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Investigation of the appropriateness of sensitized luminescence to determine exciton motion parameters in pure molecular crystals

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A wealth of experimental data has been collected over the years regarding the sensitized luminescence of molecular crystals. Indeed, such observations have played a primary role in attempts to characterize the dynamical aspects of exciton transport in these materials. Nonetheless, as has been noted previously, serious questions of interpretation remain concerning the relationship between primary experimental observables and microscopic parameters which govern exciton transport and capture. In the past these questions have led to an uncertainty, not always acknowledged, in the values of exciton diffusion constants reported in the literature. On the other hand, careful analysis of some recent experiments suggests that this uncertainty is much larger than is commonly assumed, and calls into question the utility of sensitized luminescence experiments as a quantitative probe of exciton transport. In this paper we carefully review these questions and show how they arise in a quantitative analysis of time-dependent sensitized luminescence in naphthalene, anthracene, and 1,2,4,5-tetrachlorobenzene crystals. This work, in conjunction with similar analyses of exciton-annihilation and transient-grating experiments, leads us to conclude that sensitized luminescence in its present form is useful as a probe of the capture process but not of exciton motion in pure crystals unless it is aided by independent additional experiments. We propose and discuss such experiments which might assist in disentangling effects arising from the capture process from those associated with exciton motion.

I. INTRODUCTION

Exciton motion in molecular crystals has been investigated very actively on the experimental[1–10] as well as the theoretical[9–15] front. It is remarkable, however, that, despite a quarter century of intense work, several basic questions have remained unanswered. One of these questions concerns the magnitude of the most elementary transport parameter of the exciton, viz., the diffusion constant. Thus, for anthracene, which is perhaps the most thoroughly studied crystal in this context, reported values of the singlet exciton diffusion constant at even the most convenient temperature, viz., room temperature, exhibit a disparity of 2—3 *orders of magnitude.*[2,16–19] The experiments most often used to deduce the diffusion constant D are based on sensitized luminescence, i.e., on the trapping of excitons moving in the host crystal by guest molecules introduced for the purpose. The common phenomenological equation used to address the experiment,

$$\frac{dn}{dt}+\frac{n}{\tau}=-kn\ , \tag{1.1}$$

describes the evolution of the host-exciton density n, τ being the host lifetime and k the energy-transfer rate. The latter is the main observable in such experiments and is normally used to deduce D through the application of the so-called Smoluchowski prescription,[1,2,20] which, in the present context, takes the form[21,22]

$$k=4\pi R_c D(\rho/v)\ . \tag{1.2}$$

Here R_c is a "trapping" radius taken usually to be of the order of the lattice constant, and the factor in the parentheses is the ratio of ρ, the mole-per-mole (dimensionless) concentration of the traps, i.e., the impurity molecules, to v, the volume per molecule of the host crystal.[23] Extensive information has been thus accumulated[1,2,4,8–10] and models have been proposed for the microscopic sources of the temperature dependence of the observations.[1,2,9,14] It should be obvious, however, that generally two *distinct* quantities govern the total rate of exciton trapping, viz., the rate at which excitons migrate into the regions occupied by trap molecules, presumably governed by D or a similar motion quantity; and the rate at which excitation decays to the trap states from neighboring host molecules once it enters the "sphere of influence" of the traps, with which process one may associate a capture rate c. Therefore, unless independent information about c is available, it is not possible to deduce more than lower bounds for D from such experiments since these experiments generally determine the single quantity k. While

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this fact has been recognized in the literature,[2] the assumption of infinite c has almost always been made in the interpretation of experiment as well as in the development of theory. This assumption is clearly a possible reason for the orders-of-magnitude disparity that one encounters in the reported values of the singlet diffusion constant.

If the capture rate c were much larger than the relevant motion rate, exciton trapping would indeed be motion-limited and the above assumption would be valid. For a long time there has been no evidence against such an assumption other than the above-discussed disparity in reported values of D. However, two recent investigations[21,24] point strongly to such evidence and suggest that the actual state of affairs might be exactly the opposite: that the observed k might be capture-limited and that therefore microscopic theories which have been constructed on the basis of the assumption that the trapping is motion-limited might have little to do with the observations.

The first is a recent reinterpretation[21] of energy-transfer and annihilation data which leads one to conclude that, if the usual assumption of short-range capture and annihilation is made, the energy-transfer rate in anthracene is *capture-limited* at least at temperatures higher than 60 K; and that, in any case, it is by no means clear that the trapping process is motion-limited. The second is a recent transient-grating experiment[24] in which the diffusion constant of singlets in anthracene is reported to be so much larger than what would be deduced from the "Smoluchowski prescription" applied to the energy-transfer data[8] that the latter must be associated *completely* with a capture process, if one is to accept the grating result. We present below a brief description of these two observations which suggest strongly that exciton-trapping experiments in pure aromatic hydrocarbon crystals such as anthracene are probably *not* motion-limited.

