Vibrational Exciton Structure in Crystals of Isotopic Benzenes

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Vibrational Exciton Structure in Crystals of Isotopic Benzenes*

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New high-resolution infrared spectra of crystalline isotopic benzenes C_6H_6, C_6H_5D, *p*-, *m*-$C_6H_4D_2$, *sym*-$C_6H_3D_3$, and C_6D_6 are presented. Using these data in conjunction with isotopic mixed-crystal data and the polarized single-crystal spectra (C_6H_6) of Zwerdling and Halford, the exciton band structures and coupling constants for nondegenerate vibrations of C_6H_6 and C_6D_6 are obtained. One vibration of *sym*-$C_6H_3D_3$ has also been analyzed. It is assumed that when the band shapes and splittings are nearly identical, the polarizations can be carried over from the C_6H_6 crystal to C_6D_6 and *sym*-$C_6H_3D_3$ crystals. It is not possible to analyze completely the degenerate bands of these isotopes since experimental data do not yield values of all the independent matrix elements appearing in the expression for the energy of the exciton components. In the isotopic modifications of lower symmetry, exciton structure is not easily interpreted due to an orientational effect, crystal induced Fermi resonance, and the inevitable presence of isotopic impurities.

I. INTRODUCTION

The infrared spectrum of the benzene crystal has had a long and interesting history beginning in 1949 with the classic paper by Mair and Hornig.[1] Not only did these authors correctly assign all of the spectrum in the infrared, but they observed and identified exciton structure on some of the bands. Their investigation, however, was somewhat limited by their low instrumental resolving power. In 1955 Zwerdling and Halford,[2] again using relatively low resolution, obtained polarized, single-crystal spectra of benzene. These still remain the only infrared polarization data published on the benzene crystal.[3] More recent infrared work on crystalline benzene (C_6H_6 and C_6D_6) was carried out by Hollenberg and Dows[5,6] using a resolution of about 0.7 cm^{-1}. These workers also measured the absolute intensities of the infrared crystal transitions of C_6H_6 and C_6D_6. The investigation of Hollenberg and Dows represented the first comprehensive and detailed study of the infrared spectrum of crystalline benzenes under high resolution.

Although it was clear in these early investigations that the observed structure in the benzene-crystal vibrations was due to the coupling of the four molecules in the unit primitive cell, it was not at all obvious how to interpret the observed splittings in terms of specific interactions. In fact, no interpretation was presented in terms of the intermolecular coupling constants of Davydov exciton theory[7] primarily because transitions to one of the four exciton components from the ground state is dipole forbidden ($A_u \nleftrightarrow A_g$), and there was therefore insufficient information to determine the three coupling constants.

Recently Bernstein, Colson, Kopelman, and Robinson[8], following Nieman and Robinson,[9] have presented a technique for determining the position of the fourth Davydov component, employing isotopic mixed-crystal data. Such data, in the limit of the *ideal mixed crystal*,[8] allow the mean of the $\mathbf{k}=0$ exciton multiplet to be determined and the unobserved level to be predicted. A knowledge of accurate, high-resolution polarization data would then enable one to evaluate the magnitude and sign of the nearest-neighbor, pairwise exciton coupling constants and, therefore, to establish the form and magnitude of the intermolecular interactions that characterize the entire exciton band[10,11] in the crystal. Clearly, such an analysis depends heavily on good dilute isotopic mixed-crystal data and accurate high-resolution single-crystal polarization ratios. The former

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‡ Contribution No. 3549.

[1] R. D. Mair and D. F. Hornig, J. Chem. Phys. **17**, 1236 (1949).

[2] S. Zwerdling and R. S. Halford, J. Chem. Phys. **23**, 2221 (1955).

[3] Although there are some questions concerning this work, a careful analysis of the experimental apparatus and procedure reveals that any difficulty can be cleared up when one considers the divergence of their light beam [R. Kopleman, (private communication)] and the fact that they employed the incorrect crystal structure. They believed that the benzene molecules were oriented parallel to the crystal axes. With the correct crystal structure[4] their oriented-gas arguments are not greatly altered, and their conclusions concerning the spectra observed along the **a** and **c** axes remain likewise unaltered.

[4] E. G. Cox, Rev. Mod. Phys. **30**, 159 (1958); E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, Proc. Roy. Soc. (London) **A247**, 1 (1958); G. E. Bacon, N. A. Curry, and S. A. Wilson, *ibid.* **A279**, 98 (1964).

[5] J. L. Hollenberg and D. A. Dows, J. Chem. Phys. **37**, 1300 (1962). Some doubt is cast on the assignments in the 3000-cm^{-1} region because of crystal enhanced Fermi resonance and combinations. Also a C_6D_5H transition was taken to be part of the C_6D_6 (ν_{11}) band. In this connection, see also Ref. 6.

[6] J. L. Hollenberg and D. A. Dows, J. Chem. Phys. **39**, 495 (1963).

[7] A. S. Davydov, Usp. Fiz. Nauk **82**, 393 (1964) [Sov. Phys.—Usp. **7**, 145 (1964)].

[8] E. R. Bernstein, S. D. Colson, R. Kopelman, and G. W. Robinson, J. Chem. Phys. **48**, 5596 (1968).

[9] G. C. Nieman and G. W. Robinson, J. Chem. Phys. **39**, 1298 (1963), but see also the paper by S. D. Colson, J. Chem. Phys. **48**, 3324 (1968) which casts doubt on the quasiresonance method for electronic exciton bands. The questions raised by Colson should not apply to the vibrational exciton problem.

[10] R. G. Body and I. G. Ross, Australian J. Chem. **19**, 1 (1966).

[11] S. D. Colson, D. M. Hanson, R. Kopelman, and G. W. Robinson, J. Chem. Phys. **48**, 2215 (1968).

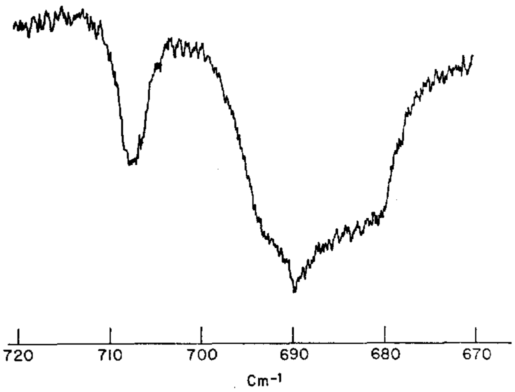

FIG. 1. Neat crystal C_6H_6 ν_{11} (a_{2u}).

are presently available[12,13] while, unfortunately, the latter are not. We must thus rely for the present on the low-resolution polarization data of Ref. 2, which are not always easy to correlate with the high-resolution line positions. A further difficulty along this line is that no polarization data are available for the deuterated benzenes. Since such information is essential to our development we will assume that bands from different isotopic modifications with "superimposable structure" are similarly polarized.

