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SPECTROSCOPIC STUDIES OF BENZENE

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1. INTRODUCTION

THE problem of interpreting the energy levels of the benzene molecule has frequently been the crucial test of a theory. As it were, the benzene molecule can be considered to be the simplest cyclic polyatomic molecule. Thus it has been the object of painstaking study, just as the hydrogen molecule has been in other branches of spectroscopy and theoretical physics.

The first experimental studies of the electronic spectrum of benzene go back to 1915,[1] while an interpretation and quantum-mechanical calculation of the energy levels of this molecule appeared in the thirties. A brilliant analysis of the absorption spectrum of benzene vapor was first carried out by Sponer.[3] Extensive studies reviewing the molecular absorption of benzene and its deuterated forms were published by Ingold and his associates in 1936 and 1948.[4]

Owing to the relatively clear conceptions of the structure of the spectrum of the free molecule, much interest has been directed toward the study of the absorption spectrum of benzene crystals at low temperatures. Attention has been drawn to the low-temperature spectra of molecular crystals by a series of papers by I. V. Obreimov, A. F. Prikhot'ko, and their associates.[5-14,47] They showed that the molecular terms in the crystal spectra undergo specific changes as are found by comparison of the vapor absorption spectrum with the sharp-line spectrum of the crystal in polarized light at liquid-hydrogen or helium temperatures.

Certain peculiarities of the spectrum of benzene crystals seem to provide a most characteristic example of exciton splitting of the molecular levels in a crystal. This phenomenon was first studied in detail and interpreted in the papers of A. S. Davydov,[15] and has since been widely studied and recognized.

Thus the spectroscopic studies of benzene in various states of aggregation have provided a wealth of material, both for theoretical calculations on polyatomic and polyelectronic molecules and for solid-state theory and the interaction of light with crystals.

This review will attempt to summarize the data, mostly experimental, on the low-temperature electronic absorption spectra of benzene in the region of its lowest electronic transition, and thus to give a unified discussion of the material on this subject which has accumulated in recent years.

2. CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES OF BENZENE

The free benzene molecule is generally considered to be a regular hexagon of carbon atoms, with the hydrogen atoms distributed around the periphery. The point-group symmetry of the molecule is $D_{6h} = 6/mmm$.

According to Cox,[16] the benzene crystal is orthorhombic, having the space group D_{2h}^{15} = Pbca. The unit cell contains four molecules. The tilt of the molecules with respect to the axes of the unit cell was determined only approximately in this study by Cox. He showed that the plane of the molecule was roughly parallel to the b axis, and formed an angle of about 40° with the c axis. In 1954 Cox and Smith[17] carried out a refinement of the crystal structure at – 3° C. They found that the normal to the plane of the ring forms an angle of 48° 04′ with the c axis, 77° 04′ with the b axis, and 44° 49′ with the a axis. The arrangement of the molecules in the unit cell is shown in Fig. 1. The molecules at the face-centered positions are generated from the molecules at the vertices of the unit cell by the operations of the a, b, and c glide planes.

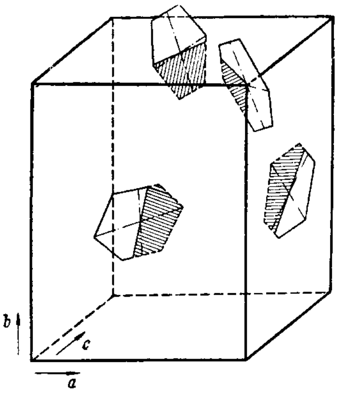

FIG. 1

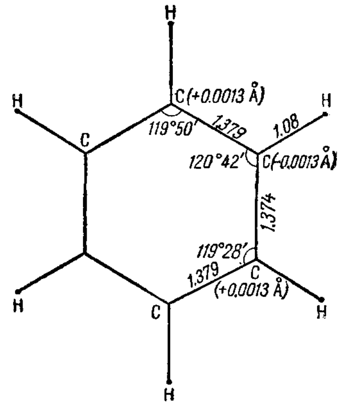

FIG. 2. Dimensions of the benzene molecule in the crystal.[17] The + and – signs indicate the deviations from coplanarity.

It has been shown from nuclear-magnetic-resonance absorption spectra that the benzene molecules reorient within the crystal structure about their plane normals within the temperature range from 90° to 120° K. Since this reorientation does not bring about any change in the structure, it obviously involves a gradual rotation of the molecules through an angle of 60°, bringing them into equivalent positions in the crystal structure.[18]

Requirements of close packing of molecules and the local symmetry of the crystal are responsible for the fact that the benzene molecule retains none of its symmetry elements but its inversion center.[19] According to Cox's data,[17] the lengths of the C—C bonds in the benzene molecule in the crystal are actually not all the same, the symmetry being $C_i = \bar{1}$ (Fig. 2).*

Benzene crystallizes at 5.43° C. Further cooling is accompanied by thermal contraction of the crystal dimensions. Table I gives the lattice parameters of benzene at various temperatures. The mean coefficients of thermal expansion of the crystal in the directions of the principal axes of thermal deformation have been estimated.[20] The values of the magnetic susceptibility and the principal indices of refraction have also been measured.[21] In crystals of the orthorhombic system, the deformation axes, the principal directions of the magnetic susceptibility, and the directions of the principal indices of refraction all coincide with the crystallographic a, b, and c axes. Table II gives the values of these quantities.

Table I

Crystallographic axis	Temperature, °C			
	-3^{17}	-20^{20}	-22^{16}	-195^{20}
a	7.460	7.43	7.44	7.277
b	9.666	9.63	9.65	9.452
c	7.034	6.99	6.81	6.728

Table II

Physical properties	Crystallographic axes		
	a	b	c
1. Lattice parameter (A)[17]	7.460	9.666	7.034
2. Refractive index[21]	1.544	1.646	1.550
3. Diamagnetic susceptibility (× 10⁶)[21]	65.2	37.9	61.3
4. Thermal expansion coefficient (× 10⁶)[20]	118	106	214
5. Energy of the electronic transition (ev)	4.686	–	4.690

A series of spectroscopic studies[23,32,45] has been conducted on a high-purity sample (99.9%) prepared in the Laboratory for Catalytic Synthesis (Institute of Organic Chemistry of the U.S.S.R. Academy of Sciences). The fundamental physical constants of the substance and the corresponding data from published tables are given in Table III.

Among the impurities found spectroscopically in this sample of benzene was phenol, which is apparently formed from it in the same way as β-naphthol is formed from naphthalene[22] by oxidation (or photooxidation) during storage. The concentration of phenol in the benzene samples studied could be estimated to be 0.03 – 0.1%. The absorption spectrum of phenol at

Table III

	Density	T_m, °C	T_b, °C	n_D^{20}
Preparation of Liberman	0.87906 (16°/4°)	5.43	80.1	1.5012
Tabulated data	0.879 (20°/4°)	5.4–5.5	80.1	1.5017

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*If one takes into account the rotational oscillations of the molecule about the six-fold axis, one must increase the bond lengths obtained from the Fourier analysis of the x-ray data by 0.015 A. The mean bond length is thus 1.377 + 0.015 = 1.392 A, with precision of 0.010 A.[17]

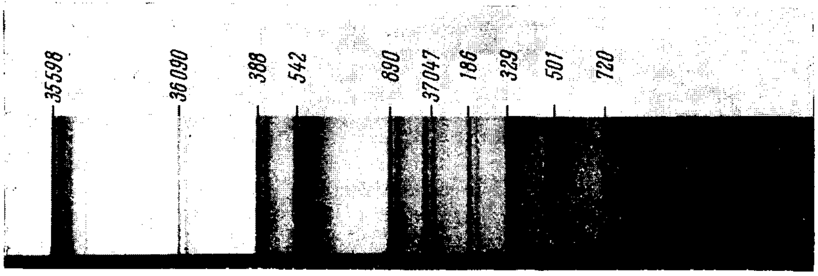

FIG. 3. The absorption spectrum of the phenol impurity in a benzene crystal. T = 20°K. Crystal thickness 0.54 mm. ISP-28 spectrograph.

77°K occurs in the region 35500 — 38000 cm^{-1} (see reference 23). Figure 3 shows the absorption of the phenol impurity in crystalline benzene at 20° K.

The Raman spectrum of liquid benzene shows a weak satellite at 984 cm^{-1}. Gerlach[24] interpreted this satellite as being analogous to the fundamental totally-symmetric vibration of the benzene molecule at 992 cm^{-1}, but arising from the isotopic molecule $C_5^{12}C^{13}H_6$. The concentration of such molecules in ordinary benzene is about 6%. As was shown by direct investigation,[25] the 984 cm^{-1} band also is about 6% as intense as the 992 cm^{-1} band, thus confirming this interpretation.

Spectroscopic studies have also been conducted on samples of deuterated benzene[28] of high deuterium content. The deuteration was performed by hydrogen exchange with liquid deuteroammonia or deuterium bromide.[26] This reaction was carried out in the Laboratory for Isotope Reactions (Karpov Institute of Physical Chemistry). Samples with degrees of deuteration from 56% to 96% have been studied.

The vapor spectra were taken in order to estimate the percent composition of the isotopic forms of the deuterobenzenes in the various samples. Detailed data on the spectra will be given below. The comparison of these spectra with Ingold's[4] data permitted us to identify the observed spectral bands with the electronic transitions of the various deuterated molecules. Then, knowing the overall degree of deuteration of the sample and the relative intensities of the bands of the individual components of the mixture, we could roughly determine the composition. We must note that traces of ordinary undeuterated benzene occur in the highly-deuterated samples.

The Raman spectrum of liquid deuterobenzene C_6D_6 exhibits a band similar to that occurring in ordinary benzene, due to the vibration of the isotopic $C_5^{12}C^{13}D_6$ molecule.[27]

3. ABSORPTION SPECTRUM OF BENZENE VAPOR

Let us recall some of the symmetry-dependent peculiarities of the energy levels of the benzene molecule.[3,28,30]

The benzene molecule has the point-group symmetry D_{6h}. A study of this molecule by the group-theoretical method gives the results presented in Table IV. The four levels obtained by solving the one-electron problem for a system of six π-electrons are A_{2u}, B_{2g}, E_{2u}, and E_{1g}, as indicated in the last column of Table IV. They are distributed in such a way[29] that the symmetry of the excited levels of the benzene molecule (the π electrons being excited) must correspond to the direct product of the representations E_{1g} and E_{2u} (the highest of the filled one-electron levels and the lowest of the free levels). By resolving this product into the irreducible representations of the group D_{6h}, we obtain the following symmetries of the excited states: B_{1u}, B_{2u}, and E_{1u}. The ground state of the molecule, as for most other molecules, possesses the

Table IV

D_{6h}	E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$	i	σ_h	$2S_6$	$2S_3$	$3\sigma_v''$	$3\sigma_v'$	m	T	R	n	Infra-red	Electronic transition	
x^2+y^2, z^2, xy, A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	2	0	0	2	Allowed		0
A_{1u}	1	1	1	1	1	1	—1	—1	—1	—1	—1	—1	0	0	0	0			0
R_z, A_{2g}	1	1	1	1	—1	—1	1	1	1	1	—1	—1	2	0	1	1			0
z, A_{2u}	1	1	1	1	—1	—1	—1	—1	—1	—1	1	1	2	1	0	1	Allowed		1
B_{1g}	1	—1	1	—1	1	—1	1	—1	1	—1	1	—1	0	0	0	0			0
B_{1u}	1	—1	1	—1	1	—1	—1	1	—1	1	—1	1	2	0	0	2			0
B_{2g}	1	—1	1	—1	—1	1	1	—1	1	—1	—1	1	2	0	0	2			1
B_{2u}	1	—1	1	—1	—1	1	—1	1	—1	1	1	—1	2	0	0	2			0
x^2-y^2, xy, E_{2g}	2	2	—1	—1	0	0	2	2	—1	—1	0	0	4	0	0	4	Allowed		0
E_{2u}	2	2	—1	—1	0	0	—2	—2	1	1	0	0	2	0	0	2			1
xz, yz, R_x, R_y, E_{1g}	2	—2	—1	1	0	0	2	—2	—1	1	0	0	2	0	1	1	Allowed		1
x, y, E_{1u}	2	—2	—1	1	0	0	—2	2	1	—1	0	0	4	1	0	3	Allowed		0
Γ_m	36	0	0	0	—4	0	0	12	0	0	0	4	36	3	3	30	7	12	6
T	3	—1	0	2	—1	—1	—3	1	0	—2	1	1	frequencies			20	4	7	4
Γ_{el}	6	0	0	0	—2	0	0	—6	0	0	0	2							

symmetry A_{1g}. The vibrationless electronic transition $A_{1g} \rightarrow \Gamma_i$ is allowed only when the direct product $A_{1g} \cdot \Gamma_{Pj} \cdot \Gamma_i$ contains A_{1g}, as may be denoted: $A_{1g} \cdot \Gamma_{Pj} \cdot \Gamma_i \propto A_{1g}$. Hence it follows that $\Gamma_{Pj} \cdot \Gamma_i \propto A_{1g}$. If we try to combine all the possible excited levels with the electric-moment vector Γ_{Pj}, we find that only one vibrationless electronic transition is allowed in the benzene molecule: $A_{1g} \rightarrow E_{1u}$. This transition is polarized in the plane of the molecule (see Table IV). Both of the other transitions, $A_{1g} \rightarrow B_{1u}$ and $A_{1g} \rightarrow B_{2u}$, are forbidden.

