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Energy transfer and spectral line shapes of impurities in crystals*

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The problem of electronic energy transport in solids is discussed. A model system of two molecules interacting with a lattice of phonons is considered. The spectral line shapes and energy transport are treated in various limiting cases, and the connection between these two phenomena is discussed.

I. INTRODUCTION

The problem of electronic energy transfer among crystal impurities has been approached theoretically by many authors from several directions. It has been investigated from the point of view of rate equations,¹ hopping models,² diffusion equations,³ and microscopically by considering the interaction of the migrating excitation with the lattice. The most useful and popular model in the latter category is that of Förster⁴ and Dexter⁵ which can be derived either from quantum mechanical⁶⁻⁹ or classical¹⁰ principles, because it treats the lattice interactions simply as a means to determine the density of states. In a variety of cases this model has been shown to give good agreement with experiment.¹¹

In a previous paper⁸ we examined a plausible microscopic model using electron-phonon coupling. A similar model has also been investigated by other workers.⁹ The model reduces to the Förster-Dexter results in limiting cases but may also treat situations for which the Förster-Dexter assumptions are not valid. This microscopic model also shows the competition between coherent and incoherent transfer processes and in that respect resembles the models of exciton migration in pure crystals.

There is another aspect of this model which is of current interest: The connection between energy transfer and absorption and fluorescence spectra in the same system. Some theories have been developed, ¹² using electron-phonon interactions, which predict spectral features of interacting impurities. Also, it has been postulated that there is a simple and direct relationship between the excitation and transfer processes in that the width of the spectral absorption line measures the same relaxation processes which appear in the energy transfer equations.^{13,14} This is true for certain models, like those treated in Refs. 13-15; however more complicated models may lead to a more complicated relationship between these parameters. For example, if appreciable lattice relaxation occurs before transfer, then there may not be a simple relationship between these processes.

Haken *et al.*, ¹⁵ Gamurar, Perlin, and Tsukerblat, ¹⁶ Avakian, Ern, Merrifield, and Suna, ¹³ Kenkre and Knox,⁹ and Grover and Silbey¹⁷ have addressed the problem of exciton migration in the presence of lattice relaxation in different ways. The latter authors have argued that in order to treat exciton transport it is sufficient to consider the density matrix in the "clothed" exciton representation (where the "clothing" process corresponds to the relaxation of the initially formed exciton by phonon emission). While it is also possible to treat exciton transport in the "bare" exciton representation, it is necessary to treat the spectral line shape in the "bare" representation (as was done by Grover and Silbey). If one assumes that the phonon part of the spectral line is governed by a correlation function which is a single exponential, $\exp(-\gamma_0 t)$, then it can be shown that the equations for the bare exciton density matrix in the Grover-Silbey model are identical to those of Haken et al.¹⁵ or Avakian et al.¹³ who do not distinguish the two representations. Thus the claim made by Ern et al.¹⁴ that the Grover-Silbey¹⁷ model cannot give the correct linewidth is based on the incorrect idea that Grover and Silbey were computing the bare exciton transport properties. The microscopic model used by Grover and Silbey as extended herein can be used to compute both the spectral line shape and the transport properties of excitons.

There are many mechanisms for the clothing process of an electronically excited molecule in a solid. This process can be visualized as the decay of the local lattice distortion produced upon vertical excitation of the impurity molecule. In a complete microscopic theory lattice relaxation and energy transfer can be treated on an equal footing and limiting cases can be examined.

In the present paper we extend the results of Rackovsky and Silbey⁸ by including a site-diagonal excitationphonon coupling (i.e., local scattering). This serves as a mechanism for vibrational and lattice relaxation of the excited molecule and host. We then derive the equations for the spectral line shape for a variety of model electron-phonon coupling schemes. We also derive the equations of motion for the density matrix averaged over the phonon states.

The paper is set out as follows: in Sec. II, the Hamiltonian and the system are defined; in Sec. III, the general formulas for spectral line shapes are given and applied to a single impurity in Sec. IV; in Sec. V, the formulas for energy transfer are given and applied to various models in Sec. VI.

II. THE SYSTEM

The system we consider consists of two impurity molecules embedded in a crystal lattice. Each molecule is viewed as having only two states: a ground state and a relatively long-lived excited state (such as a lowest singlet or triplet). Within the formalism developed in this paper, the vibrational states of the two impurities can be treated on the same footing as either the impurity electronic states or the lattice phonons. For this reason we shall not deal with them explicitly; however, for concreteness, we may assume that the electronic state referred to in what follows is the lowest vibronic state of the impurity molecule.

The two impurity excited states are coupled to each other via dipole-dipole, exchange, or other mechanism. This coupling is of course modified by the properties of the lattice.¹⁸ Idealizing the problem, however, we assume that there is no interaction between the impurity and the crystal electronic states; in this respect the lattice is "inert." At the same time each impurity interacts with the acoustic and optical phonons of the lattice (electron-phonon scattering). The strength of this interaction differs between the ground and excited states of each molecule. Since we are concerned only with the excitation and de-excitation processes of the two molecules, we can simply consider the difference between the excited and ground state interactions. In other words, we limit ourselves to the excitation-phonon interactions.

The Hamiltonian of a single impurity then is

$$\tilde{H} = \tilde{\Delta}c^*c + \tilde{Z}c^*c + H_{\text{phon}} , \qquad (2.1)$$

where $c^*(c)$ are the creation (annihilation) operators for the vertical (or bare) excitation. $\tilde{\Delta}$ is the excited state energy,

$$H_{\rm phon} = \sum_{q\lambda} \omega_{q\lambda} b^{*}_{q\lambda} b_{q\lambda}$$

is the harmonic phonon Hamiltonian in which $b_{q\lambda}^{\star}(b_{q\lambda})$ creates (annihilates) a phonon of wave vector q, branch λ , and energy $\omega_{q\lambda}$. The operator \tilde{Z} describes the coupling of the localized impurity excited state to the lattice vibrations. Part of this excitation-phonon interaction can be easily diagonalized by use of a unitary transformation. There may however be a residual part of \tilde{Z} , representing the effect of the phonon bath on the impurity energy levels (such as the decay of an intramolecular vibration), which cannot be diagonalized exactly in a simple manner. This part will be treated by perturbation theory.

Thus, for $\tilde{Z} = \tilde{Z}_d + \tilde{Z}_r$ as described above, we can diagonalize \tilde{Z}_d by the transformation

$$H = \Theta \,\tilde{H} \Theta^{+} = \Delta a_{1}^{*} a_{1} + Z_{r} \,a_{1}^{*} a_{1} + H_{\text{phon}} \,, \qquad (2.2)$$

where

$$a^* = \theta c^*, \quad a = \theta^* c, \quad Z_r = \theta Z_r \theta^*.$$

We also include in Z_r terms which change the local energy of the site which may be due to complicated factors

(strain, imperfections, etc.) whose total effect is nevertheless small and gives rise to a broadening of the spectral line of the noninteracting impurities. It should be pointed out that if a method for diagonalizing the part of H containing Z_r could be found, then of course we could proceed with no "local" scattering present in the Hamiltonian [see Eq. (2.2)]. We assume, however, that Z_r is small and thus treating this as a perturbation is an excellent approximation.

The operator $a^*(a)$ represents the creation (annihilation) operator for a "clothed" excitation, that is, an excitation in which the phonon terms are treated explicitly and separately from the electronic excitation. Thus, $\theta^*(\theta)$, the transformation operator, can be thought of as representing the creation (annihilation) of a phonon cloud which, together with the "purely electronic" excitation (a^*) comprise the full "vertical" excitation (c^*) . For the two-impurity system the Hamiltonian is

$$\begin{split} \bar{H} &= \tilde{H}_{mo1} + H_{phon} + H_{mp} \\ &= \tilde{\Delta}(c_1^* c_1 - c_2^* c_2) + J_B(c_1^* c_2 + c_2^* c_1) + \sum_{q\lambda} \omega_{q\lambda} b_{q\lambda}^* b_{q\lambda} \\ &+ \tilde{Z}_1 c_1^* c_1 + \tilde{Z}_2 c_2^* c_2 + \tilde{\Phi} c_1^* c_2 + \tilde{\Phi}^* c_2^* c_1 . \end{split}$$
(2.3)

The indices refer to impurity sites 1 and 2, J_B is the intermolecular interaction, and Z_i and Φ are phonon operators describing local and nonlocal scattering processes, respectively. This Hamiltonian can also be treated by a similar unitary transformation to give

$$H = \Delta' (a_1^* a_1 - a_2^* a_2) + J_B(\theta_1^* \theta_2 a_1^* a_2 + \theta_2^* \theta_1 a_2^* a_1) + H_{phon} + Z_1' a_1^* a_1 + Z_2' a_2^* a_2 + \Phi' a_1^* a_2 + \Phi'^* a_2^* a_1, \qquad (2.4)$$

where θ_1 and θ_2 are the operators which result when one diagonalizes Z_{1d} and Z_{2d} , respectively.

In the clothed exciton representation the terms proportional to J_B give "nonlocal" excitation-phonon scattering. This describes the scattering that results from phonons carried along with the relaxed excitation during the transfer process, and leads to the Förster-Dexter results in the appropriate limit.⁷⁻⁹ The terms in Φ' correspond to scattering of the vertical excitation (c_i^*) and is due to residual heat bath interactions during the transfer process.

