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Effect of an External Electric Field on Electronic Excitation Energy Transfer in Molecular Crystals

A new probe of the microscopic dynamics

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While several mechanisms can be imagined by which an external electric field can affect electronic excitation energy transfer in crystals, the simplest possibility involves changing the energy level spacings of neighboring molecules. Energy transfer from one molecule to another is affected by an energy mismatch or loss of resonance. In a band model, presumably valid at low temperatures, this loss of resonance decreases the exciton bandwidth and reduces the exciton group velocity. When the bandwidth is comparable to the inhomogeneous broadening, an abrupt decrease in the rate of energy transfer can be expected, reflecting the phenomenon of Anderson localization. At higher temperatures, the energy mismatch can be accommodated by phonon emission and absorption processes. The dependence of the energy transfer rate constant on electric field and temperature for the case of coherent energy transfer and for the limit of incoherent energy transfer is predicted for a simple model system.

I. INTRODUCTION

For some time a dichotomy existed in many studies of the electronic states of molecular crystals.[1,2] Spectroscopic observations were interpreted in terms of the stationary states of a perfect, rigid lattice Hamiltonian,[3] whereas observations of excitation energy transfer phenomena were interpreted in terms of localized excitations hopping from molecule to molecule.[4]

In this context various spectroscopic experiments were designed to measure or determine the excitation transfer matrix elements that are the fundamental parameters of Frenkel exciton theory.[5,6] One objective of this work was to demonstrate whether or not these parameters and the theory could explain a wide variety of observations related to *exciton band structures*. Another objective, which only now is beginning to be realized, was to explain *exciton* *dynamics*, the observations of excitation energy transfer, in terms of these same parameters.[7,8]

The case of coherent energy transfer has been defined[8] as the situation where the mean free path of the exciton wave packet is greater than one lattice site. The incoherent limit therefore is the situation where the mean free path is one lattice site. It is the purpose of the present paper to show that definite and qualitatively different effects of an external electric field on energy transfer are predicted for the case of coherence and the limit of incoherence. For the usual model[9] of coherence, these predictions are independent of any adjustable parameters and lead to the conclusion that the external field may abruptly stop energy transfer due to the phenomenon of Anderson localization.[10]

These electric field effects therefore serve to test the model for coherent energy transfer, elucidate the role of phonons in energy transfer processes, and may reveal the controversial Anderson localization of excitation energy.[11,12]

II. THE MACROSCOPIC PARAMETERS

The situation of sensitized luminescence or energy transfer to guest or defect molecules (x-traps) in the host lattice is considered. Changes in the rate of energy transfer can be observed by monitoring the relative steady-state luminescence yield of the guest or host or by monitoring the time evolution of the guest or host luminescence following pulsed excitation. With the appropriate experimental conditions,[9] one can expect these observations to be described by the following kinetic equations.

$$\dot{N}_H(t) = -(K_H + K_T)N_H(t) + P(t) \tag{1}$$

$$\dot{N}_G(t) = K_T N_H(t) - K_G N_G(t) \tag{2}$$

The number of excitons or host molecules in the lowest excited singlet state is N_H, and the number of excited guest molecules is N_G. The pumping rate by the external source is $P(t)$, and the rate constant for unimolecular decay of the host is K_H, of the guest is K_G, and for host-guest energy transfer is K_T. Only the energy transfer rate constant is considered here to depend upon the external electric field. The origin of this dependence will be described in the following sections.

Under steady state conditions, the ratio of host to guest excitations, from Eq. (2), is K_G/K_T. Since the intensity of luminescence is proportional to the number of excitations, the following expressions are obtained for the relative luminescence yields of the guest and host provided the luminescence quantum yields in the absence of energy transfer are the same for both guest and host. This condition is most likely to be valid for x-traps or isotopic mixed crystals.

$$RLY(G) = \frac{I_G}{(I_G + I_H)} = \frac{K_T}{(K_T + K_H)} \tag{3}$$

$$RLY(H) = \frac{I_H}{(I_G + I_H)} = \frac{K_H}{(K_T + K_H)} \tag{4}$$

One can see from Figure 1, the graph of Eq. (3), that changes in the energy transfer rate constant caused by the electric field will be difficult to detect in the guest luminescence unless the energy transfer rate constant is comparable to the host decay rate constant. Fortunately this constraint poses little difficulty because the energy transfer rate can be varied by varying the guest concentration, and in cases where the trap concentration is uncontrollably high so $K_T \gg K_H$, for example a crystal with numerous x-traps, the exciton luminescence, if it can be detected, is sensitive to changes in the energy transfer rate. See Eq. (4).

