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Host-Sensitized Energy Transfer in Molecular Crystals[†]

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The time evolution of the fluorescence intensities of tetracene-doped anthracene and anthracene-doped napthalene crystals was investigated for various concentrations of activators and different methods of excitation. Singlet exciton diffusion, generally invoked to explain energy transfer in these systems, cannot explain the observed time dependence, which indicates that energy transfer is more efficient at short times than at long times. Such a variation of energy-transfer efficiency is characteristic of long-range resonant interaction, but the predictions of the normal mathematical formulation of this theory also disagree with the results. A combined theory of long-range interaction and exciton diffusion can be made to fit the data only with a critical energy-transfer distance R_0, which is much greater than that determined from spectral considerations and a diffusion coefficient D, which is much smaller than that measured by other techniques.

I. INTRODUCTION

Energy transfer between an anthracene-host crystal and tetracene-impurity molecules was first observed about 35 yr ago.[1] Since that time, an extensive amount of work has been done in studying energy transfer in tetracene-doped anthracene and similar systems and the results of these investigations are summarized in several review articles.[2–7] In most of the recent investigations, energy transfer in these systems is attributed to singlet exciton diffusion where the transfer of energy is considered to be short-range process occurring between an excited host molecule and a nearest-neighbor impurity.[8–10] The singlet exciton diffusion coefficient D has been measured by several techniques and is reported to be on the order of 10^{-3} cm^2 sec^{-1} for anthracene crystals[10–13] and on the order of 10^{-4} cm^2 sec^{-1} for napthalene crystals.[14]

We recently reported experimental results on the time evolution of anthracene and tetracene fluorescence intensities in tetracene-doped anthracene crystals.[15,16] The usual mathematical formulation of singlet exciton diffusion theory cannot explain the observed time dependence. The results indicate that energy transfer is more efficient at short times than at long times, which is characteristic of long-range resonant interaction. It was found that the best fit to the data is obtained using a combined theory of diffusion plus long-range interaction. This theory yields a value for the diffusion coefficient on the order of ~ 4×10^{-6} cm^2 sec^{-1} and a value for the critical energy-transfer distance R_0, on the order of 100 Å, which is much greater than the value of 30 Å predicted from spectral considerations.

In this paper we extend our previous investigations to several other anthracene crystals with various concentrations of tetracene and to crystals of anthracene-doped napthalene. Data obtained using laser excitation are also presented. All the results described in this paper are consistent with those reported earlier. The data obtained on the anthracene-doped napthalene system also disagree with the predictions of exciton diffusion theory, and fitting the data with the combined energy-transfer theory again gives an anomalously large value for R_0 and small value for D. Other theories of energy transfer are also discussed and compared with these data.

II. THEORETICAL

The nonradiative transfer of electronic excitation energy between two optically active centers in solids with no net charge migration is generally explained in one of two models: (i) exciton diffusion and (ii) long-range resonant interaction. Several attempts have also been made to develop theories of long-range energy transfer in which the sensitizer excitation is allowed to migrate. The mathematical expressions for these various theories are derived below. The most important consideration for our purpose is the time dependence of the energy-transfer rate. In the exciton diffusion model, the sensitizer excitation wanders randomly throughout the lattice until it is trapped by an activator and, in this case, the energy-transfer rate is independent of time. In the long-range interaction model, the sensitizer excitation is localized at given lattice sites. The excited sensitizers located close to activators transfer their energy rapidly, and as their number decreases, energy transfer takes place from excited sensitizers located at increasingly greater distances from activators. The energy-transfer rate decreases with increasing sensitizer-activator separation and thus in this model the energy-transfer rate decreases with time.

A. Exciton Diffusion Theory

In the exciton diffusion model,[17–19] the equations describing the time rate of change of the sensitizer exciton concentration n_S and the concentration of excited activator molecules n_A are

$$\dot{n}_S(t)=G(t)-\beta_S n_S(t)-k n_S(t)\ , \qquad (1)$$

$$\dot{n}_A(t)=k n_S(t)-\beta_A n_A(t)\ . \qquad (2)$$

Here $G(t)$ is the rate of generation of sensitizer singlet excitions assumed to be proportional to the instantaneous intensity of the excitation pulse. β_S and β_A are the reciprocals of the decay times of the sensitizer excitons τ_S and the excited activator molecules τ_A, respectively, including both radiative and nonradiative processes, but in the absence of energy transfer. k is the probability per unit time that an activator molecule will trap an exciton times the concentration of activator molecules. k is given by[20]