However, a quite essential feature in the benzene problem, just as for a series of other molecules, is the fact that the spectrum exhibits bands belonging to these forbidden transitions, since in such cases the electronic-vibrational transitions have non-zero matrix elements, although the purely-electronic transitions do not.

In fact, an electronic-vibrational transition is allowed when $\Gamma_{Pj} \cdot A_{1g} \cdot \Gamma_i \cdot \Gamma_k \propto A_{1g}$. When $\Gamma_i = B_{1u}$, we find: $\Gamma_{Pj} = \Gamma_{Px,y} = E_{1u}$. Then, $\Gamma_{Pj} \cdot A_{1g} \cdot \Gamma_i \cdot \Gamma_k = E_{1u} \cdot A_{1g} \cdot B_{1u} \cdot \Gamma_k \propto A_{1g}$, which is possible only when $\Gamma_k = E_{1u} \cdot B_{1u} = E_{2g}$. When $\Gamma_{Pj} = \Gamma_{Pz} = A_{2u}$, we have in precisely the same manner: $\Gamma_{Pj} \cdot A_{1g} \cdot \Gamma_i \cdot \Gamma_k = A_{2u} \cdot A_{1g} \cdot B_{1u} \cdot \Gamma_k \propto A_{1g}$, which is possible only when $\Gamma_k = A_{2u} \cdot B_{1u} = B_{2g}$. Thus, although we cannot observe the purely-electronic 0—0 band of the $A_{1g} \rightarrow B_{1u}$ transition in the spectrum, we can observe the 0—1 transitions (and the progression of combinations of the totally-symmetric oscillations with them). These transitions involve combination of the purely-electronic transition with the vibrations of symmetry E_{2g} polarized in the plane of the molecule, as well as combination with the vibrations of symmetry B_{2g}, polarized along the z axis perpendicular to the plane of the molecule.

Correspondingly, we obtain for $\Gamma_i = B_{2u} : \Gamma_k = A_{2u} \cdot B_{2u} = B_{1g}$, the transition being polarized along the z axis, and $\Gamma_k = E_{1u} \cdot B_{2u} = E_{2g}$ with polarization in the plane of the molecule. Since the benzene molecule has no vibrations of symmetry B_{1g} (see Table IV), the spectrum exhibits only the 0—1 transition (and its combinations) involving the combination of the 0—0 transition with the vibrations of symmetry E_{2g}. This absorption is polarized in the plane of the molecule.

The molecular spectrum of benzene in the near ultraviolet is well known, since the absorption of light by its vapor and solutions in the range 2600 — 2200 A has been studied repeatedly.[4,30,31] This absorption has been ascribed to the electronic-vibrational bands of the transition $A_{1g} \rightarrow B_{2u}$ for the following reasons:

1. The theoretical calculations of the positions of the excited levels, as carried out by various approximate methods, show that the lowest excited level of the benzene molecule is the B_{2u} level.[29]

2. The systematics of the bands in the vapor spectra[3,31] support the hypothesis that the vibrationless electronic transition is forbidden, while the vibration allowing the transition to take place has the symmetry E_{2g}. In broadest outline, this conclusion indicates that we must select between the two excited states B_{1u} and B_{2u}.

3. The study of the spectra of crystalline benzene in polarized light at low temperatures, as will be seen below, has shown most convincingly that the observed exciton splitting of the purely-electronic transition in the crystal spectrum corresponds to a symmetry B_{2u} of the excited level, and contradicts the other two possibilities.[23,32,33]

Figure 4 (see reference 3) shows a diagram of the absorption bands of benzene vapor in the region 2600 — 2200 A, and makes clear the structure of the spectrum.

The position of the forbidden purely-electronic transition corresponds to a frequency of 38089 cm^{-1}. The E_{2g} vibration, which has the value of 520 cm^{-1} in

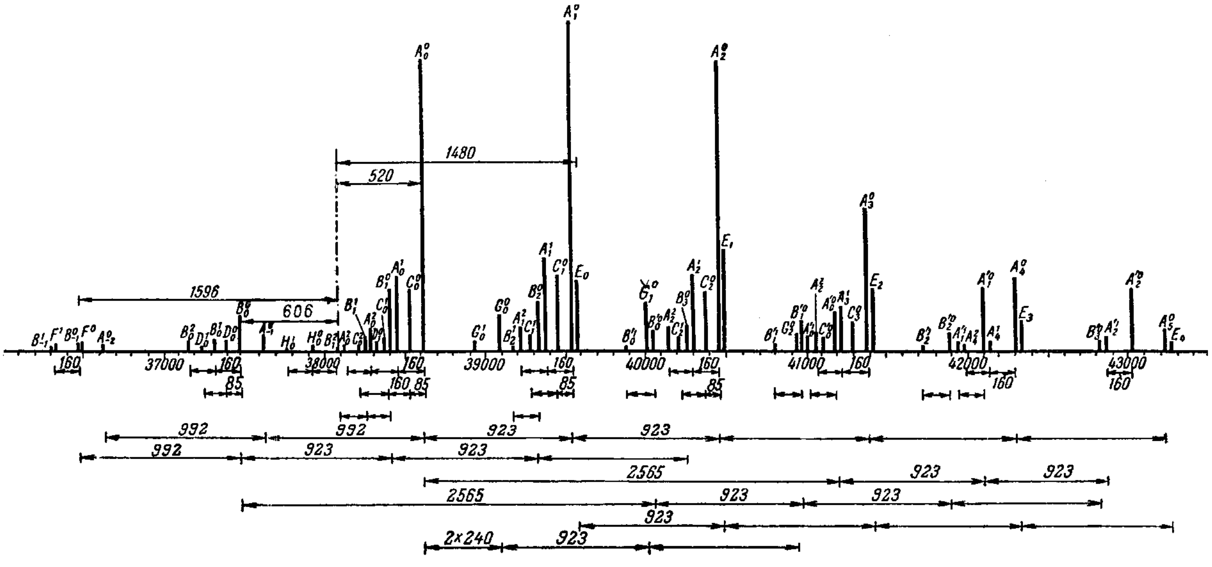

FIG. 4

the excited state, allows the transition, and gives rise to the first intense band in the spectrum at 38607 – 38612 cm^{-1}. We may easily discern in the spectrum the totally-symmetric breathing vibration of the molecule, which has the frequency 923 cm^{-1} in the excited state, and which forms a progression of bands containing many terms. In the long-wave portion of the vapor spectrum, many absorption bands are observed arising from excited vibrational levels of the ground state. The strongest of these is the band at 37482 cm^{-1}, which is interpreted as the transition with the vibrational level at 606 cm^{-1} corresponding to the E_{2g} vibration in the ground state. The bands in this portion of the spectrum are associated in a series by means of the same breathing vibration of the molecule, but the value for this vibration frequency in the ground state is larger, being 992 cm^{-1}. The portion of the bands of these latter series involving the excitation of several vibrational quanta in the excited state is located in the region of shorter wavelengths. Thus, the entire spectrum consists of several intercalated series having fundamental periodicities of 923 and 992 cm^{-1}. The correctness of such an interpretation of the vibrations of the benzene molecule is confirmed by the discovery in the Raman spectrum of an intense depolarized band at 606 cm^{-1}, as well as of an intense but polarized band at 992 cm^{-1} (see reference 34). In addition, the fluorescence spectrum of benzene vapor begins with a band at 37482 cm^{-1} (see reference 3), precisely coinciding with the absorption band at $37482 = \nu_{00} - \nu_{E_{2g}} = 38089 - 606$ cm^{-1}. This also confirms the correctness of the given interpretation of the spectrum. Thus, when the 0—0 transition is forbidden, the fluorescence spectrum must naturally begin with the band involving transition from the vibrationless level of the excited state to an E_{2g} vibrational level of the ground state (a 0—1 transition). That is, it must coincide with the corresponding absorption band.

If we increase the density of the vapor, the spectrum also exhibits absorption bands at longer wavelengths, due to multi-quantum combinations with the frequency 992 cm^{-1}. These bands coincide with the corresponding bands in the fluorescence spectrum.

More intense systems of absorption bands have been observed in the spectrum of benzene vapor in the vacuum-ultraviolet region. The first system (2050 – 1850 A) consists of broad bands arranged in groups of three. The total oscillator strength of this system is about 0.1. A second system starts below 1850 A, forming a strong continuous absorption, upon which a Rydberg series of absorption lines is superimposed. The oscillator strength in this transition is as great as 0.88.[35–37]

The vapor absorption spectra of the deuterated benzenes show an analogous structure. The 0—0 transition is forbidden in the spectrum of hexadeuterobenzene. Its combination with the non-totally-symmetric vibrations is allowed. The corresponding band occurs at 38788 cm^{-1}. In the studied samples,[38] the degree of deuteration was less than 100%, and thus the spectra of these samples exhibited bands of both completely deuterated benzene and of partially deuterated molecules containing from one to five atoms of deuterium. Figure 5 shows the initial portions of the absorption spectra of benzene vapor at various degrees of deuteration. Table V gives the frequencies of the bands of the electronic-vibrational transitions in the spectra of the various deuterated benzenes, as well as the positions of the forbidden 0—0 transitions and the values for the totally-symmetric and non-totally-symmetric vibrations.[38]

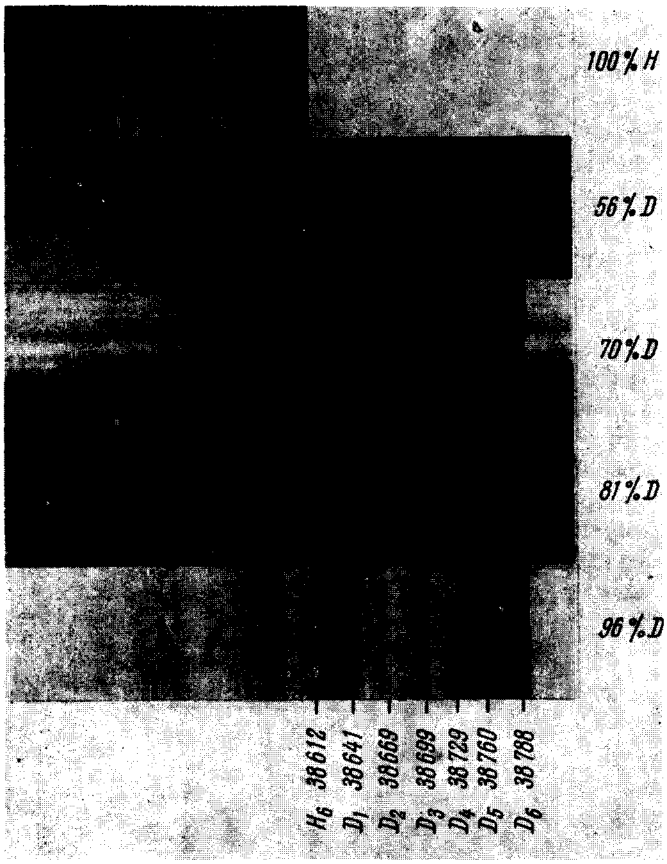

FIG. 5. Absorption spectra of benzene vapor at various degrees of deuteration. KS-55 spectrograph. Path length 1 cm. Side-arm at 15°C.

Table V

	$A_{1g}(\to B_{2u}\cdot E_{2g})$	$0\text{—}0_{\text{theor}}$	E_{2g}	A_{1g}
C_6H_6	38610 (av)	38089	521	923
C_6H_5D	38641	38124	517	920
$C_6H_4D_2$	38669	38155	511; 516.5	909
$C_6H_3D_3$	38699	38186	513	893 (?)
$C_6H_2D_4$	38729	38222	505; 510	895
C_6HD_5	38760	38260	~500	890
C_6D_6	38788	38289	499	879

According to the analysis, none of the deuterated benzenes exhibits the 0—0 transition, in spite of the loss of regular (D_{6h}) symmetry. The spectral region of this transition is devoid of bands. In the region of the 0—1 band ($0-0 + E_{2g}$), the bands in the spectra of the partially deuterated compounds occupy positions intermediate between the bands of ordinary and fully-deuterated benzene (from 38612 to 38788 cm^{-1}). They are spaced at practically identical intervals, varying from 27 to 31 cm^{-1} ($38788 - 38612 = 176 \cong 6 \times 29$). Thus, a calculated shift of 29 cm^{-1} per deuterium atom toward shorter wavelengths is observed. Here the bands of partially deuterated isomers (e.g., sym- and asym-trideuterobenzene $C_6H_3D_3$) are so close that it has not been possible to resolve them in the vapor spectra. A general analysis of the spectra shows that the vapor spectra of mixtures of the various deuterated molecules exhibit complete superposability of the bands of the individual components of the mixture.