With impulse excitation, the effect of $P(t)$ appears as a boundary condition; namely, $N_H(0)$ excitons are formed initially. This approach is valid if the duration of the pulse is much less than the host lifetime $1/K_D$ where $K_D = K_T + K_H$. The subsequent time evolution of the number of excited states and hence the time course of the luminescence is given by

$$N_H(t) = N_H(0)\exp(-K_D t) \tag{5}$$

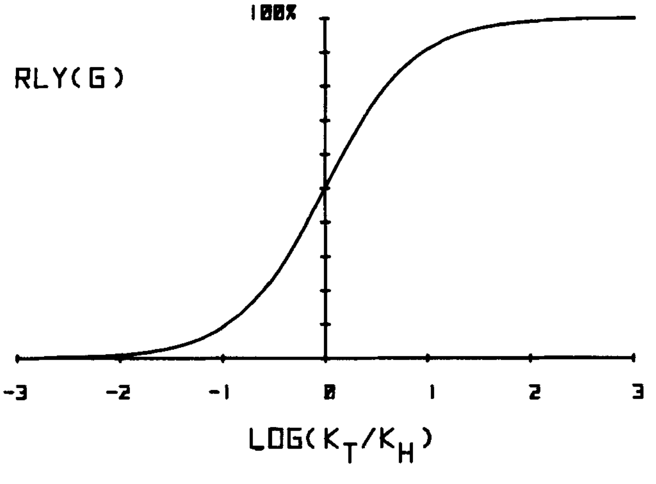

FIGURE 1 The relative yield of sensitized luminescence as a function of the ratio of the energy transfer rate constant to the unimolecular decay rate constant of the host.

$$N_G(t) = N_G(0)\,(\exp(-K_G t) - \exp(-K_D t)) \tag{6}$$

where $N_G(0) = K_T N_H(0)/(K_T + K_H - K_G)$.

Measurements of the host decay rate K_D from the exponential decay of the host luminescence or the corresponding rise of the guest luminescence will reveal changes in the energy transfer rate caused by the external field.

III. THE MICROSCOPIC VARIABLES

a. A model for the coherent case

The model for coherent energy transfer in the presence of an external electric field follows the ideas described by Harris and coworkers,[8] in particular Shelby, Zewail, and Harris.[9] The model describes linear (one dimensional) crystals with exclusively nearest neighbor excitation transfer interactions. The energy transfer rate constant is taken to be proportional to the thermal average group velocity[13] of the exciton wave packet.

The details of the constant of proportionality between the rate constant and the average group velocity are of no concern in the present analysis. This constant presumably contains the trapping probability, an average coherence length, and an average distance to a trap. These quantities are taken to be independent of the external field. The use of a thermal average group velocity is appropriate if the frequency of exciton-phonon scattering is large compared to the exciton decay rate to allow thermal equilibration but small compared to the frequency of exciton motion past the lattice sites ($\approx \beta/\hbar$) to allow the exciton propagation to be described by a single wave packet group velocity for some distance.

The electric field effects considered here arise because the molecules are taken to be polar, arranged in an antiferroelectric array, and are coupled to the external electric field by the dipole interaction. The exciton dispersion then is given by[8,14]

$$E(k) = E_0 \pm \left(4\beta^2 \cos^2\left(\frac{ka}{2}\right) + (\Delta\mu F)^2\right)^{1/2} \tag{7}$$

where E_0 is the ideal mixed crystal excitation energy,[15] β is the nearest neighbor excitation transfer matrix element, a is the lattice constant and $a/2$ the nearest neighbor spacing, $\Delta\mu$ is the difference between the ground state dipole moment and the excited state dipole moment of the molecule, and F is the local electric field. Actually the variable in the theory is the shift in the electronic transition energy caused by the field. This shift can be measured spectroscopically and symbolized by $\Delta\mu F$ so no concern is necessary for the approximate explanation of $\Delta\mu F$ given here.