$$k=4\pi\ DRN_A\ [1+R(\pi Dt)^{-1/2}]\ , \qquad (3)$$

where R is the interaction distance and N_A is the concentration of activator molecules. This expression for k is valid as long as the diffusion equation can be used to describe the exciton motion. This will be valid for a large number of steps in the random walk of each particle. Both these criteria are fulfilled for the case of interest. The second term in the brackets in Eq. (3) is important only at short times and is generally neglected. This is justified for times $t \gg R^2/D$, and for the normally accepted values of R and D we find R^2/D is on the order of 10^{-11}sec. Also, we point out that attempts to fit the experimental data including this term have been unsuccessful.[15]

Assuming k is independent of time, the solutions to Eqs. (1) and (2) can be written as

$$n_S(t)=\exp[-(\beta_S+k)t]\int_0^t G(\xi)\exp[(\beta_S+k)\xi]\,d\xi\ , \qquad (4)$$

$$n_A(t)=k\exp(-\beta_A t)\int_0^t n_S(\xi)\exp(\beta_A\xi)\,d\xi\ . \qquad (5)$$

The sensitizer and activator fluorescence intensities are proportional to $n_S(t)$ and $n_A(t)$, respectively.

The dependence of the quenching of the host fluorescence on the concentration of impurity molecules can be expressed in terms of the fluorescence decay times as

$$\tau_S^0/\tau_S^e=1+\tau_S^0 k\ , \qquad (6)$$

where τ_S^0 is the fluorescence decay time of the undoped host material and τ_S^e represents the same quantity in the doped crystal.

B. Long-Range Resonant Energy Transfer

The theory of long-range resonant energy transfer[21,22] through multipole-multipole interaction has been developed by Förster[21] and Dexter.[22] The probability per unit time for energy transfer through dipole-dipole interaction can be written as

$$\omega_{SA}^{dd}=\frac{3f^A\,\Phi}{4(2\pi n)^4\tau_S^0\,\overline{\nu}_{SA}^4 R_{SA}^6}\left(\frac{e^2}{mc^2}\right)\int g_S(\tilde{\nu})\,g_A(\tilde{\nu})\,d\tilde{\nu} \qquad (7)$$

or

$$\omega_{SA}^{dd}=(1/\tau_S^0)(R_0/R_{SA})^6, \qquad (8)$$

where

$$R_0=\left[\frac{3f^A\,\Phi}{4(2\pi n)^4\bar{\nu}_{SA}^4}\;\left(\frac{e^2}{mc^2}\right)\int g_S(\tilde{\nu})g_A(\tilde{\nu})\,d\tilde{\nu}\right]^{1/6}. \quad (9)$$

Here $g_S(\tilde{\nu})$ and $g_A(\tilde{\nu})$ are the spectral distribution functions of the sensitizer emission and activator absorption spectra, respectively. $\bar{\nu}_{SA}$ is the mean wave number in the region of spectral overlap. R_{SA} is the distance between sensitizer and activator molecules. f^A is the oscillator strength of the transition in the activator. Φ is a molecular orientation factor equal to $\frac{2}{3}$ for random orientations.[23] The "critical concentration" is defined by $C_0=(\frac{4}{3}\pi R_0^3)^{-1}$, where R_0 is the distance between sensitizer and activator sites at which the energy-transfer probability is equal to the probability for deexcitation in the absence of energy transfer.

For δ-function excitation, Eqs. (1) and (2) can still be used to describe the kinetics of the fluorescence intensities in this model with $k=(1/\tau_S^0)\sum_j(R_0/R_{ij})^6$. In this case the fluorescence intensities are proportional to

$$I_S(t)\propto I_S(0)\sum_i \exp[-t/\tau_S^0-(t/\tau_S^0)\sum_j(R_0/R_{ij})^6], \quad (10)$$

$$\begin{aligned}I_A(t)\propto I_S(0)\sum_{i,j}(R_0/R_{ij})^6\,\{&\exp(-t/\tau_A)\\&-\exp[-t/\tau_S^0-(t/\tau_S^0)\sum_j(R_0/R_{ij})^6]\}/\\&[1-(\tau_S^0/\tau_A)+\sum_j(R_0/R_{ij})^6]\,. \quad (11)\end{aligned}$$

