THE JOURNAL OF CHEMICAL PHYSICS VOLUME 51, NUMBER 12 15 DECEMBER 1969

Impurity Pairs in Mixed Molecular Crystals

BAT-SHEVA SOMMER AND JOSHUA JORTNER
Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

(Received 14 April 1969)

In this paper we consider the energy levels and the polarization ratios of an impurity pair in mixed molecular crystals using the one-particle Green's function method. The off-diagonal matrix elements of the weighted density of states function for the first singlet exciton band in crystalline benzene have been obtained and applied for the splitting of the energy levels of an isotopic impurity pair. An extension of Rashba's formula for the polarization ratio of the impurity pair has been derived.

I. INTRODUCTION

The electronically excited states of pure molecular crystals can be described in terms of exciton (one-particle) states which are characterized by a dispersion relation $E(\mathbf{k})$ which relates the energy to the crystal quasimomentum $\hbar\mathbf{k}$.[1] Complementary useful information can be obtained from the density of states function $g_0(E)$, which is related to the dispersion relation and to the Green's function $\mathbf{G}^0$ of the pure crystal by the well-known expressions[2–4]

$$g_0(E)=(1/N)\sum_{\mathbf{k}}\sum_{j}|B_{\alpha j}(\mathbf{k})|^2\delta[E-E_j(\mathbf{k})]$$

$$=(1/\pi N\sigma)\ \mathrm{Im}\mathrm{Tr}\mathbf{G}^0(E-i\delta), \quad (1)$$

where the summation over j is performed over all the branches of the exciton band $j=1\cdots\sigma$, where σ is the number of molecules per unit cell; N is the number of unit cells. $B\alpha j(\mathbf{k})$ are the elements of the unitary matrix which transforms the exciton site representation to the crystal wavefunctions. $Ej(\mathbf{k})$ is the energy dispersion relation for the jth exciton branch.

Frenkel exciton states in molecular crystals of aromatic molecules were extensively studied.[5] However, most of the optical studies concentrated on $k=0$ exciton states which provide information only concerning interactions sums over translationally inequivalent molecules. Information on the total density of states function can be derived from the following sources: (a) hot-band spectroscopy;[6,7] (b) electronic-vibrational cooperative excitations[8,9]; (c) studies of single impurity states[10–14]; (d) properties of impurity pairs.[2,11,14b,15]

Earlier theoretical work on single impurity states[10,11] utilized the Koster–Slater relations[16] which require complete information on the exciton dispersion curve. Recently the dispersion relations between the Green's function and the exciton density of states function were utilized leading to simple manageable expressions for the (bound or virtual) impurity energy levels, excitation amplitudes, and optical properties of impurity states.[3,4] This treatment provides an important consistency check concerning the adequacy of the exciton density of states function. Complementary information pertinent to this problem can be obtained from the study of impurity pairs in molecular crystals.[2,14b] No detailed information is available on the energy levels and the optical properties of an impurity pair. In the present work such theoretical information is presented for a realistic physical system, that is, the first excited singlet state of the isotopic impurities in crystalline benzene. Further theoretical information required for the interpretation of experimental spectroscopic data concerns the polarization ratio. The effect of the host exciton band is expected to alter the polarization ratio of an impurity pair, which will result in serious deviations from what might be expected on the basis of the oriented gas model. Indeed, the theoretical study of mixed molecular crystals originated in Rashba's work on the polarization ratio for a single impurity.[17,11,12] The extension of the general theory for an impurity pair is of some interest.

---

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

[2] I. M. Lifschitz, Advan. Phys. **13,** 485 (1964).

[3] Y. A. Izyumov, Advan. Phys. **14,** 569 (1965).

[4] B. S. Sommer and J. Jortner, J. Chem. Phys. **50,** 187 (1969).

[5] (a) D. P. Craig and S. H. Walmsley, *Physics and Chemistry of the Organic Solid State*, D. Fox and M. Labes, Eds. (Interscience Publishers, Inc., New York, 1963), Vol. 1, p. 201. (b) S. A. Rice and J. Jortner, *ibid.*, Vol. 3 (1967), p. 199.

[6] E. I. Rashba, Fiz. Tver. Tela **5,** 1040 (1963) [Sov. Phys.—Solid State **5,** 757 (1963)].

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

[8] E. I. Rashba, Zh. Eksp. Teor. Fiz. **50,** 1064 (1966) [Sov. Phys.—JETP **23,** 708 (1966)].

[9] M. Philpott, J. Chem. Phys. **48,** 5361 (1968).

[10] R. E. Merrifield, J. Chem. Phys. **38,** 920 (1963).

[11] D. P. Craig and M. R. Philpott, Proc. Roy. Soc. (London) **A290,** 583 (1966); **A290,** 602 (1966); **A263,** 213 (1966).

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

[13] S. D. Colson, J. Chem. Phys. **48,** 3324 (1968).

[14] (a) B. S. Sommer and J. Jortner, J. Chem. Phys. **50,** 822 (1969); (b) **50,** 839 (1969).

