Kinetic Models for Energy Transfer*

Richard C. Powell[†] and Zoltán G. Soos[‡]

Sandia Laboratories, Albuquerque, New Mexico 87115

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It has recently been suggested that host-exciton traps are responsible for the observed time dependence of host-sensitized energy transfer in doped organic crystals. Although the previously proposed model does not fit the experimental results, it is possible to formulate kinetic models with host traps which fit the time-resolved spectroscopy data by postulating traps with specific characteristics and distributions. However, experimental investigations failed to reveal any effects of trapping at room temperature; no evidence of trap fluorescence was observed in the low-energy tail of the host fluorescence and no change in the time dependence of the energy-transfer rate was observed on introduction of impurities which do not directly take part in the energy transfer. The two most important observations which eliminate trapping effects as a possible explanation for the time dependence of the energy-transfer rate at room temperature are the fact that the same results are obtained on samples grown by different techniques which have greatly different optical quality and chemical purity and the fact that thermal detrapping from shallow traps should exhibit a temperature dependence. Results reported here on the temperature dependence of the energy-transfer rate in naphthalene crystals as well as those reported earlier on anthracene crystals indicate that trapping effects become important only at temperatures less than about 125 °K. The recently proposed theory for energy transfer based on a modulated random walk with a finite trapping range is shown to be consistent with the experimental observations discussed here.

I. INTRODUCTION

Although for many years host-sensitized singlet energy transfer in doped molecular crystals has been attributed to exciton migration, the normal mathematical formulation of exciton diffusion fails to explain recent time-resolved spectroscopy results.[1-6] Four attempts have been reported thus far to explain this discrepancy. The initial proposal[7] that radiative reabsorption was responsible for the anomalous experimental results was disproved by subsequent experiments on thin crystals at low temperature.[4] The second proposal[8] was to describe the exciton motion by a random walk, with trapping on the first visit to a trapping site. However, this model was shown[9] to be equivalent to exciton diffusion for the times of interest and consequently to be inconsistent with experiment. The third proposal[10] was to postulate defects, or host traps, in the host crystal in order to fit the time evolutions of both host and activator fluoresences. Such kinetic models, generalized to include thermal detrapping and activator-induced traps, are analyzed in the present paper. The final proposal,[11] which in our opinion is the only model consistent with all available data on host-sensitized energy transfer in doped organic crystals, is based on a modulated random walk with a finite range for the trapping interaction.

A variety of host traps can be postulated: Both chemical and mechanical defects are unavoidably present and the addition of activators raises the possibility of activator-induced defects as well. A rich variety of kinetic schemes is possible with the additional flexibility of unknown trap depths, concentrations, and radiative characteristics, especially when thermal detrapping and radiative reabsorption are included. Several kinetic models based on rather different physical pictures are shown in Sec. III to fit the time-resolved spectroscopy results[1-6] for particular dopings.

We focus in this paper on very simple and general *experimental* restrictions which severely limit the adjustable parameters in kinetic schemes and which decisively eliminate several otherwise sound theoretical possibilities. For example, properties dominated by uncontrollable host traps should vary widely from sample to sample, as illustrated in Sec. IV by the difficulties in obtaining a consistent interpretation of temperature effects. However, the time dependence of the energy-transfer rate at high temperature was not affected by the optical quality of the host crystals,[2,5,6] by growing crystals in vacuum from either the vapor or the melt,[2] or even by growing thin films by cooling in air.[6] Only activator-induced host traps can readily account for such similarities in crystals prepared by widely different methods.

Fortunately, many of the experimental parameters bearing on kinetic models based on host traps were examined[1-6] in the course of demonstrating that the anomalous time-resolved spectroscopy results were not experimental artifacts. We report in Sec. II three additional experiments testing specific kinetic schemes. No evidence for host traps at room temperature was obtained by observing the red edge of

the host fluorescence. Either the host traps are not significantly populated or they have radiative properties very similar to those of free excitons. The second experiment is based on "scattering" traps, or nonfluorescing chemical impurities whose singlet exciton band is above that of the host. Even large concentrations of inactive impurities did not change the time dependence of the energy transfer rate, thus ruling out long mean free paths for singlet excitons at room temperature. The third experiment is to measure the temperature dependence of the energy-transfer rate in doped napthalene crystals. An increase in the rate was found between 300 and about 125 °K. The exponential decrease below 125 °K demonstrates the usual low-temperature effects of host traps.

Kinetic models based on host traps are discussed in Sec. III and are analyzed in terms of both the previous experimental data and the data reported here. Severe difficulties are shown for all of them, with activator-induced host traps and thermal detrapping as the relatively best possibility. The temperature dependence of the energy-transfer rate is summarized in the Appendix. Although not fully understood either experimentally or theoretically, temperature must play an important role in models with thermal detrapping. It is concluded in Sec. IV that a detailed analysis of the exciton motion and of the trapping mechanism is required to understand energy transfer to randomly distributed microscopic traps. The modulated random walk with a finite trapping range provides such an analysis.[11]

Most energy-transfer data in doped organic crystals are based on the concentration quenching of either the host fluorescence or decay time.[12] Exciton-diffusion theory can be used to analyze such data. Powell and Kepler (PK) observed[1–6] the complete time evolution of the fluorescence intensities of both the host and the activator in tetracene-doped anthracene crystals and in anthracene-or tetracene-doped naphthalene crystals. Their results are consistent with diffusion theory at long, but not at short, times. The difficulty is due to the time dependence of the energy-transfer rate, $k(t)$, which is a constant in diffusion theory except at short times of no interest here.[3] In order to fit the PK data, it is necessary to assume that $k(t)$ decreases with time, as shown in Fig. 1. The method of obtaining these curves is discussed in detail in Ref. 11. We emphasize that for each host the curves represent the average of data obtained under different experimental conditions. It is evident that $k(t)$ decreases with time and approaches an asymptotic value beyond about 40 nsec for anthracene and, less certainly, beyond about 70 nsec for naphthalene.