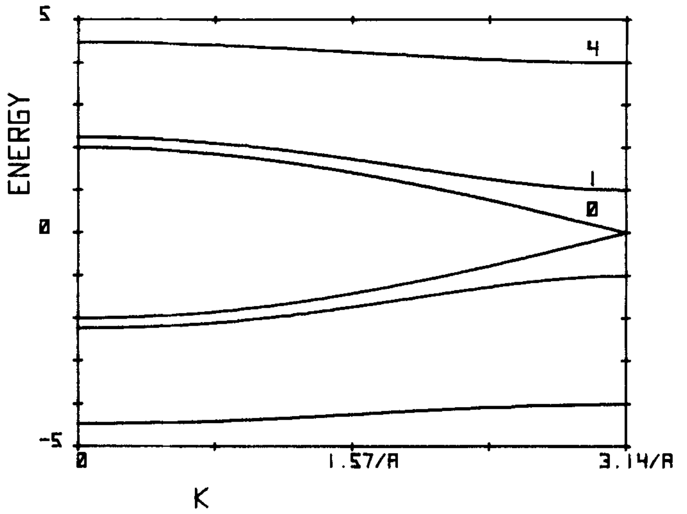

FIGURE 2 The exciton energy measured in units of β as a function of the wave vector for three values of the field energy: $\Delta\mu F = 0$, 1β, and 4β. The ideal mixed crystal level is taken as the zero of energy.

Plots of this dispersion relation for some values of the field energy $\Delta\mu F$ are given in Figure 2. At zero field the dispersion relation is just that for a linear crystal with two molecules per unit cell separated by half the lattice spacing. Because of the antiferroelectric arrangement, the external field makes the two molecules in the unit cell inequivalent, thereby causing the exciton band with two branches at zero field to split into two inequivalent bands separated by $2\Delta\mu F$. Since only nearest neighbor interactions are assumed, the dispersion in these bands comes from the so-called "superexchange" interactions.[16,17] In the perturbation limit, this interaction scales as $\beta^2/2\Delta\mu F$, thus the interaction decreases, and the bands flatten, the dispersion becomes less, as the field increases.

This flattening has a significant effect on the rate of coherent energy transfer since the group velocity is given by the derivative of the dispersion relation.

$$|V_g(k)| = \left|\frac{(\partial E(k)/\partial k)}{\hbar}\right|$$

$$= \left|\left(\frac{2a\beta^2}{\hbar}\right)\cos\left(\frac{ka}{2}\right)\sin\left(\frac{ka}{2}\right)\Big/\left(4\beta^2\cos^2\left(\frac{ka}{2}\right) + (\Delta\mu F)^2\right)^{1/2}\right| \qquad (8)$$

Plots of the group velocity throughout the Brillouin zone for some values of the field energy are given in Figure 3.

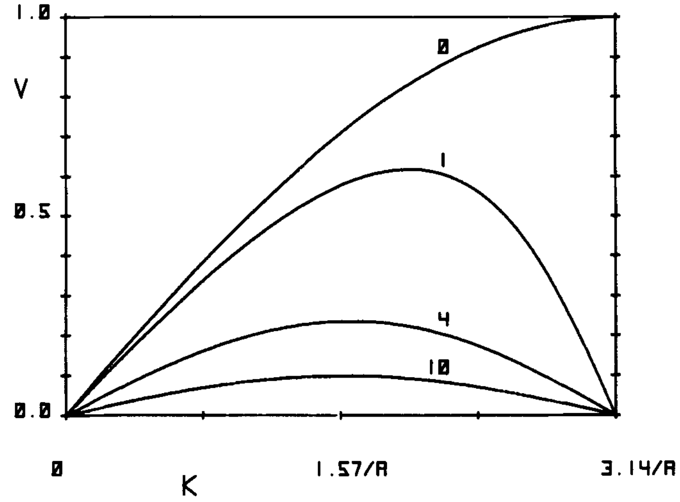

FIGURE 3 The ratio of the exciton group velocity to the maximum group velocity in zero field ($a\beta/\hbar$) for four values of the field energy measured in units of β.

The thermal average group velocity is calculated as the sum of the group velocity of all k states of both bands weighted by the appropriate probability factor $\exp(-E_b(k)/k_BT)/Q$ where $Q = \Sigma_b\Sigma_k \exp(-E_b(k)/(k_BT))$. Plots of the thermal average group velocity as a function of temperature for some values of the field energy are given in Figure 4.