The purpose then of this paper is fourfold: (1) to report a portion of the complete set of experimental data required to test a later calculation[14] of vibrational interactions in crystalline benzene; (2) to understand vibrational exciton interactions in neat crystals of the isotopic benzenes; (3) to study the relationship between isotopic mixed-crystal data and vibrational exciton structure of the various benzenes; and (4) to determine what, if any, are the effects of isotopic substitution upon the vibrational-exciton coupling constants in the neat crystal.

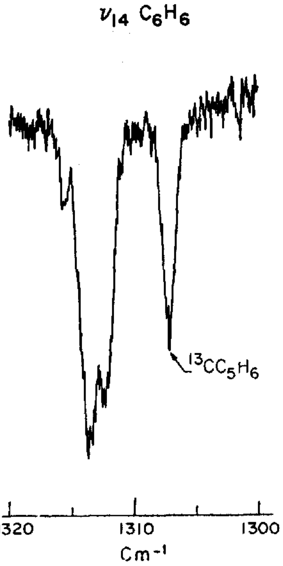

FIG. 2. Neat crystal C_6H_6 ν_{14} (b_{2u}). The feature at ~1307 cm^{-1} is due to $^{13}CC_5H_6$ (Ref. 12).

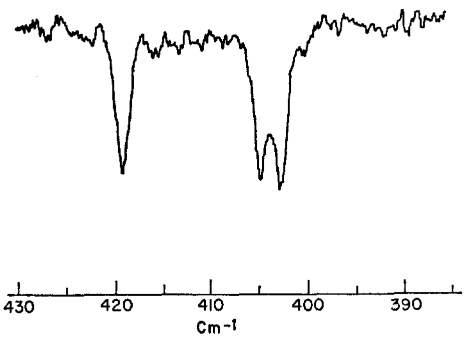

FIG. 3. Neat crystal C_6H_6 ν_{16} (e_{2u}).

II. THEORY

Exciton band theory in the Frenkel limit has recently been discussed for the case of benzene in a paper by Bernstein, Colson, Kopelman, and Robinson.[8] Pertinent earlier references to the general theory are discussed in that work. For the purposes of this paper we shall require the energies of the four Davydov components $(\mathbf{k}=\mathbf{0})$,

$$E(A)=4(+M_{\mathrm{I\,II}}+M_{\mathrm{I\,III}}+M_{\mathrm{I\,IV}})$$

$$E(B_1)=4(+M_{\mathrm{I\,II}}-M_{\mathrm{I\,III}}-M_{\mathrm{I\,IV}}) \qquad \|\,\mathbf{a}$$

$$E(B_2)=4(-M_{\mathrm{I\,II}}+M_{\mathrm{I\,III}}-M_{\mathrm{I\,IV}}) \qquad \|\,\mathbf{b}$$

$$E(B_3)=4(-M_{\mathrm{I\,II}}-M_{\mathrm{I\,III}}+M_{\mathrm{I\,IV}}) \qquad \|\,\mathbf{c}$$

in terms of the pairwise intermolecular coupling con-

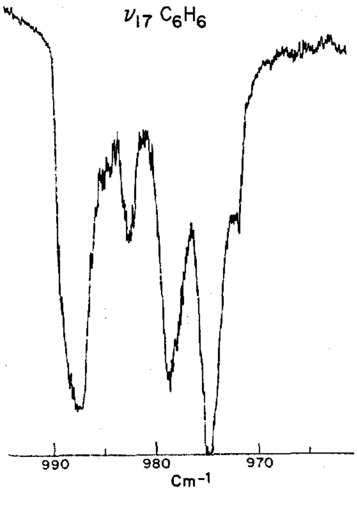

FIG. 4. Neat crystal C_6H_6 ν_{17} (e_{2u}).

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[12] E. R. Bernstein, "Site Effects in Isotopic Mixed Crystals—Site Shift, Site Splitting, Orientational Effect and Intermolecular Fermi Resonance in the Vibrational Spectrum of Benzene" (unpublished).

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

[14] E. R. Bernstein, "Calculation of the Ground State Vibrational Structure and Phonons of the Isotopic Benzene Crystals" (unpublished).

TABLE I. C_6H_6 exciton structure (cm^{-1}).

Vibration number[a]	D_{6h} symmetry	Gas-phase value[b]	IMC value[c]	Exciton components[d]	Polarization[e]
ν_{11}	a_{2u}	672	696.9	681–683	a B_{1u}
				689.2	c B_{3u}
				707.8	b B_{2u}
				[709.0][f]	A_u
ν_{12}	b_{1u}	1011	1011.3	1006.9	c B_{3u}
				1008.6	b B_{2u}
				1009.7	a B_{1u}
				[1020.0]	A_u
ν_{14}	b_{2u}	1309	1312.6	1312.2	
				1313.4	g
				1315.3	
				[1309.5]	A_u
ν_{15}	b_{2u}	1146	1146.9	1142.5	c B_{3u}
				1148.6	a B_{1u}
				1150.3	b B_{2u}
				[1146.2]	A_u
ν_{16}	e_{2u}	398	404.8	402.5	
			413.0	404.7	i
				419.0	
ν_{17}	e_{2u}	967	978.3	972.0	
			983.9	974.7	
				978.6	g
				982.3	
				987.5	
				988.1	
ν_{18}	e_{1u}	1037	1034.8	1030.0	
			1038.6	1032.5	g
				1033.5	
				1034.6	
				1038.9	
				1039.8	
ν_{19}	e_{1u}	1482	1470[h]	1469.8} ^{13}C	
				1470.2}	
				1473.5	
				1474.9	
				1475.6	g
				1477.7	
				1478.9	
				1480.2	

[a] ν_{20} and ν_{13} are strongly coupled by Fermi resonance in the crystal and are omitted because of the resulting complexity.

[b] J. H. Callomon, T. M. Dunn, and I. M. Mills, Phil. Trans. Roy. Soc. (London) **A259**, 499 (1966).

[c] Ideal mixed-crystal energy—see text and Ref. 8.

[d] Component in brackets not observed—calculated from IMC level and other exciton components, see Refs. 8 and 12.

[e] Reference 2.

[f] Position not well known due to inaccuracy in the determination of the *a*-polarized component.

[g] Polarization data not conclusive due to low resolution of Ref. 2.

[h] Broad and structureless.

