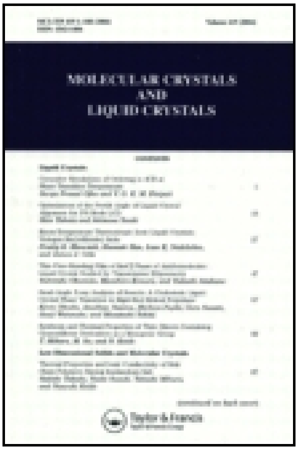

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Energy Transfer in Doped Organic Crystals†‡

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Abstract—This paper summarizes the results we have obtained in studying energy transfer in doped organic crystals as a function of temperature, dopent concentration, sample size, method of crystal growth and method of excitation. Neither the theory of energy transfer by exciton diffusion nor the theory of long range resonance energy transfer can adequately explain the experimental observations. We also show that the predictions of exciton diffusion do not agree with the observed fluorescence rise times reported previously by other workers. Unsuccessful attempts to fit the data with a theory of exciton diffusion in two dimensions are also reported.

1. Introduction

Host sensitized energy transfer in doped organic crystals has been studied extensively by measuring relative fluorescence intensities or decay times as a function of activator concentration. Energy transfer in such systems as tetracene doped anthracene and anthracene doped naphthalene is usually attributed to the diffusion of singlet excitons.(1)

We recently demonstrated the importance of studying the complete time evolution of the fluorescence intensities in investigating energy transfer.(2–5) This technique elucidates the time dependence of the processes involved and can thus be used to distinguish between different types of energy transfer mechanisms having different time dependences. The two most common energy transfer mechanisms are exciton diffusion and long range resonance. The former has a constant energy transfer rate while the latter has an energy transfer rate that depends on $t^{-1/2}$. Thus the two theories can give distinctly

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different predictions for the time evolutions of the fluorescence intensities.

The results obtained in our investigations of energy transfer in tetracene doped anthracene and anthracene doped naphthalene can not be explained by exciton diffusion theory. The time dependence of the energy transfer is consistent with the predictions of long range resonance energy transfer. However, this theory can be made to agree with the experimental results only if an anomalously large interaction strength is used.

In this paper we summarize all the experimental results we have obtained and all the different attempts that have been made to theoretically explain the data. Some earlier results obtained by other workers on different systems are analyzed and shown to exhibit the same anomalies. Finally an attempt to fit the data with a theory of exciton diffusion in two dimensions is discussed.

2. Theoretical

Since fluorescence intensities are proportional to excited state populations the time dependence of the sensitizer and activator intensities can be derived from simple rate equations. Assuming delta function excitation and neglecting direct excitation of activators, the excited state populations for sensitizers, $n_s(t)$, and activators, $n_a(t)$, are[4]

$$n_s(t) = n_s(0)\, e^{-\beta_s t - \int_0^t k(t')dt'} \qquad (1)$$

$$n_a(t) = e^{-\beta_a t}\int_0^t n_s(t')k(t')e^{\beta_a t'}dt' \qquad (2)$$

where β_s and β_a are the reciprocals of the decay times of the sensitizer, τ_s, and the activator, τ_a, respectively, including both radiative and nonradiative processes but in the absence of energy transfer, and $k(t)$ is the energy transfer probability per unit time.

For exciton diffusion theory the energy transfer rate is independent of time,[6]

$$k_E(t) = k = 4\pi D R N_a, \qquad (3)$$

where D is the diffusion coefficient, R is the interaction distance, and N_a is the concentration of activators.

The energy transfer rate for long range resonant energy transfer by dipole-dipole interaction has been derived to be(4,7,8)

$$k(t) = \frac{1}{\tau_s}\sum_j \left(\frac{R_0}{R_{ij}}\right)^6 \tag{4}$$

where

$$R_o = \left[\frac{3f^a\Phi\eta}{4(2\pi n)^4\tilde{\nu}_{sa}{}^4}\left(\frac{e^2}{mc^2}\right)\int g_s(\tilde{\nu})g_a(\nu)\,d\tilde{\nu}\right]^{1/6}. \tag{5}$$