It is clear from the above discussion and figures that an external electric field can only alter the average exciton group velocity and hence affect the energy transfer rate constant significantly when the field energy ($\Delta\mu F$) is comparable to the excitation transfer interaction (β). The few polar molecular crystals that have been characterized with respect to the above properties, including the requirement of one dimensional interactions, have $\Delta\mu \approx 1D$ and $\beta \approx 1\ \mathrm{cm}^{-1}$. Consequently even liquid helium temperatures (2–4°K) are in or close to the high temperature regime of Figure 4 for these systems.

In this high temperature limit, because of the narrow exciton band width and small splitting, the average exciton group velocity is independent of temperature. The energy transfer rate constant similarly should exhibit little temperature dependence at these low temperatures unless exciton scattering by low frequency phonons is significant. This model for coherent energy transfer therefore predicts that for these systems the ratio of the energy transfer rate constant in the presence of an electric field to the constant in the absence of the electric field should be equal to the ratio of the corresponding high temperature thermal average group velocities. This ratio as a function

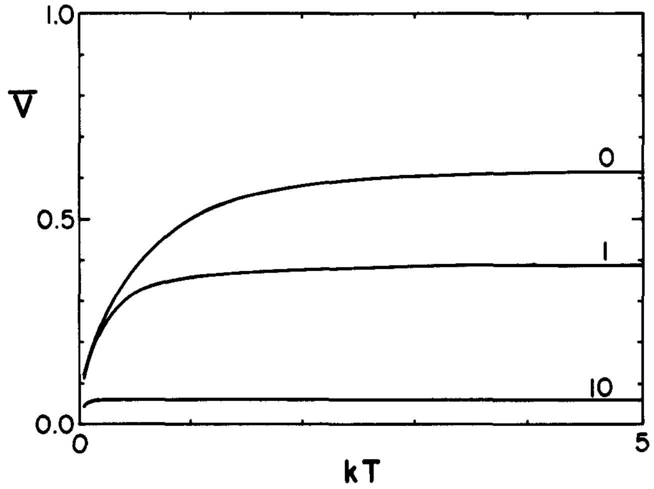

FIGURE 4 The ratio of the thermal average group velocity to the maximum group velocity in zero field as a function of thermal energy in units of β for three values of the field energy: $\Delta\mu F = 0, 1\beta$, and 10β.

field energy is shown in Figure 5 and is given by the following equation.

$$\frac{K_T(F)}{K_T(0)} = \left(1 + \left(\frac{\Delta\mu F}{2\beta}\right)^2\right)^{1/2} - \frac{\Delta\mu F}{2\beta} \tag{9}$$

The decrease in the energy transfer rate caused by an external electric field for the model of coherent energy transfer is fixed qualitatively and quantitatively by spectroscopic observations. The Davydov splitting and Stark splitting measured[14] in the absorption spectrum is simply related to β and to $\Delta\mu F$. These two quantities uniquely determine the effect of the electric field on the energy transfer rate constant.

This ratio can be measured experimentally in a pulsed excitation experiment. If K_D is measured as described in Section II for several values of the field, then $K_D(F = \infty)$ can be determined by extrapolation. For $F = \infty$, it is clear from Figure 4 that $K_T = 0$ so $K_D(\infty) = K_H$; consequently,

$$\frac{K_D(F) - K_D(\infty)}{K_D(0) - K_D(\infty)} = \frac{K_T(F)}{K_T(0)}. \tag{10}$$

Note that if K_D contains small contributions from energy transfer mechanisms not considered here, e.g. long range direct transfer or transfer in the second and third dimension, these will still contribute to $K_D(\infty)$ and tend to be subtracted in Eq. (10) to leave the right ratio. Thus, the proposed method of measurement tends to correct for the fact that real systems may differ slightly