[15] R. D. Levine and A. T. Amos, Phys. Status Solidi **19,** 587 (1967).

[16] G. F. Koster and J. C. Slater, Phys. Rev. **95,** 1167 (1954).

[17] E. I. Rashba, Opt. Spectrosk. **2,** 516 (1957).

II. IMPURITY ENERGY LEVELS

The energy levels of an impurity pair are determined by the off-diagonal elements of the density of states matrix which are determined by the crystal symmetry and by the intermolecular interactions. Such interactions are of considerable interest in the study of virtual coupling and electronic energy transfer between traps.[11,14b] Isotopically substituted impurity pairs which introduce local perturbation are expected to provide useful information concerning these intermolecular interactions. From earlier work[2,11,14b] it is known that the energy levels for a pair of isotopic impurity molecules (characterized by a sufficiently strong local perturbation strength to yield localized levels) are obtained from the equation

$$\begin{vmatrix} 1-U_0F_{qq}(E) & -U_0F_{qq'}(E) \\ -U_0F_{q'q}(E) & 1-U_0F_{q'q'}(E) \end{vmatrix} =0, \qquad (2)$$

where the impurity molecules are located at the sites $q\equiv n\alpha$ and $q'\equiv m\beta$, the double index refers to the unit cell and to the appropriate site in the unit cell. U_0 is the perturbation strength which is given by $U_0=\Delta\epsilon_{\text{guest}}{}^f-\Delta\epsilon_{\text{host}}{}^f+D_{\text{guest}}{}^f-D_{\text{host}}{}^f$, where $\Delta\epsilon^f$ corresponds to the gas phase excitation energy and D^f the pure crystal environmental shift. The matrix elements $F_{qq'}(E)$ are related to the elements of the density of states function by the dispersion relation. The Green's function in the localized excitation representation is given in the form[3,4]

$$G_{qq'}{}^0(E-i\delta)=F_{qq'}(E)+i\pi g_{qq'}{}^0(E), \qquad (3)$$

where $g_{qq'}{}^0$ is the matrix element of the weighted density of states function[3,4] (for the pure crystal) while[2–4]

$$F_{qq'}(E)=P\int\frac{g_{qq'}{}^0(E')dE'}{E-E'}, \qquad (4)$$

where P represents the Cauchy principle part of the integral.

In the deep trap limit the moment expansion method[12,14b] leads to the pair energy levels $E_\pm=U_0\pm m_{qq'}{}^{(1)}$ and to the level splitting $\Delta E=2m_{qq'}{}^{(1)}$ where the first moment $m_{qq'}{}^{(1)}$ is just the intermolecular coupling term $\epsilon_{qq'}$ between the molecules at q and at q'.[11,13,14] Thus in the case of a deep trap the impurity pair splitting of the energy levels is just $\Delta E=2\epsilon_{qq'}$, while in the case of virtual coupling between shallow or intermediate traps a full-fledged treatment based on Eq. (2) is necessary. This requires the calculation of the off-diagonal matrix elements of the weighted density of states function.[14b] These off-diagonal terms were calculated by us (see Appendix) for a typical system where the exciton band structure is determined by short-range interactions.

III. NUMERICAL CALCULATIONS FOR CRYSTALLINE BENZENE

The band structure for the first singlet exciton state of crystalline benzene is dominated by short-range electrostatic interactions.[5a,7,13] A similar situation prevails for the first singlet exciton band of crystalline naphthalene.[5a,7,14b] The individual intermolecular coupling terms in crystalline benzene which provide a reasonable fit to the density of states function and to its second moment were given by Colson.[13] Thus it appears that the singlet exciton band structure is dominated by three-dimensional short-range interactions between translationally inequivalent molecules.[13] The energy dispersion relations for the four exciton branches are then given in the form

$$E_j(k_x,k_y,k_z)=\begin{array}{c}+\\+\\-\\-\end{array}4\epsilon_{(a+b)/2}\cos\tfrac{1}{2}k_x\cos\tfrac{1}{2}ky\begin{array}{c}+\\-\\-\\+\end{array}4\epsilon_{(b+c)/2}$$

$$\times\cos\tfrac{1}{2}k_y\cos\tfrac{1}{2}k_z\begin{array}{c}+\\-\\+\\-\end{array}4\epsilon_{(a+c)/2}\cos\tfrac{1}{2}k_x\cos\tfrac{1}{2}k_z, \qquad (5)$$

where

$$j=1\cdots4;\qquad -\pi\leq k_x,k_y,k_z\leq\pi.$$

The density of states was calculated from the diagonal matrix element[4]:

$$g_0(E)=g_{n\alpha,n\alpha}{}^0(E)$$

$$=\frac{d}{dE}\frac{1}{(2\pi)^3}\sum_j\iiint_{(E)}|B_{\alpha j}(k)|^2dk_xdk_ydk_z \qquad (6)$$

while the off-diagonal matrix elements of the weighted density of states functions are obtained from

