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# *ELECTRON ABSORPTION SPECTRA OF ISOTOPIC IMPURITIES IN DEUTEROBENZENE CRYSTALS*

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A complete quantitative description of the experimental characteristics of isotopic impurity absorption in deuterobenzene crystals is presented. The 1) position, 2) integral intensity, 3) polarization ratio and 4) shape of the impurity bands are measured and the effect of impurities on the absorption spectrum of the solvent crystal is observed. The measurements are performed with 12 impurity crystals differing with respect to the value of the exciton coupling energy in the impurity molecule, $\Delta_e$. The dependence of all quantities studied on $\Delta_e$ is found. An independent numerical calculation of all measured characteristics is carried out on the basis of the current theory of isotopic impurity absorption, using data on the state-density function of crystalline benzene and known values of $\Delta_e$. Good agreement between the experimental data and calculations in all respects signifies correctness of the theory and implies that a complete picture has been given of the experimental manifestation and a complete theory proposed for describing absorption by isotopic impurities in molecular crystals.

## 1. INTRODUCTION

A complete quantitative description of the experimental impurity absorption would include: 1) determination of the position of the impurity bands, 2) measurement of their integral intensity, 3) investigation of their form, 4) establishment of the dependence of the intensity of the impurity absorption on the direction of polarization of the light incident on the crystal (in other words, determination of the anisotropy of the absorption; the most frequently used quantitative measure of the absorption anisotropy is the ratio of the integral intensities of the impurity bands for two directions of light polarization, coinciding with preferred crystallographic directions—the polarization ratio), and finally, 5) finding the influence of the presence of impurities in the crystal on the intrinsic-absorption spectra. Until recently the experimental investigations of the spectra of isotopic impurities were limited only to a determination of the band positions[1-5]. The polarization ratios were measured only for a few isotopic-impurity deuteronaphthalene crystals[6]. In the present study, we investigated quantitatively all the indicated five characteristics of electronic impurity absorption, and as a result we obtained a complete quantitative description of its properties.

The experimental investigations were performed on two groups of crystals, consisting of six impurity systems having the same solvent. In the first group, the solvent was a benzene crystal without any deuterium ($d_0$), and the impurities were the benzene d $-d_1$, $-d_2$, $-d_3$, $-d_4$, $-d_5$ and $-d_6$ molecules. The subscript of d denotes the number of deuterium atoms in the corresponding deuterobenzene molecule. In the second group, the solvent was the crystal benzene $-d_6$, and the impurities were all the light isotopes ($d_5$, $d_4$, $d_3$, $d_2$, $d_1$, and $d_0$). The principal quantitative characteristic of the impurity is the isotopic shift $\Delta_e$ of the electronic terms of its molecules, placed in the chosen crystal, relative to the terms of the crystal molecules. This shift amounts on the average to 30 $\text{cm}^{-1}$ for each act of substitution of a hydrogen atom with deuterium, and is positive (negative) on going from the lighter (heavier) isotope to the lighter (heavier) one[3]. The two investigated crystal groups differed from each other in the sign of $\Delta_e$, and within each group the value of $\Delta_e$ assumed a number of discrete values. Electronic impurity bands were observed in the spectra of all the investigated crystals. In the crystals of the first group, they were located above the exciton band of the solvent, and in the crystal of the second group below the band. Thus, it became possible to investigate the dependence of the indicated experimental characteristics on the value of $\Delta_e$.

According to present-day theoretical notions[7-10], the excited states of isotopic impurity molecules in molecular crystals are the states of an exciton localized on the impurity molecule. Consequently, the quantitative theoretical parameters of the impurity center are the binding energy of the exciton on the impurity center, equal to $\Delta_e$, and also the parameters of the exciton bands, such as width and the density of states $\rho(\omega)$. If $\rho(\omega)$ is known, then the theory makes it possible to calculate exactly the aforementioned quantitative characteristics of the impurity spectrum.

We have carried out numerical calculations[1)] of all five characteristics of the impurity absorption on the basis of the presently known function $\rho(\omega)$ for the benzene crystal[11]. From a comparison of the calculation results with the experimental data and from the obtained agreement between them, it is concluded that a complete experimental and theoretical picture has been obtained for the optical properties of the isotopic impurities in molecular crystals.

We present below a separate description of each

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[1)] All the calculations were performed with the M-20 computer. The authors thank N. V. Rabin'kina for compiling the program.

