Triplet exciton transport in isotopic mixed naphthalene crystals. I. Kinetic analysis of trapping and fusion[a]

Stuart T. Gentry[b] and Raoul Kopelman
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

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Time-resolved triplet exciton transport in binary mixed crystals has been studied for $C_{10}H_8$ in $C_{10}D_8$ (20%–100%) at liquid helium temperatures. The delayed fluorescence decays are exponential and range from milliseconds to nanoseconds as C_g goes from 0.2 to 1.0. The analysis is based on the presence of a BMN supertrap in large amounts (10^{-3}) and on the fact that supertrapping of the guest excitons dominates the kinetics while heterofusion (triplet guest-triplet supertrap annihilation) dominates over the homofusion (guest–guest annihilation) and was used to monitor the kinetics. We also investigated in detail photodetrapping and the relative efficiencies of the various fusion channels. An analysis of the transport data is given in paper II.

I. INTRODUCTION

There has been a perennial interest in studying the dynamics of triplet energy transfer in molecular crystals. Part of this interest is due to the similarities and differences between exciton transport and electron transport with respect to band theory, phonon coupling, and order–disorder transitions.[1] Most of the previous experimental time-resolved work on triplet excitons for the case of two-dimensional transport excitons, however, can be divided into two nonoverlapping regimes: nominally pure crystals at high temperatures[1-3] > 77 K; or dilute isotopically mixed molecular crystals (conducting site concentrations less than ~ 0.20 mole fraction) at low temperatures[4] < 10 K. This paper will present an experimental technique and results which help span the gap between these two extensively studied regimes in naphthalene crystal systems.[1-4]

We confine ourselves to the ternary crystals containing perdeuteronaphthalene ($C_{10}D_8$), napthalene ($C_{10}H_8$), and betamethylnaphthalene (BMN). We will refer to these species respectively as host, guest, and trap or supertrap. The BMN concentration C_s is kept small relative to the $C_{10}H_8$ concentration C_g. The electronic energy levels are such that the host sites act as an inert matrix. An exciton moves on the guest quasilattice until it irreversably transfers onto a supertrap site.

Ahlgren and Kopelman[5] demonstrated that triplet exciton transport in mixed naphthalene crystals exhibits a critical dependence on the guest concentration in the range of $C_g \simeq 0.10$–0.20 mole fraction. This has been confirmed by Klymko and Kopelman.[6,7] The Ahlgren, Kopelman, and Klymko work was limited by an upper bound of $C_g \simeq 0.20$–0.30. One of the goals of this current study, therefore, was to find out what form this concentration dependence takes for C_g values higher than 0.20. A second question which we were interested in is what controls the triplet decay kinetics in our crystal system. Evidence by Klymko and Kopelman[6,7] suggests that exciton annihilation can be a prevalent decay mechanism in $C_g = 0.10$–0.20 crystals. On the other hand, it is often assumed[8-10] that the dominant decay mechanism in pure crystals at low temperatures is trapping.

In order to study these questions we monitored the decay of the delayed fluorescence intensity following the direct excitation of triplet excitons. This fluorescence signal is a result of heterofusion, i.e., the annihilation of a naphthalene exciton with a BMN exciton. The exciton densities are such that the BMN exciton density remains constant at its steady-state value during the course of a decay measurement. We will show that the result of this conclusion is that the decay of the delayed fluorescence maps out the rate at which free excitons find BMN sites.

Section II of this paper provides the details of our experimental techniques, Sec. III outlines the kinetic model that we used to analyze our time-resolved spectra, as well as the consequent transport vs C_g results. We found that the time necessary to find a supertrap site decreases by over five orders of magnitude as we go from a guest concentration of 0.20 to a concentration of ~ 1.0 mole fraction. The functional form of this concentration dependence is a simple power law with the exponent equal to 6.5 (at 1.8 K). In Sec. IV we show that homofusion is negligible for $C_g > 0.20$ crystals and that trapping has a larger effect on the delayed fluorescence decay rate than heterofusion. We analyze the partitioning of the possible heterofusion products in Sec. V. We show that the most likely outcome of the annihilation between a trap and guest exciton is the production of a guest exciton which does not remain correlated with the BMN site of annihilation. Section VI presents evidence for a related phenomenon: optical detrapping of BMN excitons by the dye laser. Section VII summarizes our results.

This paper will be followed by another one which relates the experimental transport results to current energy transport theories (paper II).[14]

II. EXPERIMENTAL

Bridgman crystals were grown from zone-refined BMN and from potassium-fused and zone-refined $C_{10}H_8$ and $C_{10}D_8$.[11] The crystals were annealed for 48 h near their melting temperature and then cleaved into 1 mm thick pieces

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[a] Supported by NSF Grant No. DMR 8303919.

[b] Present address: Hughes Aircraft Co., 600/F245, P. O. Box 3310, Fullerton, California 92631.

along the *ab* crystal plane. These crystals were then mounted in a strain-free holder and immersed in liquid helium. We measured the BMN concentration using optical absorption at 1.8 K.

The optical excitation source was a Coherent Inc. argon ion laser pumped dye laser. The dye laser was set to excite directly either the $C_{10}D_8$ (4692 Å) or the $C_{10}H_8$ (4714 Å) first triplet transition ($^3B_{1u} \leftarrow {}^1A_{1g}$). We used a Lasermetrics electro-optic modulator (EOM) to shutter the laser. The EOM is able to reduce the argon laser UV power to a level below the dye laser lasing threshold. Therefore, by putting the EOM between the two lasers we were able to convert the 1000:1 EOM extinction rate into an infinity:1 laser system extinction ratio. The EOM was driven by a Lasermetrics avalanche mode pulse driver system which was able to follow a 3 V signal from dc to 1 kHz with a rise time of 20 ns. We typically used a square signal with a pulse duration sufficient to allow the exciton population distribution to reach a steady-state value. The delayed fluorescence signal was filtered by using two Corning 7-54 filters which effectively eliminated any laser scatter and phosphorescence intensity. The signal was processed with either a PAR boxcar gated averager or a PAR signal averager, depending on the necessary instrumental time constant.

