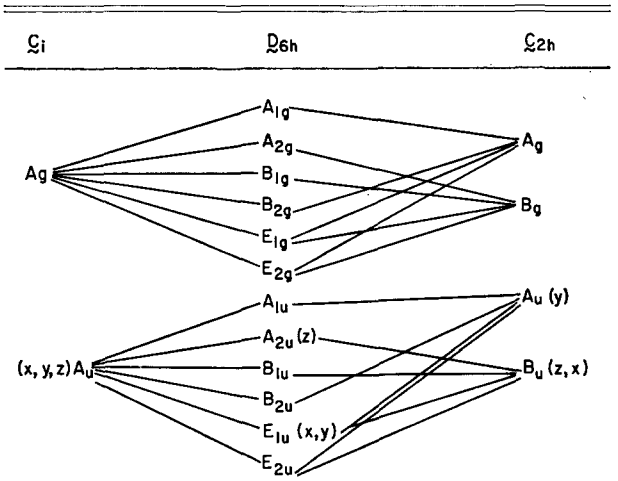


The C_6D_6 factor group structure obscures the *sym*-$C_6H_3D_3$ ν_{16} transition. For the ν_{17} vibration the interesting case of the *sym*-$C_6H_3D_3$ splitting may be complicated again by the presence of host vibrations. Since the change in site splitting with host for ν_{17} is in the opposite direction from that of ν_{18}, a simple explanation in terms of zero-point effects does not seem possible.

One point of importance is indicated by these data. The out-of-plane site splittings appear roughly twice as large as those for the in-plane vibration, and parallels the effect observed for the site shift Δ. The data show no obviously large isotope effects from either the host or guest molecules on the site splitting. This was also found to be the case for the site shift.

The fact that there is a measurable site group splitting

TABLE VIII. Correlation diagram for D_{6h}, C_{2h}, and C_i (x axis C_2 preserved).



for the degenerate molecular fundamentals of isotopic benzenes shows that the benzene molecule in the crystal has lost its threefold axis. Certainly because of zero-point motions the ground state can, at least in principle, be considered nontrigonal.

E. Orientational Effect

The last section was concerned with the effect of the crystal site environment on molecular degenerate states of benzene. In this section, the effect of the site on nondegenerate molecular states is considered.

It is clear that for the placement of H(D) atoms on a space-fixed hexagonal carbon framework there exists

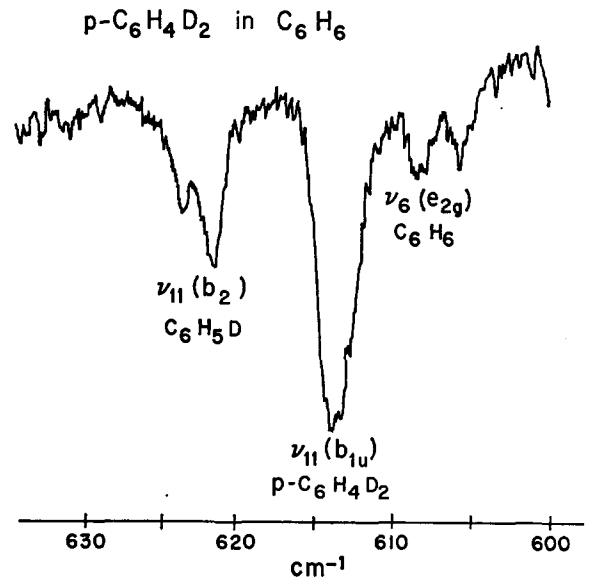


FIG. 9. Intermolecular Fermi resonance. The ν_6 (e_{2g}) transition of C_6H_6 has been induced by ν_{11} (b_{1u}) of p-$C_6H_4D_2$. C_6H_5D occurs as an impurity in the p-$C_6H_4D_2$—C_6H_6 system. Note the orientational effect on ν_{11} C_6H_5D.