| Impurity | Solvent | $\omega$, cm$^{-1}$ | $\Delta_e$, cm$^{-1}$ | $\omega_0$, cm$^{-1}$ experiment | $\omega_0$, cm$^{-1}$ calculation | $p^{imp}_{ac}$ | $\frac{I_a}{M_a^2}$ | $\frac{I_c}{M_c^2}$ |
|---|---|---|---|---|---|---|---|---|
| $d_0$ | $d_6$ | 37853 | −191 | −164 | −164 | 0,94 | 1.35 | 0.96 |
| $d_1$ | $d_6$ | 37884 | −160 | −133 | −133 | 0,92 | 1.30 | 0.90 |
| $d_2$ | $d_6$ | 37913 | −131 | −104 | −104 | 1,12 | 1.40 | 0.90 |
| $d_3$ | $d_6$ | 37948 | − 98 | − 69 | − 72 | 1,38 | 1.80 | 0.90 |
| $d_4$ | $d_6$ | 37979 | − 67 | − 38 | − 41 | 2,35 | 2.10 | 0.60 |
| $d_5$ | $d_6$ | 38000/38009 | − 32 | − 8 | − 10 | | | |
| $d_6$ | $d_0$ | 38033 | +194 | +230 | +229 | 0,41 | 0.71 | 1.04 |
| $d_5$ | $d_0$ | 38001 | +163 | +198 | +198 | 0,46 | 0.70 | 0.90 |
| $d_4$ | $d_0$ | 38038 | +133 | +163 | +163 | 0,33 | 0.70 | 1.20 |
| $d_3$ | $d_0$ | 37933 | + 94 | +130 | +129 | 0,29 | 0.40 | 1,10 |
| $d_2$ | $d_0$ | 37903 | + 61 | +100 | +100 | 0,22 | 0,35 | 0.80 |
| $d_1$ | $d_0$ | 37874 | + 31 | + 71 | + 71 | 0.17 | 0,30 | 1.00 |

quantitative characteristic of impurity absorption. To obtain experimental data for each of the characteristics it was necessary to perform special experiments, the features of which will be pointed out in the corresponding sections. Common to all was the fact that the samples were single crystals grown in a thin quartz cell. Deuterobenzene crystals crystallize readily with different developed planes. To obtain data on the intensity, polarization ratios, and spectral distribution within the bands, we used only crystals with developed ac planes parallel to the plane of the cell. The investigations were carried out at 4°K using the high-dispersion instruments KSA-1 and DFS-13, with the incident light polarized along the a and c axes of the crystal. The impurity concentration in individual samples amounted to 1–10% and was measured with a mass spectrometer$^{2)}$. The intensities were determined by quantitative-photometry methods.

## 2. POSITIONS OF IMPURITY BANDS

The absolute positions of the electronic impurity bands in the spectra of the investigated crystals are listed in the table. The table also gives the values of $\Delta_e$ determined by Broude[3] with allowance for the dissolution effect[2,3]. These data were used in Fig. 1 to plot the dependence of the distance of the impurity band to the bottom of the exciton band of the solvent crystal as a function of the reciprocal binding energy of the exciton with the impurity molecule. The shaded regions correspond to the exciton energy spectra of the crystal benzene-$d_6$ on Fig. 1a[3] and $-d_0$ on Fig. 1b[4,11,12]. The bottom of the exciton band coincides in both crystals with the position of the a-band of the Davydov electronic-absorption multiplet[3,14]. The centers of gravity of the exciton spectra, or the positions of the unsplit electronic terms of the crystals, reckoned from the bottom of the band $\overline{\omega}_p$, are 36 and 27 cm$^{-1}$, respectively[3]. The values of $\Omega$ correspond to the boundaries of the exciton spectra on the high-energy side. $\Omega$ = 60 cm$^{-1}$ in the benzene-$d_0$ crystal[4,11,12]. The value of $\Omega$ in the benzene-$d_6$ crystal is unknown. We assumed it to be 45 cm$^{-1}$, and decreased $\Omega$ proportionally for the crystal $d_0$ in accordance with the ratio of the Davydov splittings for the a and c bands of the benzene-$d_0$ and $d_6$ crystals[3]. The experimental data for the impurity crystals with $\Delta_e < 0$ are given in the lower part of Fig. 1, and for $\Delta_e > 0$ in Fig. 1b.

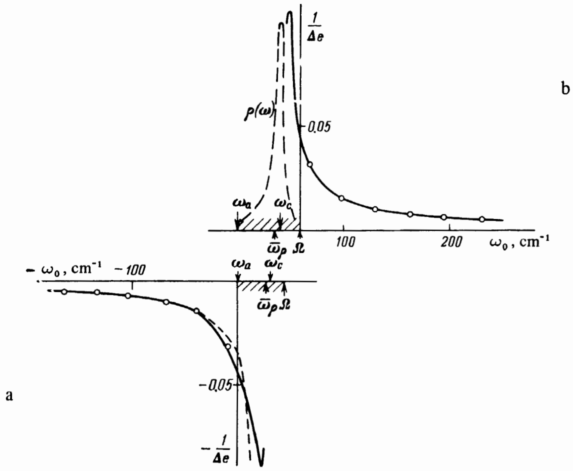

FIG. 1. Dependence of the distances from the impurity bands to the bottom of the exciton band on the reciprocal of the isotopic shift $\Delta_e$. a–Isotopic impurities in the benzene-$d_6$ crystal, b–isotopic impurities in the benzene-$d_0$ crystal. $\omega_a$ and $\omega_c$–positions of the a and c bands of the Davydov electronic-absorption multiplet of the solvent crystal.