Here $g_s(\tilde{\nu})$ and $g_a(\tilde{\nu})$ are the spectral distribution functions of the sensitizer emission and activator absorption spectra, respectively, $\tilde{\nu}_{sa}$ is the mean wave number in the region of spectral overlap, R_{ij} 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, and η is the sensitizer quantum efficiency. 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 de-excitation in the absence of energy transfer. The values of C_0 and R_0 can be determined from the observed quenching of the sensitizer fluorescence decay time(4) and intensity(7) from the equations

$$\tau_s/\tau_s{}^0 = 1 + 0.5\sqrt{\pi}\gamma(\sqrt{\pi}\gamma - \sqrt{\pi\gamma^2+4}) \tag{6}$$

$$I_s/I_s{}^0 = 1 - \sqrt{\pi}\gamma\, e^{\gamma^2}[1 - erf\gamma] \tag{7}$$

where $\gamma = N_a/C_0$, $\tau_s{}^0$ is the sensitizer decay time in undoped samples, τ_s is the time at which the fluorescence intensity in the doped sample reaches the value of $1/e$ of its maximum value, and I_s and $I_s{}^0$ are the sensitizer fluorescence intensities in doped and undoped samples, respectively.

Förster(7) simplified the expression for $n_s(t)$ given by inserting Eq. (4) into Eq. (1) by replacing the sum over sensitizers by an integration and expanding the integrand in a power series. This resulted in an energy ransfer rate that is time dependent,

$$k_F(t) = \frac{\gamma}{2}\sqrt{\frac{\pi\beta_s}{t}}. \tag{8}$$

The time dependence of $k_F(t)$ for long range resonants energy transfer arises from the fact that the energy transfer rate is a function of the separation between sensitizer and activator and therefore excited sensitizers located close to activators transfer their energy and decrease in number more rapidly than those located at greater distances from activators. The random distribution of sensitizers and activators present at zero time becomes less random with time as fewer excited sensitizers are located near to activators. The efficiency of energy transfer thus decreases with time.

In contrast to this situation, exciton diffusion is a multi-step process in which the excitation wanders randomly throughout the lattice until it is trapped by an activator. In this case the distribution of excited sensitizers remains random with time and the energy transfer rate is constant.

The time at which the activator fluorescence reaches its maximum value, t_m, can be determined by setting the time derivative of Eq. (2) equal to zero. For exciton diffusion theory this is given by

$$t_m = \frac{\ln(\tau_a/\tau_s')}{\tau_s'^{-1} - \tau_a^{-1}} \tag{9}$$

where $\tau_s'^{-1} = \tau_s^{-1} + k_E$ is the measured sensitizer decay time in the presence of energy transfer. It is not possible to derive a comparable simple expression for t_m in long range interaction theory because of the time dependence of $k_F(t)$.

3. Summary of Previous Results and Theoretical Considerations

We originally investigated the time evolution of anthracene and tetracene fluorescence intensities of thick vapor grown tetracene doped anthracene crystals with dopant concentrations between 1 ppm and 83 ppm excited by a flash X-ray pulse of a few nanoseconds duration. Neither the usual mathematical formulation of singlet exciton diffusion theory generally invoked to explain energy transfer in this system nor long range interaction theory can explain the observed time dependence. Both theories can be made to fit the anthracene fluorescence data but their predictions for the tetracene fluorescence of lightly doped samples do not agree with the experimental observations as shown in Fig. 1. At higher concentrations the predictions of the two theories become indistinguishable but quite sensitive to the magnitudes of the adjustable parameters. Thus, Eqs. (1) and (2) can be used to fit the data with k in Eq. (3)

