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# Resonance of electronic and electron-exciton complex modes in molecular crystals

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New modes are predicted to exist in molecular crystals. These are the result of a resonance coupling between an electron-exciton complex, bound by the additional polarizability of an excited molecule (Frenkel exciton), and a free conduction band electron. The dispersion relation for the complexlike branch can show a minimum at nonzero momentum. A case is made for benzene. These modes, however, are extremely fragile with respect to electron-phonon interactions. They are expected to be stable only for times short in comparison to their thermal lifetime. This restricts their detection to experiments utilizing fast nonequilibrium probes, such as electron injection in thin films.

A number of authors have examined the possibility of a coupling between electrons and excitons.<sup>1-8</sup> It is only recently that their binding was shown to exist in molecular crystals. It was argued that it would arise through the additional polarizability of an excited molecule.<sup>1-3,7,8</sup> Calculations for benzene (also valid for cyclohexene, 1,3- and 1,4-cyclohexadiene) and for 1,3-5-cycloheptatriene yielded numbers which link complexes to observed structures in low energy electron transmission spectra of thin films.<sup>1-3</sup> This provides the most direct evidence yet of their existence.

Complexes would be bound states formed from a Frenkel exciton and an electron in either (a) a tight binding molecular orbital conduction band, as described by Singh<sup>8</sup> who argues that the electron may or may not be on the same site as the exciton depending on the intramolecular potential, or (b) in a free conduction band. In case (a), if the electron is present on the same site as the exciton, the situation is somewhat similar to a molecular excited negative ion, but most frequently the exciton and the electron are on adjacent sites.<sup>8</sup> In case (b), the electron is localized between the excited molecule (Frenkel exciton) and the neighboring molecules.<sup>2,3</sup> This bound state does not necessarily exist in gases. The effect of the solid (hard core property) is to "compress" the electronic wave function around the exciton and thus to enhance the probability of a bound state. We wish to point out, however, a major difference between our definition of this complex and that in Ref. 4. These authors studied the equation of motion of a Green's function  $\langle\langle\alpha_i(t); b_{i'}^*(0)\rangle\rangle$ , where  $\alpha_i(t)$  destroys a conduction electron on site  $i$  at time  $t$  and  $b_{i'}^*(0)$  creates an exciton on site  $i'$ . They were thus interested in the resonant transformation of an electron into an exciton and not in a bound electron-exciton pair (which would have been described by  $\langle\langle\alpha_i(t)b_{i'}(t); \alpha_{i''}^*(t)b_{i''}^*(0)\rangle\rangle$  or alternately by the Gorkov function  $\langle\langle\alpha_{i''}^*(t); b_{i''}^*(0)\rangle\rangle$  similar to the one used in superconductivity). In either case (a) or (b), the bound state can be resonant with an extended electron state in the free conduction band. This resonance phenomena describes modes associated with the cyclic recurrent capture of an electron by the exciton it creates (formation of a complex) and the subsequent non-

radiative annihilation of the complex with ejection of the electron. These modes are nondecaying with respect to the electron-exciton interaction since they are eigenstates of the full Hamiltonian. We shall postpone any discussion of their lifetime with respect to photon or phonon emission until the end.

We wish to propose a simple model which will generalize the static picture in (a) or the dynamic structure in (b) by including this resonance mechanism. This model is able to describe the overall physical behavior of the resonance phenomenon while avoiding unnecessary microscopic details.

The ingredients used in building a Hamiltonian for this model are:

- (1) Electrons described by

$$H_e = \sum_{\alpha, \vec{k}} \epsilon_{\alpha, \vec{k}} c_{\alpha, \vec{k}}^{\dagger} c_{\alpha, \vec{k}}, \quad (1)$$

where  $c_{\alpha, \vec{k}}^{\dagger}$  creates an electron of wave vector  $\vec{k}$  in the  $\alpha$  band with energy  $\epsilon_{\alpha, \vec{k}}$  (spin neglected).