TABLE I. Triplet (T) exciton kinetic processes.

Equation	Description
$C_g^0 \xrightarrow{\tilde{\alpha}} T_g$	$C_{10}H_8$ (guest) exciton creation
$T_s \xrightarrow{\tau_s^{-1}} C_s^0$	BMN (supertrap) natural decay
$T_g \xrightarrow{\tau_g^{-1}} C_g^0$	$C_{10}H_8$ (guest) natural decay
$T_g \xrightarrow{k} T_s$	Trapping (by supertrap)
$T_s \xrightarrow{k_0(\alpha)} T_g$	Optical detrapping
$T_s \xrightarrow{k_t} T_g$	Thermal detrapping
$T_g + T_g \xrightarrow{\gamma_1 f_1^{(1)}} S$	Homofusion-singlet channel
$T_g + T_g \xrightarrow{\gamma_1 f_1^{(2)}} T_g$	Homofusion-triplet channel (guest/triplet exciton creation)
$T_g + T_s \xrightarrow{\gamma_2 f_2^{(1)}} S$	Heterofusion-singlet channel (guest + supertrap singlet exciton creation)
$T_g + T_s \xrightarrow{\gamma_2 f_2^{(2)}} T_g$	Heterofusion-triplet channel
$T_g + T_s \xrightarrow{\gamma_2 f_2^{(3)}} T_s$	Heterofusion-triplet channel
$f_1^{(1)} + f_1^{(2)} \equiv 1$	
$f_2^{(1)} + f_2^{(2)} + f_2^{(3)} \equiv 1$	
$\alpha \equiv \tilde{\alpha} \times C_g^0$	

III. KINETIC EQUATIONS

There are a number of competing processes which must be considered when doing a kinetic analysis of the exciton dynamics. Table I lists the relevant terms. The table does not distinguish between the individual singlet species (S_s and S_g). The resultant rate-law equations are

$$\frac{dT_g}{dt} = +\alpha - \tau_g^{-1} T_g - kT_g + k_0 T_s + k_t T_s - \gamma_1 T_g^2 (f_1^{(1)} + f_1^{(2)}) - \tfrac{1}{2}\gamma_2 T_g T_s (f_2^{(1)} + f_2^{(3)}) , \tag{1}$$

$$\frac{dT_s}{dt} = -\tau_s^{-1} T_s + kT_g - k_0 T_s - k_t T_s - \tfrac{1}{2}\gamma_2 T_g T_s (f_2^{(1)} + f_2^{(2)}) . \tag{2}$$

Equations (1) and (2) can be simplified. By monitoring the emission after the laser is turned off, we can ignore all of the laser-induced processes. (The optical detrapping term will be discussed in Sec. VI.) We kept the temperature below 16 K so as to make thermal detrapping negligible.[9,12,13] The time scale of our experiments (2.3×10^{-7} to 1×10^{-2} s) allows us to ignore the singlet exciton kinetics (lifetime = 1.2×10^{-7} s) and to ignore the triplet natural decay ($T_g = 2.6$ s). If it had been required, we could have taken into account either of these two effects. We monitored all of the emission from 2600 to 3800 Å so as to sample both the $C_{10}H_8$ and BMN fluorescence. The time-resolved spectra did not change if we monitored only $C_{10}H_8$ or only BMN emission, giving further evidence that we can ignore the time effects of the singlet states. Finally, we will show in a subsequent section that the steady-state exciton populations are such that the $C_{10}H_8$ exciton density is much lower than both the BMN excited state density and the BMN ground state density, i.e., $T_g \ll T_s$ and $T_g \ll C_s^0$. The consequences of this last statement are: (1) $C_{10}H_8$ exciton trapping and annihilation events will not significantly alter the BMN exciton and ground state populations during the course of a decay measurement and (2) homofusion is negligible. The simplified kinetic equations are

$$\frac{dT_g}{dt} \simeq -kT_g - \tilde{\gamma}_2 T_g T_s , \tag{3}$$

$$\frac{dT_s}{dt} \simeq 0 , \tag{4}$$

$$\tilde{\gamma}_2 \equiv \tfrac{1}{2}\gamma_2 (f_2^{(1)} + f_2^{(3)}) . \tag{5}$$

The rate constants k and $\tilde{\gamma}_2$ are defined to be independent of time. These equations can be solved to give

$$T_g(t) = T_g(0) \exp[-(k + \tilde{\gamma}_2 T_s)t] , \tag{6}$$

$$T_s(t) = T_s(0) . \tag{7}$$

The delayed fluorescence intensity is proportional to the product of the BMN and $C_{10}H_8$ triplet exciton densities (assuming homofusion is negligible). T_s is constant; therefore *the delayed fluorescence intensity and the naphthalene triplet exciton density decay with the same exponential rate constant* K:

$$K \equiv k + \tilde{\gamma}_2 T_s . \tag{8}$$

The parameter K describes the rate at which a $C_{10}H_8$ triplet exciton is either trapped or is destroyed by heterofusion. The important thing is that both trapping and heterofusion depend on the rate of exciton transport through the guest quasilattice. A free $C_{10}H_8$ triplet exciton moves through the crystal until it finds a BMN site. If this BMN site is in its ground state then the free exciton can become trapped. If the BMN site is already occupied then the incoming exciton can be effectively destroyed by annihilation. In either case, there will be a reduction in the $C_{10}H_8$ triplet exciton population and the delayed fluorescence intensity should be indicative of this change.

