PHYSICS

V. L. BROUDE, É. I. RASHBA, and E. F. SHEKA

1961

SovietRxiv

Abstract

Full Text

PHYSICS

V. L. BROUDE, É. I. RASHBA, and E. F. SHEKA

ANOMALOUS IMPURITY ABSORPTION NEAR EXCITON BANDS OF MOLECULAR CRYSTALS

(Presented by Academician I. V. Obreimov on 30 March 1961)

In typical molecular crystals the energy of intermolecular interaction is relatively small, and impurity absorption can usually be described on the basis of the oriented-gas model. In accordance with this model, the intensity and polarization of impurity absorption are determined by the magnitude and orientation of the dipole moment of the transition in the impurity molecule. However, the picture of the phenomenon becomes essentially different when the excited level of the impurity lies near the edge of the exciton band of the solvent crystal ([1,2]). If the distance ε of the impurity level from the edge of the exciton zone is less than, or of the order of, the width of the exciton zone M, then absorption of light in the region of the impurity band leads to the formation of quantum states in which not only the impurity molecule is excited, but also the nearby molecules of the solvent. For $\varepsilon \ll M$, the dimensions of the region in which the excitation is concentrated may substantially exceed the lattice constant.

Under such conditions the oriented-gas model naturally becomes inapplicable, and sharp anomalies of impurity absorption may be observed. Since $M \gg \varepsilon$, the structure of the exciton band near its edge has the determining influence on the features of impurity absorption. In particular, when the impurity molecule differs from the solvent molecules only by a shift of the energy levels (see below), the intensity of impurity absorption decreases as $\varepsilon^{1/2}$ if the optical transition to the edge of the exciton band is forbidden for the given polarization of light, and increases as $\varepsilon^{-1/2}$ if the optical transition is allowed*; the coefficients in these dependences are determined by the effective mass of the exciton. Correspondingly, the polarization ratio also depends sharply on ε. In addition, for $\varepsilon \lesssim M$, ε itself becomes a complicated function of the distance $2f$ between the levels of the solvent and impurity molecules in a pair.

Thus, the features of impurity absorption open up the possibility of drawing definite conclusions about the structure of exciton bands. This is all the more important because at present effective methods for analyzing exciton bands are almost lacking.

Convenient objects for the study of the phenomena described should be mixtures in which molecules differing only in isotopic composition serve as the solvent and the impurity. In this case the lattice around the impurity molecule is practically not deformed, the absorption bands of the impurity and the solvent are close to one another, and other differences in the spectral properties of the molecules (intensities, polarizations, etc.) are negligibly small (^{3}), so that all regularities are simplest. In solutions of various deutero-benzenes (^{4,5}), phenomena of the same nature as those described above were indeed observed, but, owing to the high con-

---

* In this latter case there occurs, as it were, a "pumping" of oscillator strength from the intrinsic absorption into the impurity absorption, since the excitation of the solvent molecules surrounding the impurity molecule makes, as $\varepsilon \to 0$, an ever increasing contribution to the impurity absorption.

the concentrations of the mixture components in the specimens studied, the regularities proved to be substantially altered.

A suitable object for studying the phenomena predicted in (^{1}, ^{2}) proved to be solutions of deutero-naphthalenes. Favorable features of these substances are the large separation ($\Delta \sim 158$ cm^{-1}) between the A and B bands, which form the Davydov doublet (^{6}, ^{7}), the small width of the A band (half-width 5 cm^{-1} at 20° K (^{8})), and the slight shift of the spectrum upon deuteration (a shift to the short-wavelength side by approximately 15 cm^{-1} per hydrogen atom replaced by deuterium). It is therefore possible to observe distinct impurity bands for which $\varepsilon \ll M$ (M has the same order of magnitude as Δ).

In the spectra studied, two absorption regions were analyzed: near the weakly polarized C band, corresponding to an electron-vibrational transition in the molecule, and in the region of the sharply polarized A and B bands of the Davydov doublet, associated with a purely electronic transition. In view of the narrowness of the exciton band of the local excitation, the impurity absorption in the region of the C band should obey the ordinary oriented-gas model. In other words, complete agreement of the polarization characteristics of the impurity and intrinsic absorption bands should be observed in this region of the spectrum. Similar regularities should also occur for absorption in the region of the purely electronic transition, if the impurity level is located sufficiently far from the exciton band. As the impurity level approaches the A-B bands, deviations from the oriented-gas model should be expected.