To determine $\omega_0$, we investigated binary solutions of the indicated impurity systems on the basis of benzene-$d_0$ and $d_6$ solvent crystals. However, the absence of the pure isotopic form of benzene $d_4$ made it impossible to obtain data for the crystal benzene-$d_0$ with a $d_4$ impurity. The data for the corresponding $\Delta_e$ = 133 cm$^{-1}$ are presented on the basis of the spectrum of the analogous benzene-$d_2$ crystal with $d_6$ impurity. All the values of $\omega_0$ were obtained for crystals with thicknesses above 10 μ to avoid stress effects[15]. The concentrations of the impurities in the crystals based on benzene-$d_0$ did not exceed 5%. In crystals on the basis of benzene-$d_6$, the concentrations of $d_0$, $d_1$, $d_2$, and $d_3$ did not exceed 5%. The concentrations of $d_4$ and $d_5$ were 2.7 and 7%, respectively. These impurities were contained in the original $d_6$.

According to the simplest impurity-center model—the oriented-gas model[16]—the position of the impurity

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2) The authors are grateful to N. N. Zatsepina for making the mass-spectrometric measurements possible.

3) The electronic exciton spectrum of the benzene crystal, strictly speaking, consists of four bands in accordance with the fact that its unit cell contains four molecules. However, owing to the presence in the crystal of helical symmetry axes of second order, the bands are pairwise in contact on the boundaries of the Brillouin zone in directions perpendicular to these axes [13]. The contact occurs without a gap in the energy spectrum [4,11,12], so that the exciton spectrum of the benzene crystal and of its isotopic forms can be represented by a continuous energy interval.

band relative to the bottom of the band is given by

$$\omega_0 = \Delta_e + \overline{\omega}_\rho. \tag{1}$$

Accordingly, the plot of $1/\Delta_e = (\omega_0 - \overline{\omega}_\rho)^{-1}$ is a hyperbola with asymptotes $1/\Delta_e = 0$ and $\omega_0 = \overline{\omega}_p$. On the lower part of Fig. 1, the experimental points, up to $\omega_0 = -5\ \text{cm}^{-1}$, lie on this curve, which is shown dotted. The positions of all the experimental points in the upper part of Fig. 1 are also well approximated by the corresponding hyperbola. Thus, only in the immediate vicinity of the red boundary of the exciton spectrum does the experimental relation $1/\Delta_e = f(\omega_0)$ cease to be hyperbolic. According to the rigorous theory of isotopic-impurity crystals[7-10], the position of the level of the isotopic impurity is determined by the equation

$$G(\omega_0) = 1 / \Delta_e, \tag{2}$$

where

$$G(\omega_0) = \int_0^\Omega \frac{\rho(\omega')}{\omega_0 - \omega'} d\omega' \tag{3}$$

is the real part of the exciton Green's function. From (2) and (3) we see that, strictly speaking, the model of the oriented gas is an approximation at which $\rho(\omega') = \delta(\omega' - \overline{\omega}_\rho)$, which is valid when $\Omega \to 0$.

It is thus obvious that such an asymptotic function $G(\omega_0)$ should be obtained at distances $\omega_0$ exceeding the width of the exciton band $\Omega$.

The solid curve of Fig. 1b represents the function $G(\omega_0)$, calculated from (3) on the basis of the well known density of states $\rho(\omega)$ of the benzene-$d_0$ crystal, shown in the upper part of Fig. 1[11]. It is seen from the figure that the function $G(\omega_0)$ coincides with a hyperbola outside the interval $\{0, \Omega\}$. A similar calculation was carried out for the systems represented in Fig. 1a. The calculation was made with the function $\rho(\omega)$ of the $d_0$ crystal with an altered center of gravity ($27\ \text{cm}^{-1}$ instead of $36\ \text{cm}^{-1}$ in accord with[3]), defined in a narrower spectral interval ($\{0, 45\}$ in place of $\{0, 60\}$). As seen from Fig. 1a, the function $G(\omega_0)$ (solid curve) coincides everywhere with the experimental points and is approximated by the hyperbola when $\omega_0 < -7\ \text{cm}^{-1}$. Since the hyperbolic asymptotic form of $G(\omega_0)$ is determined only by the center of gravity of the density of states of the exciton spectrum, the fact that it coincides with the experimental data for the systems of both groups denotes that the correct centers of gravity of the functions $\rho(\omega)$ of the benzene-$d_0$ and $d_6$ crystals were chosen for the calculation[4)].

Thus, the position of the bands of the isotopic impurities in the benzene-$d_0$ and benzene-$d_6$ crystals at all possible values of $\Delta_e$, with the exception of $\Delta_e = -30\ \text{cm}^{-1}$, does not depend on the form of the state-density function $\rho(\omega)$ in the exciton band of the solvent crystal, and is determined only by the value of its center of gravity. This should be connected with the fact that $|\Delta_e| \geq \Omega$ for all the investigated crystals (with the exception of $\Delta_e = -30\ \text{cm}^{-1}$). Consequently, the hyperbolic asymptotic form of $G(\omega_0)$ sets in at $|\Delta_e| < \Omega$. A similar conclusion was arrived at from the results of the investigations of the positions of the bands of isotopic impurities in deuteronaphthalene crystals[1,2,10].