It is convenient to write the Hamiltonian as

$$H = H_0 + V$$
, (2.5a)

where H_0 corresponds to the canonical average of the H for the given temperature and V takes into account the thermal fluctuations.

$$H_{0} = \Delta(a_{1}^{*}a_{1} - a_{2}^{*}a_{2}) + J_{c}(a_{1}^{*}a_{2} + a_{2}^{*}a_{1}) + H_{phon},$$

$$\Delta = \Delta' + \frac{1}{2} \langle Z'_{1} - Z'_{2} \rangle,$$

$$J_{c} = J_{B} \langle \theta_{1}^{*}\theta_{2} \rangle + \langle \Phi' \rangle,$$

(2.5b)

$$V = Z_{1}a_{1}^{*}a_{1} + Z_{2}a_{2}^{*} + \Phi a_{1}^{*}a_{2} + \Phi^{*}a_{2}^{*}a_{1},$$

$$Z_{i} = Z_{i}^{\prime} - \langle Z_{i}^{\prime} \rangle,$$

$$\Phi = J_{B}\theta_{1}^{*}\theta_{2} + \Phi^{\prime} - J_{c}.$$
(2.5c)

The energy zero in the above equation has been shifted to $\frac{1}{2} \langle Z_1 + Z_2 \rangle$ for convenience. We will now compute the

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line shapes and energy transfer parameters to second order in V.

III. SPECTRAL LINE SHAPES

The spectral line shape for a system interacting with light is given by the imaginary part of the Fourier-transformed retarded Green function. In our system in which the excited electronic state is not thermally populated, the line shape can be reduced to:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \, e^{-i\,\omega t} \, \langle \mu \circ \mu(t) \rangle \,, \qquad (3.1)$$

where $\langle \mu \mu(t) \rangle$ is the transition dipole-dipole correlation function and the angular brackets denote the average taken over the canonical phonon ensemble of our crystal. For a single impurity with one excited state

$$\mu = \mu_1(c_1 + c_1^*), \qquad (3.2)$$

where μ_1 is the dipole matrix element for the transition between the ground and the excited state.

The dipole-dipole correlation function then is

$$\langle \boldsymbol{\mu} \cdot \boldsymbol{\mu}(t) = \mu_1^2 \langle c_1 c_1^{\star}(t) \rangle = \mu_1^2 \langle a_1 \theta_1 a_1^{\star}(t) \theta_1^{\star}(t) \rangle$$

$$\cong \mu_1^2 \langle a_1 a_1^{\star}(t) \rangle \langle \theta_1 \theta_1^{\star}(t) \rangle .$$

$$(3.3)$$

The last equality in (3.3) holds within the Born-Oppenheimer approximation. The absorption spectrum then is given by

$$I(\omega) = \int_{-\infty}^{+\infty} d\omega' g_{11}(\omega') \mathfrak{D}_{11}(\omega - \omega'), \qquad (3.4a)$$

where

$$g_{11}(\omega) = \int_{-\infty}^{+\infty} dt \, e^{-i\,\omega t} \langle a_1 a_1^*(t) \rangle \tag{3.4b}$$

$$\mathfrak{D}_{11}(\omega) = \int_{-\infty}^{+\infty} dt \, e^{-i\,\omega t} \langle \theta_1 \theta_1^*(t) \rangle \tag{3.4c}$$

are the Fourier transforms of the clothed exciton correlation function and the phonon-cloud correlation function respectively. Thus, within the Born-Oppenheimer approximation, the line shape can be considered as the combination of two parts; an "electronic transition [given by $g(\omega)$], which can be described by the correlation functions of the clothed representation, and an accompanying multiphonon transition [given by $\mathfrak{D}(\omega)$] which is described by the relaxation (or clothing) process of the vertical excitation. $g(\omega)$ is obviously not entirely electronic in origin, but this nomenclature will be used throughout.

For the two impurity system the transition dipole operator is

$$\mu = \mu_1(c_1 + c_1^*) + \mu_2(c_2 + c_2^*), \qquad (3.5)$$

where the indices refer to the two impurity sites. Thus, the absorption spectrum is

$$I(\omega) = \mu_{1}^{2} \int_{-\infty}^{+\infty} g_{11}(\omega') \mathfrak{D}_{11}(\omega - \omega') d\omega' + \mu_{2}^{2} \int_{-\infty}^{+\infty} g_{22}(\omega') \mathfrak{D}_{22}(\omega - \omega') d\omega' + \mu_{1} \cdot \mu_{2} \int_{-\infty}^{+\infty} d\omega' \{ g_{12}(\omega') \mathfrak{D}_{12}(\omega - \omega') + g_{21}(\omega') \mathfrak{D}_{21}(\omega - \omega') \}, \qquad (3.6)$$

where the decoupling assumption of Eq. (3.3) is again invoked and g_{ij} and D_{ij} are defined by analogy to Eqs. (3.4b), (3.4c), and $\mu_1 \circ \dot{\mu}_2$ is the scalar product of the two transition dipole vectors.

The problem is to determine \mathcal{G}_{ij} and \mathcal{D}_{ij} in the presence of the intermolecular interaction terms. We will assume that $\mathcal{D}_{ij}(\omega)$, which is effectively the phonon spectrum of the crystal-impurity system, is not affected by the presence of these interaction terms. We will carry out the calculations of $\mathcal{G}_{ij}(\omega)$ to second order in J, the intermolecular interaction.

In Appendix A we calculate the equations of motion of

$$\hat{\mathbf{g}}_{ij}(t) = \langle a_i a_j^*(t) \rangle$$

and obtain

$$\dot{\hat{g}}_{11}(t) = i\Delta \hat{g}_{11}(t) + iJ_{\sigma} \hat{g}_{12}(t) - \int_{0}^{t} d\tau \{ \hat{A}(\tau) \hat{g}_{11}(t-\tau) + \hat{B}(\tau) \hat{g}_{12}(t-\tau) \},$$
(3.7a)

$$\hat{g}_{12}(t) = -i\Delta \ \hat{g}_{12}(t) + iJ_c \ \hat{g}_{11}(t) -\int_0^t d\tau \{ \hat{C}(\tau) \ \hat{g}_{12}(t-\tau) + \hat{B}(\tau) \ \hat{g}_{11}(t-\tau) \}$$
(3.7b)

with similar equations for $\hat{g}_{21}(t)$ and $\hat{g}_{22}(t)$.

To obtain $g_{ij}(\omega)$ we simply Laplace transform the differential equation for $g_{ij}(t)$ [Eq. (3.7)] and solve for the real part of $g_{ij}(p)$ evaluated at $p = i\omega$.

The coefficients $\hat{A}(t)$, $\hat{B}(t)$, $\hat{C}(t)$ consist of oscillatory terms of frequency Γ and decaying terms (i.e., the phonon correlation functions such as $\langle \Phi \Phi^*(t) \rangle$ [Eq. (A5)]. The real part of their Laplace transforms will be functions peaked near $\omega = \pm \Gamma$ with a width like the inverse of the characteristic time for the decay. We will assume that this width is large enough so that we can replace the functions $A(\omega)$, $B(\omega)$, $C(\omega)$ by their values at $\omega = \pm \Gamma = \pm (J_c^2 + \Delta^2)^{1/2}$. Also, near the spectral peaks at $\omega = \pm \Gamma$, we expect the imaginary part of these functions to be negligible.

With these approximations, we find

$$S_{11}(\omega) = \frac{1}{2} \operatorname{Re} \left\{ \frac{1 + (\Delta + \frac{1}{2}i(A - C))\Lambda^{-1}}{i(\omega - \Lambda) + \frac{1}{2}(A + C)} + \frac{1 - (\Delta + \frac{1}{2}i(A' - C'))\Lambda'^{-1}}{i(\omega + \Lambda') + \frac{1}{2}(A' + C')} \right\},$$

(3.8a)

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$$g_{22}(\omega) = \frac{1}{2} \operatorname{Re} \left\{ \frac{1 - (\Delta + \frac{1}{2}i(A - C))\Lambda^{-1}}{i(\omega - \Lambda) + \frac{1}{2}(A + C)} + \frac{1 + (\Delta + \frac{1}{2}i(A' - C'))\Lambda'^{-1}}{i(\omega - \Lambda') + \frac{1}{2}(A' + C')} \right\},$$
(3.8b)

$$S_{12}(\omega) = S_{21}(\omega) = \frac{1}{2} \operatorname{Re} \left\{ (J_c + iB) \Lambda^{-1} \left(\frac{1}{i(\omega - \Lambda) + \frac{1}{2}(A + C)} - \frac{1}{i(\omega + \Lambda') + \frac{1}{2}(A' + C')} \right) \right\},$$
(3.8c)

where

$$\Lambda = \left[(\Delta + i\frac{1}{2}(A - C))^2 + (J_c + iB)^2 \right]^{1/2}$$

and the primed coefficients are evaluated at $\omega = -\Gamma$ while the unprimed are evaluated at $\omega = \Gamma$.

IV. LINE SHAPES IN A ONE-IMPURITY SYSTEM

We consider a single impurity molecule imbedded in an inert lattice having the Hamiltonian of Eq. (1). An expression for the spectrum of such a system is given in Eq. (9) as consisting of an electronic and a phonon part.

