ELECTRONIC ENERGY TRANSFER IN MOLECULAR CRYSTALS[1]

❖2622

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INTRODUCTION

In the last ten years, a number of reviews of properties of molecular crystals have appeared in this series (1, 2, 3). The spectral properties of insulating molecular crystals [which are often described within the framework of the Frenkel theory of excitons (4, 5)] have been reviewed by Hochstrasser (1) and by Robinson (2). The properties of charge transfer crystals have been reviewed recently by Soos (3). In addition, the review by El-Sayed (6) on double resonance techniques applied to triplet states of organic molecules concerned itself with organic molecular crystals.

In the present review, I focus on a different aspect of molecular crystals: the transport of electronic excitation from molecule to molecule. This process, and its effect on optical spectra, electron paramagnetic resonance spectra, and fluorescence, has been of great interest in the last few years; I present a critical review of the theoretical developments in this field. Specific attention is paid to the theory of exciton transport in molecular crystals, the theory of exciton-molecular vibration and exciton-phonon interactions, and finally, to a quite different topic, the theory of excitation transport across surfaces.

Those works dealing with the optical properties of molecular crystals within the coupled oscillator model are not dealt with. It will be assumed that the interaction of light with the system is weak enough so that retardation effects and the formation of polariton states may be neglected. Only work dealing with excitation transport is dealt with herein.

We begin by discussing the simplest type of system in which excitation transfer takes place in order to define the terms necessary to treat excitation transfer in more complex systems.

TWO MOLECULE SYSTEMS

To introduce the topics to be studied, we consider a system consisting of two molecules in an inert lattice. The two molecules are simple: each has only two

electronic states, the ground state (ϕ_g) and an excited state (ϕ_e). The singly excited states of the system arc $\psi_2 = \phi_{1g}\phi_{2e}$ and $\psi_1 = \phi_{1e}\phi_{2g}$, where the numbers label the molecules. The matrix elements of the electronic Hamiltonian for this system between these two states are $\langle\psi_1|H|\psi_1\rangle = E_1$, $\langle\psi_2|H|\psi_2\rangle = E_2$, and $\langle\psi_1|H|\psi_2\rangle = V = \langle\psi_2|H|\psi_1\rangle$. To make matters as simple as possible, let us assume that no other states are important and that transitions to the ground state ($\phi_{1g}\phi_{2g}$) are weakly allowed, so that such transitions can neglected for times that are short compared to the radiative lifetime.

If at some initial time the system is in the nonstationary state ψ_1 (i.e. molecule one excited), then the excitation will travel from molecule one to molecule two in a simple oscillatory manner. To illustrate this, we compute the probability amplitudes $\langle\psi_2|e^{-iHt}|\psi_1\rangle$ and $\langle\psi_1|e^{-iHt}|\psi_1\rangle$. We write the Hamiltonian in second quantized form:

$$H = \Lambda(a_1^\dagger a_1 - a_2^\dagger a_2) + V(a_1^\dagger a_2 + a_2^\dagger a_1). \qquad 1.$$

The operator $a_{1(2)}^\dagger$ creates an excitation on molecule one(two) and $E_1 - E_2$ is equal to 2Δ. Note that $(a_1^\dagger a_1 - a_2^\dagger a_2)$ can be represented by the Pauli matrix σ_z, while $a_1^\dagger a_2 + a_2^\dagger a_1$ can be represented by the Pauli matrix σ_x. Since $\sigma_z^2 = \sigma_x^2 = 1$, we have

$$H^2 = \Delta^2 + V^2 = \Gamma^2, \qquad 2.$$

and thus

$$e^{-iHt} = \cos\Gamma t - i\Gamma^{-1}(\sin \qquad 3.$$

Thus the probability amplitudes are given by

$$\langle\psi_1|e^{-iHt}|\psi_1\rangle = \cos\Gamma t - i(\Delta/\Gamma)\sin\Gamma t, \qquad 4.$$

$$\langle\psi_2|e^{-iHt}|\psi_1\rangle = -i(V/\Gamma)\sin\Gamma t, \qquad 5.$$

and the corresponding probabilities by

$$P_1(t) = 1 - (V/\Gamma)^2\sin^2\Gamma t, \qquad 6.$$

$$P_2(t) = (V/\Gamma)^2\sin^2\Gamma t. \qquad 7.$$

Here the transfer of excitation is a wavelike or coherent process in this simple model with no heat bath. We note that, in the case of different molecules that are coupled by a dipolar interaction. $V\alpha R^{-3}$ and usually $\Delta \gg V$, so that $P_2\alpha R^{-6}$. Also, in the limit that $\Delta = 0$ (identical molecules), $\Gamma = V$ and the probabilities are very simple.

The above calculation is for two isolated molecules. When a coupling to a heat bath is present a more complicated time dependence is introduced. The heat bath is formed by a crystal lattice in which these two molecules are placed. For simplicity we assume that the lattice has no electronic levels of importance (that is, the ground to excited electronic energy level spacing of the lattice is much larger than Γ). Then the sole role of the lattice is as a collection of vibrational normal modes that may be coupled to the electronic degrees of freedom of the two molecules. This coupling can be thought of as arising from the nuclear position dependence of Δ and V.

Accordingly, we can approach the problem of the dynamics of the excitation in two ways: (a) introduce terms in the Hamiltonian representing the phonon bath and the coupling and attempt to solve for the probabilities once more, or (b) assume

that the coupling can be approximated by a time-dependent Δ and V and then solve for the probabilitics. The latter approach customarily treats thc phonon bath in a classical manner and therefore should be valid at high temperature.

We first pursue approach (b), and replace the Hamiltonian by

$$H(t) = \Delta(t)[a_1^\dagger a_1 - a_2^\dagger a_2] + V(t)[a_1^\dagger a_2 + a_2^\dagger a_1].$$ 8.

It is necessary to specify the time dependence of $\Delta(t)$ and $V(t)$. Since this time dependence is due to the excitation phonon coupling terms, it will be extremely complicated (we will see some microscopic examples later on). Following Sewell (7) and Haken & Strobl (8) we regard $\Delta(t)$ and $V(t)$ as randomly fluctuating Gaussian Markov processes with nonzero averages and delta function correlation times:

$$\langle \Delta(t) \rangle \equiv \langle \Delta + \delta\Delta(t) \rangle = \Delta,$$ 9a.

$$\langle V(t) \rangle \equiv \langle V + \delta V(t) \rangle = V,$$ 9b.

$$\langle \delta\Delta(t)\delta\Delta(t') \rangle = \gamma_0 \delta(t-t'),$$ 10.

$$\langle \delta V(t)\delta V(t') \rangle = \gamma_1 \delta(t-t'),$$ 11.

$$\langle \delta\Delta(t)\delta V(t') \rangle = 0,$$ 12.

where the average is over the fluctuations. The probability that molecule one will be excited at time t, given that it was excited at time zero, is given by

$$P_1(t) = \left\langle |\langle \psi_1 | U(t) | \psi_1 \rangle|^2 \right\rangle,$$ 13.

where the outer brackets represent the average over the fluctuating fields and $U(t)$ is the time-ordered evolution operator:

$$U(t) = \exp_0 \left[-i \int_0^t H(\tau') d\tau' \right].$$ 14.

We may also write $P_1(t)$ in the second quantized notation as

$$P_1(t) = \langle\!\langle 0 | a_1 a_1^\dagger(t) a_1(t) a_1^\dagger | 0 \rangle\!\rangle$$ 15.

where $a_1^\dagger | 0 \rangle = \psi_1$.

In order to solve for $P_1(t)$ we must consider the time development of the other operators in the system. The complete description is given in terms of

$$Z(t) \equiv P_1(t) - P_2(t),$$ 16.

$$X(t) \equiv \langle\!\langle 0 | a_1 [a_1^\dagger(t) a_2(t) + a_2^\dagger(t) a_1(t)] a_1^\dagger | 0 \rangle\!\rangle,$$ 17.

and

$$Y(t) = i \langle\!\langle 0 | a_1 [a_1^\dagger(t) a_2(t) - a_2^\dagger(t) a_1(t)] a_1^\dagger | 0 \rangle\!\rangle,$$ 18.

since $P_1(t) + P_2(t) = 1$. By using the properties of a Gaussian Markov process we may derive the equation of motion for these (8):

$$\dot{Z}(t) = 2VY(t) - 2\gamma_1 Z(t),$$ 19.

$$\dot{Y}(t) = 2\Delta X(t) - 2VZ(t) - 2(\gamma_0 + \gamma_1)Y(t),$$ 20.

$$\dot{X}(t) = 2\Delta Y(t) - 2\gamma_0 X(t).$$ 21.