4. ABSORPTION SPECTRA OF BENZENE SOLUTIONS

The spectra of solutions of benzene in various solvents permit us to study the absorption of light by individual molecules, just as the vapor spectra do. However, in solutions the interactions of the benzene molecules with the solvent molecules are substantial, and lead to small, but appreciable changes in the spectrum.

At room temperature, the spectrum of a solution of benzene in hexane[39] consists of eight strong bands in the region 2700 — 2200 A (Fig. 6). They are distributed at intervals of 920 cm^{-1}, and are easily superimposable on the intense groups of bands in the vapor spectrum, so that the contours of the solution bands form the envelope of the vapor bands. The shift in the beginning of this band series (38310 cm^{-1}) from the A^0 series of the vapor spectrum is about 300 cm^{-1}. There is a weak absorption band on the long-wavelength side of the spectrum, displaced by 1120 cm^{-1} from the first intense band; a second series of bands begins at a spacing of 920 cm^{-1} from it. On the photometric curve, the bands of this series appear as inflections on the sides of the bands of the principal series. Naturally, we must correlate this second series of bands with the vapor-spectrum series beginning with the 37482 cm^{-1} band, corresponding to the transition from the 606 cm^{-1} vibrational level of the ground state (the B^0 series).

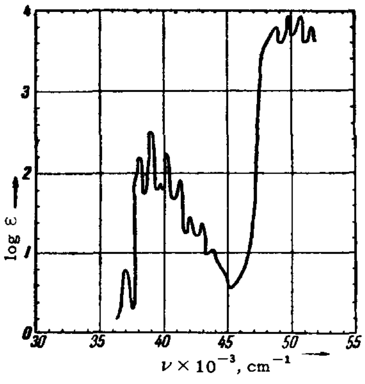

FIG. 6

The spectra of solutions of benzene in hexane have been studied[39] out to 1900 A (see Fig. 6). Another, more intense transition occurs at 2100 A, corresponding to the 2050 — 1850 A transition in the vapor spectrum.

The spectra of frozen solutions of benzene exhibit a somewhat different picture.[40] The bands of the fundamental series are retained, and are merely narrowed and shifted to shorter wavelengths by several cm^{-1} ($T = 77$°K, solvent dioxan or ethanol). On the other hand, all of the bands of the second series totally vanish, and are replaced by a new series of weak bands. The first of these is situated in the region of the 0—0 transition (at a spacing of about 500 cm^{-1} from the beginning of the first series). The disappearance of the second series of bands in the solution spectra upon lowering the temperature is normal, as expected from the resultant sharp decrease in the Boltzmann factor of the 606 cm^{-1} vibration, since combination with the latter is responsible for the existence of this series.

The appearance of a new series of bands in the solution spectrum at 77°K is apparently associated with the allowing of the 0—0 transition in the benzene molecule due to the field of the solvent molecules. This is confirmed by the fact that the intensity of the bands of the new series depends on the type of solvent. The relative intensities of the bands of this series with respect to those of the principal series are affected both by the polarity of the solvent (solutions in alcohol and dioxan were compared[40]) and by the structure of the solvent at 77°K (glassy solutions in alcohol and finely-crystalline solutions in hexane, dioxan, etc.[40]). A new series of bands has been found to appear in the spectrum of benzene upon addition of a few percent of carbon tetrachloride to a glassy hydrocarbon mixture at 77°K.[41]

A special type of benzene solution consists in the crystalline mixtures of benzene with its deuteration products. The spectroscopic characteristics of these solid solutions of benzene will be discussed below (Sec. 8).

5. CRYSTALLIZATION OF BENZENE AND GROWTH OF SPECIMEN CRYSTALS

When a thin film of liquid benzene in a cuvette is cooled and observed under the polarizing projection microscope,[42] microcrystals are seen to grow in the form of thin plates whose growth planes may coincide with various crystallographic planes. The crystals of benzene are biaxial, and hence the birefringence when the light is propagated normal to each of the planes varies. This determines the particular interference colors of crystal specimens with different growth planes.

When the liquid is cooled slowly in a quartz cuvette with a two-micron gap, flattened needles are found to grow, together with other crystals. These needles show a brown interference color between parallel polarizers and a gray color between crossed polarizers (path difference of about 200 mμ).

In observations carried out subsequent to crystal growth,[23] we have noted the growth of certain single crystals at the expense of others possessing different interference colors. This takes place in a narrow temperature range near the melting point, and is terminated by the melting of the specimen. The various stages of this process may be seen in the photographs in Fig. 7.

The onset of recrystallization most often coincides with the appearance of small droplets of liquid at the boundaries of the individual crystals. We may note simultaneously that the crystals begin to grow at the expense of one another. As the temperature is raised, the dimensions and number of the droplets increases, while the rate of encroachment of certain crystals upon others increases. Then the droplets merge into large regions of liquid, and the process ends with complete melting of the specimen. If we cool the cuvette at this moment, then instead of the conglomerate of various small crystals, only one or a few large single crystals grow. This fact has been widely utilized[23] for the growth of needed specimen crystals of benzene.

The phenomenon of growth of certain crystals at the expense of others is well known in metals, where it is called grain-boundary migration. It has also been observed in organic compounds, e.g., octachloropropane,[43] and has also been noted in the crystallization of orthorhombic bromine crystals and cubic cyclohexane crystals.[40] An analogous recrystallization is observed near the melting point of the deuterated benzenes.

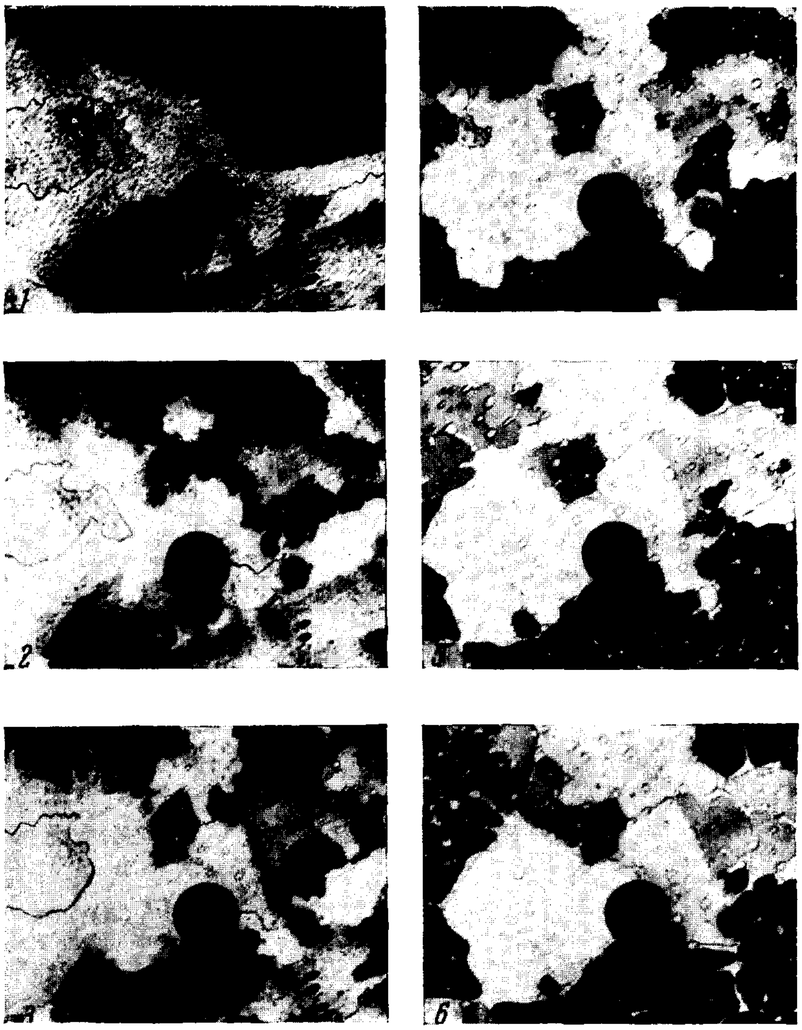

FIG. 7

Another characteristic of the recrystallization process is the fact that it may be halted at any moment by abrupt cooling. By making use of this peculiarity of the crystallization process, it has been possible to grow the three most common types of crystal, as identified by their interference colors. By cooling the prepared crystals to any required temperature (liquid nitrogen, hydrogen, or helium), one may obtain the necessary specimens for spectroscopic study.

We must note that when one subjects a conglomerate of small crystals to strong cooling, inhomogeneous strains may appear in the crystals, as manifested by patches of light against the dark background of the crystal between crossed polarizers. On the other hand, the larger crystals grown by grain-boundary migration exhibit good extinction between crossed polarizers even at very low temperatures. This may indicate that the reason for the growth of certain crystals at the expense of others is the mechanical (thermal) stresses arising at the crystal boundaries. The removal of these stresses near the melting point, when the mobility of the molecules in the crystal sites is enhanced, leads to the recrystallization of the individual grains of the conglomerate. This is also evidenced by a certain diffuseness in the absorption bands of finely-crystalline specimens, which, as we know,[44] may be caused by internal strains in the crystals. It is also not a coincidence that recrystallization has been found in crystals of high symmetry (cubic and orthorhombic). A characteristic of these crystal systems is the absence of well-defined cleavage planes. Thus, during growth of these crystals, various lattice planes may serve as the growth planes. Only by prolonged maintenance of the crystal near its melting point can we grow a specimen with a developed cleavage plane by recrystallization.

The crystal-optic measurements on the benzene specimens were carried out on a five-axis Fedorov stage at temperatures from – 5° to – 10° C. It was found that most of the benzene crystals showed the growth of planes containing the axis of lowest refractive index α, within an accuracy of 3° — 5°. The other index of the refractive-index ellipse lying in the plane of the various specimens formed an angle of from 2° — 3° to 45° with the axis of intermediate refractive index β. Thus, the lower the birefringence of the specimen was, the nearer the crystal plane was to the $\alpha\beta$ plane. This fact permits us to prepare quite thin benzene crystal plates with varying orientations of the refractive-index axes for spectroscopic studies.

We had previously carried out an analysis of the spectra of crystalline benzene,[45] and from indirect reasoning we proposed that the most probable orientation of the indicatrix was: $\alpha \parallel c$, $\gamma \parallel b$, and $\beta \parallel a$, where a, b, and c are the unit-cell axes. We later became acquainted with the studies of Guy and Lemanceau,[21] who directly measured the refractive indices of a benzene crystal. They established by a Laue pattern of the crystal that the b axis is the acute bisectrix of the angle between the optic axes. The results of this measurement are as follows: the indices of refraction for the sodium D line are given in Table II; the crystal is optically positive, and the angle between the optic axes $2V = 25° 20'$; and the orientation of the ellipsoid is $\alpha \parallel a$, $\gamma \parallel b$, $\beta \parallel c$. Because of the small difference between α and β, the crystal is nearly uniaxial, and hence the angle between the optic axes is unusually small.

The crystallization of hexadeuterobenzene and the other deuterated benzenes, as well as of mixtures of the various deuterated molecules, is completely similar to the crystallization of ordinary benzene. In the crystallization of mixtures of the deuterated benzenes, there are no indications of segregation, perfect single crystals are formed, and we may assume that these compounds form a continuous series of solid solutions.

6. ABSORPTION SPECTRUM OF BENZENE CRYSTALS

The optic properties of anisotropic crystals are characterized by the triaxial refractive-index ellipsoid, or indicatrix. Light incident normal to the plane of any section of the indicatrix is resolved in the crystal into two waves with mutually-perpendicular vibration directions. Each of these waves exhibits its own spectrum, which is a part, or component, of the absorption spectrum of the crystal as a whole. The spectra corresponding to absorption along the three principal axes of the indicatrix are called the principal components of the spectrum of the crystal. The set of three principal components characterizes the spectroscopic properties of the crystal in precisely the same way that the set of three principal indices of refraction characterizes its refractive properties. Among orthorhombic crystals, which include the benzene crystal, the crystallographic axes coincide with the axes of the indicatrix. The pinacoids naturally coincide with the principal sections of the indicatrix. Hence, the principal components of the spectrum of the benzene crystal are obtained with vibration directions of the incident polarized light lying parallel to the crystallographic axes.