The electronic part of the spectrum is

$$\mathcal{G}_{11}(\omega) = \frac{1}{2} \operatorname{Re}[i(\omega - \Delta) + \zeta]^{-1}$$
(4.1a)

$$\zeta = \int_{-\infty}^{+\infty} dt \langle ZZ(t) \rangle , \qquad (4.1b)$$

calculated easily from Eq. (3.8) and Eq. (A7) with J=0. We note that the electronic part consists of a Lorentzian line shape whose finite width arises from the residual phonon scattering processes.

To obtain an expression for the phonon part we consider the simplest excitation-phonon interaction which is linear in the phonon operators

$$\tilde{Z}_{d} = \sum_{q} z_{q} \omega_{q} (b_{q} + b_{q}^{*}) , \qquad (4.2)$$

where z_q is the dimensionless coupling constant of the qth phonon mode to the electronic transition, ω_q is the phonon frequency, and $b_q^*(b_q)$ are the phonon creation (annihilation) operators. This interaction corresponds to a local lattice deformation due to a change in equi-librium positions of the impurity and its neighboring host molecules. The problem has been treated extensively by several authors.¹⁹ We will outline here the main results without their mathematical derivation, as a point of reference for the discussion of the two-impurity spectrum.

The linear interaction of Eq. (4.2) is diagonalized by

$$\Theta = \exp\left[\sum_{q} z_{q}(b_{q} - b_{q}^{*})\right].$$
(4.3)

Therefore the cloud correlation function is

$$\hat{\mathbb{D}}_{11}(t) = \exp\left\{-N^{-1}\sum_{q} z_{q}^{2}[(2n_{q}+1) + n_{q} e^{-i\omega_{q}t} + (n_{q}+1) e^{i\omega_{q}t}]\right\},$$
(4.4)

where

 $n_q = (e^{\beta \omega_q} - 1)^{-1},$ $\beta = (kT)^{-1}.$ This gives for the phonon part of the spectrum

$$\mathfrak{D}_{11}(\omega) = e^{\beta\omega/2} \exp\left[-N\sum_{q} z_{q}^{2}(n_{q}+1)\right] \sum_{\{N_{q}\},\omega} P(N_{q} \mid \omega, T),$$
(4.5)

where the sum is over all phonon combinations of total energy ω and $P(N/\omega, T)$ is the temperature-dependent relative probability for each such combination. The form of these factors is

$$P(N_q/\omega, T) = \prod_q I_{N_q}(z_q^2 \operatorname{csch}(\beta \omega_q/z)), \qquad (4.6)$$

where I_N is the hyperbolic Bessel function of order N, and N_q equals the number of q phonons participating in the process. We note that since hyperbolic Bessel functions obey

$$I_{-N}(x) = I_N(x)$$

we have

$$P(N_q/-\omega, T) = P(N_q/\omega, T)$$
(4.7)

and

$$\mathfrak{D}_{11}(-\omega) = e^{-\beta \omega} \mathfrak{D}_{11}(\omega) . \qquad (4.8)$$

For dispersionless (Einstein) phonons

 $\hat{D}_{11}(t) = \exp\{-z^2[(2n+1) + ne^{-i\omega t} + (n+1)e^{i\omega t}]\}$

$$=e^{-z^{2}(2n+1)}\sum_{k=-\infty}^{+\infty}\left(\frac{n}{n+1}\right)^{k/2}e^{ik\omega_{0}t}I_{k}(2z^{2}n^{1/2}(n+1)^{1/2})$$
(4.9a)

so that

$$\mathfrak{D}_{11}(\omega) = e^{-\kappa^2(2n+1)} \sum_{k=-\infty}^{+\infty} \left(\frac{n}{n+1}\right)^{k/2} \times I_k(2z^2n^{1/2}(n+1)^{1/2})\,\delta(\omega-k\omega_0)\,.$$
(4.9b)

Because of the factor $e^{z^{2}(2n+1)}$ the integrated intensity of the spectrum is normalized to unity at all temperatures. Thus, at high temperatures $\mathfrak{D}_{11}(\omega)$ will consist of a broad band composed of densely spaced δ -function peaks for all the multiphonon excitations, each combination having relative intensity $P(\{N_q\} | \omega, T)$. At low temperatures $\mathfrak{D}_{11}(\omega)$ will be dominated by the zero-phonon peak, since the relative probability (intensity) of the other peaks will be small. That is,

$$I_n(z^2 \operatorname{csch}\beta \omega_0/2) \cong \delta_{n0}, \qquad (4.10)$$

for $z^2 \operatorname{csch}(\beta \omega/2) \approx 0$. In this model the zero-phonon line has no width at low *T*. The full spectrum (i.e., convolution of phonon and electronic parts) will therefore be a broad band at usual temperatures with its maximum near the multiphonon maximum. At low temperatures, where Eq. (4.10) is satisfied, the spectrum will consist of an intense Lorentzian line of width ζ [see Eq. (4.1b), the zero-phonon line] and a less intense phonon wing.

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In the time domain the multiphonon band gives a description of the clothing process, while the zero-phonon line corresponds to the creation of a "relaxed" electronic excitation. We can visualize the relaxation process by considering a vertical excitation as consisting of an electronic excitation and an accompanying local lattice distortion given by Eq. (4.3). Since the Hamiltonian [Eq. (1)] treats only harmonic nondecaying phonons the relaxation of the distortion will be due to the time evolution of the phonon combinations describing it, and appearing in the multiphonon band of the spectra. That is, when the phonons become de-phased, the local lattice distortion disappears and the excitation appears relaxed by the emission of phonons. However, the relaxation due to anharmonic and other effects can be introduced phenomenologically by giving the phonon correlation function an exponential decay.²⁰ Since the relaxation is into the phonon continuum, the decay rate will be proportional to the width of the phonon band which acts as the continuum. For strong lattice relaxation, as is the case at high temperatures, the spectrum is dominated by the multiphonon band making the clothing process extremely fast. For weak relaxation there is a finite probability of creating a relaxed species during excitation at temperatures near 0°K, given by the relative intensity of the zero-phonon line.

The situation is completely analogous for the emission process, assuming that lattice relaxation is fast compared to the excited state lifetime: The relaxed excited impurity radiates to produce a "vertical" (or "bare") excitation and upon relaxation a "clothed" ground state. The emission spectrum therefore is the exact mirror image of the absorption.

At low temperatures the absorption and emission zero-phonon lines will be exactly coincident. At higher temperatures the absorption and emission maxima will not coincide since they correspond to the multiphonon maxima. This gives rise to the "Stokes" shift.

V. INTERMOLECULAR ENERGY TRANSFER

We consider the system of two impurities embedded in an inert lattice with the Hamiltonian given in Eq. (3). In order to understand energy transfer in this system, we must find the probability of excitation localized at each site as a function of time.

We can study this process either in the c_i^* representation (i.e., looking at vertical excitations) or in the a_i^* representation (i.e., accounting only for relaxed excitations). Since we expect lattice relaxation to be fast on the time scale of energy transfer, it is more *convenient* to calculate the population of "relaxed" (or "clothed") excitations. This assumption is definitely correct for separated impurity molecules. For near pairs, however, one ought to study the intertwining of the relaxation and the transfer processes.²¹ This is difficult to do mathematically (except in a kinetic scheme) and we therefore have no knowledge of the transfer process before lattice relaxation is complete.

To study the transfer process, we assume that site 1 was excited at time zero, and then derive the equations of motion for the density matrix elements averaged over the phonon ensemble in the same manner as discussed by Rackovsky and Silbey⁸ or Grover and Silbey.¹⁷

For the case in which radiative and nonradiative decay of the excitation is neglected the three independent density matrix elements can be expressed as:

$$f(t) = \langle \rho_{11}(t) - \rho_{22}(t) \rangle, \qquad (5.1a)$$

$$n(t) = \langle \rho_{12}(t) + \rho_{21}(t) \rangle,$$
 (5.1b)

$$m(t) = \langle \rho_{12}(t) - \rho_{21}(t) \rangle$$
. (5.1c)

The subscripts 1, 2 refer to the two sites (in the a_i^* representation) and the angular brackets denote an average over the phonon ensemble. Since all other decay routes are neglected, $\rho_{11}(t) + \rho_{22}(t) = 1$ for all time.

We may now find the equations of motion for the above matrix elements using a projection operator technique. Since this was done in detail in previous work, ⁸ we will not repeat the derivation here. It is sufficient to note that the exact equations are approximated again by replacing the modified propagator which appears in the projection operator scheme by the zeroth order propagator. This makes the equations tractable and is equivalent to calculating the matrix elements to second order in J, the intermolecular interaction.