The general solution can be given in terms of the roots of a third order algebraic equation, but interesting results can be obtained without this procedure. First, it can easily be seen that for long times, X, Y, and Z go to zero. This means that at long times, the probability that the excitation would be at site 1 is equal to the probability that it would be at site 2, regardless of the value of Δ. Thus the distribution of excitations at equilibrium corresponds to *infinite* temperature in approach (b). This is a consequence of treating the lattice classically and has been discussed in the context of spin relaxation by Redfield (9).

In the limit that $\Delta = 0$, equations 19, 20, and 21 may be solved to yield:

$$Z(t) = (\tfrac{1}{2})\left[(1 \cdot \gamma_0/\lambda)e^{\lambda t} - (1 - \gamma_0/\lambda)e^{-\lambda t}\right]e^{-(\gamma_0 \cdot 2\gamma_1)t}. \qquad 22.$$

where

$$\lambda = [\gamma_0^2 - 4V^2]^{1/2}. \qquad 23$$

Since $Z(t) = P_1(t) - P_2(t)$, we see that $P_1(\infty) = P_2(\infty) = 1/2$. The limit $\gamma_0 = \gamma_1 = 0$ yields $Z(t) = \cos 2Vt$, recovering the result of our earlier analysis with no fluctuating terms. The limit $\gamma_0 = 0$ reduces to Sewell's result (7):

$$Z(t) = e^{-2\gamma_1 t} \cos 2Vt. \qquad 24.$$

We see that the result of the fluctuating terms in the Hamiltonian is to allow the probabilities to relax to equilibrium values characteristic of infinite temperature. Note, however, that we can introduce a phenomenological temperature dependence into γ_0 and γ_1 (8) if we so desire, and thus make the rate of relaxation temperature dependent. Note too, that the wavelike nature of the solution disappears entirely if $\gamma_0 > 2V$ in equation 23, for then $Z(t)$ has damping terms only. From this simple model, we see that the transfer of electronic excitation has a wavelike (or coherent) part and an incoherent (or diffusive) part. In the limit that $\gamma_0 \gg V$, we find $Z(t) = \exp(-2\gamma_1 t)$, and so the probabilities (of excitation on a molecule) obey a simple master equation with transition probability for excitation transfer equal to γ_1. This reveals that when the fluctuations are sufficiently large, the off-diagonal density matrix elements decay rapidly so that the equation of motion involves probabilities only.

The term γ_0 is usually said to represent local (i.e. site diagonal) energy fluctuations, while the term γ_1 represents nonlocal (i.e. site nondiagonal) fluctuations.

Note that in the absence of thermal fluctuations ($\gamma_0 = \gamma_1 = 0$), if the initial state had been a stationary state of the Hamiltonian (i.e. $\psi_1 \pm \psi_2$ in the case $\Delta = 0$), then the probabilities would have been independent of time. In the presence of the fluctuations, the probabilities would relax to one half even if the initial state had been $\psi_1 \pm \psi_2$. The fluctuations take the density matrix to an equilibrium state, independent of the initial conditions, which reflects the fact that coupling to a heat bath drives a system to thermal equilibrium.

For this same model, we may compute the spectral line shape for transition from the ground state to the excited states. The line shape is given by the following

formula (in the limit that the electronic excitation energy is large compared to $k_B T$):

$$I(\omega) = (\tfrac{1}{2}\pi)\,\mathrm{Re}\int_0^\infty dt\,e^{-i\omega t}\hat{\varepsilon}\cdot\langle\!\langle 0|\boldsymbol{\mu}\boldsymbol{\mu}(t)|0\rangle\!\rangle\cdot\hat{\varepsilon}. \qquad 25.$$

where $\boldsymbol{\mu}$ is the transition moment and $\hat{\varepsilon}$ is the polarization of the incident light. For simplicity, assume both molecules are identical and translationally equivalent, then

$$I(\omega) = (\mu^2/2\pi)\,\mathrm{Re}\int_0^\infty dt\,e^{-i\omega t}\langle\!\langle 0|(a_1+a_2)(a_1^\dagger(t)+a_2^\dagger(t))|0\rangle\!\rangle. \qquad 26.$$

This may be easily calculated using the properties of the Hamiltonian; one finds a Lorentzian line:

$$I(\omega) = \mu^2\pi(\gamma_0+\gamma_1)/[(\omega+V)^2+(\gamma_0+\gamma_1)^2/4]. \qquad 27.$$

Thus the line shape and position can be used to find V and $\gamma_0+\gamma_1$. Since the molecules were assumed to be identical and translationally invariant only one peak occurs. In the general case, the line shape is a sum of two Lorentzians. Note, however, that the experimental line width also has a contribution from the different site energies due to crystal strains etc (inhomogeneous broadening), which are absent in this model Hamiltonian. Care has to be taken, therefore, in equating dynamical broadening parameters (γ_0 and γ_1) to experimental widths.

More detailed treatments of this and related problems using this approach have been given by Haken and coworkers (10–21) and by Aslangul & Kottis (22–25). Haken & Strobl (10) have derived the full density matrix equations for the dimer and for exciton states. Haken & Reinecker (11) have applied these results to the two-molecule problem in order to calculate the optical line shape. Reinecker & Haken (12) also computed the influence of excitation transfer on spin resonance absorption. Reinecker then extended this treatment to triplet excitons in crystals with two molecules per unit cell (13, 14, 15). Reinecker & Kühne (16, 17) derived an approximate master equation and diffusion equation for the case in which γ_0 is large. These authors point out that, even in the incoherent limit, there are effects due to the coherent transfer parameter (V). Finally, Schwarzer and Haken (18–21) have solved the Haken–Strobl model and applied this to optical absorption and emission and electron paramagnetic resonance experiments.

Aslangul & Kottis (22–25) have solved the Haken–Strobl model using the super-operator technique and examined optical line shapes and EPR line shapes.

The procedure of replacing the excitation-phonon-interactions by random processes has permitted a full description of the excitation transfer and the line shapes in this model. The costs of this approach are the lack of knowledge of γ_0 and γ_1 (which must be computed in a separate microscopic calculation) and the fact that treating the lattice as classical (and having a delta function correlation time) leads to incorrect equilibrium populations. In addition, many interesting physical effects do not emerge in this approach; for example, examination of excitation transfer before lattice relaxation is excluded since the lattice is assumed to relax infinitely quickly.

We have assumed that each molecule has one excited state. In fact, even if only

one electronically excited level is considered, the molecule has many vibronic states in that electronic level. The above analysis implicitly assumes that only the ground vibrational level of the electronically excited molecule is important (i.e. that vibrational relaxation is fast in the excited electronic manifold).

We now discuss the various treatments of excitation transfer in two-molecule systems using approach (a) that have been considered in recent years (26–33). We begin by writing the Hamiltonian for the two-molecule system including the molecular vibrations of each molecule. This has been considered by many authors (34–39) in the case of harmonic vibrations. In the second quantized form, the Hamiltonian is

$$
\begin{aligned}
H = & E_1 a_1^\dagger a_1 + E_2 a_2^\dagger a_2 + \sum_{n,i} \Omega_{ni}(B_{ni}^\dagger B_{ni} + \tfrac{1}{2}) \\
& + V(a_1^\dagger a_2 + a_2^\dagger a_1) + \sum_{n,i} g_{ni}\Omega_{ni}(B_{ni} + B_{ni}^\dagger)a_n^\dagger a_n \\
& + \sum_{n,i} k_{ni}\Omega_{ni}(B_{ni} + B_{ni}^\dagger)^2 a_n^\dagger a_n .
\end{aligned}
\qquad 28.
$$

In this Hamiltonian, E_1 and E_2 are the vertical energies of the two electronic states (at the ground state nuclear geometry) relative to the ground state, V is the energy transfer matrix element, Ω_{ni} are the normal vibrational frequencies of molecule n, and B_{ni} and $B_{ni}^\dagger$ are the usual boson annihilation and creation operators for the harmonic normal modes of each molecule. The terms involving $(B_{ni} + B_{ni}^\dagger)$ represent displacements of the equilibrium positions of the normal modes upon excitation. The terms involving $(B_{ni} + B_{ni}^\dagger)^2$ represent frequency shifts upon excitation. This Hamiltonian represents a simple model of excitation-molecular vibration coupling and is the prototype of models of exciton-phonon coupling as well. In most cases considered in the literature, the frequency shift terms have been neglected, and usually only one normal mode per molecule is taken into account. The problem can then be solved numerically (39) for $E_1 = E_2$.