[i] Not observed by Zwerdling and Halford (Ref. 2).

stants $M_{qq'}$ for translationally inequivalent molecules. In Ref. 8 it was shown that the mean energy of these four components lies at a position $\bar{\epsilon}+\Delta+L'(0)$, where $\bar{\epsilon}$ is the gas-phase excitation energy, Δ is the total static field gas-to-crystal shift (site shift), and $L'(0)$ is the translation group shift. The value of Δ corresponds so the shift between the gas-phase excitation energy and that in an *ideal mixed crystal*.[8] The value of $L'(0)$, relative to the $M_{qq'}$ values, is small for short-range intermolecular interactions, such as those that occur for vibrational and certain electronic excitons since it depends upon the interaction between the relatively distant translationally equivalent molecules in the benzene crystal. (See Fig. 1 of Ref. 8.) Thus the mean energy of the Davydov components can for our purposes be obtained to high precision from ideal mixed-crystal results. Isotopic mixed-crystal data properly corrected for quasiresonance effects[8,9,12] approach the *ideal mixed crystal* closely. The measured positions of the three "allowed" Davydov levels (B_1, B_2, B_3) in addition to the mean energy of all four (B_1, B_2, B_3, A) levels allow the coupling constants $M_{\mathrm{I\,II}}$, $M_{\mathrm{I\,III}}$, and $M_{\mathrm{I\,IV}}$ to be determined, and thus the position of the "forbidden" A component to be ascertained.

TABLE II. C_6D_6 exciton structure (cm^{-1}).

Vibration number[a]	D_{6h} symmetry	Gas-phase value[b]	IMC value[c]	Exciton components[d]	Polarization[e]
ν_{11}	a_{2u}	498	511.2	502.0	a B_{1u}
				506.0	c B_{3u}
				519.0	b B_{2u}
				[518.0][g]	A_u
ν_{12}	b_{1u}	970	971.0	966.8	c B_{3u}
				969.6	b B_{2u}
				970.3	a B_{1u}
				[978.1]	A_u
ν_{14}	b_{2u}	1285	1285.1	1286.2	
				1287.5	
				1288.7	
				[1278.0]	
ν_{15}	b_{2u}[h]	824	820.6	823.4	c B_{3u}
				824.1	a B_{1u}
				826.9	b B_{2u}
				[808.0][j]	A_u
ν_{16}	e_{2u}	348	354.8	351.3	
			364.6	353.7	
				354.0	i
				367.3	
				370.1	
				373.2	
ν_{17}	e_{2u}	787	791.3	789.4	
			797.8	790.3	
				795.0	
				795.4	
				797.8	
				801.2	
ν_{18}	e_{1u}[h]	814	810.5	808.2	
			814.6	809.3	
				811.2	f
				812.5	
				814.9	
				815.5	
ν_{19}	e_{1u}	1333	1329.2	1325.4 ^{13}C	
				1328.4	
				1329.5	f
				1330.3	
				1335.1	
				1336.0	

ν_{20} and ν_{13} are in Fermi resonance in the crystal.

[b] Table I, Footnote b.

[c] Ideal mixed-crystal energy—see text and Ref. 8.

[d] Components in brackets are obtained from IMC level and observed exciton components.

[e] These polarizations are obtained from the C_6H_6 data by assuming the same band structure for the two isotopes; square brackets indicate Fermi resonance.

[f] Due to low resolution, the C_6H_6 polarizations are not known (Ref. 2).

[g] Not well known due to inaccuracy in the determination of the polarized components.

[h] ν_{15} and ν_{18} are in resonance in the pure crystal and to a lesser extent in the IMC.

[i] Not studied by Zwerdling and Halford in C_6H_6 (Ref. 2).

[j] Calculated on the basis of the ideal mixed-crystal level in the same fashion as the other bands. Not believed to be the true neat crystal-exciton structure due to the increase of Fermi resonance between ν_{18} and ν_{15} in the neat crystal with respect to the mixed crystal. See text for discussion of this point.

Another result of Ref. 8 that should be kept in mind here is that site splitting of a molecular degenerate state is best defined in terms of ideal mixed-crystal data. It is not necessarily a useful concept in the neat crystal because of the large number of independent off-diagonal interaction matrix elements associated with a pair of degenerate or nearly degenerate crystal states. For example, in the case of benzene, there are only three independent off-diagonal elements for a molecular nondegenerate state but ten for a doubly degenerate state. This complication arises when both site states map into the same irreducible representation of the site group, as in the case of benzene, and is particularly important when the magnitude of the site splitting in the ideal mixed crystal is comparable to the width of the exciton band in the neat crystal. The latter condition applies to many vibrational exciton bands in crystalline benzene.

It is important to realize too that vibrational states of the crystal are more susceptible to Fermi resonance

TABLE III. Nearest-neighbor pairwise exciton interaction constants for C_6H_6 and C_6D_6 nondegenerate u ground-state vibrations (in cm^{-1}).

Vibration	IMC (C_6H_6)	IMC (C_6D_6)	Coupling constants C_6H_6	Coupling constants C_6D_6
ν_{11} a_{2u}	696.9	511.3	$M_{\mathrm{I\,II}}=0.5\pm0.5$	-0.3 ± 0.5
			$M_{\mathrm{I\,III}}=0.4$	0.2
			$M_{\mathrm{I\,IV}}=2.8$	1.8
ν_{12} b_{1u}	1011.3	971.0	$M_{\mathrm{I\,II}}=0.9\pm0.2$	0.7 ± 0.2
			$M_{\mathrm{I\,III}}=0.8$	0.7
			$M_{\mathrm{I\,IV}}=0.6$	0.3
ν_{14} b_{1u}	1312.6	1285.1	$M_1{}^{a}=-0.4\pm0.2$	-0.8 ± 0.2
			$M_2=-0.3$	-0.6
			$M_3=0.1$	-0.5
ν_{15} b_{2u}	1146.9	820.6	$M_{\mathrm{I\,II}}=0.4\pm0.2$	-1.1 ± 0.2[b]
			$M_{\mathrm{I\,III}}=0.1$	-0.8
			$M_{\mathrm{I\,IV}}=-0.7$	-1.2

[a] Polarizations not known and thus it is not possible to assign each coupling constant to a given pair of molecules.

[b] Not correct values of the exciton coupling constants due to Fermi resonance between ν_{15} and ν_{18} (see text).

than vibrational states of the free molecule.[12] There are more levels in the crystal, and therefore more chance for accidental degeneracies to occur,[15] the symmetry restriction on interactions are more relaxed, and intermolecular coupling as well as intramolecular anharmonicity can mix the states.