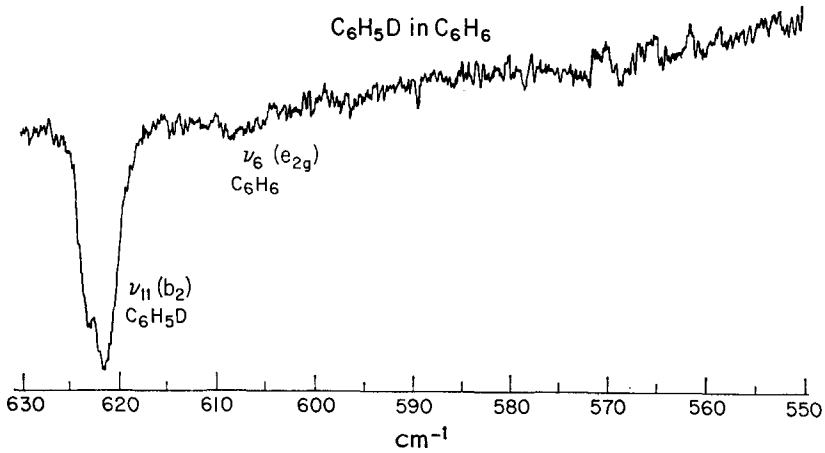


FIG. 10. A further example of a C_6H_6 host transition induced by the isotopic C_6H_5D guest. Note the effect of increased energy separation on the intensity of the induced transition. Compare Fig. 9.

generally a number of distinguishable configurations: 1 for C_6H_6 and C_6D_6; but 2 for *sym*-$C_6H_3D_3$; 3 for *p*-$C_6H_4D_2$(*p*-$C_6H_2D_4$); 6 for *m*-$C_6H_4D_2$($C_6H_2D_4$), C_6H_5D(C_6HD_5), *o*-$C_6H_4D_2$($C_6H_2D_4$), C_6H_5D(C_6HD_5), and 1, 2, 3$C_6H_3D_3$; and 12 for 1, 2, 4$C_6H_3D_3$. Since the benzene isotopic guest molecules in a host crystal are free to orient randomly with respect to rotations by $2\pi M/6$ ($M=1$, 6) about the molecular sixfold axis,[14] the number of distinct orientations of a molecule in the crystal site, and thus the number of possible different energies that can be observed in the crystal spectrum of a given gas-phase transition, is governed by the site symmetry. For the lowest possible site symmetrv $\mathbf{C}_1$, the number of distinct orientations are just those given above. For a site symmetry higher than $\mathbf{C}_1$, some of the orientations of the molecule in the site become equivalent by symmetry, thus reducing the total number of physically distinct orientations. C_6H_6 and C_6D_6 will, of course, show no orientational effect for any site symmetry, and no extra lines are expected to show up in the spectrum. The case of *sym*-$C_6H_3D_3$ is not so obvious, but again no orientational effect can occur for $\mathbf{C}_i$ or $\mathbf{C}_{2h}$ site symmetry. This can be understood by observing that the two distinct orientations in space, related to one another by a rotation of $2\pi/6$, are energetically equivalent in the site by inversion symmetry.

The isotopic molecules of $\mathbf{D}_{2h}$ symmetry and lower will show an orientational effect in a $\mathbf{C}_i$ or $\mathbf{C}_{2h}$ site. Consider 1, 4-$C_6H_4D_2$. No two of the three distinct orientations in space are equivalent by simple inversion symmetry, so for a $\mathbf{C}_i$ site three energetically different possibilities are expected. However, when a plane of symmetry perpendicular to the benzene molecular plane is added, two of the three orientations do become equivalent. Thus three energetically distinct orientations are expected for a $\mathbf{D}_{2h}$ isotopic modification of benzene at a $\mathbf{C}_i$ crystal site, while only two are expected for a $\mathbf{C}_{2h}$ crystal site (plane of site symmetry perpendicular to molecular plane). In the latter case, one of the orientations has a weight twice that of the other. One may continue on with this type of reasoning to show that for $\mathbf{C}_i$ site symmetry the number of orientational components associated with a particular molecular point group are 1 for $\mathbf{D}_{6h}$ and $\mathbf{D}_{3h}$, 3 for $\mathbf{D}_{2h}$ and $\mathbf{C}_{2v}$, and 6 for $\mathbf{C}_s$. For a $\mathbf{C}_{2h}$ site (plane perpendicular to molecular plane) one has for the number of orientational components, 1 for $\mathbf{D}_{6h}$ and $\mathbf{D}_{3h}$, 2 for $\mathbf{D}_{2h}$ and $\mathbf{C}_{2v}$, and 3 for $\mathbf{C}_s$ symmetry. Kopelman[15] has given a general group-theoretical treatment of this problem.