If the interaction of the excitation with lattice phonons is now introduced, terms representing excitation-phonon coupling arise of exactly the same form as the excitation-molecular vibration coupling terms just discussed. In addition, non-site diagonal coupling terms will also arise. The Hamiltonian is

$$
\begin{aligned}
H = & \sum_{n=1}^{2} E_n a_n^\dagger a_n + \sum_{n,i} \Omega_{ni}(B_{ni}^\dagger B_{ni} + \tfrac{1}{2}) + \sum_{\alpha} \omega_\alpha(b_\alpha^\dagger b_\alpha + \tfrac{1}{2}) \\
& + V(a_1^\dagger a_2 + a_2^\dagger a_1) + \sum_{n,i} \Omega_{ni} a_n^\dagger a_n [g_{ni}(B_{ni} - B_{ni}^\dagger) + k_{ni}(B_{ni} + B_{ni}^\dagger)^2] \\
& + \sum_{n,\alpha,\alpha'} a_n^\dagger a_n [\delta_{\alpha\alpha'} g_{n\alpha} \omega_\alpha(b_\alpha + b_\alpha^\dagger) + k_{n\alpha\alpha'}(b_\alpha \\
& + \sum_{\alpha} v_\alpha(a_1^\dagger a_2 + a_2^\dagger a_1)(b_\alpha + b_\alpha^\dagger)
\end{aligned}
\qquad 29.
$$

where b_α and $b_\alpha^\dagger$ are the annihilation and creation operators for the lattice phonons. Since the molecular vibrations play exactly the same role as the phonons (note though that the frequencies and coupling will be very different in general), we can

treat the molecular vibrations as just another set of phonon modes. On the other hand, we may assume that only the lowest vibronic states of the molecules need be considered, and thus discuss the coupling of these vibronic states with the lattice phonons as was done in the stochastic treatment. The latter point of view is usually adopted, although it is not necessary to do so. We subsume both points of view in the Hamiltonian by omitting the terms in the molecular vibrations in equation 29, and extending the sum of α to include those modes when desired. The Hamiltonian becomes

$$H = \sum_n E_n a_n^\dagger a_n + V(a_1^\dagger a_2 + a_2^\dagger a_1) + \sum_\alpha \omega_\alpha (b_\alpha^\dagger b_\alpha + \tfrac{1}{2})$$

$$+ \sum_{n\alpha\alpha'} a_n^\dagger a_n [g_{n\alpha} \delta_{\alpha\alpha'} \omega_\alpha (b_\alpha + b_\alpha^\dagger) + k_{n\alpha\alpha'} (b_\alpha + b_\alpha^\dagger)(b_{\alpha'} + b_{\alpha'}^\dagger)]$$

$$- \sum_\alpha v_\alpha (a_1^\dagger a_2 - a_2^\dagger a_1)(b_\alpha + b_\alpha^\dagger). \qquad 30.$$

This Hamiltonian is complicated but can be exactly diagonalized in two limiting cases.

If the nondiagonal terms are neglected ($V = v_\alpha = 0$) then the Hamiltonian reduces to two noninteracting harmonic systems. If either molecule is excited we can find the frequencies of the new normal modes. In the model considered by Soules & Duke (27), Rackovsky & Silbey (28), and Kenkre & Rahman (33), $v_\alpha = k_{n\alpha\alpha'} = 0$. Then, for $V = 0$, the unitary transformation of H, given by $\tilde{H} = UHU^\dagger$ where $U = \exp(S)$ and

$$S = \sum_{n,\alpha} g_{n\alpha} a_n^\dagger a_n (b_\alpha - b_\alpha^\dagger), \qquad 31.$$

produces a Hamiltonian whose eigenstates can be immediately determined

$$\tilde{H}(V = v_\alpha = k_{n\alpha\alpha'} = 0) = \sum_n \left(E_n - \sum_\alpha g_{n\alpha}^2 \omega_\alpha \right) a_n^\dagger a_n + \sum_\alpha \omega_\alpha (b_\alpha^\dagger b_\alpha + \tfrac{1}{2}). \qquad 32.$$

The eigenstates of H are given by $U^\dagger$ acting on the eigenstates of $\tilde{H}(V = v_\alpha = k_{n\alpha\alpha'} = 0)$, but no excitation transfer can take place.

In the opposite limit, where all excitation-phonon coupling is set equal to zero ($g_{n\alpha} = k_{n\alpha\alpha'} = v_\alpha = 0$), the eigenstates are also easily found, since the Hamiltonian reduces to the isolated interacting dimer. In the case $k_{n\alpha\alpha'} = v_\alpha = 0$ but $V \neq 0$ and $g_{n\alpha} \neq 0$, an exact solution cannot be found. However, Young (38) has attempted a variational solution of the problem including one vibration per molecule (with no phonons); Soules & Duke (27) and Rackovsky & Silbey (28) have attempted perturbative calculations based on the exactly soluble cases. The idea is to transform the Hamiltonian (equation 30) so that it exhibits both limiting solutions. We accomplish this by performing the unitary transformation discussed above (see equation 31) on the Hamiltonian of equation 30. An equivalent procedure is to

define new operators

$$A_n \equiv e^S a_n e^{-S} = a_n \exp\left\{\sum_\alpha \mathbf{g}_{n\alpha}(b_\alpha - b_\alpha^\dagger)\right\} \equiv a_n \theta_n, \qquad 33.$$

$$B_\alpha = e^S b_\alpha e^{-S} = b_\alpha - \sum_n a_n^\dagger a_n \mathbf{g}_{n\alpha}, \qquad 34.$$

and substitute these definitions into equation 30 to find (for $k_{n\alpha\alpha'} = v_\alpha = 0$):

$$H = \sum_n \left(E_n - \sum_\alpha \mathbf{g}_{n\alpha}^2 \omega_\alpha\right) A_n^\dagger A_n + \sum_\alpha \omega_\alpha (B_\alpha^\dagger B_\alpha + \tfrac{1}{2})$$
$$+ V A_1^\dagger A_2\, \theta_1^\dagger \theta_2 + V A_2^\dagger A_1\, \theta_2^\dagger \theta_1. \qquad 35.$$

The operator $A_n^\dagger$ now creates an excitation with a cloud of phonons at site n. This represents a vibrationally relaxed (or "clothed") electronic excitation. Note that in this representation there are no longer any site diagonal excitation-phonon couplings; this means that if equations are derived that are analogous to 19–21, and if the assumption is made that the species that is moving is the relaxed excitation (created by $A_n^\dagger$, not that created by $a_n^\dagger$), then γ_0 will be zero. If the quadratic phonon terms were kept (i.e. those proportional to $k_{n\alpha\alpha'}$), then a site diagonal term would be present in the perturbation, and a γ_0 term would also appear in the final equations. This is reminiscent of the results for the width of the zero phonon line of isolated impurities in solids (40–44), where a linear phonon coupling produces a delta function line and a quadratic phonon coupling produces a Lorentzian line shape.

Rackovsky & Silbey (28) calculated the equations of motion in the relaxed representation using projection operator techniques (45, 46). After introducing some approximations, they found (using the same notation as in equations 19–21):

$$\dot{Z}(t) = 2VY(t) - 2\int_0^t d\tau \gamma(\tau) Z(t-\tau) - \eta(t), \qquad 36.$$

$$\dot{Y}(t) = 2\Delta X(t) - 2VZ(t) - 2\int_0^t d\tau \gamma'(\tau) Y(t-\tau), \qquad 37.$$

$$\dot{X}(t) = 2\Delta Y(t). \qquad 38.$$

There are two important differences between this set of equations and equations 19–21. First, convolution integrals appear in the present analysis. In the limit that the phonon relaxation is fast compared to changes in Z and Y, so that $\gamma(\tau)$ and $\gamma'(\tau)$ go to zero quickly, then $Z(t-\tau)$ and $Y(t-\tau)$ may be replaced by $Z(t)$ and $Y(t)$ respectively, and the convolutions disappear. Secondly, the present equations contain a term, $\eta(t)$, which is absent in equation 19. It is just this term that gives the correct equilibrium populations at infinite time. Thus, by treating the phonon dynamics quantum mechanically the correct equilibrium results are obtained.

Recently, Abram & Silbey (29) have discussed the same system, including terms that give rise to a γ_0-like term. They also present spectral line shapes and transport equations.