Orientational effects in isotopic mixed crystals of benzene have been observed recently[12,13] for C_6H_5D, *p*, *m*$-C_6H_4D_2$, *m*$-C_6H_2D_4$, and C_6HD_5 in host crystals of C_6H_6 and C_6D_6. The apparent splitting of *nondegenerate* transitions in the molecules having symmetry lower than D_{3h} is due to an orientational multiplicity in the $\mathbf{C}_i$ site of the crystal. This observation indicates that the *non*symmetry related site directions or positions can and do affect the site vibrations differently. In other words, when the molecular vibration can have specific orientations with respect to its environmental field and the molecule can orient itself in more than one way in this field, the differently oriented vibrational transitions can have different energies and thus display an orientational effect. These energy differences δ_{OE} have been empirically determined to be roughly of the same order as the site group splittings and the exciton splittings (~2–10 cm^{-1}). It can be further shown[14] that all these energy "splittings" originate from the same interactions, namely, the intermolecular atom–atom couplings in the crystal.

III. EXPERIMENTAL METHODS AND RESULTS

The general technique for the preparation of samples has been described previously.[16] The isotopic benzenes used in these experiments were either unpurified or cesium purified. The C_6H_6 was obtained from Phillips Petroleum Company (Research Grade), and the isotopic modifications from Merck, Sharp and Dohme of Canada, Ltd.

For weak transitions, such as ν_{14} in C_6H_6, or any of the "*gerade*" vibrations of an isotopic modification with no center of symmetry, a 0.015-in. indium spacer was used between the two CsI cell windows to fix the sample thickness. In this manner the cell produces a sample of the order of 150 μ thick, estimated from both the measured compression of the indium spacer and the intensity of the transitions. For strong transitions, such as the e_{1u} and a_{2u} vibrations of C_6H_6 and C_6D_6, the samples were made with flat, ground and polished windows, to give sample thicknesses of roughly 10–20 μ. Both techniques produce very transparent polycrystalline samples containing no empty volume. These samples are then attached to the cold finger of a helium Dewar and brought to 77°K in about 10–15 min. Although many runs were carried out at 4.2°K, most of the data were obtained at 77°K. Using 0.5 cm^{-1} in-

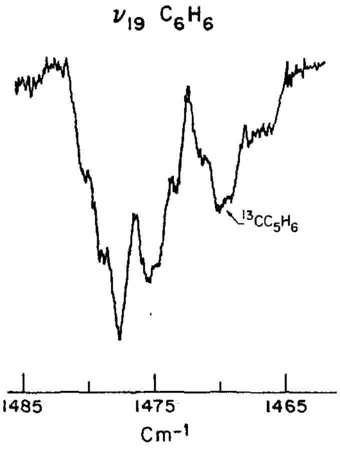

FIG. 5. Neat crystal C_6H_6 ν_{19} (e_{1u}). The feature at ~1470 cm^{-1} is due to $^{13}CC_5H_6$ and should contain two lines due to the removal of the ν_{19} degeneracy (Ref. 12).

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[15] V. L. Strizhevsky, Opt. Spektrosk. **8**, 165 (1960) [Opt. Spektrosc. **8**, 86 (1960)].

[16] S. D. Colson and E. R. Bernstein, J. Chem. Phys. **43**, 2661 (1965).

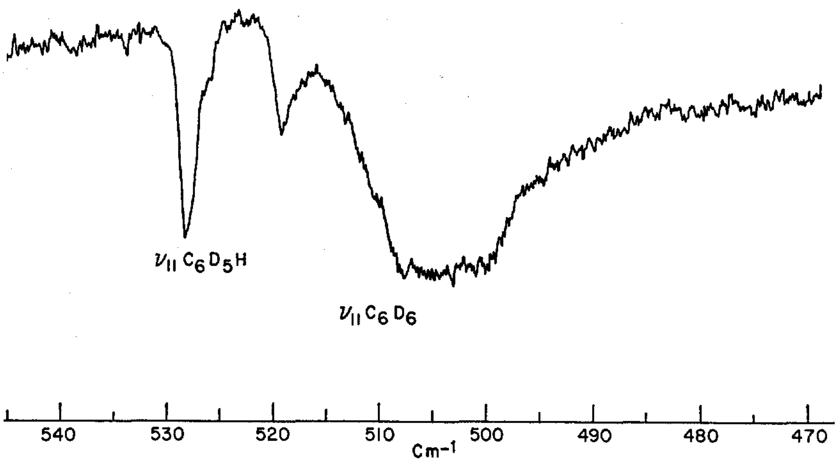

FIG. 6. Neat crystal C_6D_6 ν_{11} (a_{2u}). The absorption at ~528 cm^{-1} is due to ν_{11} of C_6D_5H. The intensity of this peak may be due to intermolecular Fermi resonance with the C_6D_6 ν_{11} level. (See Ref. 12.)

strumental resolution, there is no observable difference in exciton structure at these two temperatures. All spectra were obtained on a Beckman IR-12 whose calibration was checked against H_2O and CO_2 spectra after each benzene experiment.

A. C_6H_6 and C_6D_6

Some of the spectra for the C_6H_6 and C_6D_6 vibrations are given in Figs. 1–9, and the data are reported in Tables I and II.[17] These results should be compared with those in Ref. 5. It is quite clear that the agreement in both absolute frequency and band shape is for the most part good.[18] We do not, however, attempt to analyze ν_{20} (~3043 cm^{-1} in C_6H_6 and ~2288 cm^{-1} in C_6D_6) and ν_{13} (~3060 cm^{-1} in C_6H_6 and ~2285 cm^{-1} in C_6D_6).[19] We feel they are inherently quite complex in the crystal because of increased Fermi resonance among the fundamentals themselves and because of numerous combinations and overtones in these regions.[6] Such complications are known to be present in the gas-phase spectrum[20] and have recently been discussed for isotopic mixed crystals of benzene.[12,13]

In Table III are contained the exciton coupling constants ($M_{qq'}$) for the nondegenerate **u** molecular vibrations (a_{2u}, b_{1u}, b_{2u}) of C_6H_6 and C_6D_6 obtained from the neat and isotopic mixed crystal data. The C_6H_6 polarization ratios of Ref. 2 are employed.