$$g_{n\alpha,m\beta}{}^0(E)=\left(\frac{1}{2\pi}\right)^3\frac{d}{dE}\sum_j\iiint_{(E)}\exp[i\mathbf{k}(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta})]$$

$$\times B_{\alpha j}(k)B_{\beta j}(k)dk_xdk_ydk_z. \qquad (7)$$

In Eqs. (6) and (7) we have labeled the impurity sites as $q\equiv n\alpha$ and $q'\equiv m\beta$. The details of these calculations are given in the Appendix. The results for the density of states are presented in Fig. 1. The theoretical curve represents quite faithfully the hot-band spectrum of benzene reported by Colson *et al.*[7] apart from a Van Hove singularity around 5 cm^{-1} which is probably smeared out in the experimental spectrum. It should be noted that the computational method employed herein is considerably more accurate than the calculations previously performed on this system.[7]

In Fig. 2 we display some typical results for the off-diagonal matrix elements of the $\mathbf{g}^0$ matrix. A consistency check on the accuracy of these calculations was obtained from the moments of the off-diagonal matrix elements of the weighted density of states function. The zeroth moment should vanish while the first moment just equals the pair interaction term.[14a,14b] Using the appropriate off-diagonal matrix elements we have calculated the dimer levels and the dimer splitting as a function of the perturbation strength U_0 for the two cases: (a) impurity molecules located at $q=(0, 0)$ and at $q'=0, \frac{1}{2}(a+b)$; (b) impurity molecules located at $q=(0, 0)$ and at $q'=0, \frac{1}{2}(b+c)$. These results are summarized in Fig. 3. As expected when $U_0^2 \lesssim M^{(2)}$ (where $M^{(2)}$ corresponds to second moment of the density of states function which for crystalline benzene[7,14] is $M^{(2)}=110$ cm^{-2}) we encounter the shallow impurity case and deviations from the simple perturbation treatment are obtained. It would be interesting to test this theoretical prediction by the study of C_6D_5H ($U_0=-31$ cm^{-1}) impurity pairs in $\mathrm{C_6D_6}$.

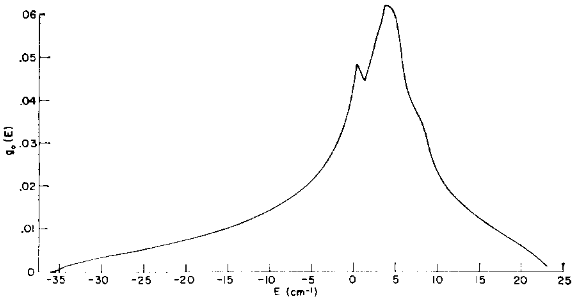

FIG. 1. The theoretical density of states curve for the first singlet exciton band in crystalline benzene as calculated from Colson's intermolecular interactions data (Ref. 13).

IV. POLARIZATION RATIOS

We shall now proceed to derive the selection rules for optical excitations of an impurity pair. The crystal wavefunctions Ψ for a mixed crystal is expanded in terms of the localized excitation basis a_l^f where $l\equiv r\gamma$ and we consider only a single (f) exciton band in the pure crystal

$$\Psi=\sum_l u(l) a_l^f. \tag{8}$$

We can express the wavefunction in the Fredholm homogenous representation

$$\Psi=\mathbf{G}^0\mathbf{V}\Psi, \tag{9}$$

where $G^0=(E-H)^{-1}$, H_0 corresponding to the pure

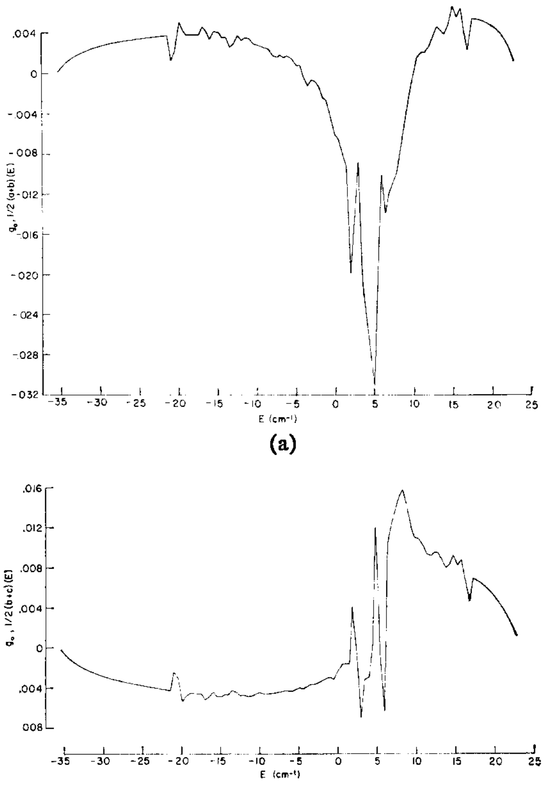

FIG. 2. The off-diagonal matrix elements of the weighted density of states matrix for the first singlet exciton band in crystalline benzene.