- (2) Excitons described by ( $\hbar = 1$ )

$$H_{ex} = \sum_r \sum_{\vec{q}} \omega_{r, \vec{q}} b_{r, \vec{q}}^{\dagger} b_{r, \vec{q}}, \quad (2)$$

where  $b_{r, \vec{q}}^{\dagger}$  creates a Frenkel exciton of wave vector  $\vec{q}$  in the  $r$  band with energy  $\omega_{r, \vec{q}}$ . Excitons are bosons by symmetry, but, considering that two of them cannot exist on the same molecule, one has

$$(b_{r, \vec{q}}, b_{r', \vec{q}'}^{\dagger}) = \delta_{r, r'} \delta_{\vec{q}, \vec{q}'} - \frac{2}{N} \sum_Q \delta_{r, r'} \delta_{\vec{q}, \vec{q}'} b_{r, \vec{q}}^{\dagger} b_{r, \vec{q}}, \quad (3)$$

where  $N$  is the number of unit cells.

- (3) Frölich terms coupling the electron and the excitons given by

$$H_{e-ex} = \sum_{\alpha, \alpha'} \sum_{\vec{k}, \vec{q}} \varphi_{\alpha', \alpha}^{\dagger}(\vec{k}, \vec{q}) c_{\alpha', \vec{k}+\vec{q}}^{\dagger} c_{\alpha, \vec{k}} (b_{r, \vec{q}} + b_{r, -\vec{q}}^{\dagger}) + \text{c. c.}, \quad (4)$$

which are responsible, among other things, for the polarizability of the molecules<sup>7,11</sup> in their ground state and for the resonance coupling.

- (4) An additional polarizability of the excited molecules representing a mean field approximation to the

<sup>a)</sup>Supported by NSERC.

modification in  $H_{e-ex}$  whenever a real exciton is present which may be written as

$$H_{\Delta} = - \sum_{\alpha, \alpha'} \sum_{\vec{k}, \vec{k}'} \Delta_{\alpha, \alpha'}^r(\vec{k}, \vec{k}', \vec{q}, \vec{q}') c_{\alpha, \vec{k}}^{\dagger} c_{\alpha, \vec{k}'} b_{\vec{q}, \vec{q}'}^{\dagger} b_{\vec{q}, \vec{q}'} , \quad (5)$$

and is essential for the binding. As described in the introductory remarks, this last term is responsible for the formation of an electron-exciton complex and is, here, described phenomenologically.

Although both cases (a) and (b) could occur simultaneously for each exciton branch, we shall consider one case at a time under the following restrictions without loss of the overall physics: (i) We neglect any Brillouin zone boundary effect. (ii) We neglect all anisotropies in order to obtain a clearer picture of the physics. (iii) In order to simplify the problem, we treat only a single exciton branch.

The effect of other exciton branches will be to renormalize the mass and energy of the conduction electron. This exciton can be a singlet or a triplet and the values of  $\omega_{r, \vec{q}}$ ,  $\Delta_{\alpha, \alpha'}^r$ ,  $\varphi_{\alpha, \alpha'}^r$  depend on this. For instance, the contribution of a triplet to the polarization potential of the ground state molecule due to its virtual excitation by the incoming electron (exchange-polarization) must be shorter ranged than in the singlet case since a spin-spin interaction is necessary in order to create a triplet exciton. We omit any details of such spin dependent interactions since they do not change the general behavior, only the size and range of the parameters. We describe the exciton by the dispersion relation given by

$$\omega_q = W_0 + \frac{q^2}{2m_{ex}} \quad (\hbar = 1) . \quad (6)$$

The exciton bands are usually narrow (less than 100  $\text{cm}^{-1}$  for a singlet and less than 40  $\text{cm}^{-1}$  for a triplet in anthracene crystals<sup>13</sup>).

(iv) We consider only two conduction bands: (1) A tight binding conduction one which is necessary for case (a) described by

$$\epsilon_{1, k} = \epsilon_{TB} + \frac{k^2}{2m_{TB}} . \quad (7)$$

(2) A free conduction band which is necessary in both cases given by

$$\epsilon_{2, k} = \epsilon_f + \frac{k^2}{2m_f} . \quad (8)$$

Here  $\epsilon_{TB}$ ,  $\epsilon_f$ ,  $m_{TB}$ , and  $m_f$  take into account the renormalization due to the phonons and the other exciton branches. In molecular crystals usually  $\epsilon_{TB} < \epsilon_f$  and evidently  $m_{TB} \gg m_f$ .<sup>12</sup> The bandwidth of tight binding bands are typically of the order of 1000  $\text{cm}^{-1}$ . This is the case in the  $a, b$  direction of anthracene crystals while it is 10  $\text{cm}^{-1}$  in the  $c$  direction.<sup>14-18</sup>