We find

$$\hat{f}(t) = 2iJ_{c}m(t) - \int_{0}^{t} F(\tau) d\tau - \int_{0}^{t} F_{f}(\tau)f(t-\tau) d\tau - \int_{0}^{t} F_{n}(\tau)n(t-\tau) d\tau, \qquad (5.2a)$$

$$\dot{n}(t) = -2i\Delta m(t) - \int_0^t N(\tau) d\tau - \int_0^t N_f(\tau) f(t-\tau) d\tau - \int_0^t N_n(\tau) n(t-\tau) d\tau, \qquad (5.2b)$$

$$\dot{m}(t) = 2iJ_c f(t) - 2i\Delta n(t) - \int_0^t M_m(\tau) m(t-\tau) d\tau . \quad (5.2c)$$

The coefficients that have been omitted vanish or give negligible contributions in most models. The expressions for the coefficients are given in Appendix C. It is obvious from Appendix C that the correlation functions which are involved in the energy transfer equations (5.2) are the same as those in the spectral line shape equations, (3.6) and (3.7). These correlation functions contain all the information needed, within our approximations, to solve both sets of equations in principle.

We note that to solve these equations we may Laplace transform and solve the resulting algebraic equations. For the long-time behavior of the solutions we may evaluate the coefficients for the transform variable p=0 as was discussed by Rackovsky and Silbey.⁸ This is done for specific models in Sec. VI.

In previous work, we found similar equations. However, we had neglected the residual local scattering, Z_i , and had treated only the portion of local scattering that can be diagonalized. This scattering was treated as nonlocal by working in the clothed representation. In the present work, however, we explicitly deal with the residual scattering at each site which arises from the fact that our system is open and interacts with the heat bath.

The equations obtained give the correct equilibrium populations at infinite time and the decay rate reduces to the expression obtained by Rackovsky and Silbey⁸ at the appropriate limits.

Lattice relaxation (and consequently the phonon part of the spectrum) enters in a different way in the treatment of energy transfer: We showed in Eq. (2.4) that the local phonon scattering responsible for lattice relaxation appears in nonlocal (off-diagonal) scattering in the clothed representation of the two-impurity system. This implies that a relaxed excitation may undergo further relaxation upon transfer, since this will create new phonon clouds at the excited and de-excited sites.

At usual temperatures where the phonon part of the spectrum appears as a wide band, lattice relaxation is extremely fast and it is certainly a good approximation to consider the relaxed excitation as the energy-transferring species, even though the vertical excitation may be the species formed by light.

At low temperatures (and weak excitation-phonon coupling) the spectrum is composed of the zero-phonon line and the phonon wing. The excitation corresponding to the phonon wing still relaxes to the clothed representa tion quickly; there is however a large probability of producing directly a relaxed state upon excitation (or energy transfer), given by the relative intensity of the zero-phonon line. This implies that at low temperatures, phonon relaxation is no longer a mechanism that can justify the distinction between the bare and the clothed representations.

In the development outlined herein, both cases can be treated easily: for weak excitation phonon coupling and low temperatures we use the unrelaxed (or bare) excitation representation throughout (i.e., $\theta = 1$). In the case of fast relaxation we use the relaxed excitation representation for transfer and the bare representation for the spectral line shapes.

VI. THE TWO-IMPURITY SYSTEM

In this section we will evaluate the expressions for the spectral line shape and energy transfer of the twoimpurity system, and relate them to experimentally measurable quantities.

We will assume for simplicity that no correlation exists between sites for the scattering process.

$$\langle Z_1 Z_2(t) \rangle = 0 \tag{6.1a}$$

and

$$\langle Z_i \Phi(t) \rangle = 0. \tag{6.1b}$$

Although this is not necessary for the present discussion, it greatly simplifies the results and is undoubtedly a good approximation in most cases in which the two molecules are not nearest neighbors.

A. Model 1: Energy transfer under fast lattice relaxation

For fast lattice relaxation the bare and clothed representations for the excitation do not coincide. We assume that the clothed excitation is the migrating species, and is formed by fast relaxation of the bare excitation produced by light.

In calculating the electronic part of the optical spectrum in this model, we shall neglect the bare excitation nonlocal scattering term $[\Phi' \text{ in Eq. } (2.4)]$. This term arises from processes such as phonon-induced transfer and we believe that it is negligible compared to the clothed excitation nonlocal scattering term $[\theta_1^*\theta_2 \text{ in Eq.} (2.4)]$.

Under these assumptions we can easily calculate the electronic part of the optical spectrum [Eq. (3.8) and Appendix A] and the coefficients that enter into it [Eq. (A7)]. To relate these coefficients to experimentally measurable quantities we consider the fact that in many cases for nonadjacent impurities [Eq. (B4)]

$$\begin{split} \langle \Phi \Phi^{*}(t) &= J_{B}^{2} \left\{ \langle \theta_{1}^{*} \theta_{2} \theta_{2}^{*}(t) \theta_{1}(t) \rangle - \langle \theta_{1}^{*} \theta_{2} \rangle^{2} \right\} \\ &\cong J_{B}^{2} \left\{ \langle \theta_{2} \theta_{2}^{*}(t) \rangle \langle \theta_{1}^{*} \theta_{1}(t) \rangle - \langle \theta_{1}^{*} \theta_{2} \rangle^{2} \right\} \,. \end{split}$$

The Fourier transform of $\langle \Phi \Phi^*(t) \rangle$ then is

$$\varphi(z) = J_B^2 \left\{ \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathfrak{D}_{11} \left(z - \omega \right) \mathfrak{D}_{22}(\omega) - \frac{1}{2\pi} \left\langle \theta_1^* \theta_2 \right\rangle^2 \delta(z) \right\}$$
(6.2)

according to Eq. (B5). Thus, $\varphi(z)$ contains the overlap integral of the phonon parts of the spectra of sites 1 and 2 when their origins are separated by energy x. We will now examine the qualitative temperature dependence of $\varphi(z)$.

We note that $\langle \theta \theta^{\star}(t) \rangle$ gives the absorption spectrum, while $\langle \theta^* \theta(t) \rangle$ corresponds to emission. Therefore $\varphi(2\Gamma)$ for $\Gamma \neq 0$ is related to the spectral overlap integral used in the Förster-Dexter theory in the limit that there is no local scattering. It represents the probability that the phonon clouds generated by the de-excitation of one site and the excitation of the other will contain phonon combinations that make the transfer process in resonance. These phonon combinations take up the energy difference of the transferred excitation (2Γ) and bring the transfer process towards equilibrium because of their fast subsequent de-phasing and scattering. The temperature dependence of $\varphi(2\Gamma)$ follows that of the overlap integral of the two spectra each normalized to unity. Thus, at high temperatures it should be an increasing function of temperature, while at low temperatures it may be either increasing or decreasing, depending on the portions overlapping.

Similarly, $\varphi(0)$ represents the probability of transfer without energy loss to the lattice. It contains the spectral overlap integral at zero energy separation of the electronic states. At low temperatures this integral consists essentially of the overlap of the zero-phonon lines of the two spectra. However, as seen in Eq. (6.2), $\varphi(0)$ is modified by $\delta(\omega)$ which is due to the coherent part of energy transfer. In the simplest case of two impurities in a lattice having dispersionless (Einstein) phonons, we would have that the magnitude of $\varphi(\omega)$ at $\omega = 0$ is

$$\begin{split} \varphi(0) &= J_B^2 e^{-(z_1^2 + z_2^2)(2n+1)} \left\{ I_0(2n^{1/2}(n+1)^{1/2}(z_1^2 + z_2^2)) - 1 \right\} \\ &= J_B^2 e^{-(z_1^2 + z_2^2)(2n+1)} \sum_{k=-\infty}^{+\infty} \left\{ I_k(2z_1^2 n^{1/2}(n+1)^{1/2}) \right. \\ &\times I_k(2z_2^2 n^{1/2}(n+1)^{1/2}) - \delta_{k0} \right\}. \end{split}$$

The value of $\varphi(0)$ therefore, is small at all temperatures. At absolute zero $\varphi(0) = 0$ rigorously in the approximation of Eq. (B4). This indicates that when there are no phonons present in the lattice, the energy-conserving transfer process can only be coherent. At finite temperatures, however, the value of $\varphi(0)$ will be finite, indicating that incoherent energy-conserving transfer processes are possible. At low temperatures, the value of $\varphi(0)$ increases with temperature; at higher temperatures $\varphi(0)$ is a decreasing function of temperature, since the probability of energy-conserving processes decreases at these temperatures. The maximum value attained by $\varphi(0)$, and the temperature at which it is attained depends on the magnitude of the total excitation-phonon coupling of the two impurities. That is, in impurities having a weak excitation-phonon coupling (so that the zero-phonon line dominates their low temperature spectra) $\varphi(0)$ reaches a maximum (typically ~ 0.3 J_B^2) at relatively high temperatures, while in cases of very strong excitation-phonon coupling (so that the zero-phonon line has a very weak intensity even at 0 °K) $\varphi(0)$ reaches its maximum at low temperatures.

Also, $\varphi(-2\Gamma)$ contains the overlap integral for the "inverse" Förster-Dexter transfer process, that is energy transfer from the low-energy site to the highenergy site with the absorption of energy 2Γ from the lattice phonons. It is therefore the overlap of the highenergy site absorption and the low-energy site emission spectra. Because of Eq. (4.8) $\varphi(-2\Gamma)$ is related to $\varphi(2\Gamma)$ by

$$\varphi(-2\Gamma) = e^{-2\beta\Gamma}\varphi(2\Gamma) . \tag{6.4}$$

At absolute zero, this overlap is rigorously zero but at higher temperatures it has some finite value for small Γ . Like $\varphi(2\Gamma)$ this function will vary very slowly with temperature.