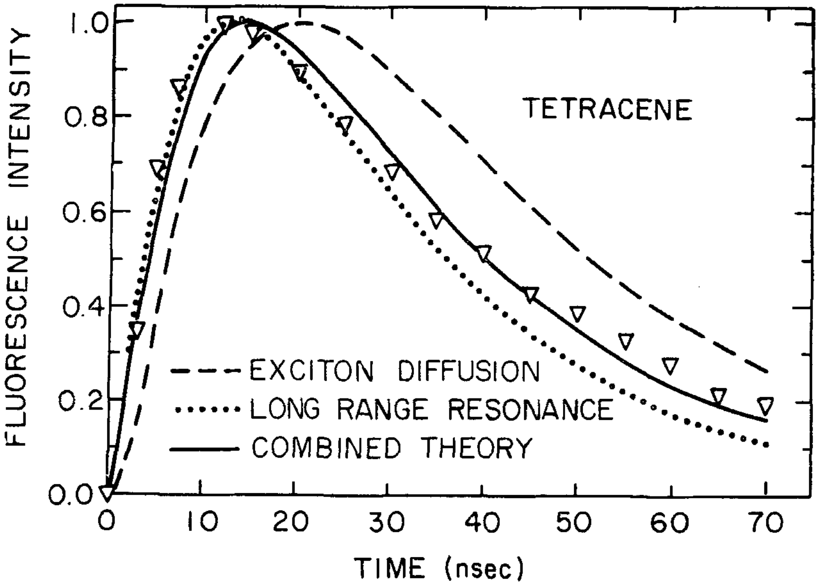

Figure 1. *Time dependence of the tetracene fluorescence intensity in anthracene doped with 1 ppm tetracene after pulsed X-ray excitation. Sample thickness is about 3 mm. See text for explanation of the theoretical lines.*

and in Eq. (8) as adjustable parameters and treating the exciting pulse as a series of equally spaced delta functions. Then k and γ are determined from the fluorescence in heavily doped samples and the different time dependences of the two theories are demonstrated for the fluorescence of the lightly doped samples. It is emphasized that sensitizer and activator decay curves for both heavily doped and lightly doped samples must be considered in establishing the best consistent fit between theory and experiment.

The only consistent fittings of the data was obtained by using a theory of long range energy transfer in which the sensitizer excitation was allowed to diffuse(9,10) (see Fig. 1). This yields a value for R_0 on the order of 100 Å whereas the value calculated from Eq. (5) and spectral parameters is ~ 30 Å. The value obtained for the phenomenological diffusion coefficient is $\sim 4 \times 10^{-6}$ cm^2 sec^{-1}. It should be noted from Eq. (5) that it would take an error on the order of 10^3 in one of the parameters determining the calculated value for R_0 to account for the observed discrepancy between the theoretical and experimental values.

The following investigations have been made in an attempt to understand the anomalously large R_0 and the small diffusion coefficient:

(1) Host fluorescent lifetime and intensity quenching data were obtained and can be successfully explained either by exciton diffusion theory using the normally accepted value$^{(1)}$ of 10^{-3} cm^2 sec^{-1} for D or by long range resonant interaction using a value for R_0 of approximately 100 Å. This is the type of data which is generally analyzed in the study of energy transfer.

(2) Differences in optical quality and impurity distribution have been observed between vapor grown and melt grown crystals of tetracene doped anthracene.$^{(11)}$ To insure that our results were not affected by these differences, four samples of the more common melt grown variety were investigated under exactly the same conditions. The results obtained were identical to those for vapor grown samples.

(3) In order to investigate the possibility that the observed anomalies might be associated with X-ray excitation to poorly defined higher excited states, 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 in this case occurs by two-photon processes to a well defined low lying singlet state providing bulk excitation in the crystal. The results were consistent with those obtained with X-ray excitation. Studies made with u.v. excitation also revealed anomalously fast fluorescent rise times as compared to the predictions of exciton diffusion theory.

(4) Similar results were obtained on crystals of anthracene doped naphthalene.

(5) An investigation of a thin (267 μ) tetracene doped anthracene crystal in which reabsorption effects were greatly reduced revealed that the predictions of long range interaction theory can be made to agree with the observed tetracene fluorescence intensity. However, to achieve this fit it is still necessary to use an R_0 on the order of 100 Å. Exciton diffusion theory can not be made to agree with the thin crystal data. It is possible that the need for including a small amount of diffusion in obtaining a theoretical fit to the thick crystal data is due to the effect of radiative reabsorption of tending to randomize the distribution of excited sensitizers.

(6) Measurements of the time evolution of the fluorescence intensities were made at numerous temperatures between 4.2 °K and 300 °K. The observations made above on thin crystals are independent of temperature. Those made on thick crystals are independent of temperature above 100 °K. At lower temperatures it is generally thought that the excitons are trapped.⁽¹⁾ Below ~25 °K the thick crystal data can be fit by long range energy transfer theory with $R_0 \approx 100$ Å. Again, exciton diffusion does not fit the data.