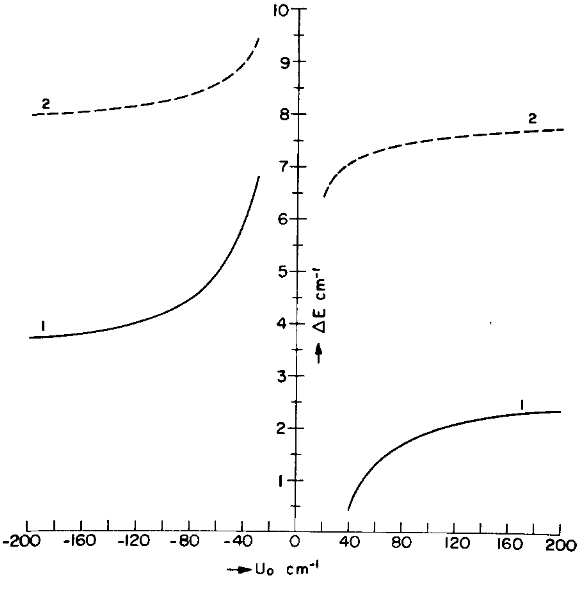

FIG. 3. The dimer splitting as a function of the perturbation strength U_0. Curve (1) corresponds to the case in which the two impurity molecules are located at the sites 00, and 0½ (**a**+**b**). Curve (2)—impurity molecules located at 00, and 0½ (**b**+**c**).

crystal Hamiltonian. V is the perturbation operator due to the presence of the impurities which in the localized representation and for local perturbation takes the form

$$\langle a_l \mid V \mid a_q \rangle = \sum_{\{p\}} U_0 \delta_{lp} \delta_{pq}, \tag{10}$$

where the sum is taken over the sites of the impurity molecules which are located at $\{p\}$. This treatment results in the following general equation for the expansion coefficients:

$$u(l') = U_0 \sum_{\{p\}} u(p) G_{l'p}{}^0. \tag{11}$$

Consider now an impurity pair with the impurity molecules located at the sites $\{p\} \equiv q$ and q'. In what follows we shall again set $q \equiv n\alpha$ and $q' \equiv m\beta$ while a general site will be denoted by $r\gamma$. The relevant expansion coefficients on the impurity sites are given in the form

$$u(q) = U_0 u(q) G_{qq}{}^0(E) + U_0 u(q') G_{qq'}{}^0(E),$$

$$u(q') = U_0 u(q) G_{q'q}{}^0(E) + U_0 u(q') G_{q'q'}{}^0(E). \tag{12}$$

We shall now make use of the identity $G_{qq}{}^0(E) = G_{q'q'}{}^0(E)$. Furthermore provided that the crystal is characterized by inversion symmetry we have $G_{qq'}{}^0(E) = G_{q'q}{}^0(E)$. Then the following simple relation results:

$$u(q) = U_0 u(q') G_{qq'}{}^0(E) / [1 - U_0 G_{qq}{}^0(E)]. \tag{13}$$

We should note in passing that Eq. (12) results in the energy relation (2). Turning our attention now to a general site in the crystal, which is occupied either by the host or by the guest molecule, we can make use of Eqs. (8) and (10) and write

$$u(l') = U_0 u(q') [\mathfrak{F}(E) G_{l'q}{}^0(E) + G_{l'q'}{}^0(E)], \tag{14}$$

where

$$\mathfrak{F}(E) = U_0 G_{qq'}{}^0(E) / [1 - U_0 G_{qq}{}^0(E)]. \tag{15}$$

The transition moment $\mathbf{M}$ from the ground state to the excited state Ψ is given in the form of

$$\mathbf{M} = \sum_{r\gamma} u(r\gamma) \langle a_{r\gamma}{}^f \mid \mu \mid \phi_0 \rangle = \sum_{r\gamma} u(r\gamma) \boldsymbol{\mu}_\gamma; \tag{16}$$

$\boldsymbol{\mu}_\gamma$ is the matrix element for the transition moment for a molecule located at site γ in the unit cell,

$$\boldsymbol{\mu}_\gamma = \langle \varphi_{r\gamma}{}^0 \mid \boldsymbol{\mu} \mid \varphi_{r\gamma}{}^f \rangle, \tag{17}$$

where φ^0 and φ^f correspond to the ground- and excited-state wavefunctions of a single molecule, respectively. Making use of Eq. (17) one obtains

$$\mathbf{M} = \sum_\gamma \boldsymbol{\mu}_\gamma \sum_r [\mathfrak{F}(E) G_{r\gamma,n\alpha}{}^0(E) + G_{r\gamma,m\beta}{}^0(E)]. \tag{18}$$

As we are interested in impurity pair states outside the band it is sufficient to consider the real part of the Green's function [Eqs. (3) and (4)], which obeys the following sum rule:

$$\sum_r F_{r\alpha,m\beta}(E) = \sum_j \{B_{\alpha j}(0) B_{\beta j}(0) / [E - E_j(0)]\}. \tag{19}$$