The relative magnitudes of $\varphi(2\Gamma)$, $\varphi(0)$, and $\varphi(-2\Gamma)$ will depend on the value of Γ , the magnitude of the excitation-phonon interaction and the temperature: (a) For small Γ as in the case of weak intermolecular coupling between similar impurities ($\Delta = 0$) we will have

$$\varphi(2\Gamma) \cong \varphi(0) \cong \varphi(-2\Gamma) \tag{6.5}$$

at all temperatures: (b) In the case where the zerophonon lines dominate the two spectra (i.e., low temperatures and weak excitation-phonon interactions) and widely separated energies for the two impurities we will have,

$$\varphi(0) > \varphi(2\Gamma) . \tag{6.6}$$

(c) If 2Γ is of the order of or greater than the width of the phonon bands coupled to the excitation we would expect the two spectra to have maximum overlap in the $\varphi(2\Gamma)$ integral thus giving

$$\varphi(2\Gamma) \gg \varphi(-2\Gamma)$$
. (6.7)

(d) For extremely large Γ , however, we will have negligible spectral overlap, making negligible the probability of any energy transfer which can bring the two site populations into thermal equilibrium.

The other parameter in these equations is $\zeta_i(x)$ [see Eq. (A7) and Eq. (4.1)]. The purely electronic spectral line has a Lorentzian shape of width $\zeta(0)$ due to local scattering with no energy loss. Thus $\zeta(\pm 2\Gamma)$ involves an energy loss of $\mp 2\Gamma$ to the lattice and corresponds to the probability of *local* relaxation in resonance with the energy transfer process.

We shall discuss in this model the spectral line shapes and energy transfer equations for two cases: (a) Weakly coupled equivalent sites, resembling the case of molecular excitons, (b) inequivalent sites with considerable spectral overlap giving Förster-like energy transfer.

1. Model 1a: Equivalent sites-molecular excitons

For similar impurities ($\Delta = 0$), the energy gap between the two exciton states is small, giving

$$\varphi(2\Gamma) \approx \varphi(0) \approx \varphi(-2\Gamma) = \varphi, \qquad (6.8)$$

$$\zeta(2\Gamma) = \zeta(0) = \zeta(-2\Gamma) = \zeta, \qquad (6.9)$$

$$e^{\beta\Gamma} \cong 1. \tag{6.10}$$

Therefore the coefficients entering in the spectral functions are [from Eq. (A7)]

$$A = C = A' = C' = \zeta + \varphi \tag{6.11a}$$

giving for the "electronic" part of the spectrum [from Eq. (3.8)]

$$g_{11}(\omega) = g_{22}(\omega) = \frac{A}{2} \left[\frac{1}{(\omega - J_C)^2 + A^2} + \frac{1}{(\omega + J_C)^2 + A^2} \right] \quad (6.11b)$$

$$g_{12}(\omega) = g_{21}(\omega) = \frac{A}{2} \left[\frac{1}{(\omega - J_c)^2 + A^2} - \frac{1}{(\omega + J_c)^2 + A^2} \right] .$$
(6.11c)

The phonon part of the spectrum consists of

$$\mathfrak{D}_{11}(\omega), \ \mathfrak{D}_{22}(\omega)$$

which are the same as in the absence of the intermolecular interaction [Eq. (4.9)] and $\mathfrak{D}_{12}(\omega) = \mathfrak{D}_{21}(\omega)$ for the phonon cross term. For nearest neighbor impurities this term has a complicated functional form, taking into account the spatial correlation of the crystal deformation. This functional form is a narrow distribution around $\omega = 0$, and as it is shown in Appendix B, it reduces to a δ function at $\omega = 0$ for separated impurities.

The electronic part of the spectrum for the two equivalent interacting impurities consists of two Lorentzian lines of width A separated by 2J [Eqs. (6.11b), (6.11c)]. The intensity ratio of these two lines is

$$\frac{I_{\star J}}{I_{-J}} = \frac{\mathfrak{D}_{11}\mu_1^2 + \mathfrak{D}_{22}\mu_2^2 + 2\mathfrak{D}_{12}\mu_1 \cdot \mu_2}{\mathfrak{D}_{11}\mu_1^2 + \mathfrak{D}_{22}\mu_2^2 - 2\mathfrak{D}_{12}\mu_1 \cdot \mu_2} , \qquad (6.12)$$

where $\mathfrak{D}_{ij} = \mathfrak{D}_{ij}(0)$. For impurities having different orientations the two lines carry different polarizations and thus the splitting between them is easily measurable.

In the full spectrum each line is accompanied by a phonon wing. Because of the very narrow distribution of the phonon cross term $\mathfrak{D}_{ij}(\omega)$, the phonon wings will be identical for the two lines within the assumptions of this model. They will only differ in the regions around $\omega = \pm J_c$ where their intensity ratios will follow Eq. (6.12).

The dynamics of exciton motion in this case are relatively simple. The solution to the energy transfer equations [Eq. (5.2)] shows that the excited state population oscillates between the two sites with a frequency

$$\omega = (J_c^2 - \zeta^2)^{1/2} \approx J_c \tag{6.13a}$$

while at the same time the oscillation is damped at a rate

$$k = \zeta + 2\varphi \tag{6.13b}$$

to achieve equilibrium. We note that these parameters may be obtained from spectral information for the isolated impurities. 22

The rate of excitation localization can be considered as the exciton hopping rate, and thus it can be related to the exciton diffusion constant. If we assume that the full spectrum of the *isolated* impurity is a Lorentzian, the overlap integral φ can be evaluated to give a migration rate (γ = width)

$$k = J_c^2 / \gamma + \zeta . \tag{6.14}$$

2. Model 1b: Inequivalent sites-Förster-like transfer

Under Förster-like conditions of large energy separation and substantial spectral overlap between the two impurities the assumptions of this model are

$$\varphi(2\Gamma) \gg \varphi(-2\Gamma) \tag{6.7}$$

and for simplicity

• •

$$\zeta_1 = \zeta_2 = \zeta \ . \tag{6.1}$$

The coefficients of Eq. (A7) then are

$$A = \zeta(0) + e^{\beta\Gamma} \epsilon(2\Gamma); \qquad A' = \varphi(0) + \zeta(-2\Gamma)$$

$$C = \varphi(0) + \zeta(2\Gamma); \qquad C' = \zeta(0) + e^{-\beta\Gamma} \epsilon(2\Gamma) \qquad (6.16)$$

where

$$\epsilon(2x) = e^{\beta x} \varphi(2x) . \tag{6.17a}$$

We note that because of Eq. (6.4) we have

$$\epsilon(2\Gamma) = \epsilon(-2\Gamma) . \tag{6.17b}$$

Solving Eq. (3.9) to order J^2 for the coefficients (6.16) the electronic part of the spectrum is found to be

$$I(\omega) = \left\{ \mu_1^2 + \mu_2^2 + \frac{\Delta}{\Gamma} (\mu_1^2 - \mu_2^2) + \frac{2J_c}{\Gamma} \mu_1 \mu_2 \right\} \frac{A}{(\omega - \Gamma)^2 + A^2} \\ + \left\{ \mu_1^2 + \mu_2^2 - \frac{\Delta}{\Gamma} (\mu_1^2 - \mu_2^2) - \frac{2J_c}{\Gamma} \mu_1 \mu_2 \right\} \frac{C'}{(\omega + \Gamma)^2 + C'^2} .$$
(6.18a)

The spectrum thus consists of two Lorentzian lines at $\omega = +\Gamma$ and $\omega = -\Gamma$. The width of these lines is $\zeta(0) + e^{\theta\Gamma} \epsilon(2\Gamma)$ and $\zeta(0) + e^{-\theta\Gamma} \epsilon(2\Gamma)$, respectively; that is, the two peaks exhibit an additional component to their width, in each case proportional to the corresponding Förster transfer rate. Their relative intensities are

$$R = \frac{\mu_1^2 + \mu_2^2 + (\mu_1^2 - \mu_2^2)(\Delta/\Gamma) + 2\mu_1\mu_2(J_c/\Gamma)}{\mu_1^2 + \mu_2^2 - (\mu_1^2 - \mu_2^2)(\Delta/\Gamma) - 2\mu_1\mu_2(J_c/\Gamma)}$$
(6.18b)

which for the case $\mu_1 = \mu_2$ reduce to

$$R = (\Gamma + J_c)/(\Gamma - J_c) . \qquad (6.18c)$$

The phonon part of the spectrum is similar to that discussed in model 1a.

The energy transfer equations (5.2) for this case reduce to

$$\dot{f} = 2iJ_c m - (4\Delta/\Gamma)\sinh\beta\Gamma\epsilon(2\Gamma) - 4[\epsilon(2\Gamma)\cosh\beta\Gamma]f,$$
(6.19a)

$$\dot{n} = -2i\Delta m - 2[\zeta(2\Gamma) + \zeta(-2\Gamma)]n, \qquad (6.19b)$$

$$\dot{m} = 2iJ_c f - 2i\Delta n - 2\{\varphi(0) + \tilde{\varphi}(0) + \zeta(2\Gamma) + \zeta(-2\Gamma)\}. \quad (6.19c)$$

The definition of $\tilde{\varphi}(0)$ is discussed in Appendix B. Energy transfer occurring according to Eq. (6.19) tends to the equilibrium value

$$f = -(\Delta/\Gamma) \tanh\beta\Gamma \tag{6.20}$$

(to order J_c^2) at long times.