1. $\nu_{11}(a_{2u})$ *[697 cm^{-1} and 511 cm^{-1}]*

The ν_{11} band for C_6H_6 and C_6D_6 (Fig. 1 and Fig. 6) look quite similar to one another. As can be seen in Table III, the exciton coupling constants are about the same though those belonging to C_6D_6 appear somewhat smaller. It should be noted, however, that the bands

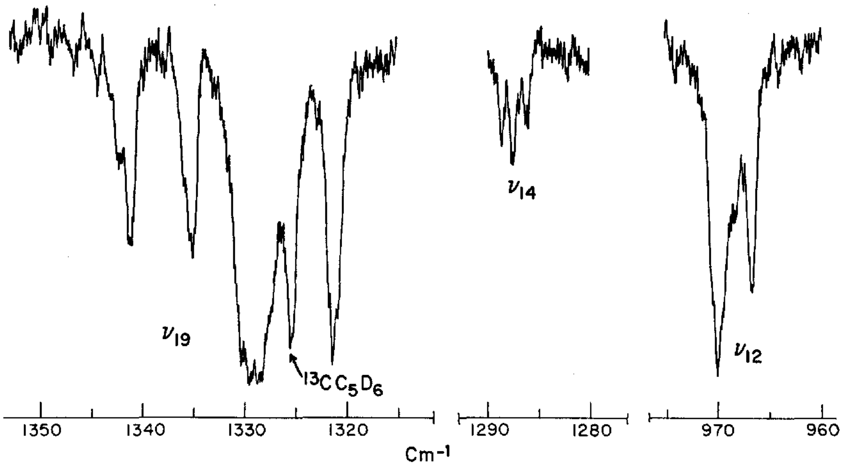

FIG. 7. Neat crystal C_6D_6 ν_{12} (b_{1u}), ν_{14}(b_{2u}), and ν_{19} (e_{1u}) absorption. The feature at ~1325 cm^{-1} is due to $^{13}CC_5D_6$ (Ref. 12). ν_{14} is the weakest observed *u* vibration in the C_6D_6 spectrum.

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[17] Some other tracings can be found in Ref. 12.

[18] We report our frequencies to 0.1 cm^{-1} and claim an absolute accuracy of ±0.5 cm^{-1}. Relative frequencies of the factor group components are of course much better than this. Our resolution seems comparable to that employed by Hollenberg and Dows in Ref. 6, where many frequencies are reported to 0.01 cm^{-1}.

[19] Here and elsewhere in this work, the normal coordinates are numbered after E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., New York, 1955).

[20] G. Herzberg, *Infrared and Raman Spectra* (D. van Nostrand Co., Inc., New York, 1964), p. 362 ff.

TABLE IV. *Sym*-(1,3,5) $C_6H_3D_3$ exciton structure.

Vibration number	D_{3h} symmetry	Gas-phase value[a]	IMC value[b]	Exciton components[c]	Polarization[d]
ν_{11}	a_2''	531	545.5	536.0 541.0 550.0 [555.0][e]	a B_{1u} c B_{3u} b B_{2u} A_u
ν_{12}	a_1'	1002	1002.7	1002.7	
ν_{15}	a_2'	912	908.1	922.0 925.0 935.0	
ν_5	a_2''	917	928.0	940.0 946.0	
ν_{17}	e''	924	935.7 939.4	955.0	
ν_1	a_1	955	954.6		
ν_{16}	e''	368	377.5 385.0	376.6 378.1 390.3 395.9 399.6	f
ν_{18}	e'	833	831.6 834.4	830.0 830.6 832.4 835.1 837.1	f

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

[b] Ideal mixed-crystal energy—see Refs. 8 and 12.

[c] Components in brackets are obtained from IMC level and observed exciton components.

[d] From the C_6H_6 data of Ref. 2.

[e] Not well known due to inaccuracy in the determination of the polarized components.

[f] C_6H_6 polarization not known.

are broad and thus the $M_{qq'}$'s can be determined to only ±0.5 cm^{-1}. Both samples were Cs purified[16] so that chemical impurities cannot be called upon to explain any of the structure. The possibility that part of the absorption in the exciton band is due to isotopic impurities is eliminated since the positions of the vibrational levels of all the isotopic benzenes in C_6H_6 and C_6D_6 mixed crystals are now well known,[12,13] and none fall within the limits of the ν_{11} exciton band absorptions. The broad lines are probably caused by the

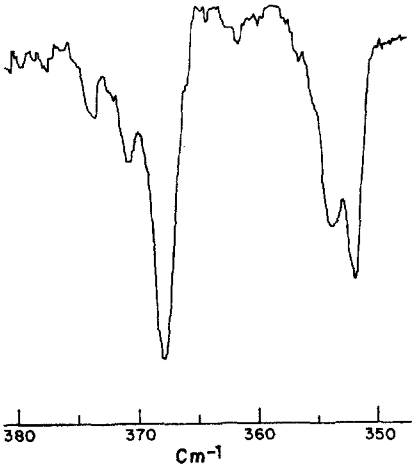

FIG. 8. Neat-crystal spectrum of C_6D_6 ν_{16} (e_{2u}).

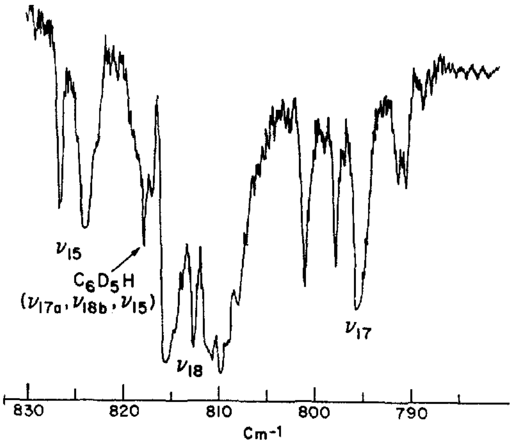

FIG. 9. Neat crystal C_6D_6 ν_{17} (e_{2u}), ν_{18} (e_{2u}), and ν_{15} (b_{2u}). There is Fermi resonance between all three of these transitions in the C_i crystal site. The absorption at ~818 cm^{-1} (to the high-energy side of ν_{18}) is due to C_6D_5H.