We can thus verify the correctness of the functions $\rho(\omega)$ in an experimental investigation of the functions $1/\Delta_e = f(\omega_0)$ only for $|\Delta_e| < \Omega$. However, to use this procedure of correcting $\rho(\omega)$, it does not suffice to have $|\Delta_e| < \Omega$; it is also necessary that there exist a discrete impurity level outside the interval $\{0, \Omega\}$. This is possible only if $\Delta_e < \Delta^-_{cr}$ at $\Delta_e < 0$, or else $\Delta_e > \Delta^+_{cr}$ at $\Delta_e > 0$. Here $\Delta^-_{cr}$ and $\Delta^+_{cr}$ correspond to the values of the function $G(\omega_0)$ on the boundaries of the exciton spectrum ($G(0) = (\Delta^-_{cr})^{-1}$, $G(\Omega) = (\Delta^+_{cr})^{-1}$ [7,9]).

In isotopic-impurity deuteronaphthalene crystals, the intervals $\Omega - |\Delta^{-1}_{cr}|$ and $\Omega - \Delta^+_{cr}$ are respectively 140 and $90\ \text{cm}^{-1}$. These intervals contain the $\Delta_e$ of a large number of impurity crystals. This is precisely why it was possible to choose for these crystals, on the basis of the relation $1/\Delta_e = f(\omega_0)$, a function $\rho(\omega)$ that gives a good quantitative description of the majority of the experimental results[10]. In the benzene-$d_6$ crystal we have $\Delta_{cr} = -27\ \text{cm}^{-1}$ (Fig. 1a), and in benzene-$d_0$ $\Delta^+_{cr} = 24\ \text{cm}^{-1}$ (Fig. 1b). Thus, the interval of $\Delta_e$ in which the function $1/\Delta_e = f(\omega_0)$ is structure-sensitive covers in the deuterobenzene crystals the segment $\{-27, -60\ \text{cm}^{-1}\}$ for $\Delta_e < 0$ and $\{24, 60\ \text{cm}^{-1}\}$ for $\Delta_e > 0$. These intervals contain deuterobenzene crystals with the single value $\Delta_e = \pm 30\ \text{cm}^{-1}$. The values of $\omega_0$ obtained for them on the basis of the functions $G(\omega_0)$ employed above coincide with the experimental values. However, agreement at only one point still does not mean that the entire calculated $G(\omega_0)$ curve is valid for small $\omega_0$.

Unfortunately, for the benzene crystal there is no isotopic substitution that gives values of $\Delta_e$ falling in the necessary interval of structure sensitivity of the relation $1/\Delta_e = f(\omega_0)$. The isotopic substitution $C^{12} \to C^{13}$ is characterized by an isotopic shift of the electronic terms $\Delta_e = 3.7\ \text{cm}^{-1}$ per substituted atom[17]. But even substitution of all the carbon atoms in the aromatic ring many not make it possible to obtain a value of $\Delta_e$ sufficient for the existence of a real impurity level. With the aid of the complete isotopic exchange $C^{12} \to C^{13}$ we can hope to refine only the quantities $\Delta^-_{cr}$ and $\Delta^+_{cr}$, and in the case of partial subsitution we can investigate the quasilocal impurity states that lie inside the exciton spectrum[9]. The corresponding $\Delta_e$ should fall in the interval $\Delta^-_{cr} < \Delta_e < \Delta_{min}$ when $\Delta_e < 0$ and $\Delta^+_{cr} > \Delta_e > \Delta_{max}$ when $\Delta_e > 0$. The values $\Delta_{min}$ and $\Delta_{max}$ correspond to the minimum (Fig. 1a) and maximum (Fig. 1b) of the function $G(\omega_0)$ and their respective values are—14 and $9\ \text{cm}^{-1}$.

## 3. POLARIZATION RATIO OF IMPURITY BANDS

The polarization ratio of the intensities of the impurity bands is a quantitative measure of the anisotropy of the impurity absorption. We measured the polarization ratio $P^{imp}_{ac}$ for all 12 crystals indicated above, defining it as the ratio of the integral intensities

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[4)] The calculation of $G(\omega_0)$ on the basis of the function for the benzene-$d_0$ crystal with $\overline{\omega}_\rho = 36\ \text{cm}^{-1}$ for the systems shown in the lower part of Fig. 1 has led everywhere to a difference of $7-9\ \text{cm}^{-1}$ between $\omega_0$ and the experimental data.