The Hamiltonians of the model can then be described as: For the case (a):

$$H = \sum_{\alpha=1}^2 \sum_{\vec{k}} E_{\alpha, k} c_{\alpha, \vec{k}}^{\dagger} c_{\alpha, \vec{k}} + \sum_{\vec{q}} \omega_q b_{\vec{q}}^{\dagger} b_{\vec{q}} + \sum_{\vec{k}, \vec{q}} \varphi_{1, 2}(q) c_{2, \vec{k}+\vec{q}}^{\dagger} c_{1, \vec{k}} (b_{\vec{q}}^{\dagger} + b_{\vec{q}}) + \text{c. c.} + H_{\Delta}^1 . \quad (9)$$

For the case (b):

$$H = \sum_{\vec{k}} \epsilon_{2, k} c_{2, \vec{k}}^{\dagger} c_{2, \vec{k}} + \sum_{\vec{q}} \omega_q b_{\vec{q}}^{\dagger} b_{\vec{q}} + \sum_{\vec{k}, \vec{q}} \varphi_{2, 2}(q) c_{2, \vec{k}+\vec{q}}^{\dagger} c_{2, \vec{k}} (b_{\vec{q}}^{\dagger} + b_{\vec{q}}) + \text{c. c.} + H_{\Delta}^2 , \quad (10)$$

where

$$H_{\Delta}^{\alpha} = - \sum_{\vec{k}, \vec{q}} \Delta^{\alpha}(q) c_{\alpha, \vec{k}+\vec{q}}^{\dagger} c_{\alpha, \vec{k}} b_{\vec{q}}^{\dagger} b_{\vec{q}} \quad (\alpha = 1, 2) \quad (11)$$

and

$$E_{1, k} = E_{TB} + \frac{k^2}{2m_{TB}^*} , \quad (12)$$

$$E_{2, k} = E_f + \frac{k^2}{2m_f^*} .$$

In writing Eq. (9), we have considered that the  $\varphi_{1, 1}$  and  $\varphi_{2, 2}$  terms have renormalized the masses and energies of the two bands. As these two Hamiltonians can be treated in the same mathematical way, we replace  $E_{2, k}$  in Eq. (9) by  $\epsilon_{2, k}$  in order to simplify the notation but one must not forget that in the (a) case,  $\epsilon_f$  and  $m_f$  take into account the renormalization by the  $\varphi_{2, 2}$  term.

We now introduce the simplifying assumption for either case that

$$\varphi(q) = \frac{\varphi}{N^{1/2}} \frac{\Omega_{\varphi}}{\Omega} \exp(-q^2/q_{\varphi}^2) , \quad (13)$$

$$\Delta(q) = \frac{\Delta}{N} \frac{\Omega_{\Delta}}{\Omega} \exp(-q^2/q_{\Delta}^2) ,$$

where  $\Omega$  is the unit cell volume and  $\Omega_{\Delta}$ ,  $\Omega_{\varphi}$  are the volumes over which the interactions are effective. We have chosen

$$\int d^3q \exp[-q^2/q_{\Delta}^2] = (2\pi)^3/\Omega_{\Delta} . \quad (14)$$

In the definition (13), we are not explicitly considering intramolecular correlations between an electron and an exciton. Such correlations are surely important. Double occupancy was not permitted although possible in case (a),<sup>8</sup> whereas in case (b) an electron can be in the same cell as the exciton although strictly not on it.<sup>2,3</sup> One should thus consider Eq. (13) as describing some sort of pseudointeractions taking into account any correlation effects in an average way. As already stated, our purpose is not to prove that complexes exist or to get detailed information on them. We only wish to study the resonance phenomena of one free conduction electron with them without being cluttered by algebra. We thus propose a model which can be adjusted to experimental data. In this way, the pseudointeractions are characterized by amplitudes  $\Delta$ ,  $\varphi$ , and ranges  $q_{\Delta}^{-1}$ ,  $q_{\varphi}^{-1}$ .