At high temperatures, the equation for $Z(t)$ reduces to a master equation and γ_1 is the transition probability for excitation transfer from site to site. The analysis of

Soules & Duke (27) or Rackovsky & Silbey (28) produces a formula for γ_1 as a function of temperature. Analysis shows that if the two molecules are coupled to different phonon bands, then γ_1 reduces to the Förster energy transfer rate expression (45, 46). If they are coupled to the same phonon bands corrections to the Förster expression arise (27).

Kenkre & Knox (30, 31) treat this problem in a different manner, reminiscent of Förster's calculation (45). They derive a rate expression for the population of excitation on a site in the same manner as Förster, but keeping a time dependence in the transition probabilities. This results in a generalized master equation

$$\dot{P}_n(t) = \int_0^t d\tau \sum_m \left[W_{nm}(t-\tau)P_m(\tau) - W_{mn}(t-\tau)P_n(\tau) \right], \qquad 39.$$

where n and m label the molecules. This reduces to a simple equation for $Z(t)$ in the two-molecule case:

$$\dot{Z}(t) = 2 \int_0^t W_{12}(\tau)\,d\tau - 2 \int_0^t d\tau [W_{21}(t-\tau) - W_{12}(t-\tau)]Z(\tau), \qquad 40.$$

where $W_{12}(\tau)$ is the time-dependent transition rate from molecule two to molecule one. This equation gives the correct equilibrium populations at infinite time, and reduces to Förster's expression for $Z(t)$ (the master equation) at long times. These authors also relate $W_{nm}(\tau)$ to the optical spectra of the individual molecules embedded in the lattice using second order perturbation theory and projection operator techniques.

Kenkre (32) and Kenkre & Rahman (33) have compared the method of Rackovsky & Silbey (28) or Abram & Silbey (29) to that of Kenkre & Knox (30, 31). They find a simple formal connection between the theories. However, there is a difference in the method of calculation: Kenkre & Knox treat all terms in $\hat{V}$ as a perturbation, while Rackovsky & Silbey treat only terms in $\hat{V} - \langle \hat{V} \rangle$ in a perturbative manner, by including the averaged $\hat{V}$ in H_0. In those cases in which $\langle \hat{V} \rangle$ is nonzero, differences can occur as we shall see when discussing larger systems.

Thus, in the last few years there have been at least four different approaches to a theoretical understanding of energy transfer between two molecules in a solid. The major new theoretical prediction not already contained in the Förster theory (45) is the possibility of wavelike motion. There has been an enormous amount of experimental work in sensitized fluorescence (47) in the last few years, and there was little or no evidence for wavelike motion. In the last two years, however, Zewail and Harris (48–51) have performed very low temperature ($\sim 1.7°$K) optically detected magnetic resonance experiments in zero magnetic field on dimers of 1,2,4,5 tetra-chlorobenzene embedded in the deuterated compound. They find that the coherence time of excited triplet state of the dimer is longer than $.10^{-7}$ sec, while the excitation exchange time ($\hbar/V$) is of order 10^{-11} sec. This implies that the dimer coherent state lasts for $\sim 10^4$ exchange times before phonon scattering destroys the coherence (or wavelike character) of the state. The fact that the molecules in the dimer are nearest neighbor equivalent molecules means that the initial state is a superposition of states in which one molecule is excited. Thus, one cannot see excitation transfer in the

sense that is usually meant in the work on sensitized luminescence, i.e. transfer of excitation from one molecule to another. In spite of this, these experiments are the first that indicate a coherent or wavelike nature to the excitation in dimeric systems.

EXTENDED SYSTEMS: THEORETICAL STUDIES

In molecular crystals, the excited electronic states are usually characterized as Frenkel excitons. The study of exciton transport phenomena is of considerable current interest both theoretically and experimentally. Studies of exciton dynamics and spectral line shapes lead to information about the intermolecular electronic interactions and the nature of exciton-phonon coupling. In addition, exciton transport processes have been used to describe excitation transfer in photosynthetic units (52).

Usually, the motion of an exciton through a molecular crystal at moderate temperatures is described as a random walk of a localized excitation from site to site (53–55), in which the transition probability for transfer is given by a Förster expression. On the other hand, at low temperatures, a wave of excitation moves through the crystal and is scattered by phonons at a temperature-dependent rate. In addition, the low-temperature spectral studies describe the excitation as delocalized over many molecules (1, 2). The physical picture is then of an excitation wave undergoing repeated phonon and impurity scattering until it finally becomes localized. Once the excitation is localized, it moves via a random walk.

Theoretical studies of this localization and transport have been given by many workers based on models for the exciton-phonon interactions. The exciton impurity scattering problem has received much less attention to date. We first discuss the theoretical work done in the last few years, and then proceed to the experimental studies of spectral line shapes and exciton dynamics.

The Hamiltonian for the molecular crystal exciton states in the absence of phonons can easily be written down in analogy with equation 1:

$$H = \sum_{n=1}^{N} E_n a_n^\dagger a_n + \sum_{n,m}^{N} V_{nm} a_n^\dagger a_m. \qquad 41.$$

In order to discuss exciton-phonon and exciton-molecular vibration interaction, we again have two options. As in the two-molecule case, we can (a) add a harmonic phonon bath and exciton-phonon interaction terms in analogy with equation 30, or (b) treat E_n and V_{nm} as fluctuating quantities in analogy with equation 8.

Haken & Strobl (8, 10) adopted the second approach, (b), and, assuming that $E_n(t)$ and $V_{nm}(t)$ were Gaussian Markov processes with delta function correlation times, derived an equation of motion for the exciton density matrix averaged over the fluctuations:

$$\langle \dot{\rho}_{nn'} \rangle = -i[\langle H \rangle, \langle \rho \rangle]_{nn'} - 2\Gamma \langle \rho_{nn'} \rangle$$
$$+ 2\delta_{nn'} \sum_m \gamma_{n-m} \langle \rho_{mm} \rangle + 2(1 - \delta_{nn'})\gamma_{n-n'} \langle \rho_{n'n} \rangle \qquad 42.$$

where [here $V_{nn}(t) \equiv E_n(t)$ for convenience]

$$\Gamma = \sum_m \gamma_{m-n} = \sum_m \int_0^\infty d\tau \langle \delta V_m \qquad \rangle \qquad 43.$$

All other correlation functions were assumed to vanish. Note that if $\langle H \rangle$ is a constant independent of n, then equation 42 for $n = n'$ reduces to a master equation for the exciton site populations $(\langle \rho \rangle_{nn})$; on the other hand, if $\gamma_{m-n} = 0$ then the equation has the wavelike solutions of Frenkel exciton theory (56); thus, this equation describes the coupled wavelike (coherent) and random walk (incoherent) motions of the exciton. The limitations of approach (b) are the same as in the two-molecule case described above. Recently, Haken and Schwarzer (18–21) and Reinecker and co-workers (13, 14, 15) have applied this equation to the study of optical, EPR, and NMR line shapes for molecular crystals with two molecules per unit cell (e.g. anthracene). In the optical case they find Lorentzian lines of width Γ whose positions are those predicted from the usual exciton analysis (4, 5).

Many authors have attempted a calculation of the exciton density matrix in the presence of exciton-phonon scattering using approach (a). Grover & Silbey (57), using a transformation similar to that in equation 31, suggested by the polaron literature (58 62), have derived an expression similar to equation 42 under the assumption of strong exciton-phonon scattering relative to inter-molecular coupling. In the limit of fast vibrational relaxation and quickly decaying phonon correlation functions, the result of this analysis is identical to equation 42 except that γ_0 is zero. This is due to the neglect of quadratic exciton-phonon interactions; when these are included in the Hamiltonian and the same procedure used, γ_0 becomes nonzero and the results for pure crystals are identical to equation 42.

Equation 42 has only been solved formally, even for the simplest case of nearest neighbor interactions; however, an equation can be derived and solved for the mean square displacement of the exciton, $\langle R^2(t) \rangle$ on a site (10, 57). The result for one dimension, nearest neighbor interactions, is

$$\langle R^2(t) \rangle \qquad \rangle$$
$$\qquad_n$$
$$+ (V^2/(\Gamma + \gamma_1)^2)[e^{-2(\Gamma + \gamma_1)t} - 1]a^2 \qquad 44.$$

where $V \equiv V_{n,n+1}$. This yields an expression for the diffusion coefficient, D,

$$D = \lim_{t \to \infty} \langle R \qquad \rangle \qquad 45a.$$

where a is the lattice constant. In three dimensions, D is a tensor, and will be given by a similar formula:

$$\mathbf{D} = \sum_{R \neq 0} \mathbf{R}\mathbf{R}[\gamma_R + \tfrac{1}{2}V_R^2/(\Gamma + \gamma_R)] \qquad 45b.$$

where $\mathbf{R}$ is the distance between two molecules in the crystal. This formula has been used to interpret the temperature dependence of the spectral line shape and diffusion coefficients for triplet anthracene (63). The data can be fit with a strong

temperature dependence of γ_0 and weak temperature dependence of V_{0n} and γ_1 over the range 118–350°K. We discuss this further below.