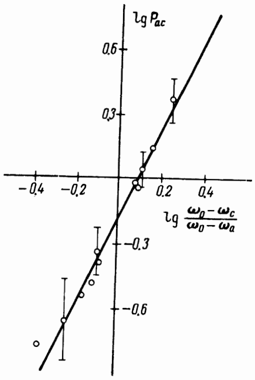

FIG. 2. Dependence of the polarization ratio in the impurity bands on their distance to the a and c components of the Davydov multiplet of the electronic absorption of the solvent crystal in isotopic-impurity deuterobenzene crystals.

of the impurity bands obtained with the incident-light polarization along the a and c axes of the crystals. To this end we investigated crystals with impurity concentrations from 5 to 10% and with thickness 4–8 μ, with an ac plane parallel to the cell plane. The ac plane of the impurity crystals with benzene-$d_0$ solvent was monitored by establishment of sharp polarization in the region of the purely electronic transition and by an analysis of the absorption in the region 38,646–655 $cm^{-1}$, for separation of the b and c components[12]. In crystals on the basis of benzene-$d_6$, the ac plane was monitored only against the character of the polarization of the purely electronic transition. Strictly speaking, it was impossible here to separate the b and c components, and therefore the measurement error for these crystals is larger than for the former ones.

In contrast to the insensitivity of the position of the impurity bands to the distance from the exciton band, their intensity varies quite sharply within the same range of variation of distances. The changes of the intensities are different for the two polarizations of the incident light, so that the value of the polarization ratio changes sharply. Thus, for the crystals of both groups $P_{ac}^{imp}$ can vary, at most, by a factor 2.5. The values of $P_{ac}^{imp}$ for the investigated systems are given in the table. It should be recalled that according to the oriented-gas method $P_{ac}^{imp}$ should be determined only by the slope of the dipole moment of the transition in the impurity molecule relative to the a and c axes of the crystal[16]. Inasmuch as the isotopic molecules replace solvent molecules isomorphically, $P_{ac}^{imp}$ for these molecules should be equal to $P_{ac}^{cr}$ in the solvent crystal. The observed discrepancy between the experimental data and the oriented-gas model signifies the existence of an influence of the exciton spectrum of the crystal on the intensity of the impurity band.

From the theory of isotopic impurity absorption it follows[7-9] that

$$P_{ac}^{imp} = P_{ac}^{cr}\frac{(\omega_0-\omega_c)^2}{(\omega_0-\omega_a)^2}. \tag{4}$$

Here $\omega_a$ and $\omega_c$ are the positions of the a and c components of the Davydov multiplet of the electronic absorption of the solvent crystal. To verify this relation, Fig. 2 shows the dependence of log $P_{ac}^{imp}$ on $\log[(\omega_0-\omega_c)/(\omega_0-\omega_a)]$. According to (4), it should be linear with a slope equal to 2. Indeed, it is possible to draw such a straight line through the experimental points. The intercept on the log $P_{ac}$ axis should give in this case the value of $P_{ac}^{cr}$. The value obtained in this manner is $P_{ac}^{cr} = 0.67$. In the benzene-$d_0$ crystal, $P_{ac}^{cr} = 0.62$ in accordance with the data of[18]. If it is recognized that thin $d_0$ crystals were used in[18] to determine the integral intensities of the a and c bands, and therefore the obtained data are subject to errors due to stress effects[15], then the relation (4) is confirmed sufficiently by the experimental data.

Figure 2 shows data obtained for both groups of impurity crystals. Within the limits of the measurement errors, they are described by a common straight line, as a result of which it can be assumed that the values of $P_{ac}^{cr}$ for the benzene-$d_6$ and benzene-$d_0$ crystals are close.

## 4. INTEGRAL INTENSITIES OF IMPURITY BANDS

The integral intensities of the impurity bands were measured in impurity crystals with developed ac plane, of thickness ~4 μ. Such benzene-crystal thicknesses cannot be measured with sufficient accuracy, and it is therefore impossible to determine in this manner the absolute intensity of the impurity bands, so that the internal-standard method was used to determine the intensities. The internal standard used in crystals with benzene-$d_0$ solvent was a benzene-$d_6$ impurity with concentration 5%. In the crystals on the basis of $d_6$, the role of the internal standard was assumed by a benzene-$d_0$ impurity of the same concentration. In both cases, the impurities farthest from the end points of the exciton spectrum were chosen. Impurities (5–10%) of the other deuterobenzenes were introduced into such binary crystals and the integral intensities of their bands relative to the bands of the standard impurity were measured. Since the impurity concentration was known, it was possible to calculate the integral intensity of the impurity absorption per molecule relative to the same value of absorption by the standard impurity.

The results obtained in this manner are given in Fig. 3. The values of a and c pertain to measurements with the light polarized along the a and c axes of the crystal. $M_a$ and $M_c$ stand for the matrix elements of the dipole moments of the transitions in the a- and c-components of the intrinsic spectrum of the crystal, calculated per molecule. The left side of the figure pertains to impurity systems with $\Delta_e < 0$, and the right side to impurity systems with $\Delta_e > 0$.

It is seen from the figure that the intensity of the impurity bands as a function of $\omega_0$ changes in different fashion for the two directions of polarization of the light, depending on whether the bands are close to the bottom or to the top of the exciton band. Thus, on the left side of the figure, the intensity of the impurity absorption increases with decreasing $|\omega_0|$ in the a component, and decreases in the c component. On the high-energy side, the intensity in the c component remains practically constant with decreasing $\omega_0$, and that in the a component decreases.