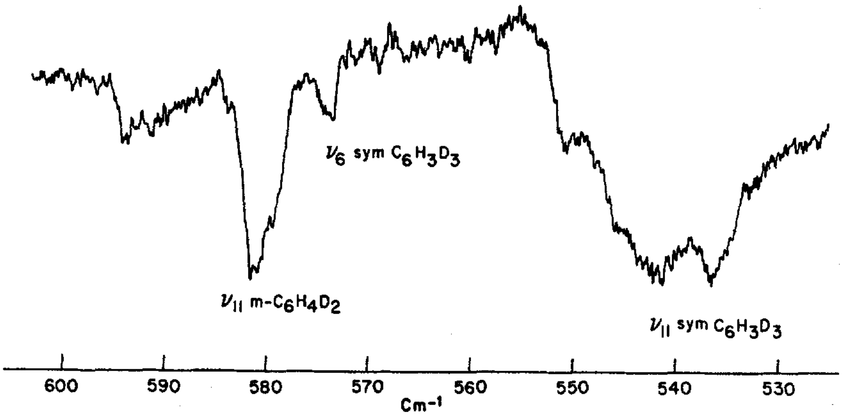

FIG. 10. Neat crystal ν_{11} (a_{2u}) of *sym*-$C_6H_3D_3$. In the region from 570–600 cm^{-1} are ν_{11} of *m*-$C_6H_4D_2$ and ν_6 (e_{2g}) of *sym*-$C_6H_3D_3$.

fact that the band has a large exciton splitting and is thus quite sensitive to crystal quality.[21]

The discrepancy between the *M*'s for C_6H_6 and C_6D_6 might be attributable to the line uncertainty, but there could be real causes for this difference. The C–C and C–H(D) contact distances are smaller in C_6D_6 than in C_6H_6 due to the smaller zero-point amplitudes for the D atoms. Thus the C–C and C–D interactions could be larger in the more closely packed C_6D_6 crystal. These changes in $M_{qq'}$ can best be termed a zero-point or bond-length effect. Just how these changes would affect the *M*'s is very difficult to judge, since in the calculation[14] of the interaction energies the geometry and number of contacts become involved in a very complicated fashion. Such changes in the exciton coupling constants should not be confused with isotopic effects on the interactions, where a change in the atom–atom potentials is brought about by a change in the electronic charge distribution in going from H to D, an effect that is expected to be vanishingly small.

2. $\nu_{14}(b_{2u})$ [*1312 cm^{-1} and 1285 cm^{-1}*]

For ν_{14} (Figs. 2 and 7) the exciton splittings in C_6H_6 and C_6D_6 are very similar. The pairwise interactions appear somewhat larger in C_6D_6 than in C_6H_6, but the experimental uncertainty does not allow a definite statement to be made.

3. $\nu_{15}(b_{2u})$ [*1147 cm^{-1} and 821 cm^{-1}*]

For this band the *M*'s for C_6D_6 and C_6H_6 obtained from the isotopic mixed-crystal data and the neat-crystal data do not agree. The major reason for this difference can be seen from Table II. The ν_{15} and ν_{18} bands of C_6D_6 (Fig. 9) interact considerably in the pure crystal since they are brought into better resonance by the exciton splitting of each band. However, they do not interact as much in the isotopic mixed crystal where the exciton splitting is missing. This difference in Fermi resonance in the pure and mixed crystals considerably shifts the band from its ideal mixed-

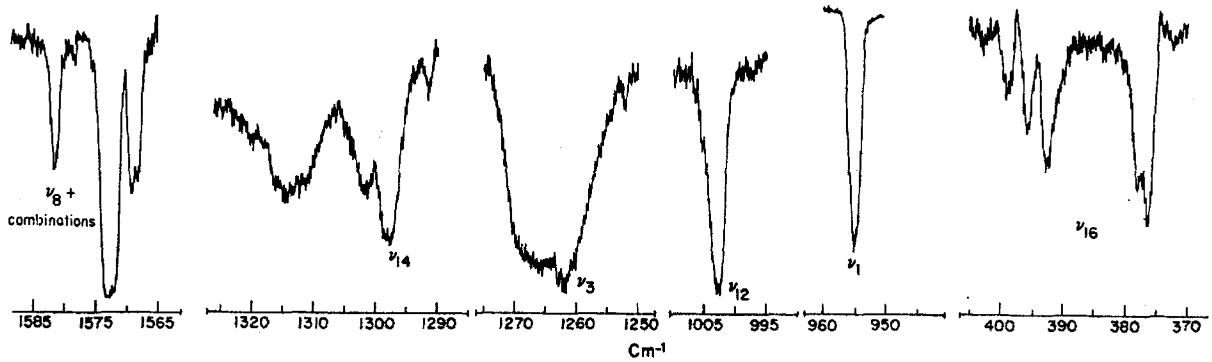

FIG. 11. A tracing of several of the *sym*-$C_6H_3D_3$ neat-crystal bands. ν_{16} is observed to show clear splitting because the various exciton components are well separated, and this band is isolated from any others. ν_1 and ν_{12} show no exciton structure but are broadened because of the various crystal effects (see text). ν_3 and ν_{14}, which mix strongly in the molecule, are broadened and distorted in the neat crystal (see text). The ν_8 region cannot be uniquely assigned because of the presence of $\nu_6+\nu_1$ and possibly other combination bands.

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[21] S. D. Colson, J. Chem. Phys. **45**, 4746 (1966).

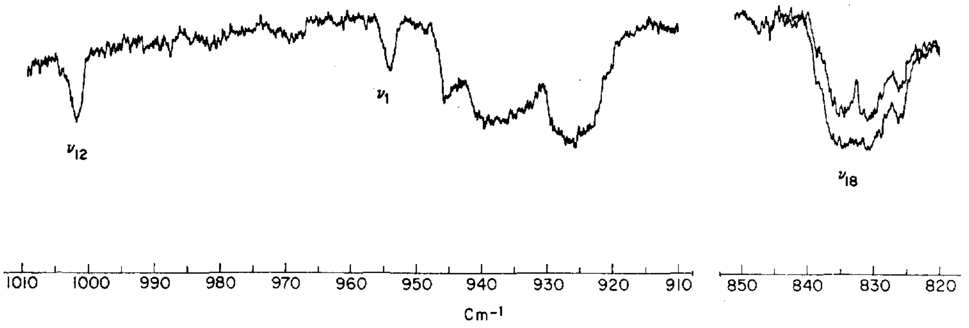

FIG. 12. A trace of the neat crystal spectrum of *sym*-$C_6H_3D_3$ showing the ν_{18} band and the ν_{12} band. The region from 920–955 cm^{-1} contains ν_5, ν_{17}, ν_{15}, and ν_1 all in resonance in the crystal. The effect of cesium purification on the isotopic composition of a non-C_6H or C_6D_6 sample can be seen from the ν_{18} trace. The upper ν_{18} spectrum was taken with a sample that was not cesium purified. ν_{18a} of *m*-$C_6H_4D_2$ and *m*-$C_6H_2D_4$ falls at 835 cm^{-1}.

crystal value. The predicted A_u Davydov level then appears to be much further away from the B_u levels than it actually is. Thus the large exciton band structure for ν_{15} of C_6D_6 is an artifact.

4. *Conclusions*

We can extract two general conclusions from the above data: (1) Isotope effects on the exciton coupling constants are probably small; and (2) increased Fermi resonance in the neat crystal compared with that in the gas and in the mixed crystal is very significant in the determination of exciton structure. Small differences in exciton coupling constants associated with isotopic substitution can probably be associated with zero-point C–H or C–D bond changes.