Förster simplified the expression for $I_S(t)$ by replacing the sum over sensitizers by an integration and expanding the integrand in a power series.[21] This resulted in the expression

$$I_S(t)\propto I_S(0)\,\exp[-\beta_S t-\gamma(\pi\beta_S t)^{1/2}]\,, \quad (12)$$

where $\gamma=N_A/C_0$. Using Eq. (12), the intensity of activator emission can be written as

$$I_A(t)\propto\gamma\beta_S^{1/2}e^{-\beta_A t}\int_0^t e^{\xi\beta_A}n_S(\xi)\,\xi^{-1/2}\,d\xi\;. \quad (13)$$

If the time dependence of the host fluorescence is characterized by the time it takes to decay to $1/e$ of its maximum value τ_S^e, then the quenching of this decay time as a function of activator concentration can be derived from Eq. (12) and is found to be

$$\tau_S^e/\tau_S^0=1+(\pi^{1/2}\gamma/2)\,[\pi^{1/2}\gamma-(\pi\gamma^2+4)^{1/2}]\quad. \quad (14)$$

C. Other Theories of Energy Transfer

Several attempts have been made to derive expressions for fluorescence emission in which both long-range interaction and diffusion have been taken into account. In the theory developed by Yokoto and Tanimoto,[24] the fluorescence intensity of the sensitizers is given by

$$I_S(t)\propto I_S(0)\,\exp(-\beta_S t)\,\exp\left[-\gamma(\pi\beta_S t)^{1/2}\times\left(\frac{1+10.91xt^{2/3}+15.74x^2t^{4/3}}{1+8.763xt^{2/3}}\right)^{3/4}\right]\,, \quad (15)$$

where γ was defined above and $x=D\beta_S^{-1/3}R_0^{-2}$. For $D=0$, this expression is the same as that obtained by Förster[21] for long-range resonant energy transfer. The fluorescence intensity of the activator molecules in this theory can be written as[25]

$$\begin{aligned}I_A(t)=\exp(-\beta_A t)\int_0^t\Bigg(&\frac{\gamma}{2}\;(\pi\beta_S)^{1/2}\,\exp(\beta_A\xi)\\&\times\xi^{-1/2}n_S(\xi)+I_S(0)\,\exp[(\beta_A-\beta_S)\xi]\xi^{-1}\\&\times\Bigg\{\exp[-\gamma(\pi\beta_S\xi)^{1/2}]-\exp\Bigg[-\gamma\,(\pi\beta_S\xi)^{1/2}\\&\times\left(\frac{1+14.05x\xi^{2/3}+23.02x^2\xi^{4/3}}{1+11.55x\xi^{2/3}}\right)^{3/4}\Bigg]\Bigg\}\Bigg)\,d\xi\;. \quad (16)\end{aligned}$$

A similar theory was developed by Kurskii and Selivanenko.[26] Their expressions for $I_S(t)$ and $I_A(t)$ are somewhat different than those given in Eqs. (15) and (16). However, the same good fit to the experimental data described in the following sections is obtained from either theory using approximately the same values for R_0 and D and, therefore, only the Yokoto-Tanimoto theory is discussed explicitly.

Voltz *et al.*[27,28] considered simultaneous energy transfer by diffusion and long-range interaction by multiplying the expression for k in Eq. (3) by 0.5 and replacing R by R_0, where R_0 is defined as the distance at which the probability for energy transfer is 0.5. This theory reduces to the exciton diffusion theory for small R_0 or large D.

In all of the theories discussed above, direct excitation of the activators by the exciting pulse has been neglected. This is justified for the systems investigated since, for example, anthracene has a quantum efficiency on the order one and in an anthracene crystal containing only 10 ppm tetracene molecules, approximately half the fluorescence is emitted by the tetracene, indicating that direct tetracene excitation is negligible compared to excitation through energy transfer.

III. EXPERIMENTAL

A. Samples and Apparatus

Five vapor-grown[29] single-crystal cylinders of anthracene containing various concentrations of tetracene molecules were cleaved to give flat faces in the a, b plane having approximate dimensions of 5×10 mm and a thickness of about 3 mm. A comparison of the results obtained on these samples with those obtained on melt-grown samples with the same range of tetracene concentration indicated that the results described below are independent of the method of crystal growth.[16]

TABLE I. Fluorescence decay times of tetracene, anthracene, and napthalene in crystals greater than 3 mm thick under bulk excitation.