The basic goal of theoretical models for energy transfer in organic crystals is to account for the

time dependence of $k(t)$. The theoretical curves in Fig. 1 are based on (i) $k(t) \propto t^{-1/2}$, which is characteristic[5] of both long-range resonant transfer (LRRT) and exciton diffusion in one dimension; (ii) $k(t) \propto 1/\ln t$, which is characteristic of two-dimensional diffusion; and (iii) $k(t) = $ const, the usual three-dimensional diffusion result. The last does not fit experiment, while the first two are decisively ruled out by other considerations.[11] The modulated random walk with a finite range for trapping can be made to fit both the anthracene and naphthalene data with reasonable physical parameters.[11] Kinetic models based on host traps and thermal detrapping can also be made to fit individual $k(t)$ curves.

II. SEARCH FOR HOST TRAPS

The fact that exciton traps are present in crystals such as anthracene and naphthalene has been well established by low-temperature fluorescence-spectra, intensity, and decay-time measurements. (See Refs. 4 and 12 and the references quoted therein.) At temperatures below 100 °K a red shift is observed in the spectra as the emitting state changes from a free to a trapped exciton. Trap depths ranging between 29 and 250 cm^{-1} have been observed and trap concentrations between 40 and 180 ppm have been reported. The presence of traps has been neglected in interpreting room-temperature data since efficient thermal activation decreases their effectiveness. The following experiments were attempts to detect the presence of host traps in anthracene and naphthalene crystals above 100 °K.

A. Red Edge of Anthracene Fluorescence

An attempt was made to observe trapped-exciton fluorescence at room temperature by observing the
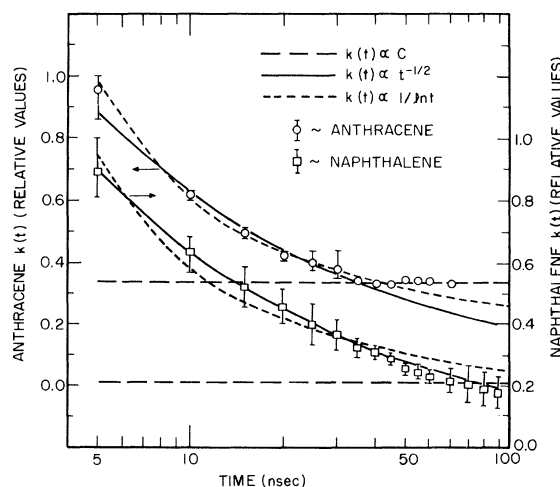

FIG. 1. Time dependence of the energy-transfer rate for anthracene and naphthalene crystals. The theoretical curves are discussed in the text, while the experimental conditions and the construction of the curves are given in Ref. 11.

red edge of the spectrum of undoped anthracene crystals using time-resolved spectroscopy. If traps are present, their fluorescence will occur on the low-energy side of the free-exciton fluorescence bands and should be observed by (a) the presence of new fluorescence bands, (b) a different fluorescence decay time, or (c) an increase in the rise time of the fluorescence emission. Both the fluorescence spectra and decay time of undoped anthracene crystals have been investigated extensively and no extraneous emission bands or double-exponential decays have been observed which could be attributed to trap fluorescence. We focus, therefore, on the third possibility listed above.

The emission spectrum of anthracene consists of three bands, the lowest-energy band being centered near 4500 Å, and a long weak tail extending to lower energies. If it is possible to isolate the trapped-exciton fluorescence, it should be observed in this low-energy tail. The time evolution of the anthracene fluorescence in an undoped sample was observed under pulsed x-ray excitation at room temperature; the experimental apparatus used for this investigation has been described previously,[3] and has an equipment-limited rise time of 5 nsec. Short-wavelength sharp-cutoff filters were used between the sample and photomultiplier tube so that only the long-wavelength emission was detected. Filters were added one at a time which began transmitting at 5100, 5250, 5550, 5750, 5900, and 6000 Å. Even with all six filters in place, the rise time of the fluorescence was observed to be 5 nsec and the fluorescence decay time remained unchanged at about 27 nsec. At longer wavelengths the signal was too weak to be detected.

The fluorescence rise time thus gives no evidence of significant exciton populations in host traps at room temperature. The analysis of the kinetic model discussed in Sec. III A predicts an observable effect in the rise time unless the host traps are directly excited and fluorescelike free excitons.

B. Effects of Nonfluorescing Impurities

An attempt was made to observe changes in the host and activator fluorescences induced by the presence of a *known* impurity which cannot be excited through the host by exciton trapping, radiative reabsorption, or long-range resonant-energy transfer. Such an impurity may act as a scattering center for excitons and may introduce lattice defects in the host.

For this investigation we chose vapor-grown anthracene crystals, with either no activators or with 5 ppm tetracene, and introduced naphthalene as a second impurity in concentrations of 500 and 1000 ppm. The naphthalene energy levels lie above those of anthracene and tetracene, and thus naphthalene cannot receive energy from either the host or activator. The experimental apparatus used for this investigation has been described previously.[3] The samples were excited with a pulsed x-ray source or with a ZnS superradiant-light target which provides light at 3450 Å. This wavelength light is strongly absorbed by anthracene but not by naphthalene or tetracene. The time evolution of the anthracene and tetracene fluorescence was then observed in these samples.