In the absence of the intermolecular interactions, V_{mn}, the diffusion coefficient reduces to that for a simple random walk with transition probabilities γ_n. In the case in which these interactions are present, and there is still strong phonon-exciton scattering, the effect of the V_{mn} is merely to modify the γ_n.

The Grover–Silbey model (57) gives a formula for the temperature dependence of the γ_n which is very similar to that found for the mobility of a polaron. By using the results of the model for the two-molecule case (27, 28, 29), we can approximately identify γ_n with the Förster expression for the exciton transfer rate in certain cases. Thus, γ_{n-m} will be approximately proportional to the overlap of the emission and absorption spectrum of the two molecules at sites n and m.

Munn (64a) has pointed out another interesting feature of the Grover–Silbey treatment: at very short times the motion of the excitation is governed by the unaveraged intermolecular transfer terms, i.e. by $\hat{V}$ not by $\langle \hat{V} \rangle$, so that this treatment is capable of dealing with exciton transfer before vibrational relaxation.

Kenkre & Knox (30, 31) have derived a generalized master equation for the diagonal density matrix elements using projection operator techniques. As pointed out by Kenkre (32), there is a simple formal connection between their theory and the result of equation 42. However, in treating the dynamical model of Grover & Silbey (57), Kenkre & Rahman (33) exhibited a limitation of this approach. In separating the Hamiltonian into a zeroth order part, H_0, and a perturbation, H_1, they chose H_0 such that it contained no V_{nm} terms at all. In contrast, earlier workers (57) had included these terms in H_0. By omitting these terms from H_0, Kenkre & Rahman (33) have limited the usefulness of their theory for crystals with $\tilde{J}$ sufficiently large. This limitation can easily be appreciated by taking the limit of no exciton-phonon interactions in their model; then their transition probability $W_{mn}(\tau)$ (cf. equation 39) becomes independent of time. If the resulting equation is solved in the simplest case of an infinite one-dimensional crystal with nearest neighbor intermolecular interactions, the result of the Rahman–Kenkre treatment for the probability of finding an exciton on site n, if it was initially on the origin, is $J_{2n}(2Vt)$, where J_n is the nth order Bessel function. The exact result (56) for this case is $[J_n(2Vt)]^2$. Thus, for $t > 1/2V$, the probabilities in the Rahman–Kenkre calculation may become negative. This always occurs if the number of sites in the crystal is larger than two. (Amusingly, in spite of the negative probabilities, the mean square displacement is given correctly.) The possibility of negative probabilities occurring if one splits the Hamiltonian in this way was pointed out earlier by Grover & Silbey (57). Of course, in a real system with exciton-phonon coupling, these negative probabilities may never show up since the decay to equilibrium may be faster than the growth of the negative probabilities. In addition, other approaches may show negative probabilities. The importance of these depends on the relative time scales of decay and oscillatory motion. Kenkre (32) has also discussed, in a rather detailed manner, the connection between excitation transport between molecules and spectral line shapes of the individual molecules.

The transport of localized excitons in molecular crystals with an exciton-phonon

coupling quadratic in the phonon operators was discussed by Munn & Siebrand (64b). These authors did not include linear terms in an attempt to study the effect of vibrational modes that are not totally symmetric on exciton transport. Results depending on the relative size of the exciton bandwidth compared to the phonon bandwidth were obtained. A novel result is the prediction of a decreased exciton transport in the limit of a small phonon bandwidth (slow phonon limit).

Iguchi (65) has also derived a formula for the diffusion coefficient that is similar to equation 45a. He also included a non-site diagonal exciton-phonon coupling term and computed the effect of this to lowest order, assuming a random walk model for the exciton motion.

Many authors have attempted to calculate the optical line shapes of exciton coupled strongly to phonons, treating the lattice phonons dynamically (approach *a*) or stochastically (approach *b*). In addition to the work of Haken and coworkers mentioned above (10–21), Kottis & Aslangul (66) have replaced the exciton phonon coupling by fluctuating terms and used super-operator techniques to compute the optical spectra. They paid particular attention to the possibility of preparing a localized exciton by light. They conclude that if the molecules are identical and translationally invariant, it is impossible to prepare an initially localized exciton by light. They also discuss the question of selection rules in great detail.

A dynamical approach to the calculation of the optical line shape of excitons coupled to phonons were carried out by Fischer & Rice (67) and Grover & Silbey (68) using a linear exciton-phonon coupling term. These authors used a Green's function technique after performing a transformation analogous to equation 31. Unfortunately, the functional form of the line shape was left as a rather formal (and formidable) expression. However, the line shape was characterized by convolutions of the exciton and phonon band widths even in the simplest case. The question of whether the line is Lorentzian in this approximation is still open.

The older theories of the exciton line shape that are summarized in reference (5), are based on weak exciton-phonon coupling. The self-energy of the exciton Green's function is expanded to second order in the exciton-phonon interaction and truncated. The theories of Fischer & Rice (67) and Grover & Silbey (68) are capable of describing both weak and strong exciton-phonon coupling (relative to the inter-molecular coupling or exciton bandwidth) since they are exact in both limiting cases.

A simplified dynamical model of the Hamiltonian, in which an Einstein phonon spectrum and site diagonal exciton-phonon coupling only are assumed, has been treated by Sumi (69, 70). In this calculation, he uses the coherent potential approximation (71, 72) in order to calculate approximately the exciton Green's function. Because of the simplicity of his model and the approximations used, he was able to get numerical results for the spectra as a function of the exciton band width, B, $(B = 2\sum_n V_{mn})$ and the exciton phonon interaction energy, $S = 1/2g^2\omega$, where g is the exciton-phonon coupling constant and ω the phonon frequency. For $B \gg S$ the spectrum consists of a single line (Lorentzian in his model because he invokes a Lorentzian broadening function); in the opposite limit $S \gg B$, he finds a series of lines of varying strength separated by ω. Because of the simplicity of his Hamiltonian (i.e. a single band of phonons of one frequency), this model represents

exciton-molecular vibration interactions better than exciton-phonon interactions. In fact, Sumi's results are a perfect illustration of the transition from strong inter-molecular coupling to weak intermolecular coupling first described by Simpson & Peterson (73). In an earlier calculation, Sumi (74) computed the optical spectrum of an exciton interacting with phonons by treating this interaction as a random variable and also using the coherent potential approximation.

In addition to this work on exciton transport and line shapes, much work has been done on the connected problem of the energy levels of an exciton coupled to molecular vibrations. Merrifield (58) used a variational method to compute the lowest state for each wave vector, k. He used the same Hamiltonian as Sumi (70): one molecular vibration per site with frequency ω, each coupled to the exciton on that site with coupling constant g. By a clever transformation, he removed the exciton variables from the problem and was left with an effective phonon Hamiltonian. Then, using a simple variational treatment, he solved numerically for an upper bound on the energy as a function of k. The results showed that (a) the main effect of the interaction is the reduction of the band width relative to the free exciton value [this reduction was not symmetric being larger at higher k, at variance with earlier ideas (73)], and (b) the effective mass of the exciton increases with the coupling as more vibrations "surround" the exciton as it moves. This calculation is very useful for the lowest band, but is incapable of describing the entire vibrational structure of the exciton.

Using the same Hamiltonian as Merrifield, Cho & Toyozawa (75a) calculated the energy levels approximately, using a Green's function technique. They diagonalized the Hamiltonian in steps: first they diagonalized the Hamiltonian for an exciton localized on a site (which corresponds to the transformation of equation 31), and then they approximately diagonalized the two-site Hamiltonian (corresponding to a dimer), and so on. Their approach is extremely complicated and is difficult to extend to more complex Hamiltonians. However, the results illustrate some simple ideas about the states of the coupled system. If the exciton band width, B, is taken as a measure of the amount of energy gained as the exciton becomes delocalized, and the exciton-phonon interaction energy S is taken as a measure of the energy to be gained upon localization of the exciton, then if $B \gg S$ the eigenstate will be almost a free exciton. If $S \gg B$, then the eigenstate will be (approximately) a highly localized exciton. Cho & Toyozawa (75a) have discussed the approximate exciton eigenstate as a function of B and S and have shown that, for large B/ω, there is an abrupt change in the character of the wave function as S becomes larger than B. This is in analogy with similar calculations on the small polaron (75b). If B/ω is small the exciton wave function does not show this abrupt change as S increases [this is also manifest in Merrifield's calculation (58)]. Most Frenkel exciton band widths in molecular crystals fall into the class $B/\omega < 1$. Thus they represent a less well-studied intermediate case.