It is of interest to note that for the benzene site symmetry ($\mathbf{C}_i$, but nearly $\mathbf{C}_{2h}$) the orientational "splittings" observed for nondegenerate vibrations of isotopic molecules with low symmetry have greater multiplicity than the (real) splittings observed for doubly degenerate vibrations of $\mathbf{D}_{6h}$ or $\mathbf{D}_{3h}$ isotopic modifications. The magnitude of the orientational effect δ_{oe} can be thought of, just as for the case of the

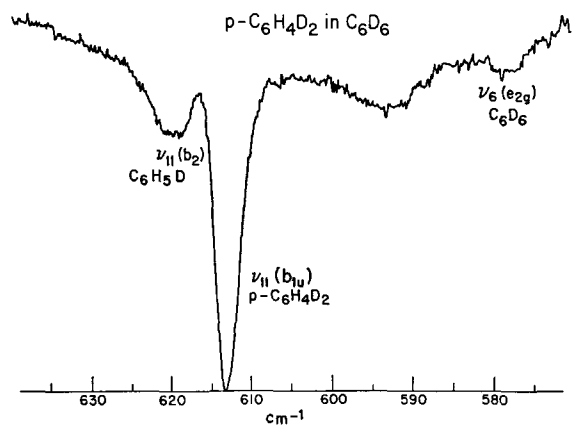


FIG. 11. The effect of increased energy separation on the induced ν_6 (e_{2g}) vibration of a C_6D_6 host.

[14] E. R. Andrew and R. G. Eades, Proc. Roy. Soc. (London) **A218**, 537 (1953).

[15] R. Kopelman, J. Chem. Phys. **47**, 2631 (1967).

site splitting, as arising from a difference in Δ terms [Eq. (2)] for different site oriented guest molecules.

The orientational effect has been observed on transitions of C_6H_5D, C_6D_5H, m-$C_6H_4D_2$, m-$C_6H_2D_4$, and p-$C_6H_4D_2$. (See Figs. 3–8, the tables, and also Ref. 9). The planar vibration ν_{18}, which for $\mathbf{D}_{6h}$ and $\mathbf{D}_{3h}$ molecules has a small site shift, can be seen for the molecules of lower symmetry to have a small orientation effect. Only two components are observed. The observed "splittings" δ_{oe} are

	C_6H_5D	p-$C_6H_4D_2$	C_6HD_5	
$\delta_{oe}^{\nu 18b}(C_6H_6)=$	[4.7]	3.7	1.5	cm^{-1},
$\delta_{oe}^{\nu 18b}(C_6D_6)=$	2.1	···	2.2	cm^{-1},
$\delta_{oe}^{\nu 18a}(C_6H_6)=$	···	···	···	cm^{-1},
$\delta_{oe}^{\nu 18a}(C_6D_6)=$	2.8	3.1	···	cm^{-1}.

Figure 5 shows the spectra of ν_{18b} of C_6H_5D and C_6H_6 in C_6D_6. The intensity change between the two components and the line shape distortion are probably due to the third, unresolved orientational line.

The out-of-plane ν_{16} components have a larger orientational effect:

	C_6H_5D	p-$C_6H_4D_2$	
$\delta_{oe}^{\nu 16b}(C_6H_6)=$	4.3	4.7	cm^{-1},
$\delta_{oe}^{\nu 16b}(C_6D_6)=$	4.6	···	cm^{-1}.

This out-of-plane vibration also has one of the largest site shifts ($\Delta\approx 10$ cm^{-1}) and site splittings ($\delta_{ss}\approx 10$ cm^{-1}). Thus there appears to be a correlation between the magnitudes of the shift, the site splitting, and the orientational effect. Unfortunately because of Fermi resonance, overlapping transitions, and the presence of isotopic impurities associated with the study of the low symmetry isotopic modifications, the data are far from complete.

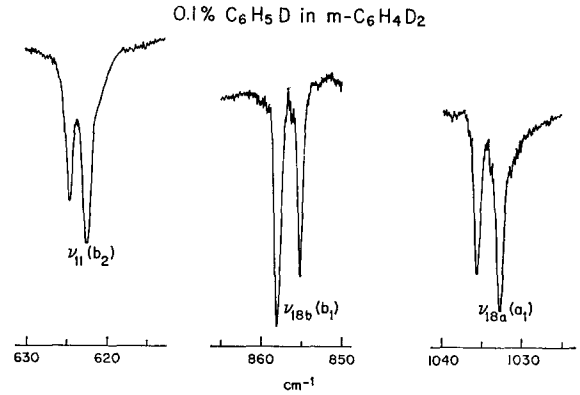


FIG. 12. C_6H_5D (0.1%) as an impurity in m-$C_6H_4D_2$, showing ν_{11} (622.3 and 624.7 cm^{-1}), ν_{18b} (855.2 and 858.4 cm^{-1}), and ν_{18a} (1032.7 and 1035.6 cm^{-1}).