Along with sensitized-luminescence observations, experiments have been performed on the mutual annihilation of excitons.[1,2,9,10] They have been interpreted with the help of an equation analogous to (1.1), viz.,

$$\frac{dn}{dt}+\frac{n}{\tau}=-\gamma n^2\ , \tag{1.3}$$

wherein γ is the annihilation constant also given by the Smoluchowski prescription[25]

$$\gamma=8\pi R_d D\ , \tag{1.4}$$

where R_d, the destruction radius within which mutual annihilation of excitons occurs, is usually taken to be identical to the lattice constant as in the case of the trapping radius R_c. Such observations have also been used to deduce values of the diffusion constant through the assumed proportionality of the observed γ to D. Under the usual assumption that R_c and R_d are both equal to the lattice constant, (1.2) and (1.4) show that γ and k are proportional to each other and must possess the same temperature dependence. However, Kenkre and Schmid[21] pointed out that the reported temperature dependence of γ and k was drastically different in anthracene as well as in naphthalene. They based their resolution of this apparent paradox and their related investigation on the simple general result

$$\frac{1}{k'}=\frac{1}{M}+\frac{1}{c}\ , \tag{1.5}$$

$$\frac{1}{\gamma'}=\frac{1}{M}+\frac{1}{d}\ , \tag{1.6}$$

where $k'=k/\rho$ and is the reciprocal of the total trapping time, $\gamma'=\gamma/v$, and is the reciprocal of the total annihilation time, $1/M$ is the motion time which can be defined[12] directly in terms of exciton-motion parameters such as D, c is the capture rate, and d is a destruction rate which, similarly to c, describes the mutual destruction process two annihilating excitons would undergo after they are within each other's influence. When c and d are large with respect to M, their reciprocals may be neglected in (1.5) and (1.6). One then obtains generalizations of (1.2) and (1.4) which reduce to the latter[12,26] for three-dimensional incoherent motion. The result (1.5) and (1.6) is valid for arbitrary degree of transport coherence and dimensionality, but for capture and destruction processes which are short-ranged in character. With this latter assumption, which is almost universally made, the analysis of Ref. 21 shows that, in anthracene, the observed $1/k'$ for $T>60$ K is so much larger than $1/\gamma$, that $1/M'$, which is bounded above by $1/\gamma'$, is negligible compared to $1/c$. Thus under the (standard) short-range assumption the observations show that, at least for $T>60$ K, sensitized luminescence in anthracene must be deduced to be capture-limited.

The analysis of Ref. 21 suggests that the exciton diffusion constant is quite different and larger than that obtained by the application of the usual prescription (1.2) to the sensitized-luminescence observations of Braun *et al.*[8] and gives the result of (1.4) as the lower bound for D. The recent transient-grating experiment of Rose *et al.*[24] not only supports these conclusions, but shows that the value of D is about 2 orders of magnitude larger than that which would be obtained through (1.2) and the sensitized-luminescence observations. The transient-grating observations[24] employ no traps and their interpretation is therefore free of the problem of disentangling the interplay of trapping and motion. They lead to D through the relation

$$D=\frac{\delta^2}{8\pi^2}\left[K-\frac{2}{\tau}\right]\ , \tag{1.7}$$

where δ is the fringe spacing of the transient grating, K is the observed exponent of the signal decay, and τ is the lifetime. The results of Ref. 24 show that D varies from 10 ± 2 cm^2/s at 1.8 K to 0.8 ± 0.2 cm^2/s at 20 K. By contrast, the application of (1.2) to Ref. 8 would result in a D that varies from 6×10^{-3} cm^2/s at 4 K to 1×10^{-3} cm^2/s at 300 K.

Clearly, the measurement of the diffusion constant involves the measurement of an appropriate transport length of the exciton, such as the diffusion length, and is possible only if the relevant characteristic length of the experimental probe is comparable to the exciton-transport length. The probe length in the transient-grating experiments of Ref. 24 is the fringe spacing and is of the order of several micrometers, whereas in the sensitized-luminescence experiments of Refs. 1, 2, 4, and 8, it is the average intertrap distance and is more than 2 orders of magnitude smaller. It is obviously impossible that both experimental techniques are able to measure the exciton-transport length since their characteristic lengths are so widely disparate. The large difference in the values of D obtained from the two experiments signals the existence of an artifact in at least one of them. We have seen above that there is evidence of a conceptual artifact in the interpretation of the sensitized-luminescence observations. It is natural, therefore, to tend to regard sensitized-luminescence observations in anthracene as reflecting only features of the capture process and none of exciton motion. Thus, the two investigations in Refs. 21 and 24 cast significant doubt both on the traditional premise that sensitized luminescence in aromatic hydrocarbon crystals such as anthracene are motion-limited, and on the compilations of exciton diffusion constants that have used that premise as their basis.