According to the theory of isotopic-impurity crystals[7-10], the integral intensity of the impurity absorption per molecule is determine by the expression

$$I_j = \frac{\Delta_e^2 |a|^2}{(\omega_0 - \omega_j)^2} M_j^2, \qquad (5)$$

where

$$|a(\omega_0)|^2 = \frac{1}{\Delta_e^2}\left[\left|\frac{dG}{d\omega}\right|_{\omega=\omega_0}\right]^{-1}. \qquad (6)$$

Here $\omega_j$ and $M_j$ are the position and the matrix element of the dipole moment of the transition, per molecule, in the j-th component of the intrinsic spectrum of the crystal, and $|a(\omega_0)|^2$ is the square of the modulus of the amplitude of the wave function of the exciton at the impurity site, or the probability of finding the excitation on the impurity molecule. The quantity $|a|^2$ describes the degree of delocalization of the impurity excitation in the lattice, and in accordance with (6), its value is calculated at the point $\omega_0$ corresponding to the position of the impurity level.

The solid lines in Fig. 3 indicate the theoretical dependences of $I_j$ on $\omega_0$ in units of $M_j^2$; j assumes values of a or c for different light-polarization directions. To be able to compare the calculated values with the experimental data, it was assumed that the experimental values of the integral intensities of the standard impurities coincide exactly with the theoretically-calculated ones for both groups of crystals. Accordingly, the data for these impurities were marked on the theoretical curves. The points corresponding to them are designated by triangles on the $\omega_0$ axis. It is seen from the analysis of the figure that the remaining experimental data for all the investigated crystals also agree with the calculated ones within the limits of the measurement error.

At the same time, the comparison of the experimental and theoretical results shown in Fig. 3 leaves a feeling of dissatisfaction, since there are no experimental points on the sharpest rise of the theoretical plot of the intensity in the a-component of the spectrum, to the left of the band. It should be noted in this connection that in this region of values of $\Delta_e$ there lie impurity bands with $\Delta_e = -30\ \text{cm}^{-1}$. In all the impurity crystals with such values of $\Delta_e$ ($d_5$ impurity in $d_6$ crystal, $d_0$ impurity in $d_1$ crystal, $d_1$ impurity in $d_2$ crystal, etc.), we observed a tremendous growth of the impurity-absorption intensity, amounting to 60–70% of the crystal-solvent intensity. This value of the intensity pertained to an impurity concentration ~7–10%. We did not succeed in investigating smaller impurity concentrations, since the impurities in all the indicated impurity crystals were contained in the original material. However, besides the tremendous growth of intensity, which in general is described by the employed theory, the impurity band was split everywhere by 9 $\text{cm}^{-1}$. As a result of this, we thought it incorrect to compare its intensity with a theory that does not describe the splitting of the impurity terms. Strictly speaking, the reduction of these experimental results should be carried out on the basis of the theory of large concentrations[19, 20].

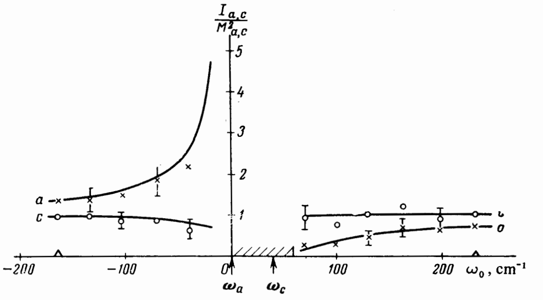

FIG. 3. Experimental (circles and crosses) and theoretical (solid lines) plots of the integral intensity of impurity absorption bands per molecule, in units of $M_a^2$ and $M_c^2$, against the distances from the impurity bands to the bottom of the exciton band of the solvent crystal in isotopic-impurity deuterobenzene crystals.

Let us examine the dependence of $I_j$ on $\omega_0$ in greater detail. According to (5), this dependence is determined by the frequency dependence of $|a|^2$ and by the factor $(\omega_0 - \omega_j)^2$. The value of $|a|^2$ is connected via the Green's function $G(\omega_0)$ with the density of states in the exciton band. For the investigated crystals, according to calculation, $|a|^2 \sim 1$. This agrees with the fact that the plot of the position of the impurity bands $\omega_0$ against $\Delta_e^{-1}$ takes the hyperbolic asymptotic form, as is characteristic of local impurity centers. Thus, the intensity of the impurity absorption does not depend on the density of states in the exciton band. However, the factor $(\omega_0 - \omega_j)^{-2}$ is still sensitive in this case to the structure of the band, since its value depends on the location of the points with $k = 0$, which correspond to the transitions for the j-th polarization of the light, relative to the end points of the exciton spectrum. It is precisely this circumstance which explains the difference in the behavior of the dependences of $I_j$ on $\omega_0$ at two directions of polarization of the incident light and when the exciton band is approached from different directions. The a band of the Davydov multiplet corresponds to a transition to the bottom of the band. This explains the sharp increase of the impurity-absorption intensity in the a component of the spectrum as $|\omega_0| \to 0$. The c band corresponds to a transition to the interior of the band. As a result, the intensity of the impurity absorption does not increase on approaching the top of the exciton band (the curve c in the right-hand side of Fig. 3).