The emission spectrum therefore will not be identical to the absorption. If we assume that equilibrium is reached in a time much shorter than the radiative lifetime, the system will radiate from its equilibrium distribution. The intensity ratio of the two peaks at $\pm \Gamma$ will be for $\mu_1 \approx \mu_2$

$$R = \frac{\Gamma + J_c}{\Gamma - J_c} \cdot \frac{\Gamma - \Delta \tanh\beta\Gamma}{\Gamma + \Delta \tanh\beta\Gamma} .$$
(6.21)

That is, in emission the bulk of the intensity shifts to the low-energy peak (sensitized fluorescence).

Observing the time evolution of the two excited state populations for the simplest case ($\Delta = 0$) we see that the excitation oscillates between the two sites with a frequency

$$\omega = \left[J_c^2 - \frac{1}{4}(\zeta(2\Gamma) + \zeta(-2\Gamma))^2\right]^{1/2} \approx J_c \,. \tag{6.22a}$$

This oscillation is damped to approach the equilibrium distribution at a rate

$$k = \varphi(0) + \tilde{\varphi}(0) + \zeta(2\Gamma) + \zeta(-2\Gamma) + 2\epsilon(2\Gamma)\cosh\beta\Gamma.$$
(6.22b)

This damping is the equivalent of the Förster energy transfer rate since it determines the rate of localization of the excitation to the low-energy site. We note however that this transfer rate differs from that obtained by Soules and Duke⁷ in that it also takes into account localization of the excitation due to randomization of phase. That is it includes the coefficients arising from both the diagonal and off-diagonal terms of the density matrix. The diagonal elements of the density matrix [Eq. (6.19a)] decay to their equilibrium value by dissipation of energy 2Γ to the lattice during the transfer process due to nonlocal scattering, $\epsilon(2\Gamma)$. On the other hand, the off-diagonal elements [Eqs. (6.19b, c)] decay to zero both because of energy fluctuations at each site [local scattering $\zeta(\pm 2\Gamma)$] and because of loss of phase coherence during an energy-conserving transfer process [nonlocal scattering $\Phi(0)$]. At high temperatures the contribution of these new terms to the localization of the

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excitation at the low-energy site may be negligible. At low temperatures on the other hand, we would expect energy-conserving transfer processes to have a greater probability thus making their contribution to excitation localization measurable.

Distinguishing between coherent and incoherent transfer processes we note that coherent energy transfer causes the excitation to oscillate between the two sites. In the frequency domain this moves the two spectral peaks to $\pm \Gamma$. Incoherent transfer processes on the other hand determine the Förster-like energy localization rate. Viewed in the frequency domain this gives rise to a transfer-dependent contribution to the width, unequally distributed between the two spectral lines and in addition to the single-impurity width (due to energy-conserving local scattering).

We also note that in the case of no local scattering all the parameters entering in the Förster-like localization rate (that is both these of the Förster process proper as shown by Soules and Duke⁷ and those due to phase randomization arising from energy-conserving transfer) are obtainable from spectral information of the isolated molecules. If however local scattering is important, the dynamics of energy transfer are not simply related to the appearance of the spectra, since the former involve local scattering terms resonant with the transfer process [i.e., $\zeta(\pm 2\Gamma)$] while the latter includes only energy-conserving local interactions [i.e., $\zeta(0)$]. However, the correlation function, $\zeta(\omega)$, contains all this information, and is, in principle, derivable from the energy transfer rate or the spectra. It may be difficult in practice to retrieve this information.

B. Model 2: Very weak excitation-phonon interactions

We assume that Z_d , the diagonalizable part of the bare excitation local phonon scattering, is negligible. The bare and clothed excitation representations thus coincide, with $\theta = 1$. This would correspond to a situation where the zero phonon line dominates the spectraum and has negligible width.

In this case, the "phonon" parts of the spectrum will be

$$\mathfrak{D}_{ij}(\omega) = \int_{-\infty}^{+\infty} dt \, e^{-i\,\omega t} \langle \theta_i \, \theta_j^*(t) \rangle = 2\pi \,\delta(\omega) \,, \qquad (6.23)$$

The structure of the one-impurity and the two-impurity spectra, therefore, will be determined completely by the features of their "electronic" part which are outlined in Eqs. (4.1) and (3.8), respectively. We will find that it is not always possible to relate the parameters in the *single* impurity spectra to the parameters in the energy transfer equations; thus we *postulate* different models for the structure of the correlation functions in what follows.

1. Model 2a: Stochastic scattering

We assume that the excitation-phonon interaction is a Gaussian-Markov stochastic process. This is a simplifying assumption, often used to calculate exciton transport models.¹⁵ Under this assumption, the correlation functions are

$$\langle Z_i Z_i(t) \rangle = 2\zeta \delta(t)$$
 (6.24a)

$$\langle \Phi \Phi^{\dagger}(t) \rangle = \langle \Phi \Phi(t) \rangle = 2\varphi \delta(t),$$
 (6.24b)

where $\delta(t)$ is the Dirac δ function. This however is an infinite temperature approximation since a δ -function correlation implies a white spectrum with all phonon frequencies excited. On the other hand, the zero-phonon line dominates in the spectrum, and in this regard the model resembles the low temperature case and at low temperatures we would expect a nonzero correlation time. We will use these assumptions, however, in order to acquire an insight into the essential features of bare excitation transfer, bearing in mind that we have chosen the assumptions which give the simplest results.

Under these assumptions the coefficients of the line shape equations [Eq. (A7)] become

$$A = C = \zeta + \varphi \tag{6.25a}$$

and therefore

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$$\Lambda = (\Delta^2 + J_c^2)^{1/2} = \Gamma.$$
 (6.25b)

The two-impurity spectrum, therefore, consists of two Lorentzian lines at $\omega = \pm \Gamma$ having width $\zeta + \varphi$. Thus, in this model also the width of the two-impurity spectral lines is affected by energy transfer.

The energy transfer differential equations under these assumptions are

$$\dot{f}(t) = -4\eta f(t) - 2iJ_c m(t)$$
, (6.26a)

$$\dot{n}(t) = -4\alpha n(t) + 2i\Delta m(t), \qquad (6.26b)$$

$$\dot{m}(t) = -2iJ_{c}f(t) + 2i\Delta n(t) - 4(\alpha + \eta)m(t). \qquad (6.26c)$$

We note that these equations are formally the same as those derived for model 1b. This indicates that the dynamics of energy transfer in the case in which the bare excitation is the migrating species is identical to the case in which lattice relaxation precedes any energy transfer. Due to the peculiarity of the δ -function correlation, however, [Eq. (6.24)], high temperature equilibrium conditions are introduced in the energy transfer equations (6.26) so that $f \rightarrow 0$ as $t \rightarrow \infty$, implying that the two site populations equalize at long times.

2. Model 2b: Temperature-dependent scattering

In order to circumvent the difficulties associated with the infinite-temperature implications of the stochastic model we postulate a temperature-dependent correlation phenomenologically which at infinite temperature reduces to the stochastic model.

$$\langle Z_i Z_i(t) \rangle = \int_{-\infty}^{+\infty} e^{-i\omega t} \zeta(\omega, T) d\omega,$$
 (6.27a)

$$\langle \Phi \Phi^{*}(t) \rangle = \langle \Phi \Phi(t) \rangle = \int_{-\infty}^{+\infty} e^{-i\omega t} e^{\beta \omega/2} \eta(\omega, T) d\omega.$$
 (6.27b)

The exact structure of the terms ζ and η depends on the particular coupling scheme postulated. For Z linear in the lattice coordinates, for example, the functional form of ζ is

$$\zeta(\omega, T) = \rho(\omega)g[n(\omega)+1], \qquad (6.28)$$

where $\rho(\omega)$ is the phonon density of states, $g(\omega)$ is the

excitation-phonon coupling coefficient and $n(\omega) = (e^{\beta\omega} - 1)^{-1}$. In order to reach the proper equilibrium value [Eq. (6.20)] we must require that

$$\eta(\omega, T) = \eta(-\omega, T), \qquad (6.29)$$

a condition which is similar to Eq. (6.17b) for the clothed excitation case.

Under these assumptions, model 2b is formally identical to model 1b. Note that some of the parameters in the energy transfer equations are not present in the single impurity spectra [i.e., $\eta(\omega, T)$]. However $\eta(\omega, T)$ will not be derivable from the overlap of the single impurity spectra, Eq. (6.2), as in the Förster theory, because Φ in this model is an inherently two molecule effect [see Φ in Eq. (2.3)].

VII. CONCLUSIONS

The system of two interacting impurities in an inert lattice was studied with respect to energy transfer and optical line shapes.