II. TIME-RESOLVED OBSERVATIONS AND TIME-DEPENDENT RATES

It should be clear from the discussion presented above that the ambiguity in the interpretation of sensitized-luminescence observations arises from *two* unknowns (for instance, D and c) making their contribution to *one* observed quantity (the energy-transfer rate k). While steady-state observations result in a single quantity such as k or the yield, time-resolved experiments provide a number of different values of the luminescence intensity, which, if it is nonexponential, would correspond to a number of different values of k. One might therefore hope that time-resolved experiments could be of help in removing the ambiguity in interpretation. For this reason, as well as for improved experimentation, time-resolved spectroscopy[27] has been introduced into this field and developed into a standard and reliable technqiue.[2,4,8,27–30] The possibility that time-resolved energy-transfer experiments in pure molecular crystals might aid significantly in the understanding of exciton transport was reinforced when some of the early time-resolved experiments on anthracene yielded apparently pronounced deviations of the luminescence intensity from exponentiality, i.e., a *time-dependent* energy-transfer rate.[2,27,29] The hope of obtaining a number of different values of $k(t)$ for the same D and c appeared to be realized. Several theoretical investigations of time-dependent rates were carried out, some of which were based on the Smoluchowski coagulation analysis,[2] and some on momentum-space evolution of excitons.[12,31] There was little agreement[12] in the various interpretations.

The activity concentrated on time-dependent energy-transfer rates in pure molecular crystals has been brought to a stop by the most recent experimental results,[4,8] which establish that, at least in anthracene pure crystals, the energy-transfer rate displays no time dependence. This is in agreement with some of the early observations.[28,30] These recent experiments have also identified the sources of some of the earlier reported time dependences and it appears, therefore, that one must conclude the latter to be an experimental artifact.

There are two important consequences of these recent findings. One is that we must conclude that time-resolved spectroscopy fails to be of assistance in disentangling the effects of capture and motion in sensitized-luminescence observables along the lines discussed at the beginning of this section. The second is that we must produce a satisfactory explanation of the observed *lack* of time dependence in the energy-transfer rate. It is trivial to show with the help of simple models, or from general considerations, that the energy-transfer rate generally does possess time dependence even for diffusive or incoherent exciton motion.[12] There are two simple explanations that can be given to show that this time dependence may be indiscernible in experiment on some systems. One of them is that the capture process may be long-ranged in character, contrary to standard assumptions. The other[12] is that, even with short-ranged capture, the motion might be so fast that its details disappear from sensitized-luminescence observations. This latter explanation can be presented in terms of the general result

$$\tilde{n}(\epsilon)=\frac{1}{\epsilon'}\left[1-\frac{\rho/\epsilon'}{(1/c)+\tilde{\nu}(\epsilon')}\right] \tag{2.1}$$

for the Laplace transform of the host intensity n, where ϵ is the Laplace variable conjugate to time, $\epsilon'=\epsilon+1/\tau$, tildes denote Laplace transforms, and the ν function contains information regarding exciton motion, being equal to the exciton self-propagator $\psi_0(t)$ for small trap concentrations. By rewriting (2.1) in terms of an "energy-transfer memory" k_m,

$$\tilde{n}(\epsilon)=\frac{n(0)}{\epsilon'+\tilde{k}_m(\epsilon')}\ , \tag{2.2}$$

one may argue[12] that, for sufficiently fast motion, $k_m(t)$ becomes a δ function in time and (2.2) gives the observed exponential time dependence

$$n(t)=n(0)e^{-t(k^s+1/\tau)}\ , \tag{2.3}$$

where

$$k^s=\tilde{k}_m(1/\tau)=\int_0^\infty dt\, k_m(t)e^{-t/\tau}$$

is the steady-state energy-transfer rate. The energy-transfer memory k_m in the Laplace domain, and the steady-state rate k^s, are given, respectively, by[12,32]

$$\tilde{k}_m(\epsilon)=\frac{\rho}{(1/c)+(1/\epsilon)[\epsilon\tilde{\nu}(\epsilon)-\rho]}\ , \tag{2.4}$$