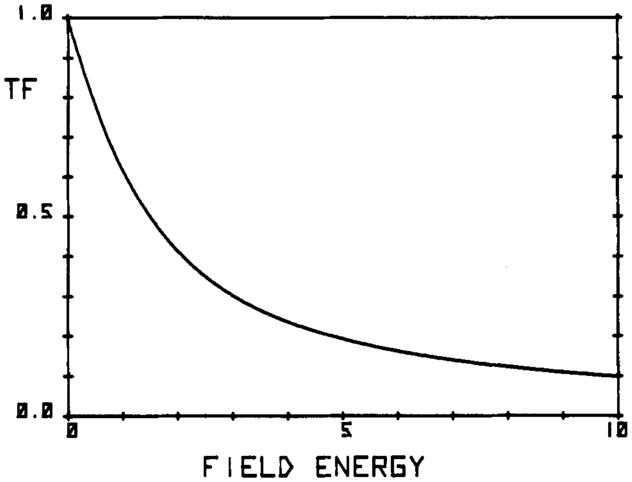

FIGURE 5 The fractional decrease (TF) in the energy transfer rate constant caused by an external electric field for the case of coherent energy transfer. The field energy is in units of β.

from the ideal model described here. Validity of the model assuming a linear array with nearest-neighbor interactions can be assessed independently by a variety of spectroscopic observations.[5,6]

b. A description of the incoherent limit

The model for the case of coherent energy transfer described in the previous section predicts that the energy transfer rate will decrease rapidly with increasing electric field and vary little with temperature in the low temperature regime. In the incoherent limit, the predictions are quite different. In this limit, presumably reached as the temperature is increased, the electronic excitation "hops" from molecule to neighboring molecule. The electronic excitation energy of neighboring molecules, however, differs by twice the electric field energy because in the model being considered neighboring molecules have dipole moments pointing in opposite directions. The "hop" therefore must be accompanied by phonon emission or absorption processes to compensate for the energy mismatch.[18]

In the incoherent limit, the energy transfer rate constant is inversely proportional to the average time needed to move one lattice constant.[9] For the present case of nonresonant energy transfer in the high temperature-high field regime, this time is determined by the rates of the phonon scattering, absorption, and emission processes involved. In the absence of relevant experimental data, the temperature and field dependence of the energy transfer rate constant is described only for the simple case of one phonon processes. The rate for one phonon absorption and emission with energy matching the energy mismatch $2\Delta\mu F$ is proportional[19] to the square of the exciton-phonon coupling matrix element, to the density of phonon states, and to their occupation number (or $n + 1$ for emission). The energy transfer rate constant therefore decreases linearly with decreasing temperature following the decrease in the phonon occupation number. At lower temperatures the rate for phonon assisted energy transfer goes to zero exponentially following the rate for absorption of a phonon. Energy transfer then occurs by the tunneling or coherent mechanism described in the preceding section. In the high temperature-high field regime the energy transfer rate constant decreases as the field decreases because the density of phonon states that can compensate the energy mismatch decreases and the exciton-phonon coupling probably decreases as well.

Since the first experiments relevant to this discussion are likely to be done on molecules with dipole moments of a few Debye, the energy mismatches will be in the range of 5–10 cm^{-1}. One phonon processes therefore will involve long wave acoustic phonons, and the density of phonon states with energy matching the mismatch will vary as $(2\Delta\mu F)^2$, following the Debye model.[19] In addition as the frequency of the phonon increases, the relative motion of neighboring molecules also increases; consequently, one might suppose that the effect of exciton-phonon coupling increases linearly with frequency or energy mismatch giving rise to an overall $(2\Delta\mu F)^3$ dependence[19] of the energy transfer rate constant on the field.

The simplest theory of phonon-assisted energy transfer therefore predicts a linear dependence of the transfer rate on temperature and a cubic dependence on electric field. The concern should not be with the validity or applicability of this simple result but rather with observing the behavior of real systems. Deviations from these predictions will provide information about the participation of higher order phonon processes, about the phonon density of states, and about the frequency or wave vector dependence of the exciton-phonon coupling.

IV. RELEVANCE TO ANDERSON LOCALIZATION

The relevance of the concept of Anderson localization to energy transport in isotopically mixed molecular crystals has been a subject of some controversy.[10–12] The basic idea is that when the inhomogeneous broadening is comparable to the exciton bandwidth then excitations are localized and energy transfer ceases or is greatly diminished. From Figure 2, it is clear that the effect of the electric field is to decrease the exciton bandwidth. In carefully selected systems where the bandwidth can be varied by the electric field from being greater than the inhomogeneous broadening to less than the inhomogeneous broadening, an electric field induced Anderson transition from extended to localized states should be obtained. This transition would be marked by a more abrupt decrease in the energy transfer rate than that predicted in Figure 5.