Interaction of the system with light creates a vertical excitation which is viewed as localized on one site to facilitate the study of the energy transfer process. The relation of the spectrum to the energy transfer process was studied using both local and nonlocal excitationphonon scattering. Two different models were adopted in this study. In the first model, the excitation created by light was assumed to relax into the clothed representation by emission of a phonon cloud. This lattice relaxation appears in the optical spectrum as a multiphonon band accompanying the transition. The clothed excitation can subsequently transfer its energy to a different site via the intermolecular coupling. Since this coupling is modulated by the lattice relaxation, spectral information can be used to evaluate some of the transport parameters. A case resembling the molecular exciton and the case of energy transfer under Förster conditions were investigated. In the second model, the energy transferring species is the same as that created by light. By using stochastic and phenomenological excitationphonon scattering it was shown that the excitation transfer parameters and the spectral line shape parameters are not related in the usual Förster way. In both cases the contributions of local and nonlocal scattering were examined and the processes leading excitation localization were discussed. In both cases formulas relating the localization processes to spectroscopic data were developed. These formulas reduce to the usual exciton diffusion expressions and the Förster-Dexter formula in limiting cases. Extra terms in our formulas arise from the consideration of the off-diagonal terms in the excitation density matrix, and thus describe the effects of phase randomization during energy transfer. At ordinary temperatures, where energy dissipation into the lattice dominates the approach to equilibrium, their contribution is probably negligible. At low temperatures, however, we would expect them to produce a measurable effect which is not taken into account by the conventional theories on energy transfer.

APPENDIX A: CALCULATION OF CLOTHED EXCITATION CORRELATION FUNCTIONS

We defined implicitly in Eq. (9b)

$$\hat{g}_{ij}(t) = \langle a_i a_j^*(t) \rangle . \tag{A1}$$

This can also be written as

$$\hat{\mathbf{G}}_{ij}(t) = \langle a_i e^{i H^{\mathbf{x}} t} a_j^* \rangle = a_i \langle e^{i H^{\mathbf{x}} t} \rangle a_j^*, \qquad (A2)$$

where H^x is the Liouville operator. So we can define a 2×2 matrix $\hat{g}(t)$ whose matrix elements are the $\hat{g}_{ij}(t)$ and is given by

$$\hat{\mathbf{g}}(t) = \langle e^{iH^{\mathbf{x}}t} \rangle \equiv P(e^{iH^{\mathbf{x}}t}), \qquad (A3)$$

where in the second equality we also define P as a projection operator which gives the phonon ensemble average of what follows (in this case the time evolution operator).

Following the procedure of Rackovsky and Silbey 8 we obtain

$$\dot{\hat{\mathbf{g}}}(t) = iH_0^x \, \hat{\mathbf{g}}(t) - PV^x \int_0^t d\tau \, e^{i\,(1-P)H^x\tau} \, (1-P) \, V^x \, \hat{\mathbf{g}}(t-\tau) \,, \tag{A4}$$

with H_0 and V defined in Eqs. (9b) and (9c), respectively.

We now approximate the correlation functions by replacing the modified propagator $e^{i(1-P)H^{\chi_{\tau}}}$ by the zerothorder propagator $e^{iH_0^{\chi_{\tau}}}$. Solving for the matrix elements of g(t) we obtain Eq. (12). The time-dependent coefficients in this equation are given by

$$\begin{split} \hat{A}(t) = & \left[\cos \Gamma t + \frac{\Delta}{\Gamma} \sin \Gamma t \right] \langle Z_1 Z_1(t) \rangle \\ & + \left[\cos \Gamma t - i \frac{\Delta}{\Gamma} \sin \Gamma t \right] \langle \Phi^* \Phi(t) \rangle \\ & + 2i \frac{J_c}{\Gamma} \sin \Gamma t \langle Z_1 \Phi^*(t) \rangle , \end{split}$$
(A5a)

$$\hat{C}(t) = \left[\cos \Gamma t + i \frac{\Delta}{\Gamma} \sin \Gamma t \right] \langle \Phi^* \Phi(t) \rangle \\ + \left[\cos \Gamma t - i \frac{\Delta}{\Gamma} \sin \Gamma t \right] \langle Z_2 Z_2(t) \rangle \\ + \frac{2iJ_c}{\Gamma} \sin \Gamma t \langle Z_2 \Phi(t) \rangle, \qquad (A5b)$$

$$\begin{split} \hat{B}(t) &= \left[\cos \Gamma t + i \frac{\Delta}{\Gamma} \sin \Gamma t \right] \langle Z_1 \Phi(t) \rangle \\ &+ \left[\cos \Gamma t - i \frac{\Delta}{\Gamma} \sin \Gamma t \right] \langle Z_2 \Phi^*(t) \rangle \\ &+ \frac{i J_c}{\Gamma} \sin \Gamma t \left[\langle Z_1 Z_2(t) \rangle + \langle \Phi \Phi(t) \rangle \right]. \end{split}$$
(A5c)

As indicated in Eq. (3.8) the Fourier transform of these coefficients at $\omega = \pm \Gamma$ is needed to evaluate the spectrum. With the simplifications of Eq. (6.1) the Fourier transformed coefficients become

$$A(\Gamma) = \frac{1}{2} \left(1 + \frac{\Delta}{\Gamma} \right) \left(\zeta_1(0) + \varphi(2\Gamma) \right) + \frac{1}{2} \left(1 - \frac{\Delta}{\Gamma} \right) \left(\zeta_1(2\Gamma) + \varphi(0) \right),$$
 (A6a)

$$C(\Gamma) = \frac{1}{2} \left(1 - \frac{\Delta}{\Gamma} \right) \left(\zeta_2(0) + \varphi(2\Gamma) \right) + \frac{1}{2} \left(1 + \frac{\Delta}{\Gamma} \right) \left(\varphi(0) + \zeta_2(2\Gamma) \right),$$
(A6b)

$$B(\Gamma) = \frac{1}{2} \frac{J_c}{\Gamma} \left(\tilde{\varphi}(0) + \tilde{\varphi}(2\Gamma) \right), \qquad (A6c)$$

where

$$\begin{aligned} \zeta_{i}(x) &= \int_{-\infty}^{+\infty} dt \, e^{-ixt} \langle Z_{i} Z_{i}(t) \rangle , \\ \varphi(x) &= \int_{-\infty}^{+\infty} dt \, e^{-ixt} \langle \Phi^{+} \Phi(t) \rangle , \\ \tilde{\varphi}(x) &= \int_{-\infty}^{+\infty} dt \, e^{-ixt} \langle \Phi \Phi(t) \rangle . \end{aligned}$$

For $\omega = -\Gamma$ we get equations similar to (A6) with Γ replaced by $-\Gamma$. Since Φ is of order J_c , $\phi(z)$ and $\overline{\phi}(z)$ are of order J_c^2 . Assuming that $\zeta(z)$ is of the same order of magnitude the equations (A6) reduce to

$$A = \zeta_1(0) + \varphi(2\Gamma), \qquad A' = \zeta_1(-2\Gamma) + \varphi(0), C = \varphi(0) + \zeta_2(2\Gamma), \qquad C' = \varphi(-2\Gamma) + \zeta_2(0),$$
(A7)

since our scheme accounts for terms up to second order only. The primed coefficients are evaluated at $\omega = -\Gamma$ while the unprimed at $\omega = \Gamma$.

APPENDIX B: PHONON-CLOUD CORRELATIONS

For the two impurity system the phonon-cloud correlation function was found to be in the case of linear phonon scattering⁸

$$\begin{split} \langle \Phi^* \Phi(t) \rangle &= J_B^2 \left\{ \langle \theta_1 \theta_2^* \theta_2(t) \ \theta_1^*(t) \rangle - \langle \theta_1^* \theta_2 \rangle^2 \right\} \\ &= J_c^2 \left[\exp \sum_q F_q(n_q e^{i\omega_q t} + (n_q + 1) e^{-i\omega_q t}) - 1 \right] , \end{split}$$
(B1)

where $F_q = z_1^2 + z_2^2 - 2z_1z_2\cos\mathbf{q}\cdot\mathbf{r}$, z_1 is the linear excitation-phonon coupling coefficient for the *i*th site to the phonon of wavevector q, and r is the distance between the two impurity sites. The Fourier transform of this phonon correlation function is

$$\varphi(x) = J_c^2 \left[e^{\beta x/2} \sum_{[N_q|x]} \prod_q I_{N_q}(F_q \operatorname{csch}\beta \omega q/z) - \delta(x) \right], \quad (B2)$$

where, as in Eqs. (4.5), (4.6) the sum $\sum_{[N_q]x]}$ is over all phonon combinations of total energy x, N_q is the number of q-phonon participating in the process, and $I_{N_{x}}$ is the hyperbolic Bessel function of order N_{q} .