It is useful to define the reduced rate constant K^R:

$$K \equiv K^R \times (C_s/C_g)\,. \tag{9}$$

K^R is the effective rate at which an exciton samples new sites while C_s/C_g is the probability that a newly visited site is a supertrap. K^R should be a measure of the diffusion coefficient.[29]

Figure 1 shows the delayed fluorescence decay rate constants for a variety of crystals at a temperature of 1.8 K. The dashed line represents the best line (using least squares linear regression) through the data. The resultant empirical equation is

$$K^R(C_g) = K^R(1.0) \times C_g^n; \quad n = 6.5 \pm 0.3. \tag{10}$$

A separate paper[14] discusses this functional relationship between K^R and C_g, and how it compares to the predictions made by several theories which are based on a master equation.[15,16] It is clear in Fig. 1, however that $K^R(C_g)$ is a smoothly varying function. It does *not* show any abrupt transition behavior, in contrast to expectations based on percolation theory[17–19] or on Anderson localization.[44,45] This is very different from the case of singlet naphthalene excitons,[20,21] and from the case of $C_g < 0.20$ triplet naphthalene excitons[5–7] where critical concentration behavior has been demonstrated.

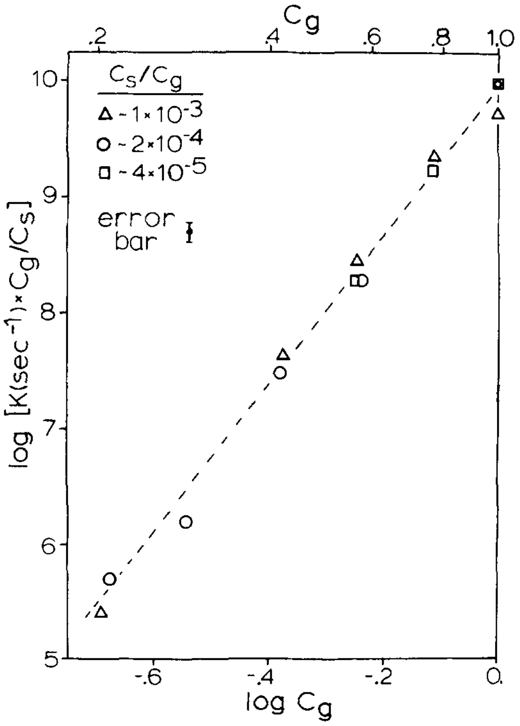

FIG. 1. Experimental K^R vs C_g data. The triangles correspond to data which were obtained using crystals having $C_s/C_g \simeq 1\times10^{-3}$; the circles correspond to $C_s/C_g \simeq 2\times10^{-4}$; and the squares correspond to $C_s/C_g \simeq 4\times10^{-5}$. All of the data were recorded at a temperature of 1.8 K. The dashed line represents the best fit using least squares linear regression through the data points. The slope of the line is 6.5 ± 0.3.

We should point out than an implicit assumption made throughout this paper is that Eqs. (1) and (2) adequately describe the time evolution of triplet excitons. Strictly speaking this is not the case. It is a well established fact that trapping in a two-dimensional lattice is controlled by a *time-dependent* rate constant $k(t)$ (e.g., Refs. 25–27). The time dependence of the trapping parameter, however, is most significant at early times relative to the nearest-neighbor transfer times. The time scale of our experiments and the noise in our spectra is such as to make the time dependence aspects insignificant. In addition, the presence of a small nonzero out-of-plane transport component will further decrease the dependence of K on time (e.g., Refs. 23 and 28).

Another implicit assumption in our kinetic analysis is that the rate determining step for trapping is finding the BMN site. The alternative is that transfer within the guest system is rapid enough to average the excitons effectively across all of the guest sites, with the rate determining step being the transfer of energy from a guest site to the supertrap.[29] Our justification for assuming that the former is true is the strong influence that guest concentration has on the trapping rate. The time necessary for an exciton to jump from a nearest neighbor guest site to a BMN site should be practically independent of guest concentration. We cannot, however, extrapolate and categorically say that in a pure naphthalene crystal there is no effect from having slower guest-trap transfer than guest–guest pairwise transfer (i.e., $\eta_t < 1.0$, see below).

IV. RELATIVE RATES OF HOMOFUSION, HETEROFUSION, AND TRAPPING

As mentioned at the beginning of this paper, there has been some disagreement about whether homofusion is a significant decay channel at low temperatures. We have found that above $C_g \simeq 0.20$ mole fraction, homofusion is negligible. This is not true below $C_g \simeq 0.20$.

We have two types of evidence in support of the conclusion that $\gamma_1 T_g^2 \ll K T_g$. The first observation is that in almost all cases, the decay is exponential and the decay constant is independent of laser intensity over two orders of magnitude attenuation of the laser power.

The second justification for ignoring homofusion arises from estimating the exciton densities. We experimentally measure an exponential decay rate constant K' while temporarily ignoring the origin of this decay. We can write an approximate kinetic equation (neglecting optical detrapping) for steady-state conditions such that

$$\frac{dT_g}{dt} = +\alpha - K'T_g = 0\,. \tag{11}$$

For a $C_g \simeq 1.0$ and $C_s = 8\times10^{-4}$ crystal at 1.8 K, we measured a value of $K' = 5\times10^{6}\ \mathrm{s}^{-1}$. We can calculate an approximate value for the optical excitation as being $\alpha = 10^{-4}$ mole fraction/s. This value of α was based on a 100 mW laser power, a 10^{-24} cm^2/molecule absorption coefficient,[22] and a 1 mm^2 illumination cross section.

Rearranging the steady-state kinetic equation gives $T_g = \alpha/K \simeq 10^{-11}$ mole fraction relative to C_g. A specific $C_{10}H_8$ exciton is thus far more likely to find a 10^{-3} mole fraction BMN site than to find a second 10^{-11} mole fraction $C_{10}H_8$ exciton.