An indication of the magnitude of the isotopic dependence of the orientation effect is given by the C_6H_5D impurity spectra (ν_{11}, ν_{18}) in m-$C_6H_4D_2$ (Fig. 12). The sharp lines arise because of good crystal quality and the very low concentration of the C_6H_5D. These transitions should be compared with those of C_6H_5D in C_6H_6 and C_6D_6 in Figs. 5 and 9. While the absolute energies are not exactly equal to those of the other hosts (see Fig. 12), the δ_{oe}'s are in very good agreement: $\delta_{oe}^{\nu 18a}(m\text{-}C_6H_4D_2)=2.9$, $\delta_{oe}^{\nu 18b}(m\text{-}C_6H_4D_2)=3.2$, and $\delta_{oe}^{\nu 11}(m\text{-}C_6H_4D_2)=2.4$ cm^{-1}.

There are three general comments to be made about these data: (1) The orientational "splittings" for a given vibrational type are about $\frac{1}{2}$ of the site group splittings observed in the more symmetrical molecules. This fact suggests a relationship between the two effects. (2) All planar vibrations are "split" into a doublet only, with an intensity ratio of about 2:1 (indicating $\mathbf{C}_{2h}$ site symmetry), while nonplanar vibrations tend to "split" into a triplet (indicating $\mathbf{C}_i$ site symmetry). From this we conclude that the site contains an approximate symmetry plane which is conserved by in-plane vibrations but destroyed by out-of-plane vibrations. (3) The orientational effect appears somewhat greater in the C_6D_6 host than in the C_6H_6 host (and also for a C_6H_5D guest compared with a C_6HD_5 guest) for the same vibration. This difference could be due to the zero-point effect mentioned in an earlier section.

Before leaving this topic it should be pointed out that the $\nu_{11}(a_{2u})$ C–H out-of-plane vibrations show a measurable orientation effect—at best quite small—for only C_6H_5D and p-$C_6H_4D_2$ while none is observed for C_6D_5H or m-$C_6H_4D_2$. This is quite surprising in light of the previous discussion but is unmistakeably true. The only possible explanation is that the a_{2u} mode is a symmetric combination of the out-of-plane C–H perpendicular bending motions and is thus not much affected by site orientation. Calculations bear this out and further comments concerning this will be made in a forthcoming paper.[16]

F. Intermolecular Intensity Enhancement

We have thus far focused our attention on the guest molecule alone. We now consider the effects of the presence of isotopic guest molecules on the host. In the case for which both guest and host molecules have inversion symmetry, the guest molecule resides at a site of inversion symmetry, at least in the limit of "infinite dilution." In a crystal of, for example, 1% C_6H_6 in 99% C_6D_6, however, approximately 10% of the C_6D_6

[16] E. R. Bernstein (unpublished calculations).

host molecules (there are 12 "nearest-neighbor" molecules in the benzene crystal) do not have inversion site symmetry. Accurately speaking, none does, but host molecules sufficiently far removed from the guest are expected to have approximate inversion symmetry. One might expect therefore to be able to observe a breakdown of the $u \leftrightarrow g$ selection rule in the infrared spectrum of the host. Obviously any type of guest molecule is expected to destroy the host site symmetry and thus change selection rules, so this effect may be of quite common occurrence. A chemically substituted guest should cause an even larger effect than the isotopically substituted ones discussed here.