The cross term $z_1 z_2 \cos(\mathbf{q} \cdot \mathbf{r})$ in F_a represents the spatial correlation of the crystal deformation upon excitation of one site. That is, its sum over all phonons $\sum_{\mathbf{q}} z_1 z_2 \cos(\mathbf{q} \cdot \mathbf{r})$ is essentially the deformation suffered by one site when the other is excited. Soules and Duke⁷ point out that if the two sites are not coupled to the same phonons, this term vanishes. In general however this condition is not met, and the sum of the cross terms will have a finite value. For dispersionless phonons, all equally coupled to the two sites, this sum reduces to

$$2z_1 z_2 (ne^{i\omega t} + (n+1)e^{-i\omega t} - (2n+1)) \frac{\sin(Nr/a_0)}{\sin(r/a_0)}, \qquad (B3)$$

where a_0 is the lattice spacing. In other words, the deformation vanishes very quickly at distances larger than the lattice spacing. For arbitrary phonon dispersions we would expect this sum to be negligibly small at large distances even though it may be difficult to show mathematically (the details of convergence depending on the particular model adopted). For nearest neighbors, on the other hand, where $r = a_0$, the sum may have some finite value. For distant impurities therefore, it is a good approximation to write:

$$\langle \theta_1 \theta_2^* \theta_2(t) \theta_1^* \rangle = \langle \theta_1 \theta_1^*(t) \rangle \langle \theta_2^* \theta_2(t) \rangle . \tag{B4}$$

The Fourier transform of this correlation function in this case reduces to

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathfrak{D}_{11}(x-\omega) \mathfrak{D}_{22}(\omega) \, d\omega - 2\pi \delta(x) \left\langle \theta_1^* \theta_2 \right\rangle^2, \tag{B5}$$

where $D_{11}(\omega)$ is defined in Eq. (3.4c).

Similarly, the probability amplitude of phonon-cloud transfer could excitation transfer is given by

$$\hat{\mathbb{D}}_{12}(t) = \exp -\frac{1}{2} \sum_{q} \left\{ (z_{1q}^2 + z_{2q}^2) (2n_q + 1) - 2z_{1q} z_{2q} \cos q \circ r [n_q e^{*i\omega t} + (n_q + 1) e^{-i\omega t}] \right\}.$$
(B6)

With a Fourier transform given by

$$\mathfrak{D}_{12}(x) = e^{\beta x/2} \exp\left[-\sum_{q} \left(z_{1}^{2} + z_{2}^{2}\right) (2n_{q} + 1)\right] \\ \times \sum_{[N_{q}]x_{1}} \prod_{q} I_{N_{q}}\left(2z_{1q}z_{2q}\cos(q \cdot r) \operatorname{csch}\frac{\beta \omega}{2}\right).$$
(B7)

Again, for nonnearest neighbors we should have

$$\hat{\mathfrak{D}}_{12}(t) \cong \langle \theta_1 \rangle \langle \theta_2^* \rangle \tag{B8}$$

making the Fourier transform in this case

 $\mathfrak{D}_{12}(x) = \left[\mathfrak{D}_{11}(0)\mathfrak{D}_{22}(0)\right]^{1/2}\delta(x).$ (B9)

Another correlation function encountered in the energy-transfer equations is $\langle \Phi \Phi(t) \rangle$. As it has been shown in the case of linear scattering⁸

$$\langle \Phi \Phi(t) \rangle = J_c^2 \left\{ \exp\left[-\sum_q F_q(n_q e^{i\omega_q t} + (n_q + 1) e^{-i\omega_q t} \right] - 1 \right\}.$$
(B10)

The Fourier transform of this function is given by

$$\tilde{\varphi}(x) = J_c^2 \left[e^{-\Re x/2} \sum_{[N_q]x]} \prod_q I_{N_q} \left(-F_q \operatorname{csch} \omega_q/2 \right) - \delta(x) \right],$$
where the symbols are defined as in Eq. (B2).
(B11)

Since the hyperbolic Bessell functions obey

$$I_{k}(y) = (-1)^{k} I_{k}(-y)$$
(B12)

we observe by comparing Eq. (B11) and (B2) that $\varphi(x)$ gives the total probability of all possible phonon processes that can occur at energy x, while $\tilde{\varphi}(x)$ consists of the probability of even-number phonon processes occurring minus the probability of the odd-number phonon processes at energy x. In our case therefore $\Phi(x)$ is the probability of energy transfer occurring with the dissipation of energy x into an *even* number of phonons.

To estimate $\tilde{\varphi}(0)$, we can assume that in the zeroenergy phonon combinations (x=0) the even numbered processes dominate, since both the zero-phonon process and the process consisting of emission of a phonon and the subsequent adsorption of the same phonon, are both even-numbered. Thus, since the odd processes are negligible, the even-minus-odd probability should approximately equal the *total* probability (even-plus-odd) and therefore we should have:

$$\tilde{\varphi}(0) = \varphi(0). \tag{B13}$$

APPENDIX C

We list here the coefficients appearing in Eq. (5.2). For these expressions we have used various properties of the Φ and Z_i . We also assume that

 $\langle \Phi(t-\tau) \Phi^{\dagger} \rangle = \langle \Phi^{\dagger}(t-\tau) \Phi \rangle$

which is true for the Φ as given in Sec. VI. In order for this to be true, it is sufficient that $|\langle n|\Phi|m\rangle|^2$ = $|\langle m|\Phi|n\rangle|^2$. This may not be true for more complex models than those considered herein.

$$\begin{split} F &= (2\Delta i/\Gamma) \sin 2\Gamma t \left\langle \left[\Phi(t), \Phi^{+}\right]_{-} \right\rangle, \\ F_{f} &= \left[\left(1 + \frac{\Delta^{2}}{\Gamma^{2}} \right) \cos 2\Gamma t + \frac{J_{c}^{2}}{\Gamma^{2}} \right] \left\langle \left[\Phi(t), \Phi^{+}\right]_{+} \right\rangle \\ &\quad - 2 \frac{J_{c}^{2}}{\Gamma^{2}} \sin^{2}\Gamma t \left\langle \left[\Phi(t), \Phi\right]_{+} \right\rangle, \\ F_{n} &= \frac{2J_{c}\Delta}{\Gamma^{2}} \sin^{2}\Gamma t \left\{ \left\langle \left[\Phi(t), \Phi\right]_{+} \right\rangle - \left\langle \left[\Phi(t), \Phi^{+}\right]_{+} \right\rangle \right\}, \\ N &= \frac{2iJ_{c}}{\Gamma} \sin 2\Gamma t \left\{ \left\langle \left[z_{-}(t), z_{-}\right]_{-} \right\rangle + \frac{1}{2} \left\langle \left[\Phi(t), \Phi^{+}\right]_{-} \right\rangle \\ &\quad - \frac{1}{2} \left\langle \left[\Phi(t), \Phi\right]_{-} \right\rangle \right\} + \frac{2J_{c}\Delta}{\Gamma^{2}} \sin^{2}\Gamma t \left\{ \left\langle \Phi\Phi(t) - \left\langle \Phi(t)\Phi^{+} \right\rangle \right\}, \\ N_{f} &= \frac{2iJ_{c}}{\Gamma} \sin 2\Gamma t \left\langle \left[z_{+}(t), z_{-}\right]_{-} \right\rangle + \frac{2J_{c}\Delta}{\Gamma^{2}} \sin^{2}\Gamma t \\ &\quad \times \left\{ \left\langle \Phi\Phi^{+}(t) \right\rangle - \left\langle \Phi(t)\Phi\right\rangle \right\}, \\ N_{n} &= 2 \cos 2\Gamma t \left\langle \left[z_{-}(t), z_{-}\right]_{+} \right\rangle - \frac{2i\Delta}{\Gamma} \sin 2\Gamma t \left\langle \left[z_{+}(t), z_{-}\right]_{-} \right\rangle \\ &\quad + \left(\frac{2J_{c}^{2}}{\Gamma^{2}} \sin^{2}\Gamma t - 1\right) \left\{ \left\langle \left[\Phi(t), \Phi\right]_{+} \right\rangle - \left\langle \Phi(t), \Phi^{+}\right]_{+} \right\rangle \right\}, \\ M_{m} &= 2 - \frac{\Delta^{2}}{\Gamma^{2}} \cos 2\Gamma t + \frac{J_{c}^{2}}{\Gamma^{2}} - \left\langle \left[z_{-}(t), z_{-}\right]_{+} \right\rangle \\ &\quad + 2\frac{i\Delta}{\Gamma} \sin 2\Gamma t \left\langle \left[z_{+}(t), z_{-}\right]_{-} \right\rangle \\ &\quad - \left(\frac{J_{c}^{2}}{\Gamma^{2}} \cos 2\Gamma t + \frac{\Delta^{2}}{\Gamma^{2}} \right) \left\{ \left\langle \left[\Phi(t), \Phi\right]_{+} \right\rangle + \left\langle \left[\Phi(t), \Phi^{+}\right]_{+} \right\rangle, \end{split} \right\} \end{split}$$

where we have assumed $\langle Z_i \Phi(t) \rangle = 0$ and have defined $Z_{\pm} = \frac{1}{2}(z_1 \pm z_2)$.

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- ²²This expression has a similar form to that of Ern *et al.*¹⁴ for the exciton diffusion constant. If we assume that φ consists of two parts, one depending on the separation of the two impurities labeled φ_R and another given by the remainder of φ (see Appendix B). The latter term can be approximately evaluated to be the *overlap* of the *isolated* impurity spectra. If we assume these to be Lorentzian with width Γ_0 , we find $2\varphi = 2\varphi_R + J^2/\Gamma_0$. Combining ξ with $2\varphi_R$, we can write $k = 2\Gamma_1$ $+ J^2/\Gamma_0$ which looks very much like the expression of Ern *et al.*¹⁴ for the diffusion coefficient. Two points should be made: (a) our expression is for two impurities, not an exciton band, so care must be taken in this comparison; and (b) the term we label "nonlocal" in the clothed representation, θ , can in the bare representation be labeled "local."