Sample	Tetracene in anthracene 1 ppm	 83 ppm	Anthracene in napthalene 1 ppm	 61 ppm	 Crystal	Napthalene Crystal
Fluorescence decay time (nsec)	13	13	11.5	15	27	107

Three crystals of vapor-grown napthalene were also investigated. Two of these contained 1 ppm anthracene molecules and the third contained 61 ppm anthracene. These samples had dimensions of approximately 1 cm^3.

To study the time dependence of the fluorescence intensity, the samples were excited by a 600-keV x-ray source having a total pulse duration of about 6 nsec and a pulse width at half-maximum of about 3 nsec. The fluorescence emission from the samples at 90° to the direction of excitation was transported through a shielded light pipe to an ITT F4030 (S-11) high current photomultiplier tube. The signal was displayed and photographed on a Tektronix 519 oscilloscope having a 0.35-nsec rise time. The sensitizer and activator fluorescence were separately isolated with the appropriate filters for each system. For the energy spectrum of the x rays from this machine, the intensity of the beam passing through 0.5 cm of anthracene will be attenuated by about 6%. Thus, the sample will essentially be uniformly excited.

Similar experiments were performed utilizing a mode-locked *Q*-switched ruby laser as the exciting source. The duration of the exciting pulse was much less than 1 nsec, and the beam size was such that the total sample was illuminated. Absorption occurs by two-photon processes to a well-defined low-lying singlet state providing bulk excitation in the crystal.[30]

In order to measure the intrinsic decay time of directly pumped tetracene in anthracene crystals, a filtered spark gap oscillator was used as an excitation source and the photmultiplier signal displayed on a sampling oscilloscope.

The measurements of the decay time of directly pumped anthracene in napthalene crystals were made utilizing a ZnS superradiant light target on a Febetron 706 electron beam machine as the excitation source.[31] The light emission occurs in a 50-Å-wide band centered at 3450 Å with a pulse half-width of about 2 nsec. The fluorescence signal was detected by a TRG 105B photodiode and displayed on a Tektronix 454 oscilloscope.

B. Results

Table I summarizes the results obtained for the fluorescence lifetimes of undoped anthracene and napthalene crystals and of tetracene- and anthracene-impurity molecules in these crystals. The same value of the decay time for crystalline anthracene was obtained for both x-ray and ruby-laser excitation. The values given in Table I are those measured on the size crystals used in these experiments and may be longer than intrinsic lifetimes because of reabsorption. The difference in anthracene lifetimes in napthalene containing different concentrations of anthracene is probably due to reabsorption. The value of 13 nsec found for the decay time of tetracene in anthracene is consistent with results of previous measurements made by Galanin and Chizhikova.[32]

The time dependence of the fluorescence intensity from five tetracene-doped anthracene samples is shown in Fig. 1. The solid lines are theoretical predictions discussed in Sec. IV., and the points represent the experimental data. Each data point is the average from three pictures, and the spread in data is ± 0.03 or less. The points for 1 ppm tetracene are the average of two samples having this concentration. The anthracene decay times decrease with increasing tetracene concentration

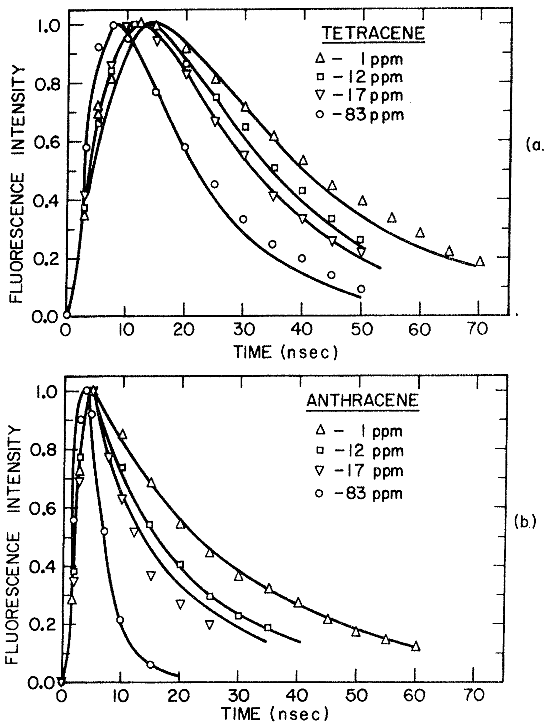

FIG. 1. Time dependence of the fluorescence intensities of anthracene doped with various concentrations of tetracene after pulsed x-ray excitation (see text for explanation of the theoretical lines).