No effects due to naphthalene impurities were detected in the time evolution of the fluorescence intensities from these samples. The anthracene crystals containing naphthalene exhibited an exponential fluorescence decay with a 27-nsec decay time, as did the undoped anthracene samples. Anthracene containing 5 ppm tetracene had a host fluorescence decay time of about 22 nsec. Samples which contained 5 ppm tetracene and 1000 ppm naphthalene exhibited the same shapes for the time variation of the anthracene- and tetracene-fluorescence intensities as did the samples with no naphthalene.

A slight decrease in the relative intensity ratio of tetracene fluorescence to anthracene fluorescence was observed when naphthalene is present as a second impurity. Faidysh et al.[13] have observed a bigger effect on the relative intensity ratio at higher concentrations of naphthalene ($\geq 1\%$). These results indicate that the presence of naphthalene quenches the efficiency of energy transfer from anthracene to tetracene but does not affect the time dependence of the energy transfer. This provides evidence for activator-induced host traps.

C. Temperature Dependence of Energy-Transfer Rate in Naphthalene Crystals

The presence of crystal defects plays an extremely important roll in the temperature dependence of energy transfer in doped organic crystals.[14-20] These can be either chemical or structural imperfections and act either as scattering centers or trapping sites. We determined the temperature dependence of the energy-transfer rate in naphthalene crystals between room temperature and 20 °K from fluorescence lifetime measurements using the expression

$$k(T) = \tau_N^{-1} - (\tau_N^0)^{-1} , \qquad (1)$$

where τ_N and τ_N^0 are the naphthalene decay times in doped and undoped crystals, respectively. Since the decay times are measured at long times where the energy-transfer rate has reached its constant asymptotic value,[11] we can make use of the expressions for $k(T)$ obtained from exciton-diffusion theory. If the exciton mean free path is less than the interaction radius of the activator, the energy-transfer rate can be expressed as[12]

$$k(T) = 4\pi D(T) R C_a , \qquad (2)$$

where D is the diffusion coefficient, R is the inter-
action distance, and C_a is the concentration of acti-
vators. Then the temperature dependence of the
energy-transfer rate is contained in the temperature
dependence of the diffusion coefficient. As sum-
marized in Table I (see Appendix), this can lead to
several different types of temperature dependences
depending on the mechanism which limits the mean
free path of the exciton and on whether or not traps
are present.

Five samples were investigated: an undoped crys-
tal about 3 mm thick, a 3-mm-thick crystal con-
taining 3.9×10^{15} cm^{-3} anthracene, an undoped crys-
tal about 20 μ thick, a 20-μ-thick crystal containing
8.6×10^{17} cm^{-3} tetracene. The first two of these
were grown from the vapor phase in a vacuum and
appeared to have relatively good crystallinity, while
the other samples were grown in air by the method
described by Ferguson[21] and were of poor crystal
quality. No attempt was made to remove any chem-
cal impurities such as β methynapthalene. The ex-
perimental setup used for these investigations has
a time resolution of about 3 nsec and has been de-
scribed previously.[3] The intrinsic decay times of
the impurity molecules in naphthalene were ob-
tained by exciting them directly using ZnS super-
radiant light for anthracene and ZnSe superradiant
light for tetracene. The decay times for anthracene
and tetracene were measured to be 10 and 13 nsec,
respectively, and found to be independent of tem-
perature. To study energy transfer in these sys-
tems, the crystals were excited with a 600-keV
pulse of x rays.

The temperature dependence of the fluorescence
decay time of undoped naphthalene has been reported
previously by El Kareh and Wolf.[22] In lowering the
temperature from 300 to 4.2 °K they observed a
minimum in the decay time at 202 °K and a maximum
of 80 °K. They attribute this behavior to the com-
petition of two processes which effect the decay
time, reabsorption and a redistribution of the ex-
cited state population between the two Davydov com-
ponents which have different decay times. The
former process becomes less important at low tem-
peratures, which tends to shorten the observed
decay time, while the redistribution of the excited
state populations enhances the emission from the
lower-lying longer-lived Davydov component, which
tends to increase the observed decay time. Our
results showed little change in the decay time of the
undoped samples above 140 °K and a decrease in
the decay time below this temperature. The dif-
ference in our results and those of Ref. 22 are
probably due to the effects of imperfections on our
samples.

For all three doped samples we observe an ex-
ponential increase in the energy-transfer-rate pa-
rameter between room temperature and about