V. SUMMARY AND CONCLUSIONS

In the case of a linear antiferroelectric array of dipolar molecules, an external field applied in the direction of the dipole moments causes the electronic excitation energy of neighboring molecules to differ by $2\Delta\mu F$.

Resonance energy transfer is still possible by tunneling through the insulating intervening molecule via superexchange interactions since only nearest neighbor interactions are included in the model. As the field increases, so does the barrier height, and the tunneling rate decreases. The decrease in the energy transfer rate constant, proportionate to the decrease in the thermal average exciton group velocity, is determined entirely by the Davydov splitting 4β and the Stark splitting $2\Delta\mu F$, both of which can be determined spectroscopically. One then has a unique correspondence between *exciton band structure* and *exciton dynamics* with no adjustable parameters. It obviously is of great interest to see if this theory of coherent energy transfer is consistent with observations of changes in the energy transfer rate caused by an external electric field. Since the effect of the electric field is to decrease the tunneling rate or from another point-of-view the exciton bandwidth, in some systems the electric field may induce an Anderson transition from extended to localized states if the bandwidth can be made smaller than the inhomogeneous broadening.

At high fields the tunneling rate becomes negligible, and at high temperatures the energy transfer should be dominated by phonon assisted processes. Under these conditions, the energy transfer rate constant is predicted, by a provocatively simple model, to vary linearly with temperature and as the cube of the electric field.

Experiments paralleling the discussion here will provide a test of the popular[8] model of coherent energy transfer, may prove the relevance of the Anderson localization concept, and will provide information about exciton-phonon coupling. With respect to exciton-phonon coupling, the experiments will allow phonon-assisted and coherent energy transfer to be identified and their rates measured as a function of temperature and electric field. The temperature dependence of the phonon assisted rate will identify the nature of the phonon process that compensates the energy mismatch while the field dependence will provide information about variations in the phonon density of states and the frequency or wave vector dependence of the exciton-phonon coupling.

References

1. R. S. Knox, *J. Am. Chem. Soc.*, **91**, 6894 (1969).
2. D. M. Hanson, *Chem. Phys. Letters*, **11**, 175 (1971).
3. D. P. Craig and S. H. Walmsley, *Excitons in Molecular Crystals* (Benjamin, New York, 1968).
4. H. C. Wolf, in *Advances in Atomic and Molecular Physics*, Vol. 3, ed. D. R. Bates (Academic Press, New York, 1967) p. 319.
5. G. W. Robinson, *Ann. Rev. Phys. Chem.*, **21**, 429 (1970).
6. V. L. Broude and E. I. Rashba, *Pure Appl. Chem.*, **37**, 21 (1974).
7. R. Silbey, *Ann. Rev. Phys. Chem.*, **27**, 203 (1976).
8. C. B. Harris and D. A. Zwemer, *Ann. Rev. Phys. Chem.*, **29**, 473 (1978).
9. R. M. Shelby, A. H. Zewail, and C. B. Harris, *J. Chem. Phys.*, **64**, 3192 (1976).
10. J. Klafter and J. Jortner, *Chem. Phys. Letters*, **49**, 410 (1977).
11. E. M. Monberg and R. Kopelman, *Chem. Phys. Letters*, **58**, 497 (1978).
12. J. Klafter and J. Jortner, *Chem. Phys. Letters*, **60**, 5 (1978).
13. M. D. Fayer and C. B. Harris, *Phys. Rev.*, **B9**, 748 (1974).
14. R. M. Hochstrasser and J. W. Michaluk, *J. Mol. Spectry*, **42**, 197 (1972).
15. E. R. Bernstein, S. D. Colson, R. Kopelman, and G. W. Robinson, *J. Chem. Phys.*, **48**, 5596 (1968).
16. H. K. Hong and R. Kopelman, *Phys. Rev. Letters*, **25**, 1030 (1970).
17. H. K. Hong and R. Kopelman, *J. Chem. Phys.*, **55**, 724 (1971).
18. T. Holstein, S. K. Lyo, and R. Orbach, *Phys. Rev. Letters*, **36**, 891 (1976).
19. B. Di Bartolo, *Optical Interactions in Solids* (John Wiley and Sons, Inc., New York, 1968) pp. 341–347.