The spectrum of crystalline benzene in unpolarized light has been known for a relatively long time.[46] However, it is essential to know the polarization of the absorption bands in order to classify them. Hence, we have obtained[23,32,45] absorption spectra in polarized light of benzene crystal plates grown along various planes. We compared these spectra with the vapor absorption spectrum in a manner analogous to that which had been applied previously to naphthalene.[47] Here we found series of bands possessing analogs in the gas spectrum, together with other series which

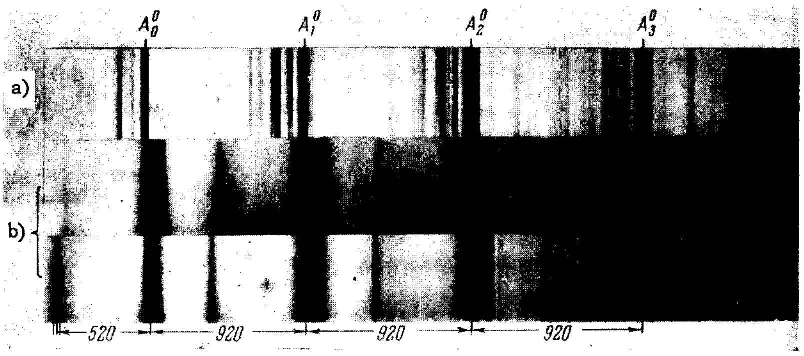

FIG. 8. (a) Vapor spectrum (path length 40 cm; side-arm temperature 18°C; Q-12 spectrograph). (b) Crystal spectrum (temperature 77°K; thickness $1\,\mu$; path difference in the crystal $10\ \mathrm{m}\mu$; Q-12 spectrograph).

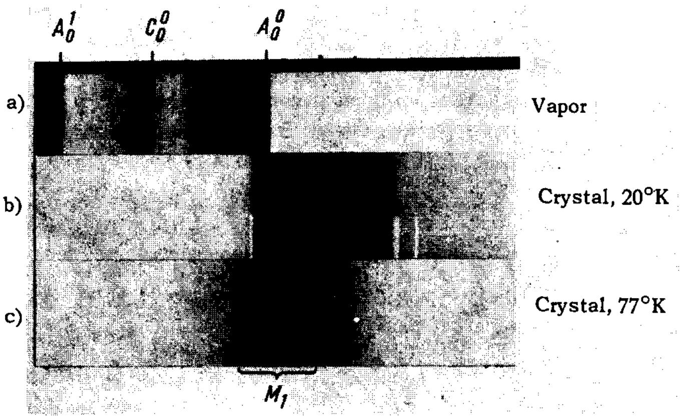

FIG. 9. (a) Vapor spectrum. (b) Crystal spectrum (20°K). (c) Crystal spectrum (77°K).

could not be correlated with corresponding bands in the gas spectrum.

The spectrum of a benzene crystal in polarized light incident normal to a plane near the $\alpha\beta$ section is shown in Fig. 8. For purposes of comparison, Fig. 8 also shows a photograph of the spectrum of benzene vapor. In order to match the crystal spectrum with the vapor spectrum, the latter has been shifted by 287 cm^{-1} toward longer wavelengths to make the intense bands of the fundamental series in both spectra coincide.

Just like the vapor spectrum, the absorption spectrum of the crystal exhibits the fundamental intense A^0 series of bands (see also Fig. 4). The first band of this series is due to the combination of the non-totally-symmetric E_{2g} vibration with the 0—0 transition. The periodicity of the series, which is ~ 920 cm^{-1}, is due to the totally-symmetric breathing vibration of the molecule. The retention of this series in the crystal spectrum shows that it is associated with the excitation of individual molecules, and may hence be termed the "molecular" M series. At 77°K, the bands of this series are broad and exhibit only a hint of structure, so that it is quite impossible to compare them with the absorption lines of the vapor. We should merely note that if the envelope of the group of bands in the vapor spectrum is sharply weakened on the long-wavelength side (see the diagram in Fig. 4), the broad bands of the crystal spectrum become practically symmetrical.*

At 20°K, the structure of the M bands becomes quite distinct, and the broad bands of the spectrum are resolved into a series of narrow bands. Figure 9 shows matched photographs of the first group of bands of the M series (the M_1 group) in the spectra of the vapor and of the crystal at 77° and 20°K. As we see, the A^0 series is the only series from the vapor spectrum which is retained in the crystal spectrum. However, besides these bands, a group of satellites on the short-wavelength side of the M bands is visible in the crystal spectrum.

A characteristic peculiarity of the bands of the M series is their low degree of polarization, amounting only to barely differing intensities of the bands in the various components of the crystal spectrum. The locations of the centers of the bands in this series are precisely the same for all components. The same is true of the satellites of the bands of the M series.

At 20°K, the fundamental band of each group in this series is split into two components: $M_1 = 38351$, 38360 cm^{-1}, $M_2 = 39275$, 39285 cm^{-1}, $M_3 = 40205\ \mathrm{cm}^{-1}$, and $M_4 = 41130\ \mathrm{cm}^{-1}$ (the doublet is not resolved in the two latter bands). The spacing between the groups of bands may be calculated even more precisely than in the spectrum at 77°K, and is found to be 924 cm^{-1}. The shift in the entire series with respect to the vapor spectrum decreases with decreasing temperature, and at 20°K is only 254 cm^{-1}, as compared with 287 cm^{-1} at 77°K. This gives the impression that the doublet structure of the bands of the M series is associated with the twofold degeneracy of the initial molecular term corresponding to this band, which has a symme-

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*The spectra in Fig. 8 have been matched according to their band maxima.

Table VI

Designation	Frequency, cm^{-1}	Intensity*	Polarization			Interpretation	Probable error of interpretation	Remarks	Analog in the vapor spectrum
			In terms of spectral components	In terms of the crystallographic axes	Distance from the 0–0 transition, cm^{-1}				
—	37200	10^{-3}**	?	?	—635	00 — 606 (E_{2g})	~30	A broad band with intensity increasing with the temperature	$B_0^0 = 37482$
K_1	803 839 846 847	4 6(II) 7(II) 6	II > I II $\left.\begin{matrix}\text{II}\\ \text{I}\end{matrix}\right\}$ I = II)	a c	—32 4 11 12	$\left.\begin{matrix}A_{1g} \to A_{2u}\\ A_{1g} \to B_{1u}\end{matrix}\right\}$ 00	—	Theoretical position of the 0–0 transition is 37835	none (38089)$_{\text{theor}}$
	874 912 ~929	1 2 2(II)	I = II I = II II	— — ?	39 77 94	00 + 39 00 + 77 00 + 94	—	Lattice vibrations (?)	none
—	38229	2	I > II	—	394	?	—		none
M_1	351 360	10 10	I > II I > II	— —	516 525	00 + 516 00 + 525	—	Splitting of the $A_{1g} \to (B_{2u} \cdot E_{2g})$	$A_0^0 = 38612$
	380 398 416 429 445 447 485	3 4 3 5 2(II) 4 1	I > II I > II I > II I > II $\left.\begin{matrix}\text{II}\\ \text{I}\end{matrix}\right\}$ I > II I > II	— — — — — —	545 563 581 594 610 612 650	00 + 520 + 25 00 + 520 + 43 00 + 520 + 61 00 + 520 + 74 00 + 520 + 91 00 + 520 + 130	—	Lattice vibrations (?)	none
—	603	1 (II)	II	?	768	?	—		none
K_1^{I}	646 655	4 2 (II)	I II	? ?	811 820	00 + 811 00 + 820	—	Splitting of the term 00 + 815 (?)	none
K_2	724 743 764 772 773	4 5 6 (II) 9 (II) 6	II > I I > II II $\left.\begin{matrix}\text{II}\\ \text{I}\end{matrix}\right\}$ I = II	a — c	889 908 929 937 938	00 + 925	—	Theoretical position of the 0–0 + A_{1g} transition is 38760	none
K_1^{II}	822 824	6 5 (II)	I II	? ?	987 989	00 + 987 00 + 989	—	Splitting of the term 00 + 988 (?)	none
	~839 ~853	2 1	II > I II > I	? ?	1004 1018	00 + 988 + 16 00 + 988 + 30	—	Lattice vibrations (?)	none
K_1^{III}	875	2 (II)	II	?	1040	?	—		none
	886 888	5 3 (II)	$\left.\begin{matrix}\text{I}\\ \text{II}\end{matrix}\right\}$ I > II	? ?	1051 1053	00 + 1051 00 + 1053	—	Spliting of the term 00 + 1052 (?)	
	895	1	I	?	1060	?	—		
	901 909	3 (II) 4	II I	? ?	1066 1074	00 + 1066 00 + 1074	—	Splitting of the term 00 + 1070 (?)	
	935	2(II)	II	?	1100	?	—		

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*The intensity was estimated visually from the negative in a ten-step system for component I of the spectrum (Fig. 14). In the cases indicated in parentheses, component II was estimated.

**The intensity is given for the spectrum of the crystal at 77°K.

Table VI. (cont'd)

Designation	Frequency, cm^{-1}	Intensity	Polarization			Interpretation	Probable error of interpretation	Remarks	Analog in the vapor spectrum
			In terms of spectral components	In terms of the crystallographic axes	Distance from the 0–0 transition, cm^{-1}				
K_1^{IV}	978 981	6 5 (II)	I II	? ?	1143 1146	00 + 1143 00 + 1146	—	Splitting of the term 00 + 1145 (?)	none
—	39016	1	I = II	?	1181	?	—		none
K_1^{V}	039 050	3 (II) 3	II I	? ?	1204 1215	00 + 1204 00 + 1215	—	Splitting of the term 00 + 1210 (?)	none
K_1^{VI}	124	3	I > II	?	1289	00 + 1289 (?)	—		none
—	159	2	I = II	?	1324	?	—		none
K_1^{VII}	205 216	3 3	I ≫ II II ≫ I	? ?	1370 1381	00 + 1370 00 + 1381	—	Splitting of the term 00 + 1375 (?)	none
M_2	275 285	10 10	I > II I > II	— —	1440 1450	00 + 520 + 920 00 + 520 + 930	0	Splitting of the $A_{1g} \to (B_{2u} \cdot E_{2g} \cdot A_{1g})$ transition	$A_1^0 = 39534$
	298 318 343 356 372	3 9 4 5 4	I > II I > II I > II I > II I > II	— — — — —	1463 1483 1508 1521 1537	00 + 520 + 925 + 18 00 + 520 + 925 + 38 00 + 520 + 925 + 63 00 + 520 + 925 + 76 00 + 520 + 925 + 92	—	Lattice vibrations (?)	none
—	391 398	3 3	I > II I > II	— —	1556 1563	00 + 516 + 2·520 00 + 525 + 2·520	0 −2	Splitting of the $A_{1g} \to B_{2u} \cdot E_{2g} \cdot A_{2u} \cdot A_{2u}$ transition (?)	$K_0^0 = 39638$
—	444 446	3 2 (II)	$\left.\begin{matrix}\text{I}\\ \text{II}\end{matrix}\right\}$ I > II	—	1609 1611	00 + 1609 00 + 1611	—	Splitting of the term 00 + 1610 (?)	none
K^{I}	529 544 559	2 4 1	I = II I ≫ II II > I	? ? ?	1694 1709 1724	?	—		none
	571 583	5 3	I > II I = II	? ?	1736 1748	00 + 925 + 811 00 + 925 + 820	0 3	Splitting of the term 00 + 925 + 815 (?)	
—	~643	1	I > II	—	1808	?	—		none
K_3	665 672 687 696	8 (II) 7 6 7	$\left.\begin{matrix}\text{II > I}\\ \text{I}\end{matrix}\right\}$ $\left.\begin{matrix}\text{II}\\ \text{I = II}\end{matrix}\right\}$	a c	1830 1837 1852 1861	00 + 2·925	—	Theoretical position of 00 + 2 · A_{1g} is 39685	none
K_2^{II}	751 756	6 4 (II)	I II	? ?	1916 1921	00 + 925 + 987 00 + 925 + 989	4 7	Splitting of the term 00 + 925 + 988 (?)	none
	766 778	1 1	I = II II > I	? ?	1931 1943	00 + 925 + 988 + 18 00 + 925 + 988 + 30	—	Lattice vibrations (?)	none

Table VI. (cont'd)