There are several interesting results that can be extracted from this calculation of the naphthalene exciton density. If we reduce C_g to 0.21 (with $C_s/C_g = 2\times 10^{-4}$) then the decay rate constant slows to 100 s^{-1}. This gives a free exciton density of 10^{-6} mole fraction as opposed to the 10^{-11} value calculated for the $C_g = 1.0$ crystal. Thus, in crystals such as those used by Klymko and Kopelman,[6,7] it is no longer appropriate to say that a free exciton is more likely to find a BMN site than to find a second free exciton. This manifests itself in the deviations from exponentiality for $C_g = 0.21$ and low supertrap concentration (Fig. 2).

Another question, now that we have shown that homofusion is negligible in crystals with $C_g > 0.20$, is how the rates of heterofusion and trapping compare to one another in these crystals. Although the physics of heterofusion and trapping are quite different, the kinetics of the two are similar. Both processes are dependent on the rate $\hat{K}$, at which an exciton can move through the guest quasilattice and find a BMN site. The kinetic processes differ only in their efficiencies η_f and η_t and in their density terms T_s and C_s^0 (BMN excited state and ground state populations, respectively),

$$k = \hat{K}\eta_t C_s^0 , \tag{12}$$

$$\tilde{\gamma}_2 T_s = \hat{K}\eta_f T_s . \tag{13}$$

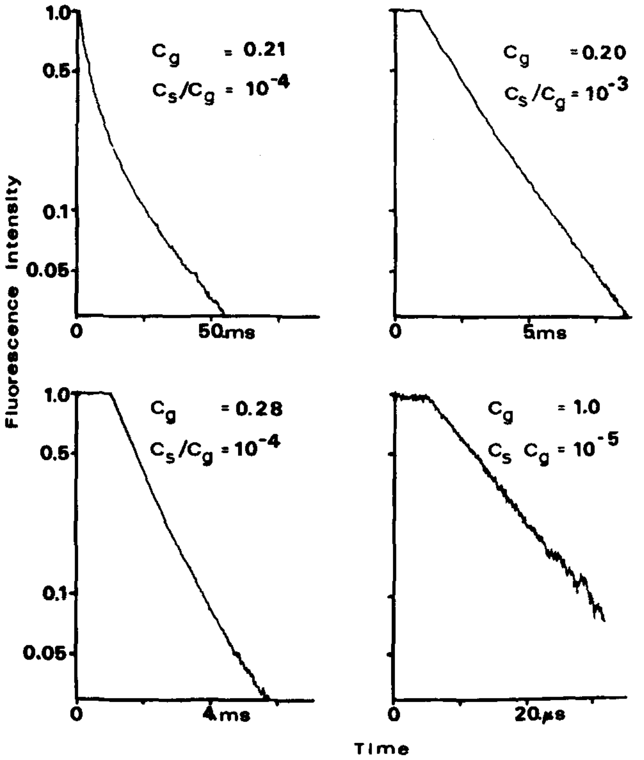

FIG. 2. Decay spectra as a function of C_g and C_s. The four spectra show the delayed fluorescence decay for several crystals. All of the spectra were recorded at 1.8 K. The crystal composed of $C_g = 0.21$ and $C_s/C_g \simeq 10^{-4}$ has a decay which was significantly nonexponential. Increasing either C_s or C_g increased the decay rate and decreased the deviation from exponential decay behavior. The $C_g \simeq 1.0$ spectrum is a representative sample of the high guest concentration range.

One method of estimating relative values for T_s and C_s^0 would be to proceed in the same fashion in which we estimated T_g. There is, however, a problem with doing this calculation for T_s. While both trapping and heterofusion destroy free excitons, one of these processes creates trapped excitons while the other destroys trapped excitons.

As an alternative to numerical calculations of the supertrap exciton density, we directly measured the ratio T_s/C_s for a crystal composed of $C_g \simeq 1.0$ and $C_s = 2.4\times 10^{-4}$. The premise was that BMN molecules which were already occupied by triplet excitons would not absorb 3219 Å photons, which induce the transition from the BMN ground state to the first excited singlet state. We measured the xenon lamp 3219 Å absorbance with and without the dye laser present to excite triplet excitons.

In order to avoid the overlap between the laser induced delayed fluorescence spectrum and the xenon lamp absorption spectrum, we used a system of shutters to alternate between the laser and lamp excitations. We used the laser to reach a steady-state triplet exciton distribution and then we shut the laser off. After waiting 5 ms for the delayed fluorescence signal to go to zero, we applied a 12 ms xenon lamp pulse and measured the absorbance as a function of wavelength. The delay time and xenon lamp pulse duration were chosen to be small relative to the natural decay time of the BMN triplet excitons. Aside from the necessary timing of the experiment, the resultant absorption spectrum resembled a common transmitted intensity vs wavelength absorption spectrum.

The result of this absorption experiment was that the absorbance was only attenuated by 5% ± 3% when the laser was turned on. Therefore *the majority of the BMN sites are available for trapping as opposed to heterofusion*, with the density of the occupied BMN sites being on the order of $T_s = 1\times 10^{-5}$ as compared to $C_s = 2.4\times 10^{-4}$ mole fraction, or consequently as compared to $C_s^0 = 2.3\times 10^{-4}$ mole fraction.

The other terms of interest in Eqs. (12) and (13) are the efficiencies η_f and η_t. While it is difficult to measure the absolute efficiencies (see Refs. 23 and 24 for relative measurements of η_f and η_t), we can discuss some of the terms which contribute to these quantities. We will see in Sec. V that η_f is substantially reduced by the fact that most of the heterofusion events do not change the guest triplet exciton density and therefore do not affect the rate of change in the delayed fluorescence intensity. On the other hand, η_t is enhanced by the presence of small energy funnels surrounding the supertrap sites on the lattice.[21,43]

Like the values for T_s and C_s^0, these contributions to η_f and η_t suggest that trapping is the primary mechanism for the decrease in the free exciton population. Heterofusion acts only as a weak nonperturbing probe of the $C_{10}H_8$ triplet density. This conclusion is further supported by our observation that our experimental values for K did not change, within 20% uncertainty, as we decreased the laser intensity by a factor of 100. If the trapping and heterofusion rates were comparable, and assuming $\eta_f \neq \eta_t$, then changing the laser intensity would have changed the ratio of steady state T_s and C_s^0 values and consequently changed the measured value of K.