(7) Attempts to explicitly account for inhomogeneous distributions of sensitizers and activators in both long range resonance energy transfer and exciton diffusion theory have not been successful in fitting these data.⁽⁴⁾ Also, it was found that the inclusion of a relativistic correction term in the interaction Hamiltonian does not change the theoretical fit of the data.⁽⁴⁾

4. Interpretation of Other Published Data

Since the major discrepancy between exciton diffusion theory and the observed time evolution of fluorescence intensities occurs in the rise time of the activator fluorescence of lightly doped samples, it is interesting to consider some of the data published previously by other workers on fluorescent rise times in doped organic crystals.

Schmillen⁽¹²⁾ has published the fluorescence rise and decay times he observed in several different systems. From his data it is possible to use Eq. (9) to obtain the fluorescence rise time of the activator emission predicted by exciton diffusion theory. The observed and predicted rise times for tetracene doped brasan (2,3 benzodiphenyleneoxide) and perylene doped chrysen are shown in Table I. We did not consider his pyrene doped systems because of the observed discrepancy in the activator decay time. The fluorescence rise times Kramer⁽¹³⁾ reports for anthracene in 2,3 dimethylnaphthalene at two temperatures are given along with the calculated values. Also shown in Table I are the observed and predicted rise times under certain conditions for the systems we investigated.

In all cases shown in Table I the observed time of the fluorescence maximum of the activator is significantly less than that predicted by exciton diffusion theory. The discrepancies are even greater in Schmillen's and Kramer's data than in our data. Schmillen's data

TABLE I. Observed and predicted activator fluorescence rise times

System	Observed t_m(nsec)	Predicted t_m(nsec)	Comments
Anthracene: Tetracene (1 ppm)	12	17	Thick crystal; two photon ruby laser excitation.
Anthracene: Tetracene (1 ppm)	10	14	Thin crystal; 100°K; X-ray excitation.
Naphthalene: Anthracene (1 ppm)	21	36	Thick crystal; X-ray excitation.
Brasan: Tetracene (1000 ppm)	1.2	9.6	Polycrystalline powder; α-excitation; Ref. 12.
Brasan: Tetracene (10 ppm)	4	15	Polycrystalline powder; electron excitation; Ref. 12.
Chrysene: Perylene (10 ppm)	4	12	Polycrystalline powder; electron excitation; Ref. 12.
2,3 Dimethylnaphthalene Anthracene (10 ppm)	6.8	18.0	Thick crystal; 300°K; u.v. excitation; Ref. 13.
2,3 Dimethylnaphthalene Anthracene (10 ppm)	8.4	22.7	Thick crystal; 77°K; u.v. excitation; Ref. 13.

were obtained with surface excitation on polycrystalline powdered samples. Under these conditions, the exciton lifetimes may be decreased by surface effects and the effects of reabsorption should be minimized.

It is also interesting to note that using Eq. (6) and the lifetime data of Schmillen(12) and Kramer,(13) the values obtained for R_0 for tetracene doped brasan and anthracene doped 2,3 dimethylnaphthalene are both on the order of 100 Å. This again is similar to what we observed in tetracene doped anthracene and anthracene doped naphthalene.(4)

It should be mentioned that the authors of references 12 and 13 do not indicate whether their t_m is defined as the time of maximum fluorescence, a e^{-1} rise time, or a 10% to 90% rise time. We assumed the first of these definitions in the comparison with the predicted t_m in Table 1. However, even if the previous authors were using one of the other two definitions of t_m, their observed values are still substantially less than those predicted by exciton diffusion theory.