In both cases, the  $\varphi$  term will be treated as a perturbation. Let us first obtain the unperturbed states. Because of  $H_{\Delta}$ , a bound electron-exciton state can occur and we use variational states  $|\psi_c^a\rangle$ ,  $|\psi_c^b\rangle$  to describe these complexes:

$$|\psi_c^a(\vec{P})\rangle = \sum_{\vec{q}} \exp[-c(q^2/q_{\Delta}^2)] c_{1, (\vec{m}_{TB}^*/M_1)\vec{P}-\vec{q}}^{\dagger} b_{(\vec{m}_{ex}/M_1)\vec{P}-\vec{q}}^{\dagger} |00\rangle ,$$

$$|\psi_c^b(\vec{P})\rangle = \sum_{\vec{q}} \exp[-c(q^2/q_{\Delta}^2)] c_{2, (\vec{m}_f/M_2)\vec{P}-\vec{q}}^{\dagger} b_{(\vec{m}_{ex}/M_2)\vec{P}-\vec{q}}^{\dagger} |00\rangle , \quad (15)$$

where  $M_1 = m_{TB}^* + m_{ex}$ ,  $M_2 = m_f + m_{ex}$  and  $c$  is the variational parameter. The energies of the complexes are then given by

$$E_c^a(P) = E_{TB} + W_0 - \Delta'_1 + \frac{P^2}{2M_1}, \quad (16)$$

$$E_c^b(P) = \epsilon_f + W_0 - \Delta'_2 + \frac{P^2}{2M_2}, \quad (16)$$

with

$$\Delta'_\alpha = \Delta \left[ \frac{2^{3/2}}{(c+2)^{3/2}} - \frac{3}{4c} \frac{q_\Delta^2}{2\mu_\alpha \Delta} \right] \quad (\alpha = 1, 2), \quad (17)$$

and

$$\mu_1^{-1} = m_{TB}^{*-1} + m_{ex}^{-1}, \quad (18)$$

$$\mu_2^{-1} = m_f^{-1} + m_{ex}^{-1}.$$

Bound states (that means complexes) exist when

$$\Delta > \frac{3^{5/2}}{16} \frac{q_\Delta^2}{2\mu_\alpha}. \quad (19)$$

The existence of a threshold is in agreement with the results of Refs. 3 and 8. In Figs. 1 and 2, we have represented by dashed lines and hatched regions the unperturbed states in both cases. In order to develop a resonance mechanism between a free conduction electron and a complex, it is necessary to have an energy degeneracy between these levels, at  $\epsilon_{2,P_c} = E_c^{a(b)}(P_c)$ . Although this condition is not necessarily fulfilled in case (a) since it means that the bottom of the free conduction band must be below  $E_c^a$ , it is certainly fulfilled in case (b) since the exciton energies are of the order of 4 eV, that is well above the possible binding energy ( $\sim 0.5$  eV) of an electron-exciton complex in this case.<sup>2,3</sup>

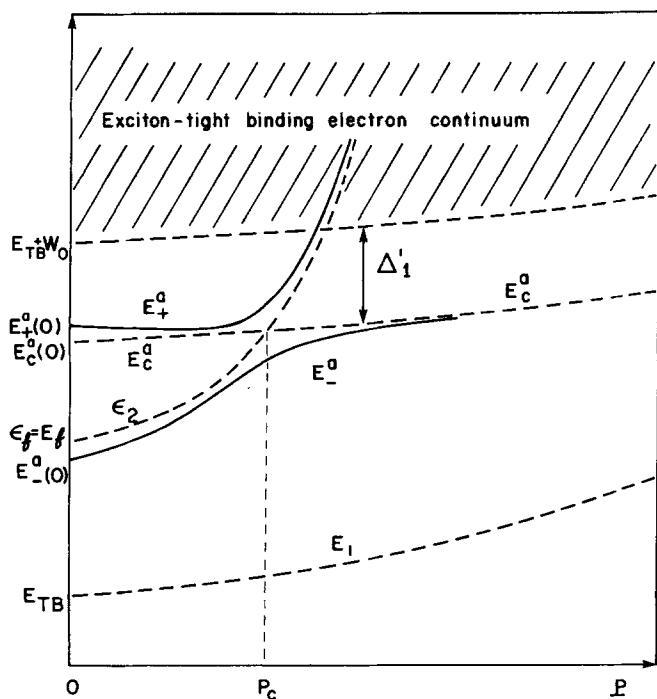


FIG. 1. Dispersion relations in case (a) (see the text) when  $E_{TB} < \epsilon_f < E_c^a(0) < E_{TB} + W_0$ . The dashed lines are the uncoupled states and the hatched region represents the electron-exciton continuum. The full lines are the resonant states.