V. ANNIHILATION PARTITION FUNCTIONS

The annihilation of a guest and trap exciton can lead to one of several products (Table I): a guest or trap singlet exciton; a guest triplet exciton; or a trap triplet exciton. The partitioning of these products is given by the respective fractions $f_2^{(1)}$, $f_2^{(2)}$, and $f_2^{(3)}$, where the sum of the three is defined to equal unity. This partitioning has a large effect on the contribution of annihilation to the delayed fluorescence. If the product is a guest triplet exciton then there is no change in the guest exciton density and consequently there is no change in the delayed fluorescence decay rate.

Statistically, one out of four annihilation events yields a singlet exciton, while a triplet exciton is produced the other three times.[30,31] (Strictly speaking this is only true for homofusion. It should be a good approximation for BMN/$C_{10}H_8$ heterofusion, however, since the orientations of the fine structure principal axes for the two species are very similar.[32]) This partition function must be modified since the resultant singlet exciton has a 0.67 probability of converting back to the triplet state via intersystem crossing.[33–35] Therefore, the final partition function for producing a singlet exciton is

$$f_2^{(1)} = 0.25 \times (1 - 0.67) = 0.08 . \tag{14}$$

The division of the remaining 0.92 probability between $f_2^{(2)}$ and $f_2^{(3)}$ will depend on the probability F_{cor} of the triplet exciton remaining correlated with the trap site during the annihilation process and during the subsequent relaxation back to the first triplet state:

$$f_2^{(2)} = [1 - f_2^{(1)}] \times [1 - F_{\text{cor}}] , \tag{15}$$

$$f_2^{(3)} = [1 - f_2^{(1)}] \times [F_{\text{cor}}] . \tag{16}$$

The end-product exciton is said to remain correlated with the BMN site if the initial product is a trapped exciton *or* if the initial product is a free exciton which subsequently undergoes rapid trapping by the now vacated BMN site.

By looking at the steady state probability P that an exciton is trapped within its lifetime, it is possible to determine F_{cor} for the case of annihilation-generated singlet excitons. The experimental expression for P is

$$P = \frac{I_s}{I_s + \alpha I_g} , \tag{17}$$

where I_g and I_s are the $C_{10}H_8$ and BMN fluorescence intensities and α is a factor which accounts for translating the realtive intensities into relative guest and trap exciton densities.[20] (See Ref. 21 for a full discussion regarding how we measured P.) We define several different trapping probabilities. P_{ann} is the overall trapping probability of singlet excitons which are produced by annihilation. Experimentally, P_{ann} is the delayed fluorescence trapping probability resulting from steady state dye laser excitation $P_{\text{ann}} = P_{\text{laser}}$. Theoretically, P_{ann} is the weighted sum of trapping probabilities P_{cor} and P_{noncor} for excitons which do and do not remain correlated with the BMN sites of heterofusion:

$$P_{\text{ann}} = [F_{\text{cor}} \times P_{\text{cor}}] + [(1 - F_{\text{cor}}) \times P_{\text{noncor}}] . \tag{18}$$

We rearrange this equation to give

$$F_{\text{cor}} = \frac{P_{\text{ann}} - \text{P}_{\text{noncor}}}{P_{\text{cor}} - P_{\text{noncor}}} . \tag{19}$$

By definition, any exciton which remains correlated with the BMN site during heterofusion will have a trapping probability which is equal to unity: $P_{\text{cor}} \equiv 1$. On the other hand, the noncorrelated production of $C_{10}H_8$ singlet excitons by heterofusion should be identical to the random production of singlet excitons by xenon lamp excitation: $P_{\text{noncor}} = P_{\text{xenon}}$.

We used Eq. (19) to determine that $F_{\text{cor}} = 0.03$ for a $C_g \simeq 1.0$, $C_s = 2 \times 10^{-5}$ crystal. If F_{cor} is the same for singlet and triplet excitons, then the value for F_{cor} can be substituted into Eqs. (15) and (16) to obtain the partition fractions listed in Table II. As can be seen, *the most probable outcome of a heterofusion event is that one exciton is destroyed while the second remains as a free (guest) triplet exciton.*

The efficiency η_f is given [cf. Eq. (5)] by the fraction of collisions giving annihilation multiplied by a numerical factor of $f_2^{(1)} + f_2^{(3)} = 0.11$. This attenuation factor of 0.11 provides support for saying that the major contribution to the decay in the delayed fluorescence intensity is trapping rather then heterofusion.

F_{cor} as a Function of Concentration: Table III lists F_{cor} values for a number of different guest and supertrap concentrations at 1.8 K. As we decrease the guest concentration from $C_g \simeq 1.0$, we see that the singlet correlation fraction rapidly increases. *This is consistent with an exciton cluster confinement model*, e.g., percolation.[17–21]

The cluster boundaries and ramified nature of the clusters in a mixed lattice make it difficult for the exciton to escape from the BMN site. The exciton must move to a different cluster, or subcluster in a ramified cluster, from the one in which the trap site resides if the exciton is to lose its correlation with the BMN site. Near $C_g = 0.20$ the correlation fraction begins to decrease with decreasing guest concentration. At this point the clusters are becoming small enough so that it may become easier for the annihilation-generated exciton to move to a different cluster from the one containing the BMN site before the highly excited exciton relaxes back to the first singlet state. Due to this cluster confinement effect, which is seen for singlet excitons at 1.8 K[20,21] but not for triplet excitons for $C_g > 0.20$, the only singlet F_{cor} value which we can treat as being equal to the triplet F_{cor} value[17,18] is that for the $C_g \simeq 1.0$ crystal.