$$k^s=\frac{\rho}{(1/c)+[\tilde{\nu}(1/\tau)-\rho\tau]}\ . \tag{2.5}$$

The above two explanations, based in one case on long-range capture and in the other on fast motion, both lead to the conclusion that the observations are capture-controlled. While that may indeed be the case, there is a third possibility which would result in practically time-independent rates *even* when the observations are motion-controlled. Detailed study[33] shows that for the systems examined, the deviations from exponential behavior are negligible for motion which is effectively two dimensional or three dimensional. As has been shown elsewhere,[34,35] (2.1) can be used along with calculations of $\nu(t)$, and, equivalently, of the exciton self-propagator $\psi_0(t)$, to obtain the host luminescence intensity $n(t)$ in the time domain with the help of numerical Laplace inversions[35] of (2.1). Thus, for two-dimensional incoherent motion via nearest-neighbor transfer rates, and for low trap concentrations as in the experiments under consideration,

$$\nu(t)\approx\psi_0(t)=e^{-4Dt/a^2}I_0^2(2Dt/a^2)\ , \tag{2.6}$$

where a is the nearest-neighbor distance. Substitution of (2.6), or of the complete expression for $\nu(t)$ valid for arbitrary trap concentrations,[35] in (2.1), followed by a Laplace inversion, produces Fig. 1(a) for parameters consonant with data in Ref. 8 1(a). The solid curve represents the extreme capture limit in which the motion is so fast as to make $\epsilon\tilde{\nu}(\epsilon)-\rho$ in the denominator of (2.4) negligible with respect to the capture time $1/c$. Then $k_m(t)$ and k^s equal $\rho c\delta(t)$ and ρc, respectively, and the host intensity $n(t)$ is an exponential as in (2.3). The dashed curve, on the other hand, represents the opposite extreme limit in which the capture rate is so large that $1/c$ effectively vanishes. The motion parameters are chosen so that the average rate of energy transfer is the same as that of the solid curve. Any system possessing motion and capture rates intermediate between these two limits, but having the same average rate of transfer, will lie between the two curves shown. Included for comparison over the same timescale we reproduce in Fig. 1(b) data collected in the experiments of Braun *et al.*[8] on singlet exciton energy transfer in tetracene-doped anthracene.

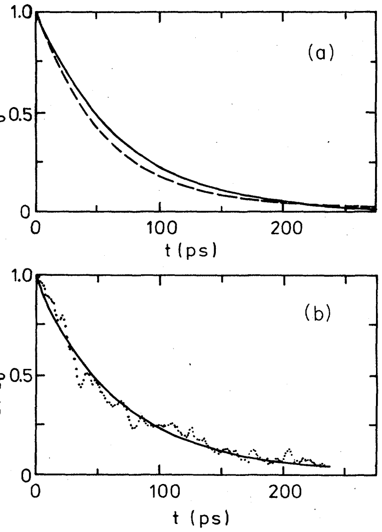

FIG. 1. Time dependence of the normalized host fluorescence in tetracene-doped anthracene. (a) Theoretical curves obtained from Eq. (1.5) for the capture-limited case (solid line), which is an exponential, and for the motion-limited case (dashed line), which shows the maximum possible deviation from the exponential consistent with the same *average* rate of decay as in the capture-limited case. The motion is assumed to be two dimensional, incoherent, and with nearest-neighbor transfer. (b) Experimentally observed decay curve from Ref. 8 (dotted curve) and an exponential fit (solid line) with a decay time of 70 ps. Parameters are $\rho=2.3\times10^{-3}$ mole/mole and $T=1.6$ K. Comparison of (a) and (b) shows that the motion-limited and capture-limited extremes (as well as all intermediate cases) lie within the scatter in the data and cannot be distinguished experimentally.

Inspection of Fig. 1(a) shows that under considerations appropriate to experiment, the extreme limits of motion-controlled and capture-controlled trapping differ very little from one another as far as the observable (host luminescence intensity) is concerned. Furthermore, a comparison with Fig. 1(b) shows that the differences lie well within the normal scatter in the data. The differences are even smaller for three-dimensional motion. Thus, as long as the effective motion is two or three dimensional (as is typical of *singlet* motion in molecular crystals), it is practically impossible to distinguish between capture-limited and motion-limited trapping from the time dependence in the first few decades of the luminescence decay. One must therefore conclude that, for such higher-dimensional systems exhibiting no discernible time dependence, there is no quantitative information contained in the time-dependent data that is not already contained in steady-state observables. Furthermore, for these systems, one must return to conclusions similar to those drawn earlier[21] that sensitized-luminescence experiments, time resolved or not, give us *only lower bounds* on the motion parameters such as the diffusion constant D. These bounds are determined by the lowest value of D consistent with maintaining the same average rate of transfer, and are implicitly expressed in the relation