## 5. SHAPE OF IMPURITY-ABSORPTION BANDS. INFLUENCE OF IMPURITY ON THE SPECTRAL DISTRIBUTION OF THE SOLVENT-CRYSTAL ABSORPTION

To obtain the quantitative results presented in the preceding sections, it was necessary to use thin crystals (no thicker than 8–10 μ), so as to be able to establish the orientation of the developed plane of the investigated crystal and to minimize the influence of the solvent-crystal background. As a result, the impurity concentrations needed for the measurements could not be lower than 5–10%. At the same time, such large impurity concentrations could cause side effects such as the occurrence of impurity exciton bands[19,20], narrowing of the exciton spectrum of the solvent crystal, the existence of cluster formations in the crystal, etc. None of these effects can at present be taken into account with sufficient accuracy. As a result, the foregoing comparison of the theory developed for the limiting case of small concentrations is to some degree incorrect. However, the good agreement be-

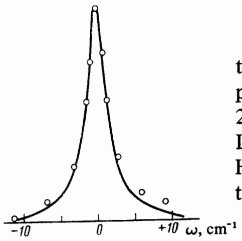

FIG. 4. Experimental shape (circles) of the absorption band of the benzene-$d_0$ impurity in a benzene-$d_6$ crystal. T = 4°K, d = 20μ, $C_{d_0}$ = 1%. DFS-13. The solid curve is the Lorentz curve $I(\omega) = I(0)\Gamma^2/(4\omega^2 + \Gamma^2)$. Here I(0) and $\Gamma = 3$ cm$^{-1}$ were obtained from the experimental data.

tween the theory and a large number of experimental data indicates that the theory is also valid for the investigated concentrations, and that the effects indicated above are apparently still small. In turn, the smallness of the effect connected, for example, with formation of impurity exciton bands, was monitored independently against the absence of measurable splitting in the impurity band. The same difficulties also arise in the analysis of the shape of the impurity absorption bands, which is most sensitive to the factors indicated above. As a result, to measure the shape of the bands we used crystals ~20 μ thick, with impurity concentrations not exceeding 1%. Such measurements could be performed only in crystals based on benzene-$d_6$ with benzene-$d_0$, $-d_1$, $-d_2$, $-d_3$ and $-d_4$ as impurities, and also in the benzene $d_0$ crystal with benzene-$d_6$ impurity. The absorption of all the remaining impurities in such thick crystals already has a rather noticeable background of intrinsic absorption. It was established that all the impurity bands have the same shape in thinner crystals with larger impurity contents.

The points of Fig. 4 represent the shape of the absorption bands of the benzene-$d_0$ impurity in a benzene-$d_6$ crystal. The half-width of the band is 3 cm$^{-1}$. The experimental points are well approximated by a symmetrical Lorentz curve with half-width $\Gamma = 3$ cm$^{-1}$. The disparity on the short-wave edge is apparently connected with the background due to the superposition of absorption with participation of optical phonons. The Lorentz Shape of the impurity absorption is evidence of the weak coupling between the electronic impurity excitation and the solvent-crystal phonons[21].

In impurity crystals based on benzene-$d_0$ at thicknesses ~ 20 μ and impurity concentrations ~10%, we succeeded in observing distortion of the solvent-crystal spectrum caused by penetration of the impurity. We investigated benzene-$d_0$ crystals with benzene-$d_1$, $-d_3$, and $-d_6$ impurities with developed ac plane parallel to the plane of the cell. In the spectra of these crystals it was observed that as the impurity becomes heavier the electronic a and c absorption bands of the benzene-$d_0$ crystal become asymmetrically broadened in a direction towards the interior of the band. This effect is most clearly pronounced in the absorption a band, since this band is sufficiently narrow and is characterized by sharply decreasing wings. Figure 5 shows the absorption of a number of impurity crystals at the base of the a band of the benzene-$d_0$ crystal[5)].

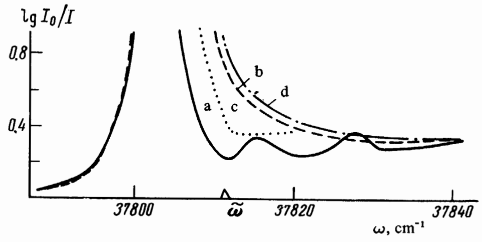

FIG. 5. Absorption in the a band of the Davydov multiplet of electronic absorption of the crystal benzene-$d_0$. a—Pure crystal, b, c, d—crystals of benzene-$d_0$ with benzene-$d_1$, $-d_3$, and $-d_6$ impurities, respectively. T = 4°K, d = 20μ, $C_{\text{imp}}$ ~ 10%, DFS-13, The light is polarized in the a direction of the crystal.