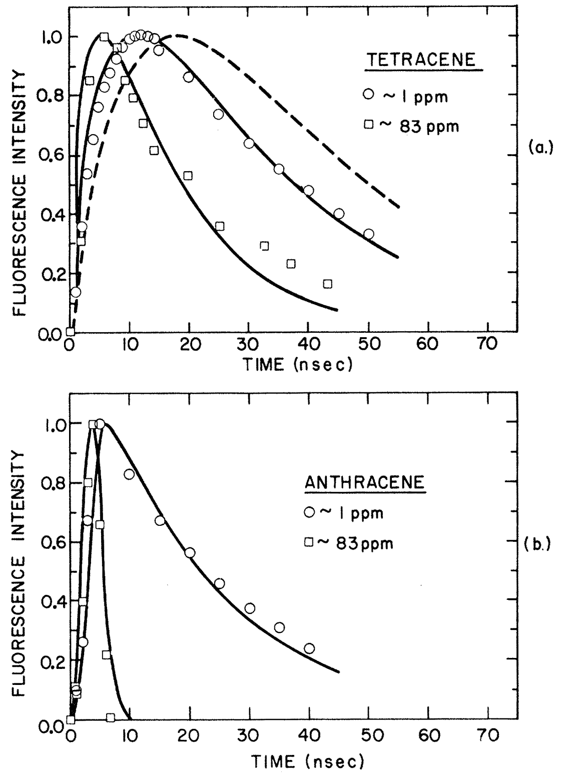

FIG. 2. Time dependence of the fluorescence intensities of tetracene-doped anthracene excited by two-photon absorption from a pulsed ruby laser (see text for explanation of the theoretical lines).

from ~25 nsec for the samples with 1 ppm tetracene to ~4 nsec for that with 83 ppm. The time at which the maximum intensity of the tetracene fluorescence occurs decreases with increasing impurity concentration form ~12 nsec for the sample with 1 ppm tetracene to ~7 nsec for that with 83 ppm. Although there is efficient generation of triplet excitons by x-ray excitation, the contribution to the fluorescence signal from triplet exciton fusion will be negligible for the time region of interest here.[33]

The results obtained using laser excitation are shown in Fig. 2. Again the 1 ppm data is the average of two samples, and the spread in data is ±0.03 or less.

Figures 3 and 4 show the time dependence of the fluorescence intensity of napthalene crystals containing 1 ppm and 61 ppm anthracene, respectively. The 1 ppm points are the average of two samples, and the data spread is ± 0.03 or less. The napthalene decay times are ~105 nsec and ~50 nsec for the 1 ppm and 61 ppm samples, respectively. The time at which the anthracene fluorescence reaches its maximum value is ~21 nsec for the lightly doped crystal and ~24 nsec for the heavily doped crystal.

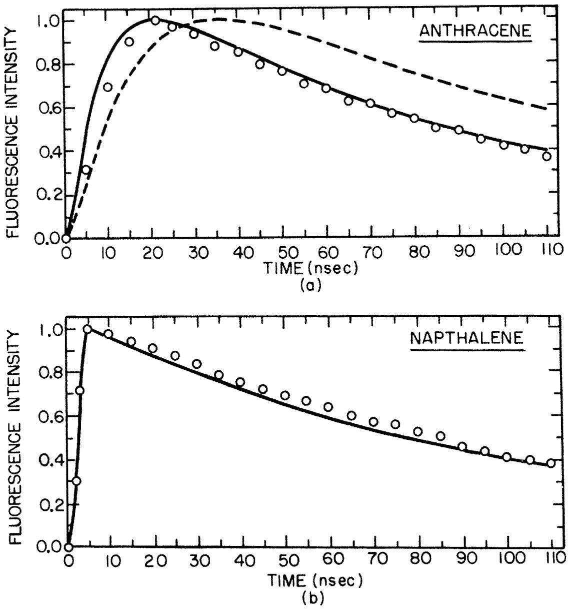

FIG. 3. Time dependence of the fluorescence intensities of napthalene doped with 1 ppm anthracene after pulsed x-ray excitation (see text for explanation of the theoretical lines).