The work of Philpott (76) on the theory of the coupling of electronic and vibrational excitations in molecular crystals should also be mentioned. He uses the weak coupling theory (1, 2, 4, 5) but includes the possibility of the total excitation (electronic plus vibrational) being split onto two or more molecules. He treats these many

"particle" states approximately and calculates absorption line shapes at $0°K$. This work is similar in spirit and results to that of Cho & Toyozawa (75a).

EXTENDED SYSTEMS: EXPERIMENTAL STUDIES

We now mention several recent experimental results on exciton-phonon coupling manifested in line shapes and exciton diffusion rates. As mentioned above, Ern et al (63) have fit optical spectral data (excitation spectral data) and exciton diffusion data to equation 45b for the lowest triplet exciton band of anthracene. They used the parameters γ_0, γ_τ, and V_τ, where the subscript τ refers to the nonequivalent nearest neighbor molecules separated by one half the sum of the lattice constants in the a and b directions. They fit V_τ to the spectra (since V_τ is approximately one eighth the Davydov splitting) to find $V_\tau \simeq 2 \, cm^{-1}$. They find γ_0 to be $65 \, cm^{-1}$ at $371°K$ falling to $15 \, cm^{-1}$ at $118°K$ (at $4°K$ it is less than $1 \, cm^{-1}$). In addition, they find $\gamma_\tau = 0.1 \, cm^{-1}$ approximately independent of temperature. The diffusion coefficient along the a axis of the anthracene crystal slowly rises from 1.6×10^{-4} $cm^2 \, sec^{-1}$ at $371°K$ to $4.0 \times 10^{-4} \, cm^2 \, sec^{-1}$ at $118°K$. The γ_τ term contributes about one half to the total diffusion coefficient at all temperatures.

Harris and Fayer (77–79) have performed a series of experiments at very low temperature that show the coherent migration of triplet excitons in 1,2,4,5 tetrachlorobenzene. The intermolecular interactions in this crystal are such that the exciton migration is almost completely one-dimensional (with occasional jumps to nearby chains). By optical detection of the phosphorescence induced by a microwave field (ODMR) (6), these authors conclude that the coherence length is between $300 \, Å$ and $10^4 \, Å$ in this material. They also report a coherence lifetime of $10^{-7} \, sec$ (80), for exciton k states, i.e. the exciton remains in a particular k (wavelike) state for as long as $10^{-7} \, sec$ until it is scattered by phonons sufficiently to be in an incoherent state. The experiments are extremely complex and the interpretation is very subtle; however, there seems little doubt that the triplet exciton in tetrachlorobenzene moves coherently below $4°K$. This is in contrast with the high field measurements on anthracene at $4°K$ (81) in which the triplet exciton moves from site to site in an incoherent fashion.

In a recent series of papers, Morris & Sceats (82–84) have presented a method for extracting exciton-phonon coupling parameters from optical spectra assuming weak exciton-phonon coupling. They have concentrated on the first singlet state of anthracene, which has been of interest for many years (85, 86) (as an example of a moderately strong transition). A very accurate reflectance spectrum was recorded and the dielectric function extracted. From this, and a theoretical expression for the self-energy of the exciton Green's function (5) in the limit of weak exciton-phonon scattering, these authors find that at $300°K$, the exciton primarily interacts with optical phonons of about $90 \, cm^{-1}$ frequency with a coupling strength of about $140 \, cm^{-1}$. They estimate the coupling parameters to be ~ 0.1 for the optical modes and $\sim 10^{-4}$ for the acoustic modes. They find little dependence of these parameters on polarization. Although there are severe difficulties with the analysis (84), the results are self-consistent in that a weak interaction was assumed for the coupling

and the results confirm this assumption. These results are the first to provide exciton-phonon coupling parameters from spectral studies. They also conclude that while at room temperature singlet exciton motion in this singlet state of anthracene can be described as a random walk with steps to nearest neighbors, at low temperature this motion may not be described in this way.

In a related series of papers, Dissado (87) has extended the analysis of weak exciton-phonon coupling to the case of two molecules per unit cell (87), and applied this to the first singlet transition of phenanthrene (87, 88). The half width of the lower Davydov component goes to zero at low temperature, while the upper component has a residual width of 70 cm^{-1}. This width has been fit to the theoretical expression for weak exciton-phonon coupling, assuming the most strongly coupled optical phonon mode is a libration. Using frequencies of $\sim 50 \text{ cm}^{-1}$ and 135 cm^{-1}, he was able to fit the spectral widths reasonably well from $\sim 80°\text{K}$ to $300°\text{K}$. Although many parameters in the theory are not known very well, Dissado was able to obtain phonon interaction energy (S) of $10-15 \text{ cm}^{-1}$, so that the exciton-phonon scattering is weak in this case, although repeated phonon scatterings cause the exciton to become localized.

Recently, Sceats & Rice (89) have commented on the low energy tail of optical absorption lines and on Raman scattering to probe exciton-phonon coupling in molecular crystals. They argue that weak exciton-phonon coupling can explain the experimental results in many molecular crystals.

Finally, mention should be made of the work on the spectra of mixed crystals, particularly isotopically doped crystals. A review of such experiments by Broude & Rashba (90) has recently appeared. This was concerned mainly with small concentrations of impurities in a host crystal. The presence of other impurities has always been a problem in the interpretation of these spectra, although progress has been made (90).

Recently a new idea has been proposed that deserves serious attention. Kopelman and co-workers suggested (91) that in heavily doped crystals, for example, naphthalene-perdeuteronaphthalene alloys, a simplification of the description of the exciton dynamics arises. In these experiments naphthalene and perdeutero-naphthalene are in mole fractions ranging from 0.01 to 0.99, while betamethyl-naphthalene (BMN) is in mole fraction 10^{-3}. The first singlet state of $C_{10}D_8$ is above that of $C_{10}H_8$, which is above that of BMN. Thus BMN acts as a trap for the excitation and its fluoresence is monitored. The $C_{10}H_8$ acts as a trap relative to the $C_{10}D_8$ but can act as a "feeder" to the BMN. As the concentration of $C_{10}H_8$ is increased, the intensity of the BMN fluorescence relative to the total fluorescence (BMN plus $C_{10}H_8$) increases rather abruptly at a mole fraction of $C_{10}H_8$ of $\sim 0.5 \pm 0.1$. The intermolecular interactions in this state of naphthalene are such that the exciton motion is almost entirely in the ab plane. Classical percolation theory (92) predicts that in the two-dimensional square net at a mole fraction of 0.6, large enough clusters arise so that a conduction path exists. Thus Kopelman (91) proposes that he is seeing the analog of an insulator to conductor transition for excitons. The picture is that a large enough concentration of $C_{10}H_8$, the exciton will transfer among $C_{10}H_8$ molecules until it finds a BMN where it is trapped and finally fluoresces.

Below this critical concentration there will be "dead-ends" for the exciton on the $C_{10}H_8$ sites, i.e., clusters that are not close enough to a BMN molecule for that to act as a trap and so the $C_{10}H_8$ fluoresces. Thus far, no temperature-dependent studies have been done and no attempt has been made to extract exciton phonon interactions from these experiments.

ENERGY TRANSFER AND FLUORESCENCE NEAR SURFACES

Kuhn and his co-workers (93–95) have reported experimental and theoretical results for electronic energy transfer over large distances. These beautiful experiments utilize the Langmuir–Blodgett monolayer deposition technique in an innovative way. A known small number of monolayers of arachidic acid salts can be deposited on a substrate by the dipping method. Each layer is 26.8 Å thick, so the total thickness of the fatty acid layer is accurately known (and checked by interference methods). Then a layer of fluorescent dye is deposited (in many of the experiments, the dye is a Eu-dibenzoylmethane complex). In some cases, the first monolayer deposited on the substrate contained molecules capable of acting as an acceptor of the electronic excitation of the dye; in other cases, the substrate acts as an acceptor. The dye is then excited by light, and the fluorescence quenching by the acceptor is measured as a function of distance from donor to acceptor (i.e. thickness of the fatty acid layer).