Designation	Frequency, cm⁻¹	Intensity	Polarization			Interpretation	Probable error of interpretation	Remarks	Analog in the vapor spectrum
			In terms of spectral components	In terms of the crystallographic axes	Distance from the 0–0 transition, cm⁻¹				
K_2^{III}	801	1	II > I	?	1966	?	—		none
	812 815	4 3	I II } I > II	— —	1977 1980	00+925+1051 00+925+1053	1 2	Splitting of the term 00 + 925 + 1052 (?)	
	826 834 843 860	3 2 4 2 (II)	I = II I I > II II > I	? ? — ?	1991 1999 2008 2025	00+925+1070 ?	~4	Splitting of the term 00 + 925 + 1070 (?)	
K_2^{IV}	887	3	I > II	—	2052	00+925+1145 (?)	—18		none
	901 904	4 (II) 5	II I	? ?	2066 2069	00+516+2·775 00+525+2·775	0 —6	Splitting of the $A_{1g} \rightarrow B_{2u} \cdot E_{2g} \cdot B_{2g} \cdot B_{2g}$ transition (?)	$W_0^0 = 40160$
K_2^{V}	964 ~974	4 (II) 4	II I	? ?	2129 2139	00+925+1204 00+925+1215	0 —1	Splitting of the term 00 + 925 + 1210 (?)	none
K_2^{VI}	~40050	5	I > II	—	2215	00+925+1289(?)	1		none
K_2^{VII}	130 139	5 4 (II)	I ≫ II II ≫ I	? ?	2295 2304	00+925+1370 00+925+1381	0 —2	Splitting of the term 00 + 925 + 1375 (?)	none
M_3	204	9	I > II	—	2369	00+520+2·925	—1	The $A_{1g} \rightarrow B_{2u} \cdot E_{2g} \cdot A_{1g} A_{1g}$ transition	$A_2^0 = 40456$
	245 267 295	8 8 8	I > II I > II I > II	— — —	2410 2432 2460	00+520+2·925+41 00+520+2·925+63 00+520+2·925+91	—	Lattice vibrations (?)	none
—	317	7	I > II	—	2482	00+3520+925 (?)	—3	The $A_{1g} \rightarrow B_{2u} \cdot E_{2g} \cdot E_{2g} \cdot A_{2g} \cdot A_{1g}$ transition	$K_1^0 = 40559$
—	367	3	I > II	—	2532	00+925+1610 (?)	—3		none
K_3^{I}	468	3	I ≫ II	?	2633	?	—		?
	495 504	4 4	I > II I > II	— —	2660 2669	00+2·925+811 00+2·925+820	—1 —1	Splitting of the term 00 + 2·925 + 815 (?)	none
K_4	600 615	4 6 (II)	I > II II > I	*a* *c*	2765 2780	00+3·925	—	$00+3 \cdot A_{1g}$	none
K_3^{II}	683	4	I > II	—	2848	00+2·925+988 (?)	10		none
K_3^{III}	~740 ~762 ~770	1 1 1	I > II I > II I > II	— — —	2905 2927 2935	00+2·925+1052 (?) 00+2·925+1070 (?)	3 11		none
K_3^{IV}	~800	1	I > II	—	2965	00+2·925+1145 (?)	30		none
	~837	2 (II)	II > I	?	3002	00+520+925+2·775 (?)	7	The $A_{1g} \rightarrow B_{2u} \cdot E_{2g} \cdot B_{2g} \cdot B_{2g} \cdot A_{1g}$ transition	$W_1^0 = ?$
K_3^{V}	~905	1	I = II	?	3070	00+2·925+1210 (?)	10		none
M_4	~41130	1	I > II	—	3295	00+520+3·925 (?)	0	The $A_{1g} \rightarrow B_{2u} \cdot E_{2g} \cdot A_{1g} \cdot A_{1g} \cdot A_{1g}$ transition	$A_3^0 = 41378$
K_5	~550	1	I = II	*a/c*	3715	00+4·925	15	$00+4 A_{1g}$	none

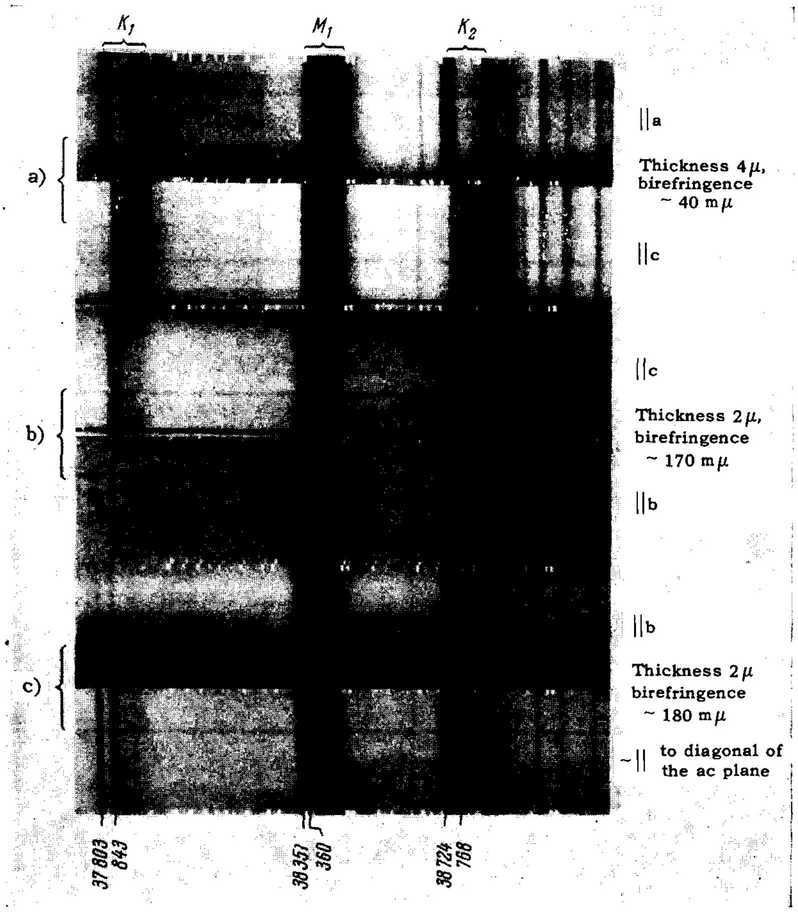

FIG. 10

try of $E_{1u} = B_{2u} \cdot E_{2g}$. This problem will be discussed in more detail in Sec. 9.

The M series and certain weak bands (see Table VI) account for the total number of coincident bands in the crystal and vapor spectra. No direct correspondence can be found for any of the other bands of the crystal spectrum in the spectrum of benzene vapor. We should note in this regard that the frequently stated similarity of these spectra is to a considerable degree illusory. An entire group of series observed in the vapor spectrum arises from transitions from the vibrational sublevels of the ground state (the B and D series, etc.). The occupancy of these levels declines exponentially with decreasing temperature, and the corresponding transitions practically do not occur at low temperatures.

Figure 10 shows a comparison of photographs of the initial regions of a series of components of the spectra of various crystals of benzene at 20° K. The crystal specimens differed from one another in orientation of the indicatrix with respect to the plane of growth.

In addition to the M series in the spectrum, there are relatively strong bands forming the K series. This series contains sharply polarized absorption bands, which appear either solely in certain components of the spectrum, or with much greater relative intensity in certain components. The first group of this series (K_1) is situated near the theoretical position of the purely-electronic transition. Its bands may hence be interpreted as the components of the 0—0 transition, which is allowed by the crystal field, since the symmetry of the crystal is lower than the symmetry of the molecule, and thus the selection rule is abolished. The detailed systematics of the absorption bands of the crystal spectrum may be found in Fig. 14 and Table VI.

7. THE DAVYDOV SPLITTING

A theoretical determination of the possible polarization of the bands forming the components of the purely-electronic transition in the benzene crystal has been carried out by Davydov[33] on the basis of his theory of exciton absorption in molecular crystals.[15] Starting with the fact that the four benzene molecules within the unit cell of the crystal are so arranged that their planes are approximately parallel to the b axis,* he obtained the following results. If we assume that

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*In the later x-ray structure analysis of the benzene crystal,[17] it was established that the planes of the molecules are tilted 13° with respect to the b axis (see Fig. 1).

the symmetries of the excited levels of the benzene molecule may be B_{1u}, B_{2u}, or E_{1u} (see Sec. 3), then in the crystal:

(1) the forbidden molecular transition to the B_{1u} level becomes allowed and must be polarized along the b axis of the crystal;

(2) the forbidden molecular transition to the B_{2u} level corresponds in the crystal to a doublet of bands, one of which is polarized along the c axis, and the other along the a axis;

(3) the allowed doubly-degenerate molecular term corresponding to the transition to the E_{1u} level becomes split in the crystal, and must appear in the form of a triplet with components along all three axes of the crystal.

A more precise calculation of the polarization of the components of the purely-electronic transition has been made,[48,49] taking into account the most recent data on the crystal structure of benzene.[17] This calculation showed that the transition to the B_{2u} level must be manifested in the crystal as a triplet with components along all three crystal axes, rather than a doublet. The inclination of the molecular planes with respect to the b axis is responsible for an additional absorption polarized along this axis (in contradiction to Davydov's results). However, the small amount of tilt (13°) may be related to the low intensity of this band. In a first-order approximation, we can neglect this absorption (see also Sec. 9). Another result of the more precise calculation[48] is the fact that the transition to the B_{1u} level must also be manifested in the crystal as a triplet with components along all three crystallographic axes.

Although a rather large number of studies have already been devoted to the absorption spectrum of the benzene crystal,[46,32,23,45,50] they have not involved any direct x-ray determination of the plane of growth of the studied specimens. As has been explained (see Sec. 5), various planes of the benzene crystal may appear as the plane of growth in the thin-film cuvette. If we take this phenomenon into account, the discrepancies among the various published papers in the identification of the polarizations of the individual bands in the spectrum are not remarkable.

In order to interpret the absorption spectrum of the benzene crystal, we must first of all solve two problems. First, what is the polarization of the components of the purely-electronic transition in the observed spectrum with respect to the crystallographic axes? Second, what is the symmetry of the excited level of the benzene molecule responsible for the absorption band being studied?

We shall attempt to make a careful review of the experimental results on the spectroscopic and refractive properties of the benzene crystal, to answer the questions posed above, and to find the most plausible interpretation of this part of the benzene problem.

Let us consider the absorption spectrum of a crystal showing a very small birefringence (with a path difference of about 10 mμ in a thickness of the order of 1μ) and having a plane of growth close to the $\alpha\beta$ section of the indicatrix. If we interpret the obtained results in the light of the data of Guy and Lemanceau,[21] we must conclude that this spectrum involves the absorption of light incident normal to the ac plane of the crystal. Then, the bands at 37786 and 37811 cm^{-1} at 77° K, or correspondingly at 37803 and 37843 cm^{-1} at 20° K (see Figs. 8 and 10) must correspond to the components of the purely-electronic transition, either along the c and a axes, respectively, or vice versa. This conclusion is quite firmly established, and has been confirmed in a number of studies.[32,33,45,50]

The problem of relating the polarization of each of these bands to a concrete direction in the crystal is more complex. It is exceedingly difficult to determine experimentally the polarization of these bands by use of a compensator or a quartz plate of known path difference to identify the directions within the crystal. The reason for this is that we must use a thin crystal having a small birefringence to obtain a distinct spectrum, and it is difficult to estimate the changes introduced by the compensator. In this regard, special studies have been made of crystals of about five microns thickness or more, exhibiting an appreciable path difference. It was thus established that the spectrum begins at shorter wavelengths for the direction showing the greater refractive index. Hence it follows (see Sec. 5) that the long-wavelength component of the purely-electronic transition (37803 cm^{-1} at 20° K) is polarized along the a axis of the crystal.

According to Davydov's calculations,[33] the observation of doublets of a and c bands in the absorption spectrum of the crystal provides evidence for the interpretation of the bands. Thus, in deciding between the two possible forbidden transitions in the benzene molecule to the B_{1u} and B_{2u} levels, we must choose the latter (B_{2u}). Hence the same calculations indicate that there should be no absorption when the incident light is polarized along the b axis of the crystal.

Figure 10 shows photographs of spectra of benzene crystals with various planes of growth. Out of the extensive collection of such photographs containing spectra exhibiting practically all possible intensity ratios of the components of the purely-electronic transition, we have selected and shown in Fig. 10 only those exhibiting especially sharp polarization of the bands. As was shown above, the spectrum of specimen a corresponds to incident light normal to the ac plane. The spectra of the two other specimens characteristically show a substantial, if not complete, diminution of one of the components of the spectrum in the region of the 0—0 transition. According to Davydov's predictions, this may be due to the fact that in the latter specimens the b axis lies in the plane of growth or near it. This conclusion has been made[23] previously as well, and correspondingly, the plane of growth in specimen b has been taken as the cb plane.