VI. OPTICAL DETRAPPING

An integral part of the experimental technique outlined in this paper is that we eliminate the prompt fluorescence by

Table II. Annihilation partition fractions for $C_g \simeq 1.0$ crystal.

fusion→S	$f_2^{(1)} = 0.08 = 0.08$
fusion→T_g	$f_2^{(2)} = (1 - 0.08) \times (1 - 0.03) = 0.89$
fusion→T_s	$f_2^{(3)} = (1 - 0.08) \times (0.03) = 0.03$

Table III. Annihilation correlation fractions (1.8 K).

C_g	C_s/C_g	P(xenon)	P(laser)	F_{cor}
1.0	8.1×10^{-4}	1.0	1.0	
1.0	1.7×10^{-5}	0.13	0.16	0.03 ± 0.09
0.76	5.3×10^{-5}	0.033	0.46	0.44 ± 0.16
0.57	1.4×10^{-3}	0.051	0.42	0.39 ± 0.15
0.57	2.4×10^{-4}	0.018	0.39	0.38 ± 0.13
0.56	3.1×10^{-5}	0.008	0.44	0.44 ± 0.14
0.42	8.8×10^{-4}	0.030	0.58	0.57 ± 0.17
0.42	1.3×10^{-4}	0.013	0.71	0.63 ± 0.17
0.20	1.8×10^{-3}	0.008	0.26	0.25 ± 0.10
0.21	2.0×10^{-4}	0.001	0.17	0.17 ± 0.06

exciting the first triplet state of naphthalene directly. This requires that we use a high-intensity laser since the $^3B_{1u}\leftarrow{}^1A_{1g}$ transition is spin forbidden. Unfortunately the large monochromatic photon flux can lead to problems which do not normally arise with an arc lamp. Specifically, we have found that triplet excitons in naphthalene mixed crystals are affected by triplet–triplet absorption.[36,37]

The oscillator strength for triplet–triplet absorption at 4714 Å is approximately[36] $f\simeq10^{-2}$, while the $^3B_{1u}\leftarrow{}^1A_{1g}$ ground state oscillator strength is roughly[22] $f=5\times10^{-10}$. This difference in absorptivities more than compensates for the 10^{-5}:1 ratio of BMN-$^3B_{1u}$ and $C_{10}H_8$-$^1A_{1g}$ absorbate concentrations which we calculated earlier. Therefore, *the same laser which is used to excite triplet excitons is also capable of cycling each of the trapped excitons through several triplet–triplet absorption and relaxation events during the excitons' lifetime.* (The time required for the system to relax back to the first triplet state following the absorption step is in the subnanosecond range.)

We found that the effect that triplet–triplet absorption has on our mixed crystal system is to detrap excitons out of the BMN sites. To demonstrate this we did a double-excitation experiment. The crystals were irradiated by both a xenon lamp and a dye laser. The xenon lamp created triplet excitons indirectly via intersystem crossing from the singlet manifold. The dye laser was set close to, but not right on, the $C_{10}H_8$ 0–0 $^3B_{1u}\leftarrow{}^1A_{1g}$ absorption wavelength (4720 and 4714 Å, respectively).

Figure 3 shows several time-resolved spectra for this double-excitation experimental design. We applied a xenon lamp pulse (using a mechanical shutter) which was long enough to reach a steady-state exciton population distribution. After a preset delay interval, we applied a laser pulse. We monitored the fluorescence intensity as a function of time during this sequence of events. The first spectrum in Fig. 3 shows the result that was obtained when we only used the xenon lamp. The lamp induced a strong emission signal composed of both delayed and prompt fluorescence. The 3 ms fall time was due to the transit time of the shutter. The second spectrum was obtained when we only used the off-resonance laser pulse. In the third spectrum, we used both the xenon lamp and the dye laser. As before, we initially saw the falloff of the xenon lamp-induced fluorescence. In this spectrum, however, when the laser was turned on a new fluorescence signal appeared.

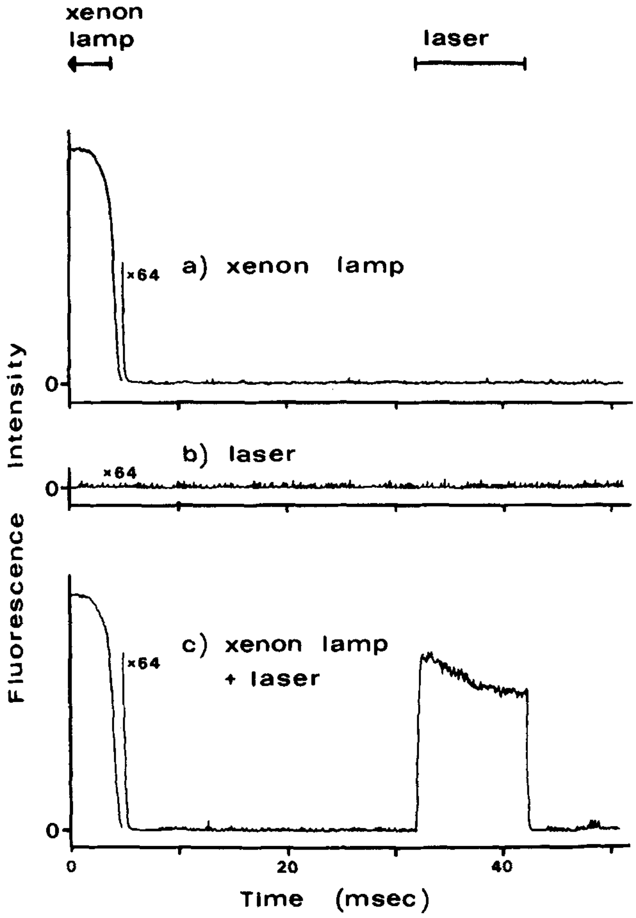

FIG. 3. Double-excitation decay spectra. The figure shows several time spectra of delayed fluorescence measured with a $C_g\simeq1.0$ crystal doped with $C_s=10^{-3}$. The three time spectra correspond to that seen using only a xenon lamp, only a 4720 A laser, and that seen using both. The timing sequence for the lamp and the laser irradiation of the crystal is shown at the top of the figure. The intensity peak at 30–40 ms in the third spectrum is induced by the laser pulse, but is only visible if the crystal was first excited by the xenon lamp.