B. *Sym*-$C_6H_3D_3$

Data for this isotopic modification are in Table IV. Although it has been shown group theoretically[22] and experimentally[12,13] that no orientational effect can occur for *sym*-$C_6H_3D_3$ in the $\mathbf{C}_i$ site of a C_6H_6 or C_6D_6 host crystal, it is clear that for the neat crystal of *sym*-$C_6H_3D_3$, where the site-symmetry group is now reduced to $\mathbf{C}_1$ due to the rotational disorder of the molecules, two distinct and, in principle energetically different, orientations can occur for this isotope. This is a consequence of the loss of inversion symmetry in the molecule itself. However, the crystal site field should not be greatly perturbed by such a change, since the bulk geometrical arrangement of the molecules remains unchanged and the isotopic effects on the potentials are small for ground-state vibrations. In other words, this orientational effect should be considerably smaller than that which occurs for a molecule like C_6H_5D or *p*-$C_6H_4D_2$ in C_6H_6 or C_6D_6 host crystals. Therefore, some bands in neat crystalline *sym*-$C_6H_3D_3$ are well resolved (for example, ν_{11}, ν_1, ν_{12}, and ν_{16} in Figs. 10 and 11).

The presumably random orientation of the molecules in the crystal will also affect the translational symmetry. Thus the entire **k**-band structure and the $\Delta\mathbf{k}=0$ selection rules[23] are in principle altered. In light of the

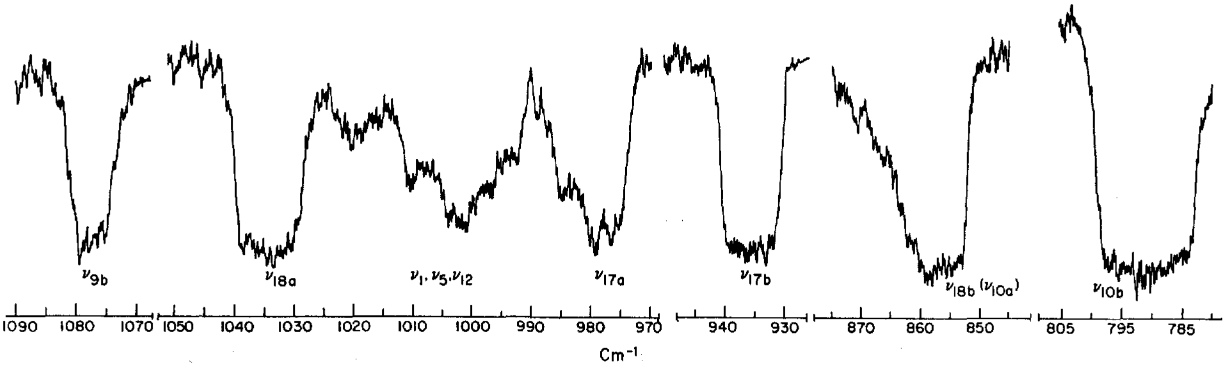

FIG. 13. Neat-crystal C_6H_5D tracing. The two causes of loss of exciton structure in neat crystals of non-D_{6h} isotopes are present. The spectral region 990–1010 cm^{-1}, where ν_1, ν_5, and ν_{12} fall, shows the effect of increased Fermi resonance in neat crystals. The other transitions show no exciton structure due to the orientational effect.

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

[23] S. D. Colson, R. Kopelman, and G. W. Robinson, J. Chem. Phys. **47**, 27, 5462 (1967).

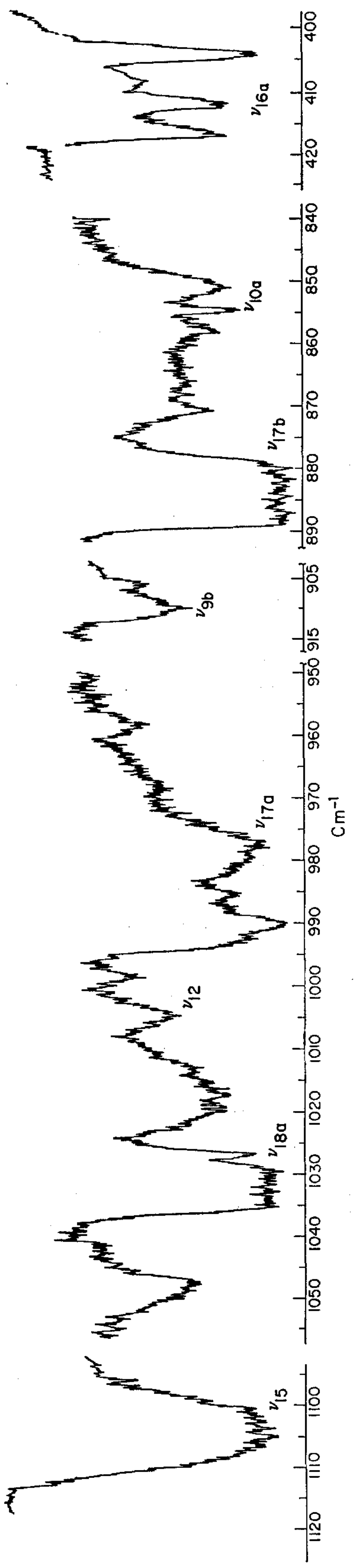

FIG. 14. Neat-crystal spectrum of p-$C_6H_4D_2$. The orientational effect can be seen to obscure most of the exciton structure. ν_{16} (~410 cm^{-1}) where the orientational and exciton splittings are both quite large shows resolved structure but the presence of $C_6H_6(\nu_{16})$ complicates this interpretation. Due to the orientational disorder of the p-$C_6H_4D_2$ molecules the g vibrations ν_{10a} (~850 cm^{-1}) and ν_{9b} (~910 cm^{-1}) are seen. This is due to the loss of the C_i site symmetry in the crystal.

above ideas, however, these effects may again be assumed to be small. Still there are many fundamentals that are quite broad, showing no discernable exciton structure (Figs. 11 and 12). The two principal causes of this (see Fig. 12) are Fermi resonance and the presence of a large amount of isotopic impurity such as m-$C_6H_4D_2$. Loss of structure due to overlapping transitions of other isotopes can be seen from the difference between spectra of the Cs purified and unpurified samples. Cs purification[16] appears to cause exchange of H and D atoms.