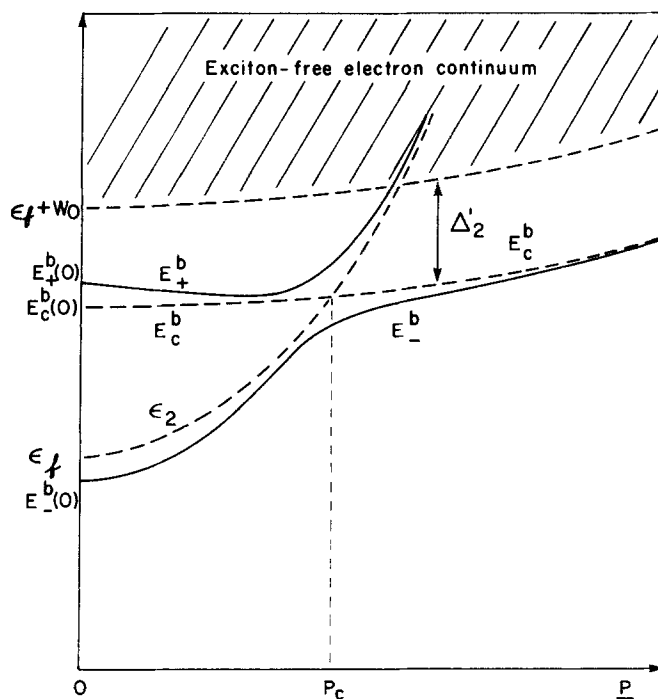


FIG. 2. Dispersion relations in case (b) (see the text). The dashed lines are the uncoupled states; the hatched region represents the electron-exciton continuum and the full lines are the resonant states.

We use now the two-level degenerate perturbation theory on the  $\varphi$  term which couples the two degenerate levels  $c_{2,P}^*|00\rangle$  and  $|\psi_c(P)\rangle$  and we get two branches:

$$E_\pm^a(P) = \frac{\epsilon_{2,P} + E_c^a(P)}{2} \pm \left[ \left( \frac{E_c^a(P) - \epsilon_{2,P}}{2} \right)^2 + a_1^2(P) \right]^{1/2}, \quad (20a)$$

for case (a), whereas for case (b) we obtain

$$E_\pm^b(P) = \frac{\epsilon_{2,P} + E_c^b(P)}{2} \pm \left[ \left( \frac{E_c^b(P) - \epsilon_{2,P}}{2} \right)^2 + a_2^2(P) \right]^{1/2}, \quad (20b)$$

with

$$a_\alpha^2(P) = \varphi^2 \frac{\Omega_\varphi}{\Omega} \frac{(2cq_\Delta^2 q_\varphi^2)^{3/2}}{(cq_\varphi^2 + q_\Delta^2)^3} \times \exp\left(-\frac{m_{ex}}{M_\alpha} \frac{P^2}{q_\varphi^2} \frac{2cq_\Delta^2}{cq_\varphi^2 + q_\Delta^2}\right) \quad (\alpha = 1, 2). \quad (20c)$$

The dispersion relations  $E_\pm$  are shown in Figs. 1 and 2 by full lines for both cases.

The important conclusions at this point are: (1) The free electrons and the complexes, whenever their energies are resonant, form coupled states which can propagate even for infinite mass complexes (within their radiative lifetimes). (2) The dispersion relation for the complex like modes can have a minimum at nonzero momentum. It is relatively easy to give the condition for such a minimum to appear. The coefficient of  $P^2$  in  $E_\pm$  must be negative for small  $P$ . For instance, whenever

TABLE I. Model parameters for benzene (first excitons) and other  $\pi$ -bonded six carbon rings. The parameters are defined in the text.

$m_f = 10^{-27} \text{ g}^{\text{a}}$
$m_{ex} = 10 \text{ } m_f^{\text{b}}$
$W_0 \approx 4 \text{ eV}^{\text{c}}$
$\Delta'_2 \approx 0.65 \text{ eV}^{\text{c}}$
$P_c \approx 10^8 \text{ cm}^{-1\text{d}}$
$q_\Delta \approx q_\phi \approx 3.5 \times 10^7 \text{ cm}^{-1\text{e}}$
$C \approx 0.5^{\text{f}}$
$\Delta \approx 2.2 \text{ eV}^{\text{f}}$
$a_2(0) \approx 0.7 \text{ eV}^{\text{g}}$
$2a_2(P_c) \approx 0.07 \text{ eV}^{\text{h}}$

<sup>a</sup>Free electron mass.