The following result is then obtained:

$$\mathbf{M} = U_0 u(m\beta) \sum_\gamma \boldsymbol{\mu}_\gamma$$

$$\times \sum_j \frac{\mathfrak{F}(E) B_{\gamma j}(0) B_{\alpha j}(0) + B_{\gamma j}(0) B_{\beta j}(0)}{E - E_j(0)}. \tag{20}$$

Using the conventional expression for the transition moment to the jth exciton branch,

$$\boldsymbol{\mu}_j = \sum_\gamma B_{\gamma j}(0) \boldsymbol{\mu}_\gamma, \tag{21}$$

our result takes the form

$$\mathbf{M} = U_0 u(m\beta) \sum_j \boldsymbol{\mu}_j \left(\frac{\mathfrak{F}(E) B_{\alpha j}(0) + B_{\beta j}(0)}{E - E_j(0)} \right). \tag{20'}$$

Let the dimer states be characterized by the energy levels E_{ri} ($i = 1, 2$), and these energies have to be substituted in Eq. (20′). Considering optical excitation by light characterized by the polarization vector $\mathbf{e}_\lambda$, then the components of the transition moment $M^\lambda = \mathbf{M} \cdot \mathbf{e}_\lambda$ for the excitation of the dimer can be displayed in the final form

$$M_i{}^\lambda = U_0 u(m\beta) \sum_j (\boldsymbol{\mu}_j \cdot \mathbf{e}_\lambda) \left(\frac{\mathfrak{F}(E_{ri}) B_{\alpha j}(0) + B_{\beta j}(0)}{E_{ri} - E_j(0)} \right). \tag{22}$$

The $\mathfrak{F}(E_{ri})$ factor is nothing but a constant. Making use of Eq. (2) we write for states outside the band

$$1 - U_0 G_{qq}{}^0(E) = \pm U_0 G_{qq'}{}^0(E). \tag{23}$$

Hence

$$\mathfrak{F}(E_{ri}) = \pm 1, \qquad i = 1, 2. \tag{24}$$

This result immediately implies that $u(n\alpha) = \pm u(m\beta)$, the amplitudes of the expansion coefficients on the two impurity sites are equal for any U_0.

The absolute intensity of the impurity pair components can be evaluated from Eq. (22). For this purpose the expansion coefficients $u(n\alpha)=\pm u(m\beta)$ have to be evaluated. Making use of Eqs. (17) and (24) one gets

$$u(l')=U_0 u(q')(\pm G_{l'q}{}^0+G_{l'q'}{}^0). \tag{25}$$

Now we can apply the normalization condition

$$1=\sum_{l'}|u(l')|^2=U_0^2|u(q')|^2 \times\sum_{l'}[|G_{l'q}{}^0|^2+|G_{l'q'}{}^0|^2\pm 2G_{l'q,l'q'}{}^0] \tag{26}$$

and utilize the relations[3]

$$\sum_{l'}|G_{l'q}{}^0(E)|^2=-(d/dE)G_{qq}{}^0(E),$$

$$\sum_{l'}G_{l'q}{}^0(E)G_{l'q'}{}^0(E)=-(d/dE)G_{q'q}{}^0(E). \tag{27}$$

Then the following relations are obtained:

$$|u(q')|^2=|u(q)|^2 =\frac{1}{-2U_0^2[(d/dE)G_{qq}{}^0(E)\mp(d/dE)G_{qq'}{}^0(E)]}. \tag{28}$$

As we are interested in states located outside the band, we can rewrite Eq. (21) in terms of the real part of the Green's function [see Eqs. (3) and (4)] in the form

$$|M_i{}^\lambda|^2=\frac{1}{2\{-(d/dE)[F_{qq}(E)\mp F_{qq'}(E)]\}_{E=E_{ri}}} \times\left(\sum_{j'}\boldsymbol{\mu}_j\cdot\mathbf{e}_\lambda\frac{\mathfrak{F}(E_{ri})B_{\alpha j}(0)+B_{\beta j}(0)}{E_{ri}-E_j(0)}\right)^2. \tag{29}$$

Making use of Eq. (2) this result can be recast in the form

$$|M_i{}^\lambda|^2=\tfrac{1}{2}U_0^2\left(\frac{dE_{ri}}{dU_0}\right) \times\left(\sum_j(\boldsymbol{\mu}_j\cdot\mathbf{e}_\lambda)\frac{\mathfrak{F}(E_{ri})B_{\alpha j}(0)+B_{\beta j}(0)}{E_{ri}-E_j(0)}\right)^2. \tag{30}$$

The coefficient in Eq. (30) can then be evaluated either from theory or from experimental data.