We found that the intensity of the laser-induced signal, relative to the xenon lamp signal, decreased exponentially with increasing delay time between the xenon lamp and the laser pulse. The rate constant for this decrease was approximately equal to the inverse lifetime of the supertrap first triplet state. We also found that under steady state lamp and laser conditions, the laser-induced increase in fluorescence intensity was accompanied by a decrease in BMN phosphorescence intensity.

These observations indicate that the laser causes optical detrapping of BMN triplet excitons. While the system is in the highly excited triplet state, or possibly during the relaxation back to the $^3B_{1u}$ state, the exciton is able to move on the lattice from the BMN site back to the guest quasilattice. This process would be similar to the motion of excitons during annihilation, as discussed in the previous section. Shirakawa *et al.*[37] report a similar detrapping observation and conclusion for betachloronaphthalene doped in naphthalene. This indirect detrapping effect is different than the direct triplet-pentacene-to-triplet-naphthalene process which was used by Morsink and Wiersma.[42]

We also considered two possible alternative explanations for the laser induced signal, both of which we subsequently concluded had negligible effects on the delayed fluorescence. The first was that the laser causes local heating of the crystal and this leads to thermal detrapping of the excitons. Measurements have shown[13] that the increase in the bulk crystal temperature due to the dye laser (under our experimental conditions) is less than 1 K. On the other hand, a minimum temperature of 17 K is necessary for significant thermal detrapping.[9,12,13] The other possible mechanism is that triplet–triplet absorption induces fluorescence via intersystem crossing from a highly excited triplet state to the singlet manifold. Keller[38] has measured the quantum yield for intersystem crossing following naphthalene triplet–triplet absorption in a glass matrix at 77 K. He found that the ratio of the number of intersystem crossing events to the number of photons absorbed by triplet–triplet absorption was only 5×10^{-7}.

The optically induced detrapping process has a number of ramifications on the use of lasers for studying exciton dynamics. One concern is that the kinetic analysis earlier in this paper, which is based on decay measurements made while the laser is off, is not applicable when the laser is on. This means that we must be careful when applying our kinetic model to steady-state experiments and to measurements of the luminescent rise times.

A second area where caution is necessary is when designing experiments which attempt to use the dye laser to excite given molecules in a crystal selectivity. As an example, it may be helpful to selectively excite a trap site and monitor the consequent phosphorescence or fluorescence spectrum and make inferences about transfer between sites or to assign emission peaks (e.g., Ref. 39). Unfortunately, while it is possible to excite a given species with the laser, the laser will also subsequently scramble those excitations across all of the sites in the lattice. There is an obvious, partial analogy to detrapping by heat pulses.[40,41]

VII. SUMMARY

In this paper we have demonstrated that the rate of decay of the delayed fluorescence intensity can be used to extract information regarding the rate of triplet exciton transport among naphthalene sites. The experimental procedure is to apply a pulse of laser radiation which is sufficient in energy to excite the $C_{10}H_8$ triplet state directly and long enough in duration to reach a steady-state exciton distribution. The decay in delayed fluorescence intensity, after turning off the laser, acts as a direct measure of the decay in the $C_{10}H_8$ exciton population, which is due to trapping and heterofusion. This technique depends on the fact that the $C_{10}H_8$ exciton density is much smaller than the density of both ground state and excited state BMN molecules.

While heterofusion is present in sufficient amounts to be able to monitor the delayed fluorescence, the dominant decay mechanism for $C_{10}H_8$ triplet excitons in our experimental system is trapping by the BMN ground state sites. There are two pieces of evidence for this. We have shown that under typical experimental conditions, only ~5% of the supertrap sites in a $C_g \simeq 1.0$, $C_s = 10^{-4}$ crystal are in their triplet excited state. We have also shown that the majority of the heterofusion events convert the guest and trap excitons into a single guest triplet exciton, which means that there is almost no change in either the triplet $C_{10}H_8$ exciton density or in the singlet exciton densities.

Heterofusion may be weak in our crystals, but homofusion is virtually nonexistent. The very rapid trapping time in concentrated crystals keeps the guest exciton density at a level which is several orders of magnitude less than the BMN density. Therefore a $C_{10}H_8$ triplet exciton is far more likely to find a BMN site than it is to find a second $C_{10}H_8$ exciton to annihilate with. If, however, the guest concentration is lowered to 0.20 mole fraction, then the trapping time slows to a level which allows homofusion to begin contributing to the decay kinetics.

We have also shown that our kinetic analysis of the delayed fluorescence intensity is only applicable when the laser has been turned off. The laser not only generates excitons but induces exciton detrapping from the BMN sites. We attribute this phenomenon to triplet–triplet absorption. The excitons are presumably able to move from a trap site to the guest quasilattice while the exciton is in the highly excited upper triplet state.

Triplet–triplet absorption is very efficient at detrapping excitons; therefore the motion of the highly excited exciton away from the trap must be equally efficient. We have also shown that the same is true for singlet excitons which are generated by triplet exciton heterofusion. For the case of a $C_g \simeq 1.0$ crystal, we showed that 97% of the singlet excitons are able to move away from the initial BMN site of annihilation. As with optical detrapping, the highly excited annihilation-produced singlet exciton must move far enough in distance so as not to be rapidly retrapped at the BMN site. We have also shown that this probability for moving away from the trap site is substantially reduced when one lowers the guest concentration from $C_g \simeq 1.0$ to $C_g = 0.3$–0.7 mole fraction. We have interpreted this result as being due to cluster confinement of singlet excitons in mixed crystals at 1.8 K.