IV. DISCUSSION

Host-sensitized energy transfer in doped organic

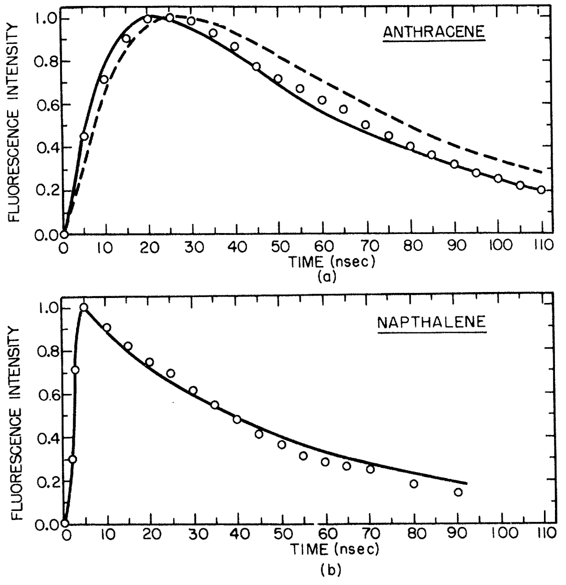

FIG. 4. Time dependence of the fluorescence intensities of napthalene doped with 61 ppm anthracene after pulsed x-ray excitation (see text for explanation of the theoretical lines).

crystals is generally attributed to exciton diffusion. The characteristics of energy transfer are usually investigated by monitoring the quenching of the fluorescence intensity or lifetime of the sensitizer as a function of activator concentration.[7] The results of such a study on our tetracene-doped anthracene samples are shown in Fig. 5. The predictions of both exciton diffusion theory, Eq. (6), and long-range resonant interaction, Eq. (14), appear to be consistent with the experimental data. To obtain agreement between exciton diffusion theory and the data, a value of $k = 3\times10^6\,\text{sec}^{-1}$ defined by Eq. (3), was used for the exciton trapping rate constant which is consistent with that found by other investigations.[8,10] A value of $C_0 = 47.7$ ppm was needed to obtain a good fit between the long-range resonant interaction theory and the data. This value will be discussed further below. The important point is that this type of experimental data connot be used to unambiguously distinguish between these two types of energy-transfer mechanisms. The predictions of the combined theories discussed in Sec. II fall between the two theoretically predicted curves shown in Fig. 5. To fit this data with the Yokota-Tanimoto theory, it is necessary to use the same values for the fitting parameters that are needed to fit the time evolution data. These values are discussed in detail below. The same values for the fitting parameters of the various theories will be obtained if integrated fluorescence intensities are analyzed instead of decay times.[7]

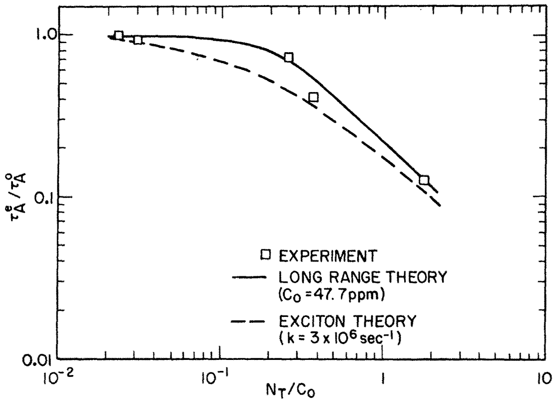

FIG. 5. Concentration dependence of the quenching of anthracene fluorescence due to energy transfer to tetracene.

The reason that we chose to investigate the characteristics of the energy transfer by monitoring the time evolution of the fluorescence intensities is that the two energy-transfer mechanisms of interest predict easily distinguishable curves for samples with low activator concentrations. The predictions for these lightly doped samples are, however, relatively insensitive to the magnitudes of the adjustable parameters of the theories; therefore, it is also necessary to fit the data obtained on heavily doped samples where the theoretical curves are less distinct for the two models but are very sensitive to the magnitudes of the adjustable parameters.

To obtain the predicted curves of the various theories discussed previously, Eqs. (4), (5), (13), and (16) can be numerically integrated, using the values of β_A and β_S from Table I and treating k and γ as adjustable parameters in the exciton diffusion theory and long-range interaction theory, respectively, and treating both γ and x as adjustable parameters in the combined theory. In Eq. (4) the experimentally determined pulse shape is used for $G(\xi)$. In order to compare the predictions of Eqs. (12) and (15) with experimental results obtained by x-ray excitation, the exciting pulse was treated as a series of equally spaced δ functions with magnitudes proportional to the height of the pulse at the time of the function. Each δ function produces a curve having the shape of Eq. (12) or (15) with different $I_s(0)$ and the sum of these curves is compared with experimental results. This procedure is not necessary for comparison with the data obtained using laser excitation, since the exciting pulse is a good approximation to a δ function. However, for this type of excitation, it was necessary to form the convolution of the photomultiplier response with the fluorescence decay function in order to determine the sensitizer fluorescence intensity at all times.