<sup>b</sup>Exciton mass for a bandwidth of  $100 \text{ cm}^{-1}$  (see the text).

<sup>c</sup>References 2 and 3.

<sup>d</sup>Free electron momentum at resonance  $P_c \approx [2 m_f (W_0 - \Delta'_2)]^{1/2}$ .

<sup>e</sup>From Eq. (13), assuming a nearest-neighbor range ( $\approx 6 \text{ \AA}$ ) which is consistent with Ref. 3.

<sup>f</sup>From the variational procedure in Eq. (17).

<sup>g</sup>From the known polarization energy of a  $\pi$  bond (Ref. 19) at the maximum electron density in the complex ( $\approx 3 \text{ \AA}$ ) which is adequate to the mode energy displacement at  $P=0$ ,  $a_2^2(0)/[E_c^b(0) - \epsilon_f]$  (singlet exciton case).

<sup>h</sup>Resonance splitting from Eq. (20).

$$\frac{m_f}{m_f + m_{ex}} \ll 1, \quad a_\alpha^2(0) \ll (E_c^{a(b)}(0) - \epsilon_f)^2 \quad (21)$$

the condition becomes

$$\frac{cq_\phi^2 + q_\Delta^2}{4cM_\alpha} \frac{(E_c^{a(b)}(0) - \epsilon_f)^2}{a_\alpha^2(0)} - (E_c^{a(b)}(0) - \epsilon_f) + \frac{cq_\phi^2 + q_\Delta^2}{4cm_f} < 0 \quad (\alpha = 1, 2). \quad (22)$$

Furthermore this condition can be simplified to

$$\frac{cq_\phi^2 + q_\Delta^2}{4cm_f} < E_c^{a(b)}(0) - \epsilon_f, \quad (23)$$

when

$$\frac{cq_\phi^2 + q_\Delta^2}{4cM_\alpha} \frac{E_c^{a(b)}(0) - \epsilon_f}{a_\alpha^2(0)} \ll 1 \quad (\alpha = 1, 2). \quad (24)$$

The interaction between these modes and the continua of one exciton plus one electron and higher energy states can be treated in second-order perturbation theory. The features just described remain qualitatively the same. One does not get pinning of the electron like modes to the continua because of the short-range nature of the interaction  $\phi(q)$ .

It is surely instructive at this point to take a closer look at benzene, which has already been proposed as a prototype for case (b). We have estimated the various parameters entering our semiphenomenological model. These appear in the Table I. It should be noted that the deduced parameter  $\Delta$  has a value quite compatible with the additional polarization energies of an exciton.<sup>2,3</sup> With these values, Eqs. (21)–(24) are all satisfied and we predict a minimum in the dispersion relation of the

upper branch with a depth of about  $0.1 \text{ eV}$ . The resonance splitting  $2a_2(P_c)$  is seen to be small.

As far as case (a) is concerned, we cannot make predictions with any great accuracy. Since the electron in the complex lies mostly on the molecular orbitals of the first neighbors around the exciton. In the Singh approach<sup>8</sup> the maximum binding energy  $\Delta'$  would be equal to the additional polarization energy at the nearest-neighbor distance ( $\approx 6 \text{ \AA}$ ), i. e.,  $\leq 0.1 \text{ eV}$ . The only crucial parameter as far as a minimum is concerned is that  $(E_c^a(0) - \epsilon_f)$  be greater than a few tenths of an eV. The minimum, if it exists, should be very shallow.