The experimental details and early theory have been reviewed by Kuhn (96). Here we review the recent theoretical work that has brought experiment and theory into exact agreement. The experiments to be discussed are those in which the substrate is a metal (Ag, Au, Cu) that acts as an acceptor. A typical plot of the experimental lifetime of the dye fluorescence (at wavelength $\lambda = 6120$ Å) as a function of distance (d) from dye to silver metal surface is given in Figure 1.

The oscillations at long distance were interpreted qualitatively by Morawitz (97) using a quantum-mechanical argument. A classical argument can also be made that if the excited dye molecule is considered as an oscillating dipole, as proposed by Kuhn (96), then the electric field reflected from the mirror surface interacts with the dipole. This field, which can be considered as arising from the image dipole, has an oscillatory dependence on d/λ. This gives rise to oscillations in the lifetime as a function of d.

The short distance (less than ~ 200 Å) behavior cannot be explained in this way, since if the metal is considered to be a perfect reflector, then the lifetime of a dipole-oriented parallel to the surface will go to infinity as d gets small, while that of a dipole oriented perpendicularly to the surface will go to one-half its value at $d = \infty$ (97). The correct qualitative explanation of the short distance behavior was provided by Kuhn (96), who pointed out that the metal absorbs at the fluorescent wavelength of the dye, and hence can act as an acceptor (in the Förster transfer sense) of the excitation energy. He took this into account in an approximate way by multiplying the reflected field (of a perfect mirror) by a factor that correctly reproduced the reflectivity and phase shift at this wavelength. This resulted in very good agreement
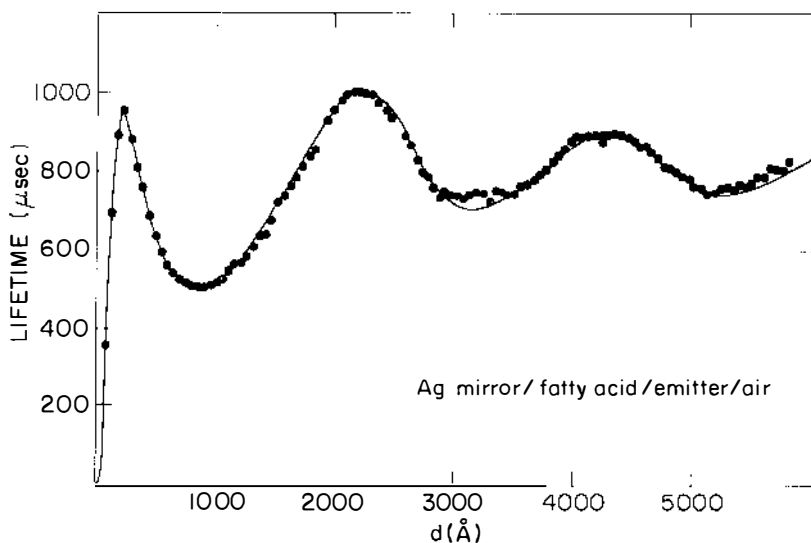
Figure 1 Fluorescent lifetime of emitter at a distance d from a silver mirror. The points are the experimental data (96); the solid line is the theoretical result (105).

at large distances, but only qualitative agreement at short distances. Drexhage (98) noted that the dye molecules are on (or near) an interface between air and fatty acid and he suggested this would have a profound effect on the emission properties of the molecule, particularly if oriented perpendicular to the surface. The question of whether this effect or the approximations introduced by Kuhn were the source of the short distance disagreement remained open.

Independently, Tews (99–101) and Chance, Prock & Silbey (102–105) extended Kuhn's calculation (96) by computing the exact expression for the reflected electric field of an oscillating dipole at a distance d from a real silver surface. These calculations were based on the discussion of radio wave transmission near the earth's surface by Sommerfeld (106) and involved the optical constants of silver, gold, and copper, which are known from the work of Johnson & Christy (107). Both these calculations improved the agreement markedly, but there was still room for improvement since, in order to achieve this agreement, it was necessary to postulate that most ($\sim 90\%$) of the dipole emitters were perpendicular to the surface. It seemed likely that only 1/3 were so oriented, so that a puzzle remained.

This puzzle was solved by Chance, Prock & Silbey (105), who followed Drexhage's suggestion (98) regarding the interface between the fatty acids and air. The agreement between experiment and theory is now essentially exact (see Figure 1) with the only adjustable parameter being the quantum yield of the luminescent state in the absence of the metal.

The explanation of the short distance effect is then that the metal acts as an

absorber of the electronic excitation in the dye. It is interesting to inquire how this absorbance changes with emission wavelength and to understand which modes of the metal are effective in absorbing the energy. These questions were examined by Morawitz & Philpott (108) and by Chance, Prock & Silbey (104). Both these groups discovered that the surface plasmon modes (109) of the metal-dielectric interface were responsible for the absorption of the energy. The rate of energy transfer, b, from the dye to the metal can be written in the small distance limit as

$$b(d) = b_0 \, \beta(\omega) \, d^{-3}, \qquad\qquad 46.$$

where b_0 is the rate in the absence of the metal and

$$\beta(\omega) = \theta Im[\varepsilon_D/(\varepsilon_D + \varepsilon_M(\omega))], \qquad\qquad 47.$$

where θ is a geometrical factor, ε_D is the dielectric constant of the fatty acid layers, and $\varepsilon_M(\omega)$ is the frequency-dependent dielectric constant of the metal. For a Drude-like metal

$$\varepsilon_M(\omega) = 1 - \omega_p^2/[\omega(\omega + i\tau)] \qquad\qquad 48.$$

and so $\beta(\omega)$ will have a peak at the surface plasmon frequency, ω_{sp}:

$$\omega_{sp} = \omega_p/(1 + \varepsilon_D)^{1/2}. \qquad\qquad 49.$$

Philpott (110) has recently discussed this by applying the results of Elson & Ritchie (111) for the quantization of the radiation field and the surface plasmon modes. His results are in agreement with the classical calculations. Since the surface plasmon mode dispersion relations of certain metals are of current interest (112, 113), it has been suggested that it may be possible to probe these with fluorescent molecules near the surface (114).

Literature Cited

1. Hochstrasser, R. 1966. *Ann. Rev. Phys. Chem.* 17:457
2. Robinson, G. W. 1970. *Ann. Rev. Phys. Chem.* 21:429
3. Soos, Z. 1974. *Ann. Rev. Phys. Chem.* 25:121
4. Craig, D., Walmsley, C. 1968. *Excitons In Molecular Crystals.* New York: Benjamin
5. Davydov, A. S. 1971. *Theory of Molecular Excitons.* New York: Plenum
6. El-Sayed, M. 1975. *Ann. Rev. Phys. Chem.* 26:235
7. Sewell, G. 1962. In *Polarons and Excitons*, ed. G. Kuper, pp. 233–44. New York: Plenum
8. Haken, H., Strobl, G. 1968. In *The Triplet State*, ed. A. Zahlan. Cambridge: Cambridge Univ. Press
9. Redfield, A. 1965. *Adv. Magn. Reson.* 1:1
10. Haken, H., Strobl, G. 1973. *Z. Physik* 262:135
11. Haken, H., Reinecker, P. 1972. *Z. Physik* 249:253
12. Reinecker, P., Haken, H. 1972. *Z. Physik* 250:300
13. Reinecker, P. 1975. *Phys. Status. Solidi* B70:189
14. Ibid, 471
15. Reinecker, P. 1975. *Z. Physik* 821:409
16. Reinecker, P., Kühne, R. 1975. *Z. Physik* B22:193
17. Ibid, 201
18. Schwarzer, E., Haken, H. 1972. *Phys. Lett.* 42A:317
19. Schwarzer, E., Haken, H. 1973. *Opt. Comm.* 9:64
20. Schwarzer, E., Haken, H. 1974. *Chem. Phys. Lett.* 27:41
21. Schwarzer, E. 1976. *Z. Physik B.* In press
22. Aslangul, C., Kottis, P. 1974. *Phys. Rev. B* 10:4364
23. Aslangul, C., Kottis, P. 1974. *C. R. Acad. Sci. B* 278:33