125 °K, as shown in Fig. 2(a). Below 100 °K all
three samples exhibit an exponential decrease in
$k(T)$, as shown in Fig. 2(b). The high-temperature
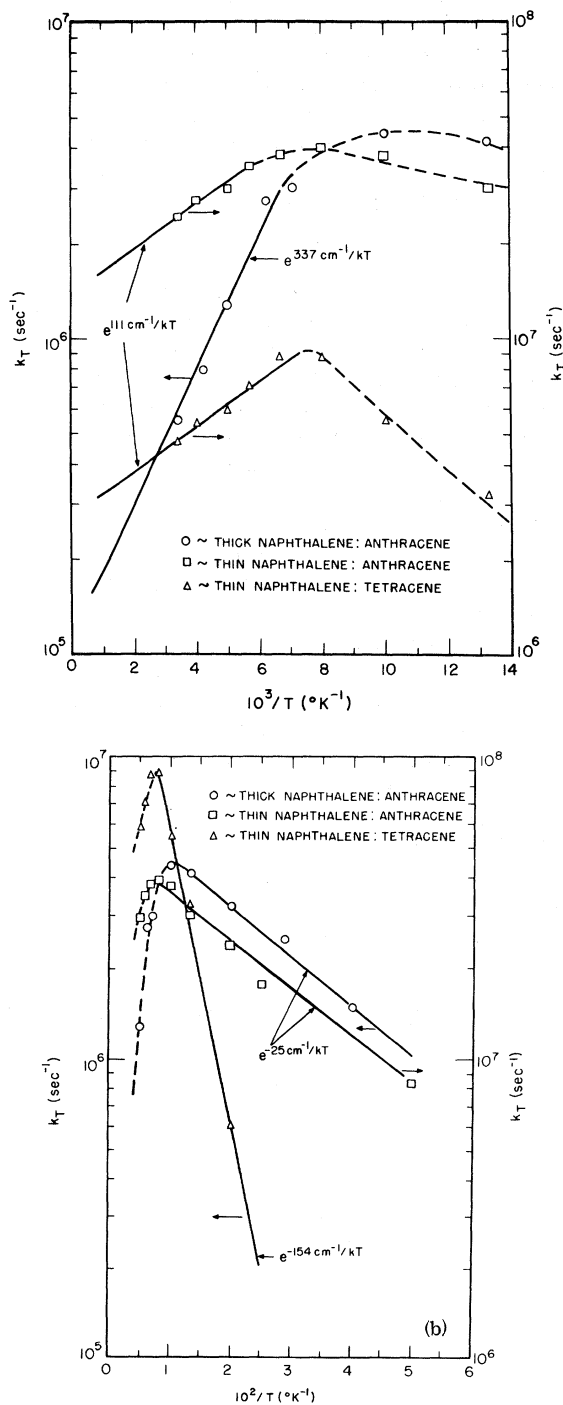data are consistent with the predictions of scattering

FIG. 2. Temperature dependence of the energy-trans-
fer rate in doped naphthalene crystals as obtained from
the quenching of the fluorescence lifetime, Eq. (1). (a)
High-temperature region; (b) low-temperature region.

of free excitons by thermally activated defects (see Appendix). The observed activation energy for the defects is 337 cm^{-1} for the thick anthracene-doped crystal and 111 cm^{-1} for the thin anthracene- and tetracene-doped crystals. The low-temperature behavior is characteristic exciton trapping for trap depths of 25 cm^{-1} for both the thick and thin anthracene-doped samples and 154 cm^{-1} for the thin tetracene-doped sample. These results indicate that exciton trapping is important below about 100 °K but no effects due to the presence of traps are observed at higher temperatures.

III. KINETIC MODELS

Kinetic models, in which microscopic rates are approximated by constant coefficients, often provide excellent descriptions of the time evolution of reacting species. Birks[10] has recently proposed that host traps can account for the PK data, but no direct comparison between theory and experiment was shown. Host excitons can be trapped by either activators or by host traps whose depths, concentrations, and radiative properties are adjustable parameters. We generalize Birk's kinetic model to include thermal detrapping from host traps and direct transfers from host traps to activators.

Thermal detrapping is important for shallow traps, which would not be easily detected in the red-edge experiment described in Section II A. Activator-induced traps, clustered around the activators, are consistent with the similar $k(t)$ time dependence observed in differently prepared crystals. Such traps would transfer energy to the activator by the familiar LRRT mechanism and would consequently not lead to significant host-trap fluorescence.

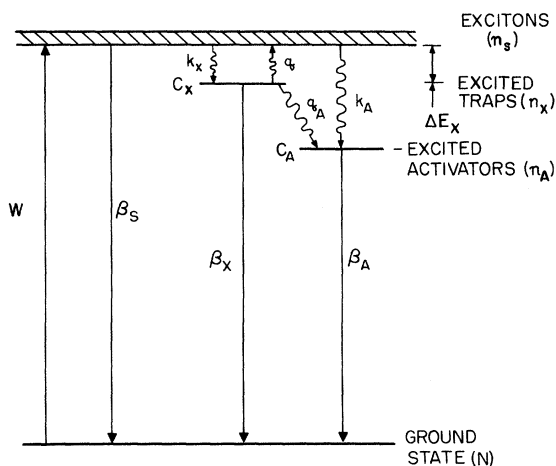An energy-level diagram for the kinetics of ex-

FIG. 3. Energy levels and rate parameters for exciton migration in the presence of both activators and host traps.

citon migration in the presence of host traps and activators is shown in Fig. 3. Here W is the rate of creation of host excitons; β_S, β_x, and β_A are the fluorescence decay rates of excitons, traps, and activators, respectively; k_x and k_A are the exciton-trapping rates for host traps and activators, while q and q_A are the rates of thermal detrapping and of transfers from host traps to activators; C_x and C_A are the concentrations of trapping sites and of activators, respectively, and ΔE_x is the depth of the host trap. Back transfer from activators to the exciton band or to host traps is neglected. This is a good approximation for systems such as tetracene-doped anthracene or anthracene-doped naphthalene. Radiative reabosrption has also been neglected for simplicity, since thin-crystal results[4] have already ruled out reabsorption as the explanation for the time dependence of $k(t)$. Finally, we neglect direct-activator and trap excitations for simplicity. Direct-activator excitation is unimportant for the concentrations in the PK experiments.[1-6] Large concentrations of host traps, and thus significant direct excitation of host trapping sites, is also ruled out experimentally at high temperature.