Fig. 1. A and B are the components of the Davydov doublet of the solvent crystal; C is the weakly polarized band of the electron-vibrational transition; Π and Π_C are impurity absorption bands. $T = 20°$ K; $\parallel a$ and $\parallel b$ correspond to the polarization of the light incident on the single crystal.

Solutions of ordinary naphthalene ($C_{10}H_8$) in octadeuteronaphthalene ($C_{10}D_8$) and in tetradeuteronaphthalenes (α-$C_{10}D_4H_4$ and β-$C_{10}D_4H_4$) were investi-

Fig. 1. Schematic of the A and B components of the Davydov doublet of the solvent crystal; C is the weakly polarized band of the electron-vibrational transition; Π and Π_C are impurity absorption bands. $T = 20°$ K; $\parallel a$ and $\parallel b$ correspond to the polarization of the light incident on the single crystal.

Figure 1: Fig. 1. Schematic of the A and B components of the Davydov doublet of the solvent crystal; C is the weakly polarized band of the electron-vibrational transition; Π and Π_C are impurity absorption bands. $T = 20°$ K; $\parallel a$ and $\parallel b$ correspond to the polarization of the light incident on the single crystal.

gated*. The concentration of the naphthalene impurity was several percent. Differences in the isotopic composition of the molecules made it possible to investigate features of impurity absorption located at different distances from the bands of the solvent crystal.

Figure 1 gives a diagram of the initial portions of the spectra obtained for the impurity crystals. For convenience of representation, the A, B, and C bands of the absorption spectra of the solvents are combined in this diagram. Attention is drawn to the intensity of the impurity Π band, which changes substantially as it approaches the A band of the solvent. In the a component of the crystal spectrum, the intensity of the Π band increases anomalously. At the closest approach of the Π and A bands (interval ~ 7 cm^{-1}), the intensity of the impurity band becomes comparable with the intensity of the intrinsic A band, i.e., increases by several tens of times. At the same time, in the "strong" b component of the spectrum, weakening of the Π band occurs, and on approaching the region of the A band it practically disappears completely. It should be noted that in the b component, together with a noticeable weakening of the impurity Π band, the appearance of weak diffuse absorption can be detected in the region corresponding to the position of the A band.

Naturally, simultaneously with the change in the intensity of the Π bands, a sharp change in the polarization ratio P_Π occurs (Table 1).

* The authors express their gratitude to Prof. A. I. Shatenshtein, who kindly supplied specimens of deutero-naphthalenes synthesized in his laboratory at the L. A. Karpov Institute of Physical Chemistry.

Table 1

Frequencies* of electronic transitions in the spectra of the crystals studied, in reciprocal centimeters at $T = 20°$K, and values of the polarization ratios**
(for notation see Fig. 1)

Solute	Solvent	A	B	C	ν_k***	$[00] \equiv C - \nu_\mathrm{k}$	$P_{A/B}$	P_C	Π	Π_C	P_Π	$P_{\Pi C}$
$C_{10}H_8$	$C_{10}D_8$	31 586	31 744	32 047	418	31 629	1:100	1:6	31 541	31 975	1:6	1:6
$C_{10}H_8$	β-$C_{10}H_4D_4$	31 549	31 707	32 027	425	31 602	1:100	1:6	31 530	31 973	1:1	1:6
$C_{10}H_8$	α-$C_{10}H_4D_4$	31 526	31 684	32 006	427	31 579	1:100	1:6	31 519	31 968	10:1	1:6

* The measurement error does not exceed ±2 cm^{-1}.

** The polarization ratios $P_{A/B}$, P_C, P_Π, and $P_{\Pi C}$ were estimated in each case from microphotograms of bands in two components of the spectrum: $P = I_a/I_b$.

*** ν_k is the intramolecular vibrational frequency of the solvent corresponding to the electronic-vibrational transition (the C-band).

In the studied range of distances between the impurity and intrinsic absorption bands this polarization ratio changes by a factor of 60 (from $1:6$ to $10:1$). It should be noted that at a sufficient separation from the intrinsic absorption bands the polarization ratio for the impurity band must be equal to the polarization ratio for the pure crystal, i.e., $1:100$ in favor of the b-spectrum ([8]). If this extrapolation is taken into account, the total change in the polarization ratio as a result of the perturbing action of the zones of the host crystal will be thousandfold.