There are two different types of experimental data which are generally accepted as proof that singlet excitons in anthracene migrate. The first is the transmission experiment of Simpson(14) in which the diffusion coefficient was determined to be $\sim 10^{-3}$ cm^2 sec^{-1}. In this experiment, the light at 3650 Å which passed through anthracene samples of different thicknesses was absorbed by a " detector " which consisted of anthracene heavily doped with tetracene. The observed tetracene fluorescence was taken as a measurement of the amount of excitation energy reaching the detector. This turned out to be greater than could be accounted for by optical transmission of the exciting light and the excess excitation was attributed to the diffusion of singlet excitons. We reported previously that it is possible to interpret these experimental results in terms of a long range resonant energy transfer theory.(4) The data shown in Figs. 6 and 7 of Ref. 14 can be fit with the assumption that the energy is transferred to the tetracene in the detector by long range dipole-dipole interaction using the same R_0 ($\sim$ 100 Å) used to fit our data.

The second type of results thought to imply singlet exciton migration in anthracene are obtained in bimolecular quenching experiments.(15,16) The nonlinear variation of fluorescence intensity with excitation dose at high levels of excitation and the decrease in fluorescence decay time at high levels of excitation have been attributed to exciton-exciton interaction. This interpretation assumes that two excitons migrate to positions close to one another before they interact. We again find that this type of data can also be interpreted using the theory of long range resonant energy transfer. The values reported(15,16) for the exciton-exciton interaction rate constant range from 4×10^{-8} to 2×10^{-9} cm^3 sec^{-1}. The values of R_0 for which Eq. (7) is consistent with the reported data range from 75 Å to 200 Å. The exact value can be determined only when more accurate data is available. Note that for this case the spectral distribution function for " activator " absorption which enters into Eq. (5) for R_0 will be the excited state absorption spectrum for singlet excitons. Thus R_0 can not be easily determined from spectroscopic considerations but the 75 Å—200 Å range of values is certainly anomalously large although it does encompass the $\sim$ 100 Å value needed to fit other results.

5. Two Dimensional Exciton Diffusion Calculations

Recently the importance of the dimensionality of exciton propogation was pointed out by Suna.(17) He considered triplet exciton motion in one and two dimensions. There are some indications that singlet exciton migration in anthracene may also be anisotropic and closer to two dimensional than three dimensional.(18,19) Since the solution to the diffusion equation in two dimensions is significantly different from the three dimensional solution, we felt it would be interesting to attempt to fit our data with the predictions of exciton diffusion in two dimensions.

The solution for the flux of particles entering a trap by two dimensional diffusion can be found in the books by Crank(20) and by Carslaw and Jaeger.(21) This flux can be converted to an exciton trapping rate by multiplying by the concentration of traps and dividing by the concentration of excitons. The solutions to the resulting rate equations assuming delta function excitation are

$$n_s(t) = n_s(o)\, e^{-\beta_s t - N_a e^{2\gamma}\, li(T)} \tag{10}$$

$$n_a(t) = ce^{-\beta_a t} \int_0^t \frac{e^{\beta_a t'}\, n_s(t')\, dt'}{\ln[T(t')]} \tag{11}$$

where N_a is the concentration of activators in molecule/molecule, γ is Euler's constant, $li(T)$ is the logarithmic integral $\int_0^T dT'/\ln T'$, $T = 4e^{2\gamma} Dt/R^2$ and $C = 4N_a D/R^2$.

Equations (10) and (11) predict curves which are good fits to the observed fluorescence for lightly doped samples. However, no close fit could be obtained for the fluorescence of heavily doped samples. Thus, considering exciton diffusion in two dimensions does not explain the anomalies we observe in the time evolution of the fluorescence intensities.

6. Summary and Conclusions

Measurements made on both anthracene doped naphthalene and tetracene doped anthracene crystals show that the normal mathematical formulation of exciton diffusion theory cannot predict the correct time dependence for the energy transfer in these systems especially with respect to the rise time of the activator fluorescence intensity in the lightly doped samples. This is true for both thick and thin samples at all temperatures between 300 °K and 4.2 °K. These results are independent of the method of crystal growth and the method of excitation and they can not be explained by radiative migration and energy transfer. The time dependence of the energy transfer is consistent with that of long range resonant interaction but it is necessary to use an anomalously large value for the strength of the interaction in order to fit the data with this theory.

In this paper we demonstrated that anomalies similar to those that we observed also occur in the data reported by other workers in several different doped organic crystal systems. We also showed that considering exciton diffusion to be a two dimensional process can not account for the anomalies.

The results indicate that the current theories of energy transfer are not adequate for explaining phenomena occurring in short times.

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