To find the time dependence of $k(t)$, it is necessary to obtain expressions for the fluorescence intensities of the sensitizers (in this case free excitons), traps, and activators as a function of time. These intensities are proportional to the populations of the excited states, $n_S(t)$, $n_x(t)$, and $n_A(t)$, respectively, and the kinetic equations describing these populations are

$$\dot{n}_S(t) = -(\beta_S + k_x + k_A)n_S(t) + qn_x(t) + W , \qquad (3)$$

$$\dot{n}_x(t) = -(\beta_x + q + q_A)n_x(t) + k_x n_S(t) , \qquad (4)$$

$$\dot{n}_A(t) = -\beta_A n_A(t) + k_A n_S(t) + q_A n_x(t) . \qquad (5)$$

These equations are readily solved for any initial condition. We will consider explicitly the case of a δ-function excitation and $n_x(0) = n_A(0) = 0$. We neglect trap saturation and exciton-exciton interactions, since there are many activators per exciton and exciton-exciton collisions are even rarer than exciton-trap collisions. A variety of rather different physical situations are nevertheless described by Eqs. (3)-(5).

A. $q = q_A = 0$

The solutions of Eqs. (3)-(5), when there is neither thermal detrapping ($q = 0$) nor direct transfer from host traps to activators ($q_A = 0$), are

$$n_S(t) = e^{-(\beta_S + k_x + k_A)t} , \qquad (6)$$

$$n_x(t) = [k_x/(\beta_x - \beta_S - k_x - k_A)]$$
$$\times (e^{-(\beta_S + k_x + k_A)t} - e^{-\beta_x t}) , \qquad (7)$$

$$n_A(t) = [k_A / (\beta_A - \beta_S - k_x - k_A)]$$
$$\times (e^{-(\beta_S + k_x + k_A)t} - e^{-\beta_A t}) , \quad (8)$$

where we have set $n_s(0) = 1$ for simplicity. These results correspond to Eqs. (9)–(12) in Ref. 10 in the special case $\beta_x = \beta_S$, $k_x = kC_x$, and $k_A = kC_A$. The total host fluorescence is

$$n_H(t) = n_S(t) + n_x(t) \quad (9)$$

if the host-trap fluorescence cannot be distinguished from the exciton fluorescence.

The suggestion[10] that case db [Eqs. (31) and (33db) in Ref. 10] describes the PK time dependence fails because the host-fluorescence decay rate for deep traps does not depend on the activator concentration, while the PK results[1-6] show such a dependence. Birk's model of deep traps thus fails even to describe the time evolution of $n_H(t)$ and $n_A(t)$. In the deep-trap model, the excitons are simply partitioned between host traps and activators. The host-trap intensity, but not the decay rate, depends on the activator concentration, contradicting experiment.

Even if the trap fluorescence does not lead to new bands, the fluorescence at the red edge of the host fluorescence should follow $n_x(t)$. Equation (7) leads to an initial fluorescence rise time following a δ-function excitation pulse and the time at which the trap fluorescence intensity reaches its maximum value is given by

$$t_m^x = (\beta_S + k_x + k_A - \beta_x)^{-1} \ln[(\beta_S + k_x + k_A)/\beta_x] . \quad (10)$$

This expression is derived for a δ-function excitation; the effect of the finite width of the excitation pulse used in our experiments is to make the observed t_m^x longer by about 3 nsec than the predicted t_m^x, and thus Eq. (10) represents a lower limit for t_m^x. An estimate for t_m^x can be obtained for undoped samples from Eq. (10) using the measured value for β_S, setting k_A equal to zero, and assuming that $\beta_x = \beta_A$. If this last assumption is not valid, it should be possible to observe β_x in the decay of the red-edge fluorescence. An estimate for k_x is obtained by assuming it is approximately equal to the energy-transfer rate measured for anthracene doped with 1 ppm tetracene.[3] This assumption implies, as in Birks's model,[10] that the exciton-trapping rate is the same for activators and host traps and that the trap concentration is about 1 ppm.

From these considerations, a value of $t_m^x = 26$ nsec is predicted as the lower limit of the fluorescence rise time. Since the rise time of the free-exciton emission in anthracene is limited by the experimental apparatus, which for our equipment is 5 nsec, it should be possible to observe a pronounced change in fluorescence rise time if the trapped-exciton fluorescence can be isolated. For larger

trap concentrations the predicted t_m^x will be less. However, an initial rise should be observable up to trap concentrations on the order of 500 ppm. This is a much higher value than would be expected in view of the smaller concentrations measured for shallow traps at low temperature.

B. Thermal Detrapping

We consider next the case of shallow host traps, with thermal detrapping and $q \neq 0$. If the traps are randomly distributed and not activator induced, they are, on the average, far from the activators and direct transfers from traps to activators are negligible $(q_A = 0)$. The solution of Eqs. (3)–(5) for a δ-function excitation is then

$$n_S(t) = \frac{W}{\lambda_+ - \lambda_-} [(\lambda_+ + k')e^{\lambda_+ t} - (\lambda_- + k')e^{\lambda_- t}] , \quad (11)$$

$$n_x(t) = \frac{Wk_x}{\lambda_+ - \lambda_-} (e^{\lambda_+ t} - e^{\lambda_- t}) , \quad (12)$$

$$n_A(t) = \frac{Wk_A}{\lambda_+ - \lambda_-} \left[\left(\frac{\lambda_+ + k'}{\lambda_+ + \beta_A} \right) (e^{\lambda_+ t} - e^{-\beta_A t}) \right.$$
$$\left. - \left(\frac{\lambda_- + k'}{\lambda_- + \beta_A} \right) (e^{\lambda_- t} - e^{-\beta_A t}) \right] , \quad (13)$$

where $k' = \beta_x + q$ and

$$\lambda_\pm = -\tfrac{1}{2}(\beta_S + k_A + k_x + k')$$
$$\pm \tfrac{1}{2}[(\beta_S + k_A + k_x - k')^2 + 4qk_x]^{1/2} . \quad (14)$$

As before, the total host fluorescence is $n_H(t) = n_S(t) + n_x(t)$ and is the observed quantity if the trap fluorescence is assumed to be indistinguishable from that of free excitons. In practice, the inclusion of $n_x(t)$ does not alter $n_S(t)$ significantly unless a substantial number of the sites are host traps, which, however, would then affect the red edge of the fluorescence.