The absolute intensity of the dimer component $\mathfrak{F}(E_{ri})=+1$ (located at E_{ri}) is determined by $U_0^2(dE_{ri}/dU_0)\{1/[E_{ri}-E_i(0)]^2\}$, where $E_1(0)$ is the energy of the $k=0$ component of the pure crystal which is closest lying to the band edge $E_C{}^0$ and which corresponds to the irreducible representation where $B_{\alpha j}(0)=B_{\beta j}(0)$. When the intermolecular coupling terms in the pure crystal are determined by three-dimensional interactions, $F_{qq}(E)$ and $F_{qq'}(E)$ are expected to reveal a Van Hove type singularity at the band edge so that both $F_{qq}(E)$ and $F_{qq'}(E)$ are proportional to $|E-E_C{}^0|^{1/2}$ and thus $(d/dE)(F_{qq}+F_{qq'})\propto|E_{ri}-E_C{}^0|^{-1/2}$ and the absolute intensity is proportional to $(E_{ri}-E_C{}^0)^{1/2}[E_{ri}-E_1(0)]^{-2}$. If the $E_1(0)$ is located at the bottom of the band (as is the case for the first singlet exciton state in naphthalene and benzene) the intensity for impurity states localized below the band ($U_0<0$) will diverge as $[E_{ri}-E_1(0)]^{-3/2}$, when E_{ri} approaches the band edge. On the other hand, if $E_1(0)>E_C{}^0$ the intensity of the dimer component will decrease when E_{ri} approaches $E_C{}^0$. The same argument holds, of course, for the dimer level $\mathfrak{F}(E_{ri})=-1$, and whereupon the $\mathbf{k}=0$ exciton component corresponds to the irreducible representation for which $B_{\alpha j}(0)=-B_{\beta j}(0)$. This result is known for the single impurity case.[4] The analogous result obtained for the impurity pair is of some interest as in view of the splitting between the dimer energy components, one of these components (for an appropriate value of U_0) can be located rather close to $E_C{}^0$, whereupon the effect of the exciton band on this dimer level will be appreciable.

Thus the final expression for the polarization ratios reduces to the form

$$\left|\frac{M_i{}^\lambda}{M_{i'}{}^{\lambda'}}\right|^2=\frac{dE_{ri}}{dU_0}\left|\sum_j\boldsymbol{\mu}_j\mathbf{e}_\lambda\frac{\mathfrak{F}(E_{ri})B_{\alpha j}(0)+B_{\beta j}(0)}{E_{ri}-E_j(0)}\right|^2\Bigg/\frac{dE_{ri}{}'}{dU_0}\left|\sum_j\boldsymbol{\mu}_j\mathbf{e}_\lambda{}'\frac{\mathfrak{F}(E_{ri}{}')B_{\alpha j}(0)+B_{\beta j}(0)}{E_{ri'}-E_j(0)}\right|^2, \tag{31}$$

where the two impurity energy levels E_{ri} and $E_{ri'}$ will be labeled as follows: $\mathfrak{F}(E_{ri})=+1$ and $\mathfrak{F}(E_{ri'})=-1$. This result can be applied either to a single component or to both components of the dimer pair measured with different polarizations.

To treat a specific example let us consider the naphthalene crystal, space group ($P21/a$), with two translationally inequivalent molecules per unit cell. There are two exciton branches with $j=1$, 2. The expansion coefficients are $B_{1\alpha}(0)=B_{1\beta}(0)=B_{2\alpha}(0)=-B_{2\beta}(0)=1/\sqrt{2}$. The two states of the pure crystal to which transitions are allowed are $E_{ac}(0)$ and $E_b(0)$ polarized along the $\mathbf{e}_\lambda\perp\mathbf{b}$ and $\mathbf{e}_\lambda\parallel\mathbf{b}$. (We shall denote the *ac* plane by $\mathbf{a}$.) Thus the corresponding transition moments are $\boldsymbol{\mu}_1\cdot\mathbf{a}=\mu_a$ and $\boldsymbol{\mu}_2\cdot\mathbf{b}=\mu_b$. Consider now the following situations:

(a) If the two impurity molecules are located on translationally equivalent sites (say of type α) only one dimer state [for which $\mathfrak{F}(E_{ri})=1$] will be amenable to observation. The polarization ratio $P_1(a/b)$ for this state will be

$$P_1\left(\frac{a}{b}\right)=\frac{\mu_a{}^2}{\mu_b{}^2}\frac{[E_{ri}-E_b(0)]^2}{[E_{ri}-E_a(0)]^2}. \tag{32}$$

(b) When the two impurity molecules are located at translationally inequivalent sites both dimer states will be experimentally observed. The polarization ratio $P_1(a/b)$ for a single component is again given by Eq. (32). The polarization ratio for the two components determined by two different polarizations **a** or **b**, which we denote by $P_2(a/b)$ is given in the form

$$P_2\left(\frac{a}{b}\right)=\frac{\mu_a{}^2}{\mu_b{}^2}\left(\frac{E_{ri}'-E_b(0)}{E_{ri}-E_a(0)}\right)^2\frac{dE_{ri}/dU_0}{dE_{ri}'/dU_0}. \tag{33}$$

These equations are generally valid for localized states of the impurity pair which corresponds to the shallow, intermediate and deep trap cases. In the case of intermediate and deep traps we expect that the ratio $(dE_{ri}/dU_0)(dE_{ri'}/dU_0)^{-1}$ will be close to unity. On the other hand, for shallow traps this ratio has to be explicitly included and it will affect the polarization ratio (28).