As was indicated above, the crystal spectrum contains no analogs of any of the series of bands in the vapor spectrum arising from transitions involving excited vibrational levels of the ground state. However, upon gradual heating of the crystal, a relatively broad band at about 37200 cm^{-1} was found to appear, its intensity increasing with the temperature.[32] This band is shifted by approximately 285 cm^{-1} from the first line of the B^0 series in the vapor (37482 cm^{-1}), and apparently may be related to it. However, there are no quantitative measurements at present on the intensity of this band at various temperatures to be tested against the exponential law to be expected from the Boltzmann factor for the 606 cm^{-1} vibration.

The luminescence of crystalline benzene at low temperatures[46,32,50,51] begins with a band at about 37200 cm^{-1}. A detailed study of the structure of this band and correlation of it with the "thermal" absorption band has not yet been carried out. Hence, the interpretation of the luminescence spectrum as involving transitions from exciton states to vibrational levels of the ground state[50] does not seem very convincing. The problem of the nature of the luminescence of the benzene crystal still awaits solution, especially in view of the known general peculiarities of the luminescence of similar crystals.[52]

Thus, an analysis of the experimental data and a comparison with the theoretical predictions permits us at present to draw the following conclusions:

1. The symmetry of the transition responsible for the absorption of benzene in the range 2600 – 2200 A is $A_{1g} \rightarrow B_{2u}$. This transition is forbidden in the free molecule, but is permitted in the form of an exciton doublet of highly polarized bands in the crystal.
2. The bands of the purely-electronic transition at 37803 and 37843 cm^{-1} are polarized along the a and c axes, respectively (at 20°K).
3. There is practically no light absorption for polarization along the b axis of the crystal in the region of the purely-electronic transition.

The fine details of the crystal spectra will be treated in Sec. 9.

8. ABSORPTION SPECTRA OF CRYSTALS OF THE DEUTEROBENZENES AND THEIR MIXTURES

The absorption spectrum of a crystal of isotopically pure hexadeuterobenzene has apparently not yet been studied.* This is due to the difficulty of carrying out a complete exchange reaction of deuterium for hydrogen. Even in the preparations containing 99% D, the concentration of C_6HD_5 could amount to 6%. However, this fact need not interfere with the analysis of the spectrum, since the presence of such an impurity hardly disturbs the crystal structure, owing to the similarity of physical and chemical properties of the isotopic molecules. This idea is confirmed by the fact that the spectrum of ordinary benzene dissolved in hexadeuterobenzene is shifted by only ~ 19 cm^{-1} from its position in a pure crystal of ordinary benzene.

The absorption spectrum of the hexadeuterobenzene crystal is completely analogous in structure to that of ordinary benzene. The region of the purely-electronic transition exhibits highly polarized absorption bands showing the same pattern as in ordinary benzene. The exact extent of the band splitting cannot be determined from the spectra of the specimens, which are not isotopically pure. One cannot do this because the splitting is considerably dependent on the concentration of deuterium, as will be seen below.[38] We may show, however, that the splitting is of the same order of magnitude as in the spectrum of ordinary benzene (about 30 – 40 cm^{-1}). The bands of the 0–0 transition are distributed about 38040 cm^{-1}, corresponding to a decrease in the E_{2g} vibration frequency to about 500 cm^{-1}. The frequency of the totally-symmetric vibration is reduced to 880 cm^{-1} (in agreement with Ingold's data[4] on the vapor spectra). The M series is shifted by 190 cm^{-1} toward shorter wavelengths.

A spectroscopic study of mixed crystals consisting of the various deuterated benzenes was of especial interest. The absorption spectrum of these mixed single crystals, just like the spectrum or vapor mixtures (see Fig. 5), consists of a superposition of the spectra of the individual components (Fig. 11) in the region of the E_{2g} combination frequency. The intensities of the bands in the group correspond roughly to the concentrations of the given deuterated benzenes. This was verified by the agreement between the average con-

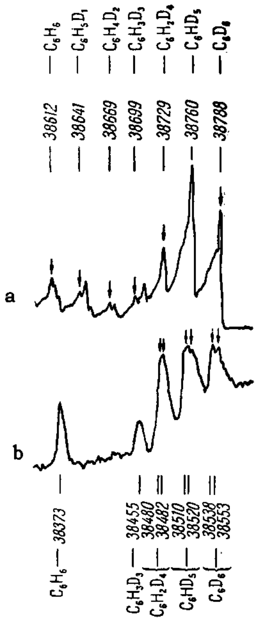

FIG. 11. Microphotometer trace of the spectrum of a mixed crystal obtained by mixing a sample having 81% D with ordinary benzene. The spectral region corresponds to the combination of the 0–0 transition with the E_{2g} vibration. The same spectral region for the vapor of the 81% D sample is shown for comparison. a – vapor; b – crystal (20°K).

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*An analysis of Zmerli's[50] data shows that the sample which he assumed to be pure C_6D_6 was actually a mixture of C_6D_6 with C_6HD_5.

centration of deuterium and the data on the degree of deuteration of the sample. The starting points of the absorption spectra of the individual isotopic forms are displaced with respect to the corresponding vapor spectra by 240 – 250 cm^{-1}. The spacings between the bands are the same as in the vapor spectrum (from 28 to 31 cm^{-1}).

The spectra of the crystals of the deuterobenzenes also exhibit splitting of the doubly-degenerate molecular vibration E_{2g} (the bands of the M series). This phenomenon is not so clearly marked as in the spectrum of benzene since the bands are somewhat diffuse, but in a number of cases it may be measured. The magnitude of this splitting is 10 – 15 cm^{-1}. The weaker the corresponding band is (the lower the concentration of the molecule of the given type), the less the splitting is found to be. A number of the samples contained ordinary benzene as an impurity (in concentrations below 10%). This component is manifested in the spectrum in the form of a sharp single absorption band at 38373 cm^{-1}. Thus, we may suppose that the magnitude and distinctness of the splitting of this electronic-vibrational level is proportional to the concentration of the given component of the mixture.

The region of the 0—0 transition in the spectra of the mixed crystals exhibits distinct groups of polarized bands belonging to the individual components of the mixture. This fact was established by comparison of the absorption spectra of crystals obtained from samples of varying degrees of deuteration. An additional criterion for the correctness of the identification of the doublet of 0—0 transition bands of each of the deuterated benzenes was the agreement between the magnitudes of the molecular vibration frequencies with the data from the vapor spectra.

The spectrum of the specimen with 96% D shows a doublet of a- and c-bands of hexadeuterobenzene with a splitting of about 22 cm^{-1}, and a doublet of the same bands of C_6HD_5 with a splitting of 14 cm^{-1} (Fig. 12). The spectrum of the specimen with 94% D shows, besides the bands of C_6D_6 and C_6HD_5, weak bands of $C_6H_2D_4$ and traces of C_6H_6. Both of these bands are unpolarized and single. The spectrum of the mixed crystal obtained from the sample containing 81% D shows in the region of the 0—0 transition a group of highly polarized doublets corresponding to C_6D_6, C_6HD_5, and $C_6H_2D_4$. Unpolarized bands of $C_6H_3D_3$ and C_6H_6 can also be seen.*

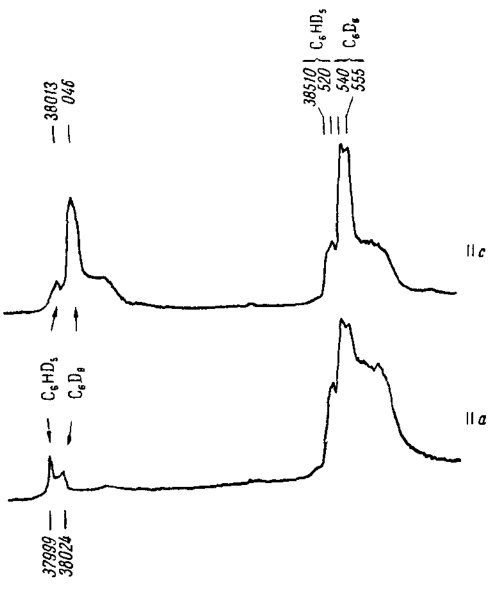

FIG. 12. Microphotometer trace of the initial region of the spectrum of a crystal obtained from a 96% D sample.

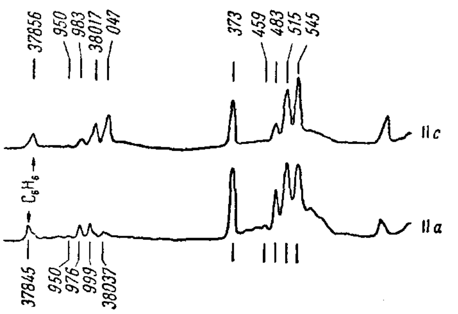

FIG. 13. Microphotometer trace of the initial region of the spectrum of a crystal obtained from a 81% D sample to which ordinary benzene has been added (in about 25% concentration).

In order to determine whether the extent of splitting of the 0—0 doublet depends on the concentration of the corresponding component in the mixture, a study was made of the spectra of specimens prepared by mixing a sample having an original concentration of 81% deuterium with ordinary benzene. It turned out that when the content of benzene in the specimen was greater than 10 – 15%, the previously unpolarized 0—0 transition underwent splitting, which amounted to 11 cm^{-1} at a benzene concentration of 25% (Fig. 13).*

Just as in the crystal spectrum of ordinary benzene, the spacing between the short-wavelength band of the doublet (the c band) to the doublet in the region of the E_{2g} combination corresponds to the frequency of this vibration in the excited electronic state. The values for this vibration frequency found from the crystal spectra are in good agreement with those determined by Ingold from the vapor spectra;[4] as the number of deuterium atoms in the molecule increases, this value decreases from 521 cm^{-1} for benzene to

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*The $C_6H_2D_4$ in the spectra of certain specimens was manifested in the form of a close doublet of spacing 5 cm^{-1}. These bands apparently belong to two isomers of this molecule, symmetric and asymmetric.

*In the study of the absorption spectra of the series of mixed crystals of the deuterobenzenes, a parallel shift was noted in the spectra, but its cause has not yet been explained. In some cases this shift was as much as 10 cm^{-1}. The shift did not disturb the relative arrangement of the absorption bands or their polarization. Hence, the data given here and below on the absolute values of the band frequencies have been adjusted on the assumption that the frequency of the band of the M_1 series for hexadeuterobenzene is 38545 cm^{-1}.

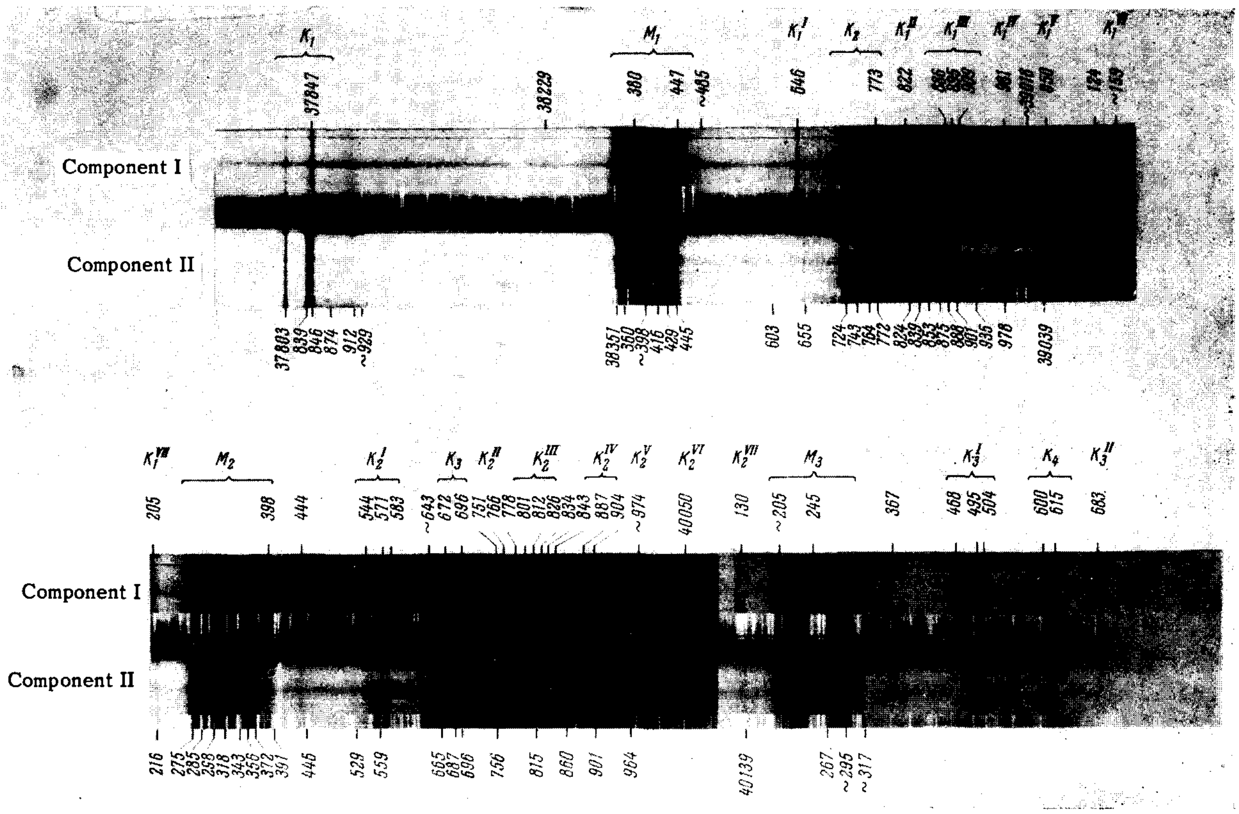

FIG. 14

499 cm^{-1} for hexadeuterobenzene. The value of the totally-symmetric breathing frequency of the molecule also decreases upon deuterium substitution from 925 to 880 cm^{-1} (see Table V).