In the ν_{11} and ν_{16} regions the complications from Fermi resonance and from isotopic impurities are believed to be small.[24] Since ν_{16} is a degenerate vibration in the free molecule, the only band for which we can obtain M's is $\nu_{11}(a_2'')$. Within an error of ±0.5 cm^{-1} these are: $M_{\mathrm{I\,II}}=0$, $M_{\mathrm{I\,III}}=1.5$, and $M_{\mathrm{I\,IV}}=1$ cm^{-1} (±0.5 cm^{-1}). The large error is due to the greater line-position error in sym-$C_6H_3D_3$. While it is difficult to comment extensively on these exciton coupling constants, they seem of the same general size as those of the ν_{11} bands of C_6H_6 and C_6D_6.

C. Other Isotopes

For C_6H_5D, m, p-$C_6H_4D_2$, and m-$C_6H_2D_4$, large orientational effects are possible. Fermi resonance is extensive, and isotopic impurities are numerous. For these reasons, the pure crystal spectra are uniformly uninformative (see Figs. 13 and 14). The ν_{16a} region of p-$C_6H_4D_2$, for example, is probably complicated due to the presence of C_6H_6 (Fig. 14). Where impurities and orientational effects do not obscure the exciton structure, Fermi resonance takes over to complicate matters.

An interesting point concerning the p-$C_6H_4D_2$ spectra shown in Fig. 14 is that the g vibrations ν_{9b} (910 cm^{-1}) and ν_{10a} (850 cm^{-1}) appear to be induced due to the loss of the $\mathbf{C}_i$ site symmetry in the crystal. This decrease in symmetry occurs because of the orientational disorder in the crystal, and graphically illustrates the importance of site symmetry for the selection rules.

IV. CONCLUSIONS AND SUMMARY

The experimental results reported in this paper demonstrate the following:

(a) For the case of benzene there appears to be no need to invoke large isotopic effects on the nearest-neighbor pairwise exciton interactions. Any change in the M's for different isotopic modifications of benzene can probably be ascribed to either Fermi resonance or to zero-point effects on the C–D and C–H bond lengths.

(b) The orientational "splittings" observed in mixed crystals occur also in neat crystals. In the neat

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[24] The ν_{11} band of m-$C_6H_2D_4$ should fall around 538 cm^{-1} and could change the band shape of the sym-$C_6H_3D_3$ band.

crystal, however, the orientational effect usually serves to broaden the exciton structure to such an extent that neither the orientational "splitting" nor the exciton structure can be extracted from the spectrum.

(c) A further orientational effect can occur in principle if there is a loss of $\mathbf{C}_i$ site symmetry in the crystal due, say, to isotopic substitution. Such an orientational effect is postulated for non-D_{6h} species because of the expected random rotational orientation of the molecules at their sites. That "splittings" or broadening caused by this effect are small is indicated by the fact that a number of *sym*-$C_6H_3D_3$ neat-crystal transitions are fairly sharp. However, *g*, *u*-selection rules have been observed to be affected by this type of symmetry loss. Other effects, such as a breakdown of the $\Delta\mathbf{k}=0$ selection rule and the disruption of the general **k**-band structure due to the loss of translational symmetry in the crystal, may also contribute to broadening of the exciton structure in non-$\mathbf{D}_{6h}$ isotopic crystals.

(d) The importance of Fermi resonance for crystal vibrational spectra is emphasized. Fermi resonance in the crystal is greatly enhanced over that in the free molecule because of the greater chance of resonance and the reduced symmetry in the crystal. Fermi resonance is particularly prevalent when the number of allowed transitions is large, such as in the low-symmetry isotopic modifications of benzene. The presence of Fermi resonance complicates and tends to obscure exciton structure in the crystal. It may also cause the ideal mixed-crystal concept[8] to break down so that it is no longer possible to obtain the mean energy of the Davydov components from isotopic mixed-crystal data.

(e) Doubly degenerate vibrations in the molecule are split because of the low symmetry of the site. For benzene, site splitting and exciton splitting appear to be of comparable magnitude and often the expected six infrared lines are resolved. However, the number of data are insufficient[8] to allow an analysis of the splitting in terms of intermolecular interactions.

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Excluded-Volume Effect of Polymethyl Methacrylate Solutions

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Osmotic pressures of polymethyl methacrylate solutions in acetone and in benzene are examined over a wide range of concentration $(0<v_2<0.17)$. The data are used to evaluate the thermodynamic parameter B appearing in the excluded-volume parameter z. The behavior of $\alpha_\eta^3=[\eta]/[\eta]_0$ over a wide range of $z\,(0<z<8)$ are compared to the theoretical predictions. The dependence of α_η^3 on z seems to be approximately described by the modified Flory–Fox relation $\alpha_\eta^5-\alpha_\eta^3=1\ 03z$. The observed dependence of $h(\bar{z})=2A_2/N_AB$ on $\bar{z}$ for polymethyl methacrylate solutions is very close to the result for polystyrene solutions. It is found that $\log h(\bar{z})$ is not a linear function of $\log z^2$ over a sufficiently wide range of $z^2\,(0<z<8)$.

The theories of dilute polymer solution are represented in terms of the parameter z given by

$$z=0.330B(6\langle s^2\rangle_0/M)^{-3/2}M^{1/2}, \tag{1}$$

where B is the free energy parameter related to the binary cluster integral, $\langle s^2\rangle_0$ is the unperturbed mean-square radius of gyration, and M is the molecular weight of polymer. The parameter B must be determined for direct assessment of the theories of dilute polymer solution. Some investigators[1–4] have evaluated B from measurements of the second virial coefficient A_2 or the intrinsic viscosity $[\eta]$ in the vicinity of the Θ temperature. We have proposed a method[5,6] of evaluating B from osmotic-pressure data of moderately concentrated solutions. This osmotic-pressure method is not limited to Θ solvents. Since B can be evaluated even in good solvents, a comparison of the theories with experiment is possible over a wide range of z.

In the previous paper,[6] we have examined the viscometric and thermodynamic behaviors for polystyrene in toluene solutions. Further examination seems to be required for evaluation of the theories of dilute polymer solution. Here we deal with the excluded-volume effect for polymethyl methacrylate in acetone and benzene solutions.

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[1] G. V. Schulz, A. Haug, and R. Kirste, Z. Physik. Chem. (Frankfurt) **38**, 1 (1963).

[2] G. V. Schulz and H. Baumann, Makromol. Chem. **65**, 101 (1963).

[3] G. C. Berry, J. Chem. Phys. **44**, 4550 (1966).

[4] H. Inagaki, H. Suzuki, M. Fujii, and T. Matsuo, J. Phys. Chem. **70**, 1718 (1966).

[5] N. Kuwahara, T. Okazawa, and M. Kaneko, J. Polymer Sci. Pt. C (to be published).

[6] N. Kuwahara, T. Okazawa, and M. Kaneko, J. Chem. Phys. **47**, 3357 (1967).