As was to be expected, the approach of the Π_C- and C-bands of the crystal spectrum is not accompanied by any anomalies.

Fig. 2. [00] is the position of the purely electronic term of the molecules of the host crystal; $[00]_\Pi$ is the position of the purely electronic term of the impurity molecule; ν^0_kp is the frequency of the intramolecular vibration of naphthalene ([9]); ν_kp is the interval between the impurity Π_C- and Π-bands.

The character of the observed features, as well as the fact that these features accompany the approach of the impurity band only to the free-exciton bands of the host crystal, indicate the detection of precisely those effects predicted by theory ([1],[2]).

A detailed study of the structure of the impurity spectra made it possible to find that, under the conditions in which anomalies in the intensity of the impurity band are observed, the magnitude of the interval between the Π- and Π_C-bands changes simultaneously. In agreement with theory ([1],[2]), the approach of the impurity Π-level and the A-zone of the host is accompanied by an increase in this interval (see Table 2).

Figure 2 shows a diagram of the crystal spectrum for the case in which the exciton zone of the host has a substantially perturbing effect on the impurity level. The dashed line $[00]_{\Pi}$ denotes the theoretical position of the impurity band in the absence of the effects under discussion.

The experimental data presented above make it possible to draw certain conclusions about the structure of the exciton A-zone. From the fact that the impurity band remains narrow over the entire range of distances from the A-band down to 7 cm^{-1}, that its intensity in the a-component of the spectrum increases continuously, and that a noticeable increase in the interval between the Π- and Π_C-bands occurs as the Π- and A-bands approach each other, it follows that the A-band corresponds to a transition to the bottom of the A-zone of the crystal. Since, moreover, in accordance with known

By the selection rule, this transition corresponds to $k \simeq 0$; the point $k = 0$ is located at the bottom of the A-band, and the effective mass of the exciton in this region is positive. If a displacement of the band bottom from the point $k = 0$ does occur, it does not exceed a few reciprocal centimeters.

Table 2*

Dissolved substance	Solvent	$e = A - \Pi$	$\nu_{\text{kp}} = \Pi C - \Pi$	ν^0_{kp} (°)	$\Delta\nu$	$[00]\Pi = \Pi C - \nu_{\text{kp}}$	$2f = [00] - [00]\Pi$
$C_{10}H_8$	$C_{10}D_8$	45	434	433	(1)	31 542	97
$C_{10}H_8$	β-$C_{10}H_4D_4$	19	443	433	10	31 540	62
$C_{10}H_8$	α-$C_{10}H_4D_4$	7	449	433	16	31 535	44

* For the notation, see Fig. 2. All frequencies are given in reciprocal centimeters.

The investigation of the quantitative regularities in the impurity spectrum as a function of the distance of the impurity band from the exciton band of the spectrum of the solvent crystal (see Tables 1 and 2) also opens up the fundamental possibility of determining the magnitude of the effective mass of the exciton. This estimate can be made both from the law governing the change in the intensity of the impurity band and from the course of the change in the magnitude of the interval between the Π- and ΠC-bands.

Institute of Physics
Academy of Sciences of the Ukrainian SSR

Institute of Semiconductors
Academy of Sciences of the Ukrainian SSR

Received
21 III 1961

REFERENCES

1. É. I. Rashba, *Optics and Spectroscopy*, **2**, 568 (1957).
2. É. I. Rashba, Reports at the Conference on Spectroscopy, L' vov, July 1956, Phys. Collect. L' vov State Univ., vol. 3, **1**, 140 (1957).
3. V. L. Broude, E. A. Izrailevich et al., *Optics and Spectroscopy*, **5**, 113 (1958).
4. V. L. Broude, M. I. Onoprienko, *Optics and Spectroscopy*, **10**, No. 5 (1961).
5. V. L. Broude, É. I. Rashba, *Physics of the Solid State*, **3**, No. 7 (1961).
6. A. F. Prikhot' ko, *Izv. AN SSSR, ser. fiz.*, **12**, 499 (1948).
7. E. F. Sheka, *Optics and Spectroscopy*, **10**, No. 5 (1961).
8. M. Coccini, *Ukr. Phys. J.*, **5**, 707 (1960).
9. D. S. McClure, *J. Chem. Phys.*, **24**, 1668 (1954).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.