It is readily seen that λ_+ is the slow decay rate which controls the host fluorescence at long time. For shallow traps, with essentially free-exciton fluorescence, we expect that $\beta_x = \beta_S$. Furthermore, if the exciton motion is interrupted by either host traps or activators, then $k_x = kC_x$ and $k_A = kC_A$, where k describes the free-exciton diffusion [see Eq. (2)]. The PK results for 1 ppm tetracene-doped anthracene can be fit quantitatively[23] by adjusting C_x, k, and q and using measured values for $\beta_S = \beta_x$ and β_A.

The physical model for thermal detrapping is the approach to thermal equilibrium between initially free excitons and initially empty trapping sites. Considering the traps to be nonfluorescing sinks for the excitions, the excition population is given by

$$n_s(t) = W[(\lambda_+ + q)/(\lambda_+ - \lambda_-)]e^{\lambda_+ t}\left(1 - \frac{\lambda_- + q}{\lambda_+ + q} e^{-(\lambda_+ - \lambda_-)t}\right) . \quad (15)$$

In the limit $\lambda_+ \to 0$ (or $\beta_S = \beta_x = 0$ and $k_A = 0$), Eq. (15)

predicts that the free-exciton concentration approaches a constant asymptotic value exponentially. Such equilibration has been observed for free-charge carriers in organic solids.[24] According to diffusion theory, free excitons are trapped by activators ($k_A \neq 0$) at a constant rate. The approach to thermal equilibration described by Eq. (15) in the presence of both host fluorescence and activators thus leads to a decreasing rate of energy transfer from excitons to activators. The $k(t)$ obtained for thermal detrapping has the same form as that found[11] for a modulated random walk with a finite trapping range and thus can be made to fit the PK data.

The most serious objection to a thermal-detrapping model based on randomly distributed host traps is that similar $k(t)$ time dependences are obtained in samples of widely different chemical and optical purity, which certainly should have very different intrinsic host-trap concentrations. In addition, the thermal detrapping should, as discussed in Sec. IV, be affected by changing the temperature.

C. Activator-Induced Host Traps

Host traps directly induced by the activators are the only kind of traps not dependent on individual crystal quality. For example, an activator can distort the electronic states of nearby hosts and produce a region of distorted sites, or host traps, around itself. Such shallow trapping sites are the basis for the finite trapping range in the modulated-random-walk model.[11] A diffusing exciton must then first reach the host traps surrounding each activator, be immobilized briefly, and then LRRT to the activator. We thus set $k_A = 0$ in Eqs. (3)–(5) to exclude direct transfer from free excitons and still neglect the energetically unfavorable back transfer from activators to surrounding shallow host traps.

The decay constants $\lambda_\pm$ in Eq. (14) are now given by

$$\lambda_\pm = -\tfrac{1}{2}(k + k') \pm \tfrac{1}{2}[(k - k')^2 + 4qk_x]^{1/2}, \qquad (16)$$

where $k = \beta_S + k_x$ and $k' = \beta_x + q + q_A$. Although the coefficients are different, we again find $n_S(t)$ and $n_x(t)$ to decay as a linear combination of $e^{\lambda_+ t}$ and $e^{\lambda_- t}$, while $n_A(t)$ again involves the additional $e^{-\beta_A t}$ time dependence. The PK data for individual samples can therefore be fit by activator-induced host traps and thermal detrapping ($q \neq 0$). The additional flexibility of choosing $n_x(0)$ to be the initial average exciton density facilitates the fit and is reasonable physically for shallow mechanical trapping sites.

However, only a few (perhaps ~10) host sites are expected to be disturbed by the presence of an activator molecule. When the host traps are very close to the activator, the trap-to-activator LRRT rate

q_A is larger than the other rate parameters in dilute samples and the kinetic equations reduce to the diffusion theory result in which the "activator" is the entire trapping region. The correspondence is exact when thermal detrapping is neglected. Thus a constant $k(t)$ is obtained, after a short time, for small trapping regions and no detrapping, in disagreement with the PK results. Thermal detrapping has little effect as long as $q_A \gg q$ and must again lead to observable temperature dependences. In order to fit the PK data for 1 ppm tetracene-doped anthracene with a kinetic model based on activator-induced traps, it was necessary to postulate many (more than 100) traps around each activator,[23] and this did not seem physically reasonable.

D. Long Mean Free Paths

The first kinetic models we postulated to understand the time-resolved spectroscopy results were based on a long-mean-free-path model for exciton motion. The mean free path defines a region in which trapping can occur before another scattering. Such a model is a variation on Sec. III C: Instead of distorting the host sites around each trap, the sites near an activator play special roles by virtue of being within a mean free path of the activator. Equations (3)–(5) must again be solved for $k_A = 0$, uniform initial exciton distribution, and equal exciton fluxes in and out of the critical region when transfer to the activator is disallowed.