To conclude this discussion we would like to point out that the selection rules for the optical excitation of an impurity pair in the mixed crystal can be related to the energies and to the polarization ratios for the $k=0$ Davydov components in the pure crystal as is the case for the Rashba formula[17] for the single impurity.

The simple treatment presented herein can be easily extended. One can apply the algebraic elimination method to treat any number of impurity aggregates, however, this problem is of little interest as configurational averaging will have to be performed. One can also easily handle the case when the perturbation strengths of the two impurity molecules are different.

APPENDIX: CALCULATION OF THE OFF-DIAGONAL MATRIX ELEMENTS OF THE WEIGHTED DENSITY OF STATES FUNCTION

These matrix elements were evaluated by numerical integration for the first singlet exciton band of benzene where the band structure is determined by three-dimensional interactions.

Let the impurity molecules be located at the sites $\mathbf{R}_{m\beta}=0$ and $\mathbf{R}_{n\alpha}=\eta_1\mathbf{a}+\eta_2\mathbf{b}+\eta_3\mathbf{c}$, where the indices η_i are $\eta_i=n_i+\frac{1}{2}$ or $\eta_i=n_i$ $(i=1, 2, 3)$ and n_i $(i=1, 2, 3)$ are integers. The components of the **k** vector are (k_x, k_y, k_z) so that

$$\mathbf{k}\cdot(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta})=\eta_1k_x+\eta_2k_y+\eta_3k_z. \tag{A1}$$

The dispersion relation $E_j(k_x, k_y, k_z)$ [Eq. (5)] was applied to express $k_y(E, k_x, k_z)$ in the form

$$k_y=2\arccos T, \tag{A2}$$

where

$$T=(E-\epsilon_4\cos\tfrac{1}{2}k_x\cos\tfrac{1}{2}k_z)/(\epsilon_2\cos\tfrac{1}{2}k_x+\epsilon_3\cos\tfrac{1}{2}k_z) \tag{A3}$$

and

$$|\epsilon_2|=4\epsilon_{(a+b)/2},\qquad |\epsilon_3|=4\epsilon_{(b+c)/2},\qquad |\epsilon_4|=4\epsilon_{(a+c)/2}.$$

The signs of the energy parameters ϵ_2, ϵ_3, and ϵ_4 for each exciton branch are determined by the corresponding representation of the D_{2h} point group.

The volume integral enclosed by a constant energy surface

$$A_{n\alpha,m\beta}=\underset{(E)}{\iiint}\exp[i\mathbf{k}(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta})]dk_xdk_ydk_z \tag{A4}$$

can be expressed in the form

$$A_{n\alpha,m\beta}(E)=\frac{1}{(2\pi)^3}\int_{-\pi}^{\pi}\exp(i\eta_3k_z)dk_z \times\int_{-\pi}^{\pi}\exp(i\eta_1k_x)dk_x\int_{-2\arccos T}^{+2\arccos T}\exp(i\eta_2k_y) \times dk_yB_{\alpha j}(k)B_{\beta j}(k). \tag{A5}$$

The off-diagonal terms [Eq. (7)] are given by

$$g_{n\alpha,m\beta}(E)=(d/dE)\sum_j A_{n\alpha,m\beta}(E). \tag{A6}$$

In a similar manner the density of states function [Eq. (6)] is obtained from the diagonal terms $A_{n\alpha,n\alpha}$. As the volume integrals $A_{n\alpha,n\alpha}$ are proportional to the number of states up to energy E, one has to bear in mind that the total number of exciton states has to increase with increasing the volume of the zone enclosed by the constant energy surface E. Integration had to be performed over the appropriate zone volume enclosed by the constant energy surface, taking into account the effect of Van Hove analytical singular points. The integrals $A_{n\alpha,m\beta}(E)$ have to be calculated on the same zone volumes enclosed by the same energy surfaces in the Brillouin zone as have been done for the diagonal terms. As the interactions are of short range we can set $B_{\alpha j}(k)=B_{\alpha j}(0)$ for all values of α, j, and k. Furthermore, as the orthorhombic crystal structure is characterized by an inversion symmetry one can show that the integrals (A5) in this particular case are real. The off-diagonal elements take the form

$$g_{00,0[(a+b)/2]}{}^0(E)=\frac{d}{dE}\sum_j 16\underset{(E)}{\int_0^{\pi}\int_0^{\pi}}\sin\tfrac{1}{2}k_y\cos\tfrac{1}{2}k_xdk_xdk_z,$$

$$g_{00,0[(b+c)/2]}{}^0(E)=\frac{d}{dE}\sum_j 16\int_0^{\pi}\int_0^{\pi}\sin\tfrac{1}{2}k_y\cos\tfrac{1}{2}k_zdk_zdk_x, \tag{A7}$$

where k_y is given by Eq. (A2).