Thus, the comparative study of the absorption spectra of ordinary and deuterated benzenes has shown that:

1. Complete or partial replacement of the hydrogen atoms by deuterium does not alter the selection rules for optical transitions. The spectrum retains the polarizations and relative intensities of the absorption bands which are characteristic of the ordinary benzene crystal.

2. Deuteration leads to a slight displacement of the spectrum to shorter wavelengths, amounting to about 30 cm^{-1} per substituted atom. At the same time, a decrease in the fundamental vibration frequencies takes place (by about 1% per substituted atom).

3. In crystalline mixtures of the various deuterated benzene molecules, the spectral region of the purely-electronic transition exhibits a superposition of the bands of the individual components. In this process, the inherent band splitting exhibited by the spectra of the pure crystals and the polarization of the corresponding bands persist. However, the magnitude of the splitting is highly dependent on the concentration of the given component. Estimates of the concentration have permitted us to determine that an appreciable splitting (3 — 4 cm^{-1}) takes place at concentration of the component of 10 — 15%. At a concentration of about 35%, the splitting becomes as great as 20 cm^{-1}. As is known, the exciton splitting is 45 cm^{-1} in the spectrum of the pure crystal. These data demonstrate a monotonic (or in a crude approximation linear) variation of the extent of splitting with the concentration. This functional relationship, together with the observed nature of the absorption bands, serves to indicate the formation in the studied specimens of impurity exciton states.*

9. THE DETAILED STRUCTURE OF THE ABSORPTION SPECTRA OF BENZENE CRYSTALS

In this section we shall note some peculiarities of the spectra of benzene crystals, which are not well understood at present. A further study of these problems may not only aid in securing a more profound interpretation of the benzene crystal spectrum, but is likely also to cast light on some yet unknown features of light absorption by crystals in general.

Figure 14 shows one of the typical photographs of an absorption spectrum of a benzene crystal at 20° K. The plane of growth of this specimen corresponds to a certain oblique section of the unit cell. Table VI gives the frequencies of the bands of this spectrum

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*The exciton absorption of an isotopic-molecule impurity as studied here is fundamentally different in its manifestations from that observed in mixed (ionic) crystals,[53] as the latter exhibit the formation of mixed exciton states of large radius.

with the interpretation of some of them. The data on the polarization of the absorption bands is also given therein.

(a) Supplementary series of polarized bands. In addition to the absorption bands discussed above, comprising the M and K series, the spectrum of the benzene crystal contains at least seven other series of narrow polarized bands indicated in Fig. 14 by indices from K^{I} to K^{VII}. It has not been possible to find analogs of these bands in the vapor spectrum. Each member of these series consists of a close doublet of narrow and relatively sharp bands with a splitting of from 2 to 11 cm^{-1}. The individual members of each series are related to one another by the totally-symmetric vibration frequency 925 cm^{-1} (see Table VI). The initial bands of the series are distributed at spacings of 815, 988, 1052, 1145, 1210, 1289, and 1375 cm^{-1} from the theoretical location of the 0—0 transition, which is at 37835 cm^{-1} [see below in (b)].

A characteristic peculiarity of the bands of these series is their anomalous polarization. The photographs of the absorption spectra of certain specimens with growth planes oblique to the crystal axes (in particular, the spectrum shown in Fig. 14) exhibit complete polarization of the components of these band doublets. Since these spectra correspond to oblique sections of the unit cell,* their components are not the principal components (see Sec. 6). Hence, it follows that the absorption bands of these supplementary series are polarized in directions other than the principal directions of the crystal. This is also demonstrated by an analysis of the principal components of the spectrum (see Fig. 10). In these photographs, the bands of the doublets of the additional series are weakly polarized, and remain visible with both polarization directions of the incident light. The two specimens in Fig. 15 give a good illustration of what has been said here.

When we apply the laws of ordinary crystal optics, the absorption is described by a second-rank tensor, whose axes coincide with the crystallographic axes for the orthorhombic crystals of benzene. The peculiarities of the bands of the additional series give evidence that this absorption in the benzene crystal corresponds to a more complex surface than a triaxial ellipsoid, and cannot be represented by a second-rank tensor.

Absorption of this type may be associated with the fact that we may not neglect the finite wavelength of the light in this case. Thus, these absorption bands may be due to transitions to those points in the exciton band for which the wave vector, which is equal to the wave vector of the light wave, differs from zero.

The finiteness of the wavelength of the light in exciton absorption (spatial dispersion) has been taken into account from the theoretical standpoint by Pekar in a series of recent papers.[56] The discovery by Gross and Kaplyanskii,[58] and by Gorban',[59] of polarization of one of the absorption bands in the spectrum of the cubic crystal Cu_2O, as well as the study of certain magnetooptic effects involving excitons in CdS crystals,[60] all demonstrate the possibility of experimental observation of the spatial-dispersion effects in crystals.

Since the molecule and crystal of benzene have been well studied and their energy diagrams have been interpreted to a considerable extent, the study of the details of the spectrum of this crystal in order to elucidate the role of spatial dispersion should be highly fruitful.

(b) The fine structure of the components of the purely-electronic transition. From the theoretical standpoint, the purely-electronic transition in the crystal spectrum may be crudely considered to be the "center of gravity" of the observed doublet of bands. In this interpretation, its frequency turns out to be 37825 cm^{-1}. On the other hand, the location of this transition may be determined by use of the data on the spectra of crystalline solutions of benzene (see Sec. 8). It has been shown that the displacement observed on going from the pure crystal to the solution is 19 cm^{-1} (38374 – 38355 = 19 cm^{-1}, where 38355 cm^{-1} is the mean frequency of the 0—0 + E_{2g} doublet). The location of the 0—0 transition in the spectrum of the solution is 37855 cm^{-1}, and hence, its location in the spectrum of the pure crystal should be 37835 cm^{-1}. This frequency has been accepted as that of the 0—0 transition in the analysis of the spectrum (see Table VI).

In determining the magnitude of the splitting of the exciton-band doublets in the crystal spectrum, it was found that this magnitude did not remain constant in the spectrum, but varied from one overtone band to another. In the K_1 group, it amounts to 40 cm^{-1}, in the K_2 group to 44 cm^{-1}, in the K_3 group to 24 cm^{-1}, in the K_4 group to 15 cm^{-1}, while in the K_5 and K_6 groups it is nearly zero (at 20°K). If we assume that the relative intensities of absorption in these groups are the same as in the bands of the A^0 series of the vapor spectrum,[31] we must conclude that the magnitude of the splitting is proportional to the oscillator strength of the given transition. This conclusion agrees with the predictions derived from Davydov's theory.[15]

A careful study of the absorption spectra of benzene crystals at 20° K in a high-dispersion instrument[45] has shown that, in distinction from the 37803 cm^{-1} band, the second band of the 0—0 transition at 37843 cm^{-1} is a doublet (37839 and 37846 cm^{-1}). Here the relative intensities of the bands of this doublet vary in relation to the crystallographic orientation of the plane of growth in the various specimens. The same splitting of the short-wavelength component of the doublet

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*We can also establish this fact from the polarization of the bands in the region of the purely-electronic transition. In oblique sections of the lattice, the spectrum does not show a clean separation of the a and c bands between the components. Both bands are observed simultaneously on both photographs (see Fig. 14 and compare with Fig. 10, specimen a).

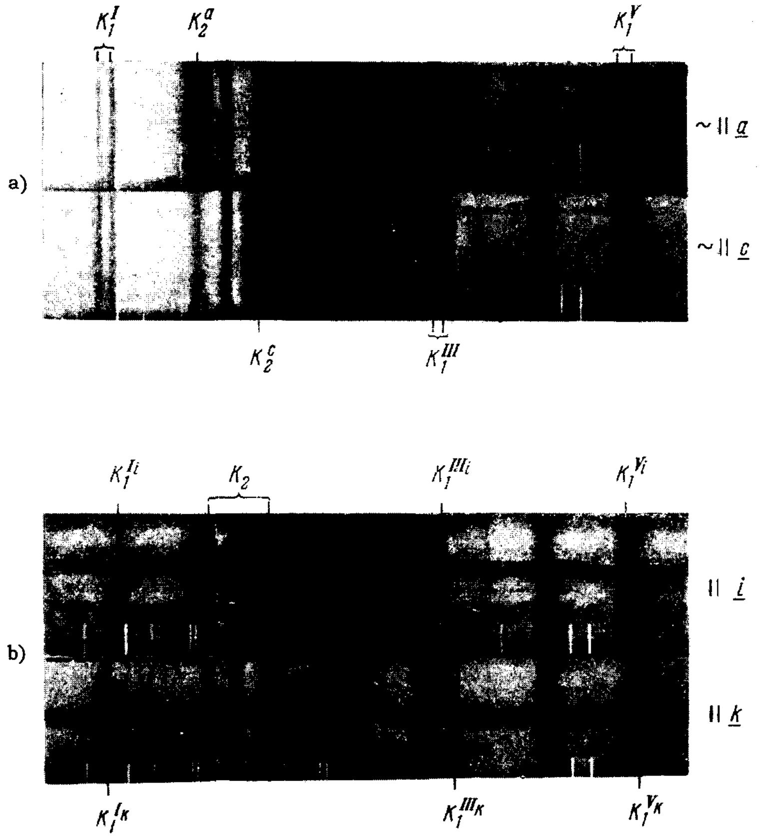

FIG. 15. Regions in the spectra of benzene crystals (20°K). (a) A crystal with a plane of growth near the ac plane; (b) a crystal with a plane of growth oblique to the lattice (the ik plane).

has also been observed in the following overtones of the K series in the crystal spectrum: 37839 — 37846 cm^{-1}, 38764 — 38772 cm^{-1}, and 39687 — 39696 cm^{-1}.

The existence of a doublet of polarized bands at 37839 — 37846 cm^{-1} in the crystal spectrum and the variation of their relative intensities for different lattice planes has led us to assume that one of these bands involves the component of the 0—0 transition polarized along the third crystal axis, i.e., the b axis (see reference 45). Its appearance in the spectrum might be explained by the small inclination of the molecule with respect to the b axis, which has not been taken into account previously. However, it has not yet been possible to relate this assumption to the general weakening of the absorption in the region of the 0—0 transition observed when the light is polarized along the b axis of the crystal (see Fig. 10).

Certain additional peculiarities are observed in individual members of the K series. The K_2 group exhibits a weakly polarized band at 38743 cm^{-1} having no analog in the other members of the series. We find in the K_3 group that the position of the a band varies in the various components of the spectrum of a crystal having an oblique plane of growth (39665 and 39672 cm^{-1} in Fig. 14). Such a variation in the positions of bands also takes place in the K_4 group.

On the short-wavelength side of the K_1 group we find some weaker and more diffuse absorption bands which we must apparently ascribe to lattice vibrations of the crystal. A certain argument in favor of this assumption is the discovery of a structurally-analogous group of stronger bands near the 0—0 + E_{2g} transition and the corresponding overtones (see Fig. 14 and Table VI).

Thus, we may describe the 0—0 transition and its overtones in the crystal spectrum of benzene in a first-order approximation as consisting of doublets of a and c bands. However, subsequent refinements of the interpretation must include the additional peculiarities in the polarization of these absorption bands such as we have described here.