Although such a long-mean-free-path coherent model for singlet-exciton motion was a severe departure from a diffusion model, the $k(t)$ data obtained by time-resolved spectroscopy could clearly not be understood by the usual diffusion model. An excellent fit to the 1 ppm tetracene-doped anthracene was obtained,[23] but examination of the parameters revealed several features that were felt to be unphysical. The introduction of scattering traps, as described in Sec. II B, decisively ruled out a long-mean-free-path model for singlet-exciton motion at room temperature, since the time evolution of $k(t)$ was not affected. We mention the long-mean-free-path model to emphasize that kinetic models must do more than simply fit particular PK curves and that such models can be decisively tested experimentally.

IV. DISCUSSION

There have been several previous investigations of the temperature dependence of host-sensitized energy transfer in doped naphthalene crystals.[14-20] The measured quantity in these studies is the ratio of the fluorescence intensities, either that of the activator to that of the sensitizer or that of the sensitizer in the doped sample to that in an undoped sample. These investigations can be divided into two groups, those in which care has been taken to

use optically and chemically pure crystals, and those in which such care has not been taken. Results which fall in the first group show that there is either no change or a slight increase in energy transfer as temperature is lowered from 300 to about 100 °K.[14,17] As temperature is lowered further, a $T^{-1/2}$ dependence is observed[14] which is attributed to the scattering of free excitons by phonons (see Appendix). Results which fall into the second category have shown[19] an exponential increase in energy transfer between room temperature and about 200 °K, which is consistent with the scattering of excitons by thermal defects with an activation energy of about 1000 cm^{-1}. Trapping effects have also been observed previously[15,16] at temperatures less than 100 °K, with trapping depths on the order of 30 cm^{-1} for traps created by chemical impurities and on the order of 165 cm^{-1} for those created by structural impurities. Values for the product DR [see Eq. (2)], which determines the magnitude of the energy-transfer rate, have been determined from these experiments to be between 2×10^{-12} and 10^{-11} cm^3 sec^{-1} in naphthalene crystals.

The results reported here on the temperature dependence of $k(T)$ as obtained from fluorescence-decay-time measurements are fairly consistent with the results obtained earlier by fluorescence intensity measurements on similar systems. The activation energies of the thermally activated scattering centers are slightly less than that reported previously; the trap depth for the anthracene-doped samples is consistent with traps induced by chemical impurities; the trap depth for tetracene-doped samples is consistent with traps induced by structural impurities; and the value of DR for our samples at room temperature range from 2×10^{-12} to 10^{-11} cm^3 sec^{-1}. As noted before, these values for the thin anthracene- and tetracene-doped samples are about equal, thus indicating no dependence of DR on spectral overlap.[6] The larger value of DR is obtained for the thick crystal and probably reflects the presence of radiative energy migration and transfer.

Results obtained on tetracene-doped anthracene crystals also show either no temperature dependence or a slight increase in energy transfer as temperature is lowered from 300 to about 100 °K and the effects of trapping appear only at lower temperatures.[4,12] Since it is shown in the Appendix that trapping effects, except for activator-induced traps, should produce a decrease in the energy-transfer rate due to the immobilization of the excitons, the results obtained on these systems above 100 °K are not consistent with the presence of trapping. For activator-induced traps, trapping can actually lead to an increase in the energy-transfer rate due to efficient LRRT from the traps to the activators. The fact that in the tetracene-doped anthracene

system some samples exhibit an increase in energy transfer at low temperatures and other samples exhibit a decrease may be due to the dominance of activator-induced traps in the former case and other types of traps in the latter case. This is a good illustration of the variation from sample to sample that is encountered with effects due to traps. Thus, the temperature dependence in the high-temperature region is again compatible with a trapping model only for activator-induced traps.

We can summarize the effects of traps on energy transfer by pointing out that both the results of previous work and the results presented here give strong evidence of the presence of host-exciton traps in molecular crystals. However, the evidence shows that these are shallow traps ($\Delta E \lesssim 200$ cm^{-1}) with relatively low concentrations (< 200 ppm). They have been shown to be important at low temperatures ($\lesssim 100$ °K) but it is generally believed that excitons are essentially unaffected by the presence of traps at higher temperatures.

In addition to fitting the time evolution of the host and activator fluorescences, kinetic models based on uncontrollable randomly distributed host traps must account for the lack of dependence of $k(t)$ in crystal quality or preparation. Only activator-induced host traps readily satisfy this criterion. Kinetic models based on thermal detrapping from shallow traps must also account for the smallness of the high-temperature variations of $k(t)$ between about 125 and 300 °K. Again activator-induced traps, which efficiently transfer energy to the activators rather than detrap, are indicated. However, the kinetic model based on activator-induced host traps discussed in Sec. III C fits selected PK data only for the unphysical case of extended trapping regions containing many (more than 100) trapping sites around each activator.[23] Less general experimental limitations on the parameters in kinetic models are found from experiments designed to detect the host traps.

We have not shown that all kinetic models fail to account for the time-resolved spectroscopy results, but have focused on severe general restrictions on the physically most reasonable host-trap models. In our opinion, however, the basic assumption of kinetic models, that detailed microscopic processes can be lumped into constant coefficients, fails for energy transfer to randomly distributed microscopic activators. Instead of Eqs. (3)–(5), the population of each site and the rates of all transfers must be considered, as in the most general master-equation approach. Such an approach would be equivalent to the modulated random walk with a finite range,[11] in which the motion of a single exciton is analyzed. This model has been shown[11] to fit the PK data. We consider here the limitations imposed by experiment.