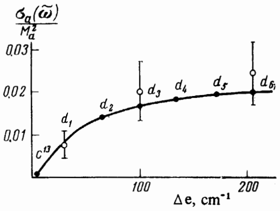

FIG. 6. Dependence of the amplitude of the impurity-induced absorption in the exciton band $\sigma_a(\tilde{\omega})$ on the isotopic shift $\Delta_e$. Solid curve—result of theoretical calculation on the basis of [21,9], light circles—experimental data.

The long-wave edge of the a bands in the investigated crystals have identical shapes, and therefore the spectra are superimposed on this absorption edge. The figure shows clearly the asymmetrical broadening of the a band, which is directed towards the interior of the band and increases on going over to the heavier impurity. The effect reaches 2—3% of the a-band intensity. It should be noted that in benzene-$d_0$ crystals with benzene-$d_1$ and $-d_3$ impurities, the broadening of the a band is not accompanied by a broadening of the remaining narrow bands of the spectrum[6)]. Introduction of the benzene-$d_6$ impurity makes the crystal spectrum more diffuse, but in this case the broadening of the a band becomes sharply pronounced.

The effect of broadening of the exciton spectrum of the solvent crystal due to scattering of the exciton by the impurity molecule was predicted earlier[22 9]. According to the theory, the spectral distribution of the absorption induced by the impurity in the region of the exciton band, when calculated per molecule, is described by the expression

$$\sigma_j(\omega) = \sigma_0(\omega)\frac{\Delta_e{}^2 M_j^2}{(\omega - \omega_j)^2} \tag{7}$$

$$\sigma_0(\omega) = \frac{\rho(\omega)}{[1 - \Delta_e G(\omega)]^2 + [\pi\Delta_e\rho(\omega)]^2} \tag{8}$$

(the notation is the same as before). If the function $\rho(\omega)$ is known, then the quantity $\sigma_j(\omega)$ can be calculated[7)]. The solid line in Fig. 6 shows the amplitude of

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[5)] In the spectrum of a pure benzene-$d_0$ crystal with developed ac plane, at thicknesses ~20μ and with the light polarized along the a direction, narrow bands are observed superimposed on the region of the exciton band (see Fig. 5). In the spectrum of the impurity crystals, these bands did not appear; they are apparently lost in the background. The origin of these bands is not clear at present.

[6)] To establish this fact, we traced the shape of the narrow band with $\nu$ = 38,229 cm$^{-1}$, which is sufficiently intense at the employed thicknesses and corresponds to excitation of a single-particle vibronic state with a narrow vibronic band.

[7)] An experimental measurement of $\sigma_j(\omega)$ leads to a new possibility, compared with [23], of determining the quantity $|a|^2$ in (5), since

$$\int_0^\Omega \sigma_0(\omega)\,d\omega = 1 - |a|^2. \tag{8'}$$

the induced absorption $\sigma_a(\tilde{\omega})$, calculated in units of $M_a^2$ on the basis of (7) and (8) for the point $\omega = \tilde{\omega}$ indicated by the triangle in Fig. 5 and located 8 $\mathrm{cm}^{-1}$ away from the center of the a band, as a function of the isotopic shift $\Delta_e$. The black dots on the curve indicate the different isotopic impurities in the $d_0$-benzene crystal. The point $C^{13}$ corresponds to isotopic substitution of one $C^{12}$ atom. It is interesting to note that in contrast to the decrease of the influence of the exciton spectrum of the crystal on the properties of the impurity absorption with increasing $\Delta_e$, the reverse effect of the impurity on the intrinsic spectrum increases under the same conditions.

Comparison of the theoretical curve with the experimental data represented by the light circles in Fig. 6 shows that there is undisputed correspondence between the theoretical and experimental relations, indicating that the effect has been observed. This correspondence has been established by us for all values of $\tilde{\omega}$ lying in the distance range 5–10 $\mathrm{cm}^{-1}$ from the center of the a band. At larger distances this relation remains in force qualitatively, but becomes quantitatively incorrect because of the existence of additional absorption of unknown nature in the spectrum of the benzene-$d_0$ crystal in the region $\tilde{\omega} > 10\ \mathrm{cm}^{-1}$.

## 6. CONCLUSION

On the basis of the experimental data given in the present paper, we can draw a complete picture of the impurity spectrum of isotopic impurity molecular crystals. The results obtained with isotopic-impurity crystals of deuterobenzenes illustrate very well the extent to which molecular crystals are convenient for the most exhaustive study of the impurity spectrum. Their principal advantage over other crystals lies in the fact that the variety of isotopic substitution makes it possible to investigate the obtainable quantitative characteristics as functions of the principal parameter of the impurity center. On the other hand, the presented comparison of the experimental data with the results of a calculation based on the presently existing theory of isotopic-impurity crystals has shown that this theory describes quantitatively correctly all the features of the impurity absorption of such systems. At the same time, the theory connects the properties of the impurity absorption quantitatively with the structure of the exciton band of the solvent crystal. This circumstance confers primacy upon investigation of isotopic crystals among the experimental methods of investigating the structure of the exciton bands of molecular crystals.

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