We present here only a few instances that seem to be free from interference by isotopic impurities or other transitions. Intensity enhancement of the $\nu_6(e_{2g})$ transition in the host ($\sim$605 cm^{-1} for C_6H_6; $\sim$580 cm^{-1} for C_6D_6) having various isotopic impurities present is monitored. A very intense guest transition $\nu_{11}(a_{2u})$ lies in the same region (697 cm^{-1} for C_6H_6; 513 cm^{-1} for C_6D_6) and we consider this the transition in resonance with the host molecule ν_6. It is believed that the effect arises because of intermolecular resonance since the e_{2g} transition is not observed in the C_6H_6 host when the guest transition is too far away—C_6D_6 (513 cm^{-1}), C_6D_5H (527 cm^{-1}), *m*-$C_6H_2D_4$ (538 cm^{-1}), or *sym*-$C_6H_3D_3$ (543 cm^{-1}). However, with either *p*-$C_6H_4D_2$ (612 cm^{-1}) or C_6H_5D (621 cm^{-1}) as guest, a doublet whose components lie at 605.5 and 608.2 cm^{-1} is observed in the C_6H_6 host. The frequencies of this e_{2g} mode occur at 606.3 and 609.4 cm^{-1} in the phosphorescence spectrum of a C_6H_6 isotopic mixed crystal.[9] It is likely, however, that the induced doublet reported here represents unresolved site-interchange split levels of the host, which appear in the Raman as a quartet (605.2, 606.3, 609.0, and 611.0 cm^{-1}).[17] Spectra to illustrate this discussion are presented in Figs. 9–11.

A possible further instance of intermolecular Fermi resonance can be found in the observed high intensity of the C_6H_5D peak (ν_{11}) (see Fig. 9), which is difficult to explain unless intermolecular resonance is invoked. C_6H_5D is an impurity in the C_6H_6–*p*-$C_6H_4D_2$ system, but certainly is not expected to be so prevalent as the spectrum suggests. Although in both cases only small energy shifts ($\lesssim$1.0 cm^{-1}) are observed, intensity enhancement seems to be the most important factor in Fermi resonance in solids.[10]

Another case of this type of intersite Fermi resonance that seems to have played a role in the benzene spectrum is that of the impurity C_6D_5H in C_6D_6. Hollenberg and Dows[18] assigned the a_{2u} vibration of C_6D_5H as a part of the $C_6D_6\nu_{11}(a_{2u})$ exciton band. The $\nu_{11}(a_{2u})$ band of C_6D_5H at 527 cm^{-1} is anomalously intense, and we propose this to be due to the intermolecular intensity borrowing through the Fermi resonance mechanism.

VI. CONCLUSION

From the four observed phenomena—site shifts, site group splitting, orientational effect, and intermolecular intensity enhancement—it is possible to make the following statements concerning the benzene crystal:

(1) C_6H_6 and C_6D_6 molecules in the crystal do not have sixfold axes of symmetry, but inversion symmetry is rigorously retained. These facts are illustrated by the observed infrared selection rules for crystal transitions.

(2) The site symmetry is $\mathbf{C}_i$ and not $\mathbf{C}_{2h}$. The possibility of $\mathbf{C}_{2h}$ site symmetry, the horizontal plane coinciding with the plane of the molecule, is eliminated by the observation that three orientational components are observed for certain vibrations of guests with $\mathbf{D}_{2h}$ or $\mathbf{C}_{2v}$ molecular symmetry.

(3) The near coincidence of two of the three orientational components in $\mathbf{D}_{2h}$ or $\mathbf{C}_{2v}$ isotopic guests indicates an approximate plane of symmetry at the site perpendicular to the molecular plane. Apparently this plane is "preserved" by planar vibrations and destroyed by nonplanar vibrations, since only out-of-plane vibrations exhibit the three orientational components expected for $\mathbf{C}_i$ site symmetry.

(4) From data on site shifts, splittings, and the orientational effect, the out-of-plane vibrations are found to be more sensitive to the nature of the site potential field than are the in-plane vibrations. The atomic displacements associated with the out-of-plane modes are larger by almost a factor of 5 on the average than those for the in-plane modes. Thus the greater amplitude atomic displacements account for the fact that the large crystal effects are always found associated with the out-of-plane modes (b_{2g}, e_{1g}, a_{2u}, e_{2u} in $\mathbf{D}_{6h}$ symmetry).

(5) To within the experimental error ($\pm$0.5 cm^{-1}), no isotopic effects on the interaction potentials can be observed.

(6) Since both the site splitting and orientational effect seem to be independent of mode classification (C–C, C–H, H–H), we can conclude, in agreement with the results of calculations,[16] that C–H as well as H–H intermolecular interactions are of importance for these splittings.

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[17] A. R. Gee and G. W. Robinson, J. Chem. Phys. **46**, 4847 (1967); relative intensities of the components in the Raman and the perturbed infrared absorption need not, of course, be the same.

[18] J. C. Hollenberg and D. A. Dows, J. Chem. Phys. **37**, 1300 (1962).