We have shown that the question of triplet exciton transport in isotopically mixed naphthalene crystals is a complex problem. It is this wealth of dynamical processes and considerations that generates continuing interest in studying energy transfer in molecular crystals. Hopefully what we learn about exciton dynamics in these crystals will help provide insight into transport phenomena in more complex disordered media.

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[1] R. Kopelman, in *Modern Problems in Solid State Physics, Vol. 4: Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, edited by V. M. Agranovich and R. M. Hochstrasser (North–Holland, Amsterdam, 1983), p. 139.

[2a] V. Ern, J. Chem. Phys. **56**, 6259 (1972).

[2b] H. Port and H. C. Wolf, Z. Naturforsch. Teil A **30**, 1290 (1975).

[3] K. von Burg, L. Altwegg, and I. Zschokke-Gränacher, Phys. Rev. B **22**, 2037 (1980).

[4] S. D. Colson, S. M. George, T. Keyes, and V. Vaida, J. Chem. Phys. **67**, 4941 (1977).

[5] D.C. Ahlgren and R. Kopelman, J. Chem. Phys. **70**, 3133 (1979).

[6] P. W. Klymko and R. Kopelman, J. Phys. Chem. **86**, 3686 (1982).

[7] P. W. Klymko, Doctoral dissertation, The University of Michigan, 1984.

[8] G. C. Smith, Phys. Rev. **166**, 839 (1968).

[9] H. Port and H. C. Wolf, Z. Naturforsch. Teil A **23**, 315 (1968).
[10] H. Asami, T. Nakayama, T. Chong, and N. Itoh, Phys. Status Solidi B **88**, 623 (1978).
[11] F. W. Ochs, Doctoral dissertation, The University of Michigan, 1974.
[12] K. W. Benz, Doctoral dissertation, The University of Stüttgart, 1970.
[13] S. T. Gentry, Doctoral dissertation, The University of Michigan, 1983.
[14] S. T. Gentry and R. Kopelman, **81**, 3022 (1984).
[15] A. Blumen and R. Silbey, J. Chem. Phys. **70**, 3707 (1979).
[16] R. F. Loring, H. C. Andersen, and M. D. Fayer, J. Chem. Phys. **76**, 2015 (1982); **77**, 1079 (1982).
[17] R. Kopelman, in *Excited States, Vol. II*, edited by E. C. Lim (Academic, New York, 1975), p. 33.
[18] R. Kopelman, in *Topics in Applied Physics, Vol. 15: Radiationless Processes in Molecules and Condensed Phases*, edited by F. K. Fong (Springer, Berlin, 1976), p. 297.
[19] A. H. Francis and R. Kopelman, in *Topics in Applied Physics, Vol. 49: Laser Spectroscopy of Solids*, edited by W. M. Yen and P. M. Selzer (Springer, Berlin, 1981), p. 241.
[20] R. Kopelman, E. M. Monberg, and F. W. Ochs, Chem. Phys. **21**, 373 (1977).
[21] S. T. Gentry and R. Kopelman, J. Chem. Phys. **78**, 373 (1983).
[22] D. M. Hanson and G. W. Robinson, J. Chem. Phys. **43**, 4174 (1965).
[23] A. Suna, Phys. Rev. B **1**, 1716 (1970).
[24] P. Argyrakis, D. Hooper, and R. Kopelman, J. Phys. Chem. **87**, 1467 (1983).
[25] R. C. Powell, J. Chem. Phys. **58**, 920 (1973).
[26] G. Zumofen and A. Blumen, J. Chem. Phys. **76**, 3713 (1982).
[27] P. Argyrakis and R. Kopelman, Chem. Phys. **78**, 251 (1983).
[28] G. Zumofen and A. Blumen, Chem. Phys. Lett. **88**, 63 (1982).
[29] V. M. Kenkre and D. Schmid, Chem. Phys. Lett. **94**, 603 (1983).
[30] R. C. Johnson and R. E. Merrifield, Phys. Rev. B **1**, 896 (1970).
[31] P. R. Groff, R. E. Merrifield, and P. Avakian, Chem. Phys. Lett. **5**, 168 (1970).
[32] M. Chabr and I. Zschokke-Gränacher, J. Chem. Phys. **64**, 3903 (1976).
[33] V. L. Ermolaev, E. B. Sveshnikova, and E. A. Saenko, Opt. Spectrosc. **22**, 86 (1967).
[34] G. Karamos, T. Kole, P. Scribe, J. C. Dalton, and N. J. Turro, J. Am. Chem. Soc. **93**, 1032 (1971).
[35] R. Li and E. C. Lim, J. Chem. Phys. **57**, 605 (1972).
[36] M. Higuchi, T. Nakayama, and N. Itoh, J. Phys. Soc. Jpn. **40**, 250 (1976).
[37] A. Shirakawa, H. Asami, T. Nakayama, T. Chong, and N. Itoh, Solid State Commun. **28**, 625 (1978).
[38] R. A. Keller, Chem. Phys. Lett. **3**, 27 (1969).
[39] Ph. Pee, J. P. Lemaistre, F. Dupuy, R. Brown, J. Megel, and Ph. Kottis, Chem. Phys. **64**, 389 (1982).
[40] J. Heber and H. Murmann, J. Lumin. **12/13**, 769 (1976).
[41] S. J. Hunter, H. Parker, and A. H. Francis, J. Chem. Phys. **61**, 1390 (1974).
[42] J. B. W. Morsink and D. A. Wiersma, J. Chem. Phys. **74**, 4734 (1981).
[43] S. T. Gentry and R. Kopelman, J. Phys. Chem. (in press).
[44] J. Klafter and J. Jortner, Chem. Phys. Lett. **65**, 100 (1979).
[45] C. M. Soukoulis, J. Klafter, and E. N. Economou, Solid State Commun. **44**, 833 (1982).