Using the above procedure, all of the various theories give the same best fit to the measured time evolution of the sensitizer fluorescence intensity. These theoretical predictions are shown as solid curves in Figs. 1(b), 2(b), 3(b), and 4(b).

We reported previously that the normal mathematical formulation of exciton diffusion theory given by Eq. (5) could not be made to agree with the experimental results of the activator fluorescence obtained from x-ray excitation of the lightly doped anthracene crystals.[15] The same observation is true for the data shown in Figs. 2(a), 3(a), and 4(a) where the predictions of exciton diffusion theory are represented by dashed lines. These theoretical curves are in marked disagreement with the experimental observations, especially with respect to the rise time of the fluorescence. For the heavily doped sample in Fig. 2(a), exciton diffusion theory gives the same fit to the data shown by the solid line.

The theoretical predictions of the normal mathematical formulation of long-range resonant interaction, Eq. (13), for the case of the activator fluorescence in the lightly doped samples fall consistently below the experimental data in the decay portion of the curve by 0.08, which is greater than experimental error.

The combined theory of exciton diffusion and long-range resonant interaction described by Eq. (16) can be made to give a good fit to the experimental results. These predictions are shown as solid lines in Figs. 1(a), 2(a), 3(a), and 4(a). The combined theory of Voltz *et al.*[27,28] cannot be made to fit the data.

Thus, the only energy-transfer theories which give the time dependence necessary for the explanation of these experimental results are those based on long-range resonant interaction which allow for some diffusion. However, a discrepancy arises even with these theories in comparing the magnitudes of the phenomenalogical fitting parameters with their values predicted theoretically or obtained from other types of measurements. For the tetracene-doped anthracene system, the theoretical fit requires a value for the critical energy-transfer distance (R_0) on the order of 100 Å, which is much greater than the value of 30 Å predicted from spectral considerations. From Eq. (9) it can be seen that the measured parameters necessary for the calculation of R_0 (such as oscillator strength and spectral overlap) are taken to the $\frac{1}{6}$ power; therefore, it would take an extremely large change in these parameters to predict a value of $R_0 \approx 100$ Å. Also, for this system the fit between theory and experiment requires a value for the diffusion coefficient on the order of 4×10^{-6} cm^2 sec^{-1}, which is more than two orders of magnitude smaller than the value generally reported for D.

The same discrepancies exist with the anthracene-doped napthalene system. For this system, the value obtained for D as a phenomenological fitting parameter is on the order of 3×10^{-6} cm^2 sec^{-1}, which is again two orders of magnitude less than the value reported from other measurements. The required value of R_0 is approximately 60 Å. Using the overlap integral measured by Zima *et al.*[34] the calculated value is $R_0 = 25$ Å.

The derivation of Eq. (12) is based on a homogeneous distribution of activators surrounding each excited sensitizer. Because of the strong dependence of the fluorescence intensity on sensitizer-activator separation, $\exp[-(R_0/R_{ij})^6]$ inhomogeneities in the distributions of activators and excited sensitizers can be important. That is, some regions of the crystal may have higher densities of excited sensitizers and activators than other regions; a better description of the long-range resonant interaction theory is obtained by solving Eqs. (10) and (11) after having the computer generate sets of random numbers for R_{ij}. Using this procedure did not alter the fit between theory and experiment. Attempts to explicitly account for inhomogeneous distributions in exciton diffusion theory have not been successful in fitting these data.[35]

Other methods have been suggested for explaining apparent long-range energy transfer. Avery[36] considered a Breit interaction Hamiltonian instead of a Coulomb Hamiltonian and this gave an added relativistic correction term in the energy-transfer probability which varied as R_{ij}^{-2} instead of R_{ij}^{-6}. Including this term does not change the theoretical fit of the data.

It is also possible in certain cases for higher-order Coulomb interactions to give rise to longer-range energy transfer. However, for the systems under consideration here, the dipole transitions are highly allowed; there is no reason to believe that higher-order multipole interactions will dominate.