We have calculated constant energy surfaces for

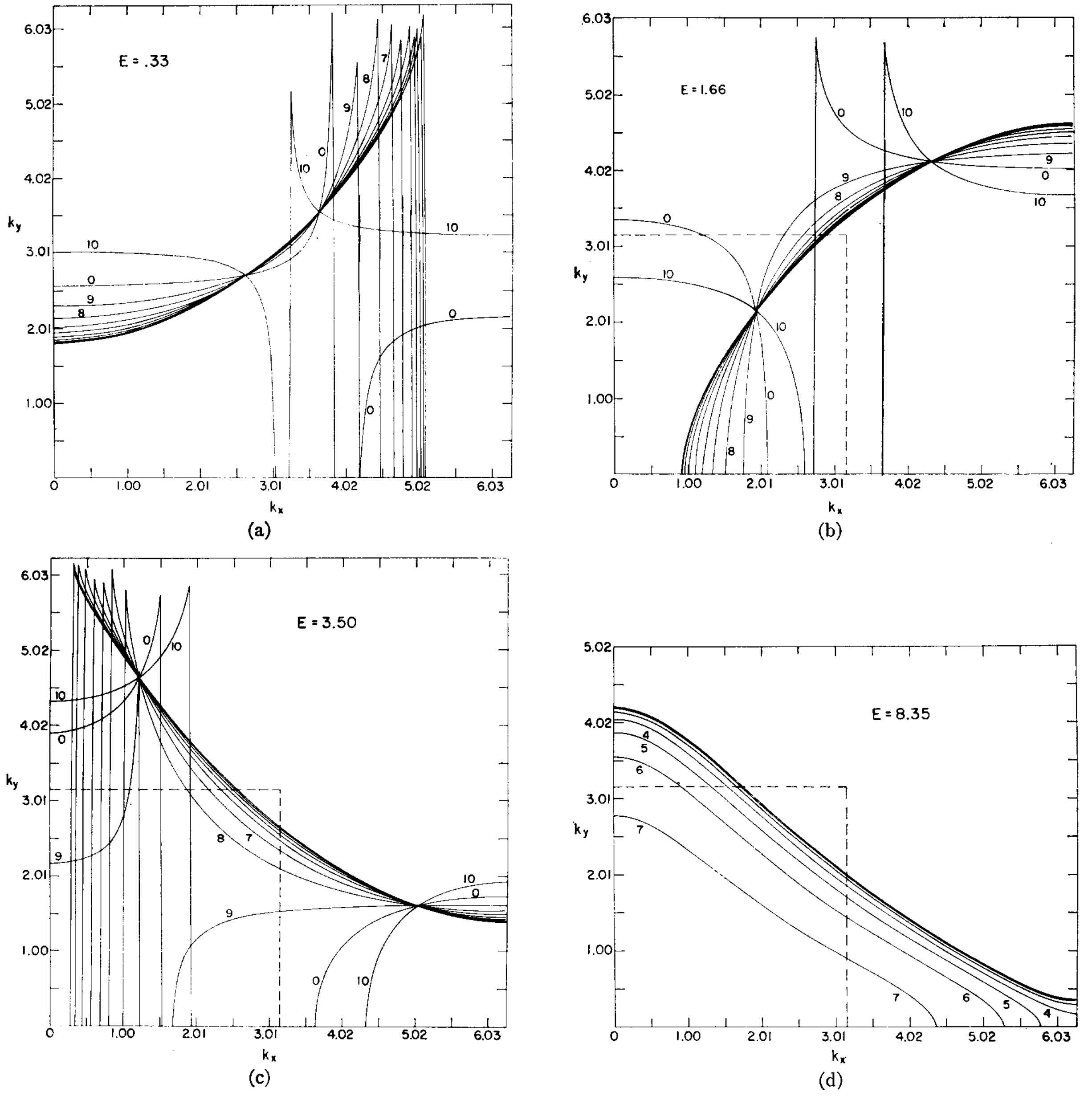

FIG. 4. Constant energy surfaces for the first singlet exciton band in benzene. Each line corresponds to a constant value (E) at fixed k_z. The dashed lines sign the region of a $\frac{1}{4}$ of the reduced Brillouin zone. Energies are given in cm^{-1}. Note that at a particular energy value E, the k_z lines behave differently. (a) $E=0.33$ cm^{-1}; (b) $E=1.66$ cm^{-1}; (c) $E=3.50$ cm^{-1}; (d) $E=8.35$ cm^{-1}.

each exciton branch and for fixed k_z (taking 400 points in the Brillouin one). The k_y values were determined from 800 points in the Brillouin zone for each fixed k_z. Typical examples for such surfaces are displayed in Fig. 4. When these energy surfaces reveal different behavior at the same energy as can be seen from Fig. 4, integration must be performed for each fixed k_z so that the number of the enclosed exciton states increases with increasing the energy of that particular exciton branch. Finally, all the contributions in the k_z direction were summed up for each exciton branch. Given the integrals of the form (A7) as a function of energy the (real) matrix elements $F_{qq'}(E)$ [Eq. (3)] were evaluated by numerical integration.