(c) The fine structure of the $A_{1g} \rightarrow (B_{2u} \cdot E_{2g})$ transition. The electronic-vibrational transition involving the non-totally-symmetric E_{2g} vibration possesses the symmetry E_{1u} ($B_{2u} \cdot E_{2g} = E_{1u}$). According to group-theoretical considerations, it is allowed both in the free molecule and in the crystal. According to Davydov's calculations, this molecular term must correspond in the crystal to a triplet of bands polarized along the three crystal axes. Actually, this transition is manifested in the spectrum by a doublet of unpolarized ("weakly polarized") bands (M_1 = 38351 — 38360 cm^{-1}). This gives the impression that we are dealing here with the ordinary removal of a twofold degeneracy (the Bethe splitting). However, this contradicts the results of experiments with solid solutions of the deuterated benzenes (Sec. 8). It has been shown that the absorption spectra of these mixed crystals also exhibit a splitting of this molecular term. Here the extent of splitting turned out to depend on the concentration of the given component of the mixture. When the concentration of benzene in the mixture of deuterobenzenes was small (below 10%), this term was not split, and appeared as a sharp single band at 38374 cm^{-1}. Apparently, this contradicts the elementary theory of Bethe splitting in a stationary external crystal field,* for which concentration dependence would be absent. This compels us to assume that resonance interactions between identical molecules plays an essential role in the creation of the 38351 — 38360 cm^{-1} doublet, in spite of the weak polarization of the corresponding bands.

In connection with the peculiarities discussed here of the absorption bands involving the $A_{1g} \rightarrow E_{1u}$ transition, the quite general problem arises of why the "Davydov splitting" exists. As applied to the case of the benzene crystal, this is a question of why the purely-electronic transition in the crystal appears in the form of a sharply polarized doublet, while the electronic-vibrational transition $A_{1g} \rightarrow E_{1u}$ forms weakly-polarized absorption bands.

This question is also very basic in the analysis of the spectra of other molecular crystals. It has been noted that not nearly all molecular terms undergo splitting nor appear in the crystal spectrum as sharply polarized bands. Experiment has shown that most often such a splitting exists only in the electronic-transition bands of longest wavelength.

According to theoretical considerations, the existence of exciton splitting must be influenced above all by the oscillator strength of the corresponding molecular absorption band. In the benzene spectrum, this cannot eliminate the difficulties, since the 0—0 transition here is several times weaker than the electronic-vibrational transition. Thus, we are left with the assumption that the decisive role in this problem must be played by the magnitude of the exciton-phonon interaction.

The distinctive peculiarity of the behavior of these absorption bands has also been found in the study of the effect of thermal deformation of crystals on the spectrum.[44,54]

All of the studies of the spectroscopic properties of benzene crystals have been carried out on specimens obtained by crystallization of the liquid between the quartz windows of a thin-film cuvette. On the other hand, it has been shown[44] that thermal stresses may arise upon cooling in a crystal in contact with a quartz substrate, owing to the differing thermal expansion coefficients of the crystal and the quartz. These stresses in the crystal distort the normal form of the absorption spectrum. In particular, this phenomenon has also been found in thin benzene crystals. If the thickness of the crystal is less than a micron, and especially, if the specimen has been prepared by direct freezing of the liquid without subsequent recrystallization near the melting point, we then may observe effects associated with the distortion of the spectrum by the internal strains of the specimen. The size of this effect increases as the thickness of the crystal diminishes. Figure 16 shows the structure of the spectra of free and stressed crystals of benzene in the region of the M_1 group (since the crystal was very thin, the absorption in the region of the 0—0 transition could not be determined). The spectral bands become appreciably more diffuse. The splitting between the original bands at 38351 — 38360 cm^{-1} increases sharply, and becomes as much as 29 cm^{-1}. A strong polarization of the short-wavelength band of this doublet appears.

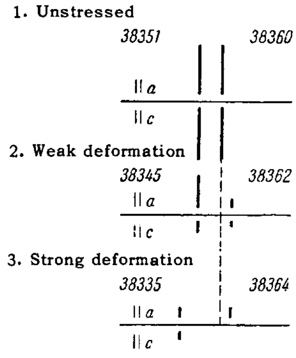

FIG. 16

Hardly any explanation has yet been found for the origin of the "induced" sharp polarization of the spectral bands in stressed crystals, not only in the benzene case, but also for other crystals studied.[44] However, it is not impossible that the behavior of the absorption bands in deformed specimens may permit in the future a more profound study of the nature of the energy levels of molecular crystals.

(d) The form and symmetry of the molecule in the crystal. The analysis of the absorption spectra of benzene in the crystalline and gaseous forms has shown that the 0—0 transition is forbidden in the free molecule owing to its high symmetry. The absorption bands corresponding to this transition are missing in the vapor spectrum. In the absorption spectrum of the crystal, the 0—0 transition is allowed, and the corresponding spectral region exhibits doublets of sharply polarized bands. The relaxation of the symmetry selection rule is associated with the influence of the anisotropic crystal field, which has a relatively low symmetry. The absorption bands which appear as a result of the relaxation of the selection rule are somewhat less intense than those involving the combination of the 0—0 transition with the non-totally-symmetric vibrations, which are allowed even in the vapor spectrum of benzene. A rough estimate shows that the ratio of the intensities of these two groups of bands (the M_1 and K_1 groups) is from three to five. The

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*The magnitude and symmetry of the field are practically unaffected by the substitution of a molecule by an isotopic molecule.

nature of the polarization of the absorption bands in the K group (i.e., the presence of doublets of a and c bands and the absence or low intensity of bands polarized along the b axis (see above)) demonstrates that the local symmetry of the crystal in the vicinity of the molecule is approximately C_{2h}.[33]

The symmetry of the free benzene molecule is D_{6h}. However, small deviations from this high symmetry occur in the crystal, according to the x-ray studies.[17] The variations in the interatomic distances and angles at the vertices of the hexagonal carbon skeleton reduce the symmetry of the molecule in the crystal to C_{2h}. The non-coplanarity of the carbon atoms noted in Fig. 2 results in the loss of some further symmetry elements. As a result, the symmetry of the benzene molecule in the crystal is described by the point group C_i. The variation in the interatomic distances amounts to 0.005 A, and in the angles to 1° 14′, or respectively, 0.4% and 0.8%. The non-coplanarity of the atoms is due to displacements from the plane by 0.0013 A.

It is only necessary to reduce the symmetry to C_{2h} to relax the symmetry selection rules for a transition in a molecule belonging to point group D_{6h}. Here, experiment shows that a variation of 0.4 — 0.8% in the bond lengths and angles is sufficient to permit the manifestation of previously forbidden transitions with appreciable intensity. The considerably smaller distortions reducing the symmetry to C_i will have a further influence on the structure and intensity of the bands due to the transition, which is now allowed.

The effect of the non-coplanarity of the carbon atoms is apparently small, and hence the spectrum basically reflects the symmetry C_{2h} (with the b absorption bands missing or very weak). Perhaps the fine structure of the absorption bands observed in the spectra at 20° K (see above) is partially due to the lowering of the molecular symmetry from C_{2h} to C_i.

Thus, we can detect distortions in the symmetry of a molecule resulting from changes in bond lengths of only 0.4% (if the allowing of a transition forbidden by symmetry is involved). This change shows its effect in the appearance of new absorption bands having intensities 3 — 5 times less than those which are allowed even in the vapor spectrum. Such a sensitivity of the spectrum is not remarkable, since the rule allowing the forbidden transition to be manifested by combination with the non-totally-symmetric E_{2g} vibration (in benzene vapor) is essentially also due to the relative displacements of atoms during this vibration. Here, the interatomic distances vary approximately by 0.015 A,[17] with the loss of the high symmetry of the molecule. This displacement is three times as large as the changes in bond lengths responsible for the allowing of the 0—0 transition in the crystal, the latter being 0.005 A. Apparently, it is this difference which is responsible for the observed intensity ratio of 3 — 5 between the transition allowed by the E_{2g} vibration and the transition allowed in the crystal by the lowering of the molecular symmetry.

It was noted above that the molecules of the partially deuterated benzenes do not appreciably exhibit the 0—0 transition in the vapor spectra in spite of the loss of D_{6h} symmetry. Apparently, this experimental result indicates that the distortion of the carbon skeleton upon deuteration is small, and in any case smaller than the changes in the structure of the molecule observed upon aggregation of the molecules into a crystal. This is also demonstrated by the small magnitude of the shift in the spectra of the deuterated molecules with respect to that of ordinary benzene. This shift (80 cm^{-1} on the average) is considerably less than the shift between benzene and toluene, and amounts to about one-fourth of the shift between vapor and crystal in the spectrum of ordinary benzene.

(e) The Rashba effect in impurity absorption. The following effect was noted in the study of the peculiarities of the spectra of mixed crystals of the deuterobenzenes.

As was stated above, the magnitude of the splitting of the purely-electronic transition of a given component was found to depend monotonically on its concentration in the mixture. However, the steepness of the curve for this dependence was found to vary for the molecules of different isotopic forms, being greater when the energy level of the given form was closer to that of the solvent crystal. Thus, for example, in a series of specimens in which the solvent was hexadeuterobenzene, the concentration of ordinary benzene was higher than that of trideuterobenzene, whereas the bands of trideuterobenzene were split by 5 cm^{-1}, but the band of ordinary benzene was not split. As we see, the energy level of the impurity of ordinary benzene was farthest removed from the bands of the solvent. The nearer the impurity level is to the exciton bands of the crystal solvent, the more readily splitting of the impurity level occurs for a given concentration.

Another peculiarity was noted in the relative intensities of the a and c bands for the various components of the mixture. It was shown that for impurity bands far enough removed from the solvent band, the relative intensities of the a and c bands were approximately those expected from an oriented-gas model, coinciding with the polarization ratio observed in the spectrum of the same plane of a pure crystal without impurities. This was true even in cases in which the concentration of the component was considerable and exciton splitting was observed. An example of this is given by the bands of ordinary benzene at 37845 — 37856 cm^{-1} in the spectrum in Fig. 13, which are separated by 90 cm^{-1} from the bands of the solvent hexadeuterobenzene. We may determine the degree of approximation of the polarization ratio of the corresponding a and c bands to the oriented-gas model (about 1 : 1, since the molecule is inclined at about 45°) by comparing it with the same ratio as observed in the bands in the region of the combination with the E_{2g} vibration (see the next footnote). On the other hand, approach of *the impurity level to that of the solvent is accompanied* by mutual perturbation, which has the effect of disturbing the polarization ratio, so that it deviates strongly from that of the oriented-gas model. This effect increases as the levels approach one another more closely (Fig. 17). In line with the determined composition of the studied mixtures of deuterobenzenes, in which the solvent was usually hexadeuterobenzene with an impurity content sometimes as high as 50%, the disturbance of the polarization ratios was especially marked among the bands of the highly-deuterated molecular species.* This ratio became almost 1 : 10 in some especially marked cases, instead of the 1 : 1 ratio expected from the oriented-gas model.

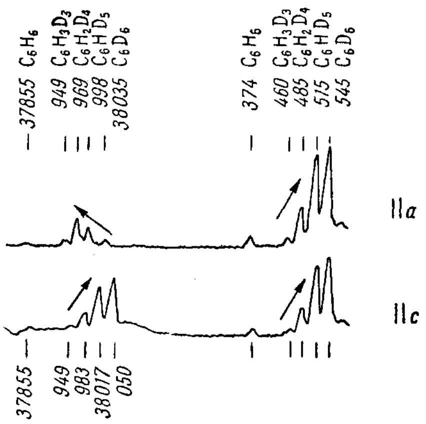

FIG. 17

Both of the above-mentioned peculiarities of the absorption spectra of mixtures of deuterobenzenes have been estimated only qualitatively; strict quantitative measurements must still be made. However, the nature of these phenomena compels us to assume that they are related to the Rashba effect,[55] which consists in an anomalous redistribution of the band intensities of impurity absorption bands in the immediate vicinity of an exciton energy band of a solvent crystal. It seems to us that the existence of these peculiarities of impurity absorption bands is facilitated by the similarity in nature of the molecules of the impurity and the solvent molecule, as occurs in solutions of isotopic molecules. The theory of this phenomenon[55] must be developed further to apply it to concentrated solutions.

10. CONCLUSION

We have attempted here to present as fully as possible the experimental results of the studies of the absorption spectra of benzene, a favorite object of spectroscopic studies, and to make the most plausible interpretation of the observed facts.

Here we have established that the general character *of the crystal spectrum, comprising the arrangement* and polarization of its most intense bands, may be satisfactorily understood on the basis of the theory developed by Davydov.[15] However, on the other hand, a number of experimental facts involving the fine structure of the spectrum, as discussed in Sec. 9, cannot yet be completely reconciled with theoretical conceptions. To a considerable extent, this is associated with the qualitative nature of the experimental results, among which there are practically no measurements of precise quantitative regularities, but it is also due to the inadequate development of the corresponding theoretical fields.

It is difficult to point out at present the general ways to solve the problems presented by the experimental facts. However, new conceptions concerning the optics and light absorption of crystals, taking into account the finiteness of the wave vector of the light wave, i.e., the theoretical field developed recently by Pekar,[56] are likely to aid in interpreting the observed data.

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*We should note that the polarization ratio for the bands in the region of the combination with the E_{2g} vibration (see Figs. 13 and 17) is the same for all of the isotopic molecular species.

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