24. Ibid, 7050
25. Ibid, 7350
26. Ibid, 279 : 5230
27. Soules, T., Duke, C. 1971. *Phys. Rev. B* 3 : 262
28. Rackovsky, S., Silbey, R. 1973. *Mol. Phys.* 25 : 61
29. Abram, I., Silbey, R. 1975. *J. Chem. Phys.* 63 : 2317
30. Kenkre, V. M., Knox, R. 1974. *Phys. Rev. B* 9 : 5279
31. Kenkre, V. M., Knox, R. 1974. *Phys. Rev. Lett.* 33 : 803
32. Kenkre, V. M. 1975. *Phys. Rev. B* 11 : 1741; Ibid 12 : 2150
33. Kenkre, V., Rahman, T. 1974. *Phys. Lett.* 50A : 170
34. Fulton, R., Gouterman, M. 1974. *J. Chem. Phys.* 35 : 1059
35. Merrifield, R. 1963. *Radiat. Research* 20 : 154
36. Fulton, R., Gouterman, M. 1964. *J. Chem. Phys.* 41 : 2280
37. Lefebvre, R., Garcia-Sucre, M. 1967. *Int. J. Quant. Chem.* 15 : 339
38. Young. J. 1968. *J. Chem. Phys.* 49 : 2566
39. Suna. A. 1971. *Phys. Status. Solidi* 45 : 591
40. McCumber, D. 1964. *J. Math. Phys.* 5 : 221
41. McCumber, D. 1964. *Phys. Rev.* 135 : 1676
42. Fitchen, D. 1968. In *Physics of Color Centers*, ed. W. Fowler, pp. 294–351. New York : Academic
43. Osadko, I. 1971. *Sov. Phys. Solid State* 13 : 974
44. Ibid 1973. 14 : 2522
45. Förster. T. 1948. *Ann. Phys. NY.* 2 : 55
46. Förster, T. 1965. In *Modern Quantum Chemistry*. ed. O. Sinanoglu, 3 : 93–138. New York : Academic
47. Dexter. D. 1973. In *Luminescence of Crystals, Molecules and Solutions*, ed. F. W. Williams. New York : Plenum
48. Zewail, A., Harris, C. B. 1974. *Chem. Phys. Lett.* 28 : 8
49. Zewail, A., Harris, C. B. 1975. *Phys. Rev. B* 11 : 935
50. Ibid, 952
51. Zewail, A. 1975. *Chem. Phys. Lett.* 33 : 46
52. Pearlstein. R. 1967. *Brookhaven Symp. Biol.* No. 19 : 8; Knox, R. S. 1968. *J. Theor. Biol.* 21 : 244
53. Trlifaj, M. 1958. *Czech. J. Phys.* 5 : 510
54. Merrifield, R. E. 1968. *Acc. Chem. Res.* 4 : 129
55. Avakian, P., Ern, V., Merrifield, R., Suna, A. 1968. *Phys. Rev.* 165 : 974
56. Merrifield, R. E. 1958. *J. Chem. Phys.* 28 : 647
57. Grover. M., Silbey. R. 1971. *J. Chem.*

Phys. 54 : 4843
58. Merrifield, R. E. 1964. *J. Chem. Phys.* 40 : 445
59. Holstein, T. 1959. *Ann. Phys. NY* 8 : 325
60. Lee, T., Low, F., Pines, D. 1953. *Phys. Rev.* 90 : 297
61. Emin, D. 1971. *Ann. Phys. NY* 64 : 336
62. Munn, R. 1973. *J. Chem. Phys.* 58 : 3230
63. Ern, V., Suna, A., Tomkiewicz, Y., Avakian, P., Groff, R. 1972. *Phys. Rev. B* 5 : 3222
64a. Munn, R. 1974. *Chem. Phys.* 6 : 469
64b. Munn, R., Siebrand, W. J. 1970. *Chem. Phys.* 52 : 47
65. Iguchi, I. 1972. *J. Chim. Phys.* 69 : 23
66. Kottis. P., Aslangul, C. *Phys. Rev.* To be published
67. Fischer. S., Rice. S. A. 1970. *J. Chem. Phys.* 52 : 2089
68. Grover. M., Silbey. R. 1970. *J. Chem. Phys.* 52 : 2099
69. Sumi. H. 1974. *J. Phys. Soc. Jpn* 36 : 770
70. Ibid 1975. 38 : 825
71. Velicky, B., Kirkpatrick, S., Ehrenreich, H. 1968. *Phys. Rev.* 175 : 742
72. Onodera, Y., Toyozawa, Y. 1968. *J. Phys. Soc' Jpn* 24 : 341
73. Simpson, W., Peterson, D., 1957. *J. Chem. Phys.* 26 : 588
74. Sumi, H. 1972. *J. Phys. Soc. Jpn* 32 : 616
75a. Cho, K., Toyozawa, Y. 1971. *J. Phys. Soc. Jpn* 30 : 1555
75b. Emin, D. 1973. *Adv. Phys.* 22 : 57
76. Philpott, M. 1971. *J. Chem. Phys.* 55 : 2039
77. Fayer, M., Harris, C. B. 1974. *Chem. Phys. Lett.* 25 : 149
78. Harris. C. B., Fayer. M. 1974. *Phys. Rev. B* 10 : 1784
79. Fayer, M., Harris, C. B. 1974. *Phys. Rev.* 139 : 748
80. Harris, C. B. 1974. *Pure Appl. Chem.* 37 : 73
81. Haarer, D., Wolf, H. 1970. *Mol. Cryst. Liq. Cryst.* 10 : 359
82. Morris, G., Sceats, M. 1973. *Chem. Phys.* 1 : 120
83. Ibid 1974. 3 : 332
84. Ibid, 342
85. Rice, S., Jortner, J. 1967. In *The Physics and Chemistry of the Organic Solid State*, ed. D. Fox, 3 : 199–497. New York : Wiley
86. Philpott, M. 1973. *J. Chem. Phys.* 59 : 4406
87. Dissado, L. 1975. *Chem. Phys.* 8 : 289; Dissado, L. 1975. *Chem. Phys. Lett.* 33 : 57
88. Tomioka, K., Animoto, H., Tomotika, T., Matsui, A. 1973. *J. Chem. Phys.* 59 : 4157
89. Sceats. M. G., Rice. S. A. 1974. *Chem.*

Phys. Lett. 25 : 9; 1975. *J. Chem. Phys.*
62 : 1098
90. Broude, V., Rashba, E. I. 1974. *Pure Appl. Chem.* 37 : 21
91. Kopelman, R., Monberg, E., Ochs, F., Prasad, P. 1975. *Phys. Rev. Lett.* 34 : 1506
92. Shante, V. K., Kirkpatrick, S. 1971. *Adv. Phys.* 20 : 235
93. For a review see Kuhn, H. 1971. *Pure Appl. Chem.* 27 : 421
94. Drexhage, K. H., Kuhn, H., Schäfer, F. 1968. *Ber. Bunsenges. Phys. Chem.* 72 : 329
95. Drexhage, K. H. 1974. *Prog. Opt.* 12 : 165
96. Kuhn, H. 1970. *J. Chem. Phys.* 53 : 101
97. Morawitz, H. 1969. *Phys. Rev.* 187 : 1792
98. Drexhage, K. H. 1970. *J. Lumin.* 1–2 : 693
99. Tews, K. 1972. Thesis. Univ. Marburg/Lahn
100. Tews, K. 1973. *Ann. Phys. (Leipzig)* 29 : 97
101. Tews, K. 1974. *J. Lumin.* 9 : 223

102. Chance, R., Prock, A., Silbey. R. 1970. *J. Chem. Phys.* 60 : 2184
103. Ibid 1974. 60 : 2744
104. Ibid 1975. 62 : 2245
105. Ibid 1976. 63 : 1589
106. Sommerfeld, A. 1949. *Partial Differential Equations of Physics.* New York: Academic
107. Johnson, P., Christy, R. 1973. *Phys. Rev. B* 6 : 4370
108. Morawitz, H., Philpott, M. 1974. *Phys. Rev. B* 10 : 4863
109. Ritchie, R. 1973. *Surf. Sci.* 34 : 1
110. Philpott, M. 1975. *J. Chem. Phys.* 62 : 1812
111. Elson, J., Ritchie, R. 1971. *Phys. Rev. B* 4 : 4129
112. Economou, E. N., Ngai, K. L. 1974. *Adv. Chem. Phys.* 27 : 265
113. Rice, S. A., Guidotti, D., Lemberg, H. L., Murphy, W., Bloch, A. 1974. *Adv. Chem. Phys.* 27 : 543
114. Chance, R., Prock, A., Silbey. R. *Sol. State Commun.* In press