The theoretical analysis has proven, thus far, the likely existence of coupled modes. Their practical importance, however, must be conditioned by their lifetime. Radiative lifetimes of excitons are typically, in anthracene for instance,  $27 \times 10^{-9}$ ,  $24 \times 10^{-9}$ , and  $10^{-11} \text{ s}$  for the first singlet, the first triplet, and the excitonic states,<sup>10</sup> respectively. The radiative lifetime of a triplet exciton may be dramatically reduced in the presence of the electron within the complex perhaps bringing it down to the singlet exciton level. Although the radiative lifetime of excitons in the presence of electrons might be small, the quasiparticles in the complexlike branch ( $E_+$ ) would be much more stable near resonance ( $P_c$ ). Their radiative decay implies a transition to the electron like branch ( $E_-$ ) with a small energy transfer [ $\sim 2a_2(P_c)$ ]. In the case of benzene, for instance, the ratio of this photon energy ( $\sim 0.1 \text{ eV}$ ) to the one involved in phosphorescence decay ( $w_0 \sim 4 \text{ eV}$ ) is large ( $\sim 40$ ). Since electric dipole transition rates are proportional to  $w^4$ , one then expects an increased lifetime of the quasiparticles with respect to the normal radiative lifetimes by a large amount ( $\sim 10^6$ ). Phonon emission may prove to have the most constraining influence on these modes. One can safely assume that the resonance conditions could not be sustained for times much longer than  $10^{-12}$ – $10^{-11} \text{ s}$  because of phonon emission (vibrations of intramolecular or lattice origin with typical frequencies of  $10^{13} \text{ Hz}$ ). These processes are responsible for energy decay and thermalization, and are quite fast. This is evident in phosphorescence and fluorescence quenching<sup>9,10</sup> which involves an energy transfer between diffusion (unbound) states of excitons and injected electrons and fast subsequent transfer to the vibrational modes. The whole concept of modes is thus restricted to the narrow time interval between the resonance period  $[2a_2(P_c)]^{-1}$ ,  $\sim 10^{-14} \text{ s}$  for benzene, and the lifetime  $10^{-12}$ – $10^{-11} \text{ s}$ . There is an obvious difficulty in making measurements in such a short time. One needs a nonequilibrium probe which is sensitive to this time interval. Electron transmission experiments in thin films<sup>1-3</sup> may well prove to be one of the few possible probes for this.

<sup>1</sup>L. Sanche, Chem. Phys. Lett. 65, 61 (1979), J. Chem. Phys. 71, 4860 (1979), also J. Phys. C 13, L 677 (1980).

<sup>2</sup>G. Bader, L. Caron, and L. Sanche, Solid State Commun. 38, 843 (1981).

<sup>3</sup>L. Sanche, G. Bader, and L. Caron, J. Chem. Phys. 76, 4016 (1982).

<sup>4</sup>G. Gumbs and C. Mavroyannis, Solid State Commun. 41, 237

- (1982).
- <sup>5</sup>E. L. Nagaev and E. B. Sokolova, *Phys. Status Solidi B* **64**, 441 (1974).
- <sup>6</sup>F. I. Dalidchik and V. Z. Slonim, *Pis'ma Zh. Eksp. Teor. Fiz.* **31**, 122 (1980); [*JETP Lett.* **31**, 112 (1980)].
- <sup>7</sup>V. M. Agranovitch and A. A. Zakhidov, *Chem. Phys. Lett.* **68**, 86 (1979).
- <sup>8</sup>J. Singh, *Phys. Status Solidi B* **103**, 423 (1981).
- <sup>9</sup>N. Wakayama and D. F. Williams, *Chem. Phys. Lett.* **9**, 45 (1971).
- <sup>10</sup>N. Wakayama and D. F. Williams, *J. Chem. Phys.* **57**, 1770 (1972).
- <sup>11</sup>Y. Toyozawa, *Prog. Theor. Phys.* **12**, 421 (1954).
- <sup>12</sup>Karl Norbert, "Organic Semiconductors," *Festkörperproblem XIV* (1974).
- <sup>13</sup>A. Davydov, *Théorie du Solide* (MIR, Moscow, 1980), see Fig. 87, p. 672 and Fig. 77, p. 514.
- <sup>14</sup>H. Sumi, *Solid State Commun.* **28**, 309 (1978).
- <sup>15</sup>L. B. Schein, *Phys. Rev. B* **15**, 1024 (1977).
- <sup>16</sup>O. H. Leblanc Jr., *J. Chem. Phys.* **35**, 1275 (1961).
- <sup>17</sup>J. I. Katz, S. A. Rice, S. I. Choi, and J. Jortner, *J. Chem. Phys.* **39**, 683 (1963).
- <sup>18</sup>R. M. Glaeser and R. S. Berry, *J. Chem. Phys.* **44**, 3797 (1966).
- <sup>19</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967).