The presence of activator-induced host traps is postulated in the modulated–random-walk model and leads to a finite range for trapping. The exciton is trapped on the first visit to the host traps surrounding an activator, since trap-to-activator LRRT over a lattice spacing or two can easily exceed the thermal-detrapping rate. Such activator-induced host traps are consistent with the experiments discussed above and are suggested by the results on scattering traps. The time dependence of $k(t)$ is then due to changes in the rate of sampling new sites, which all have equal *a priori* probabilities for being activators, rather than to changes in the free-exciton population. Resampling previously sampled sites cannot lead to trapping, since the exciton would have been trapped on the first visit.

The finite range for trapping increases the initial trapping rate when there are 10–20 host traps around each activator, but also increases the resampling due to short steps of the order of the range. Both nearest-neighbor diffusive steps and longer steps have been attributed to LRRT in molecular crystals.[25] Long host-to-host LRRT interrupts the resampling due to short steps and controls the time dependence of $k(t)$. The modulated random walk with a finite trapping range thus gives a detailed analysis of the motion of a free exciton. It is consistent with all experimental data discussed above, and there is no need to postulate contributions to $k(t)$ due to randomly distributed host traps.

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Note added in proof. Another paper has appeared recently purporting to explain the PK results with a model based on host traps [R. M. Pearlstein, K. Lakatos-Lindenberg, and R. P. Hemenger, Phys. Rev. Letters 27, 1509 (1971)]. This model is equivalent to the one we discussed in Sec. IIIB where thermal detrapping is effective, and the objections we stated there still apply.

APPENDIX: TEMPERATURE DEPENDENCE OF $k(T)$

Three different types of temperature dependences are possible for the diffusion constant $D(T)$:

$$D(T)_{\text{loc}} \propto e^{-\Delta E\,'/kT} \ , \quad T \ge T_D \tag{A1}$$

$$D(T)^{\text{ph}}_{\text{free}} \propto \begin{cases} T^{-1/2} \ , & T > T_D \\ \text{const} \ , & T < T_D \end{cases} \tag{A2}$$

$$D(T)^{\text{def}}_{\text{free}} \propto e^{\Delta E /kT} \ , \tag{A3}$$

where T_D is the Debye temperature.

The first case is for localized excitons where lattice distortions move with the electronic excitation energy.[25] Here $\Delta E'$ is the potential barrier due to the lattice distortion which must be overcome for the exciton to make a jump. The last two cases are for free excitons where the exciton jumps before the lattice relaxes around the excited molecule. Equation (A2) is derived for the situation where the dominant mechanism limiting the mean free path of the exciton is scattering by phonons,[26] and Eq. (A3) holds when defect scattering is dominant.[27] In the latter case the thermal motion of the molecules at the defect is different from the surrounding molecules and the equilibrium concentration of "thermal defects" is proportional to $e^{-\Delta E /kT}$, where ΔE is the activation energy for the formation of defects. When no traps are present, the temperature dependence of $k(T)$ will be contained in $D(T)$ through Eq. (2). This is summarized in Table I.

The temperature dependence of $k(T)$ due to the presence of host traps can be deduced from the expression for the ratio of the relative fluorescence intensities which is found by solving Eqs. (3)–(5) in the steady-state condition where all the time derivatives are set equal to zero,

$$\frac{I_A}{I_H} \propto \left(\frac{1 - \beta_x/q}{\beta_A(1 - \beta_x/q + e^{\Delta E T /k_B T})} \right) k_A(T) \ . \tag{A4}$$

I_A /I_H is then proportional to $k'(T)$, where

$$k'(T) = \frac{k_A(T)\,B}{\beta_A(B + e^{\Delta E T /k_B T})} \tag{A5}$$

and

	FREE EXCITON		LOCALIZED EXCITON
	PHONON SCATTERING	DEFECT SCATTERING	
NO TRAPS $[k(T) \propto D(T)]$	$k \propto T^{-1/2}, T > T_D$ $k \propto \text{CONST}, T < T_D$	$k \propto \exp(\Delta E/kT)$	$k \propto \exp(-\Delta E'/kT), T \ge T_D$
WITH TRAPS $[k(T) \propto D(T)\exp(-\Delta E_T/kT)]$	$k \propto T^{-1/2}\exp(-\Delta E_T/kT), T > T_D$ $k \propto \exp(-\Delta E_T/kT), T < T_D$	$k \propto \exp[(\Delta E - \Delta E_T)/kT]$	$k \propto \exp[-(\Delta E' + \Delta E_T)/kT], T \ge T_D$

TABLE I. Temperature dependence of the energy-transfer parameter $k(T)$. $k(T) = 4\pi DRC_A$, $\lambda < R$.

$$B = 1 - \beta_x / q \ . \tag{A6}$$

Here we have assumed that the free- and trapped-exciton populations are in thermal equilibrium, with

$$q/k_x = e^{-\Delta E_T / k_B T} \ , \tag{A7}$$

where ΔE_T is the trap depth and k_B is the Boltzmann constant. Trap-to-activator energy transfer has been neglected. If thermal detrapping is also neglected ($q = 0$), the presence of traps does not introduce any new temperature dependence in I_A / I_H.

At low enough temperatures, where the exponent in the denominator of Eq. (A5) is larger than B and $q \neq 0$,

$$k'(T) \approx \frac{k_A(T)B}{\beta_A} e^{-\Delta E_T / k_B T} \ . \tag{A8}$$

At high enough temperatures $k'(T)$ will be approximately constant. The total temperature dependence of $k(T)$ in the presence of traps is found by substituting Eq. (2) along with either Eqs. (A1), (A2), or (A3) into Eq. (A5), as summarized in Table I.

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