Other experimental observations have been reported of anomalously long-range energy transfer in molecular crystals. Zhevandrov[37] has investigated energy transfer in tetracene-doped anthracene by studying polarization effects. His results indicate the existence of energy transfer between tetracene molecules in anthracene over distances on the order of 200 Å, whereas calculations in the Förster-Dexter model predict $R_0 \approx 10$ Å. Zhevandrov suggests that the discrepancy in R_0 might be due to energy transfer by virtual excitons of the host lattice according to the suggestions of Agranovich.[38] However, recent calculations by Dow[39] indicate that the virtual exciton mechanism is effective only over very short distances and cannot compete with dipole-dipole interaction.

Radiative reabsorption has also been proposed as the mechanism for energy transfer in these systems.[40] However, this model predicts that for the tetracene-doped anthracene system, the anthracene decay time will not be shortened by energy transfer to less than 10 nsec. As shown in Figs. 1(b) and 2(b), the decay time for anthracene in the heavily doped samples is much less than 10 nsec. At low temperatures the anthracene decay time is less than 10 nsec even for the lightly doped samples.[16] This indicates that energy transfer by radiative reabsorption is not the dominant mechanism. It is certainly possible, however, to have reabsorption of the host fluorescence by other host molecules.[40,41] It is difficult to account for the effects of such processes since none of the existing theories of reabsorption have been developed to the extent that they can be compared to the type of data of interest here. The use of bulk-crystal sensitizer decay time accounts for the effect of host reabsorption on lengthening the amount of time that the sensitizer excitation remains in the crystal. The fact that the general observations made on the room-temperature data described here appear to remain valid for preliminary data obtained at low temperatures[16] where reabsorption effects are negligible indicates that these observations are not associated with the effects of reabsorption.

V. SUMMARY AND CONCLUSIONS

This paper questions the validity of attributing energy transfer in doped molecular crystals to the diffusion of singlet excitons as is now commonly done. It also demonstrates that existing theories of enregy transfer are inadequate for describing the time variation of the activator fluorescence in these systems.

The time evolution of the fluorescence intensity of tetracene-doped anthracene and anthracene-doped napthalene crystals was investigated and the results are found to disagree with the predictions of singlet exciton diffusion theory and with the normal mathematical formulation of energy transfer by long-range resonant interaction. A combined theory of exciton diffusion and long-range resonant interaction can be made to fit the data only if an anomalously large value is used for the critical energy-transfer distance. These observations are independent of both the method of crystal growth[16] and the method of excitation.

The results reported here appear to be more consistent with a long-range resonant energy-transfer mechanism than with exciton diffusion which is quite surprising, since it is generally believed that energy transfer in these systems takes place by the latter mechanism. It is interesting to note that the experiment by Simpson,[11] usually cited as proof that singlet excitons in anthracene can move and the diffusion coefficient describing their motion is on the order of 10^{-3} cm^2 sec^{-1}, can be equally well explained by long-range resonant interaction theory. The data shown in Figs. 6 and 7 of Ref. 11 can be fit with the long-range interaction model of energy transfer using the same R_0 (on the order of 100 Å) that was used to fit the data described in this paper.

We do not feel that the results and observations presented in this paper represent concrete proof of long-range energy transfer in these systems. They do demonstrate the inability of the normal mathematical formulation of exciton diffusion theory to explain all aspects of energy transfer in these systems and show that the correct model for energy transfer must allow for a decrease in the rate of energy transfer with time similar to that contained in the long-range resonant interaction model.

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Phase Transitions in Perovskitelike Compounds of the Rare Earths

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High-temperature powder x-ray diffraction photography and differential thermal analysis give 1643 K for the rhombohedral-to-cubic transition temperature of $PrAlO_3$; for $NdAlO_3$, this transition temperature is estimated to be 2020 K. The 800 K transition temperature of $LaAlO_3$ is further confirmed. A rhombohedral-to-cubic transition temperature of 1230 K is predicted for $CeAlO_3$. The orthorhombic-to-rhombohedral transition temperatures of $LaFeO_3$, $LaGaO_3$, and $SmAlO_3$ have been corroborated; these are 1260, 1150, and 1075 K, respectively. Ruiz *et al.* have reported an orthorhombic-to-rhombohedral transition in $LaCrO_3$ at 550 K, and the rhombohedral-to-cubic transition near 1300 K. The former occurs actually at 533 ± 3 K, the latter above 1873 K and probably near 2000 K.

INTRODUCTION

There has been substantial interest in the nature of the crystallographic transition in $LaAlO_3$.[1] A number of perovskitelike compounds of the rare-earth ions are, in some temperature range, isostructural with $LaAlO_3$. Our purpose was to examine some of these and to determine their transition temperatures.

Two techniques were employed in two different