$$[\tilde{\nu}(1/\tau)-\rho\tau]^{-1}\geq k^s/\rho\ , \tag{2.7}$$

which follows from (2.5). For the small trap concentrations that occur in the system studied, (2.7) reduces, for two-dimensional incoherent motion with nearest-neighbor transfer rates F, to

$$4\pi F[\ln(32F\tau)]^{-1}\geq k^s/\rho\ . \tag{2.8}$$

Equation (2.8) is obtained with the help of results explained elsewhere.[35] While it is true that singlets do not move via nearest-neighbor transfer interactions, the use of (2.7) and (2.8) and the resultant bounds should be of value in order-of-magnitude estimates of the limits of transport parameters. Bounds of this sort were presented[36] in Refs. 21 and 37 for several systems. We present a more detailed compilation in Table I. It should be noted that the value of F for anthracene given in Table I is about twice the value quoted in Ref. 37. The reason for this apparent discrepancy is the fact that in Ref. 37 only information obtained from energy-transfer experiments were used, whereas in Table I the information obtained from annihilation experiments[8] was also taken into account.

At least a part of the problem associated with the systems we have discussed stems from the recognized fact that deviations from exponentiality become less pronounced as the dimensionality increases. As a result of the strong anisotropy prevalent in the interaction matrix elements, the nature of transport in some molecular crystals is effectively one dimensional. Triplet exciton motion in 1,2,4,5-tetrachlorobenzene (TCB) is a case in point.[39] It

TABLE I. Bounds for the transfer rate ("hopping rate") F and the diffusion constant D obtained from various experiments assuming two-dimensional incoherent short-range exciton motion.

Host	Guest	Type	Temperature (K)	F (10^{12} s^{-1})	D (10^{-2} cm^2/s)
anthracene[a]	tetracene	singlet	5—300	>56	>15
naphthalene[b]	anthracene	singlet	4	>3.9	>1
naphthalene[b]	anthracene	singlet	300	>0.21	>0.054
p-terphenyl[c]	tetracene	singlet	80	>1.5	>0.36
p-terphenyl[c]	tetracene	singlet	250	>9	>2.2
tetracene[d]	pentacene	singlet	170	>33	>8.2
naphthalene[e]	β-methyl-naphthalene	triplet	6	>0.016	>0.004
naphthalene[e]	β-methyl-naphthalene	triplet	16	>0.0076	>0.002

[a] Reference 8.
[b] Reference 29.
[c] Reference 7.
[d] Reference 28.
[e] Reference 38.

is to be expected, therefore, that nonexponential behavior in the luminescence intensity, equivalently a time-dependent k, might arise in this system and lead to the resolution of the ambiguities discussed in the beginning of this section. Indeed, Parris and Kenkre[40] found that if the motion were *known* to be diffusive, the phosphorescence data[41] on triplet motion in TCB would be compatible with largely motion-limited trapping. Thus, under the assumption of incoherent motion, it is indeed conceivable that one could determine transport information in one-dimensional systems from an analysis of the time dependence of the energy-transfer rate. However, in the case of TCB a new problem appears. Spin-echo experiments have recently been used[42,43] to conclude that triplet motion in TCB at low temperatures is not diffusive at all, but coherent over large distances. The analysis in Ref. 40 indicates that, if one accepts the degree of coherence obtained in the spin-echo work,[42] one is forced to conclude that the energy-transfer data[41] are capture-limited. In Fig. 2 we show fits[40] based upon these respective assumptions to the time-resolved X-trap emission in TCB from Ref. 41. The solid curve is a fit based on the value of the scattering rate (or degree of coherence) given by the spin-echo work,[42] but with the capture rate c varied. The best-fit value of c is 6×10^{3} s^{-1}. The dashed curve is based on incoherent transport (infinite scattering rate) and infinite capture rate c, but with the hopping rate F varied. The best-fit value of F is 3.3×10^{10} s^{-1}. From these one-parameter fits it is obvious that coherent motion as envisaged in Ref. 42 is as capable of explaining the luminescence data as incoherent motion. Furthermore, in the former case the trapping process is seen to be capture-limited as had been suggested earlier for TCB.[44] When two-parameter fitting is attempted by varying both the scattering rate and the capture rate c, it is found[40] that the best fit gives the scattering rate to be 9×10^{8} s^{-1} and c to be 10^{7} s^{-1}. This would lead one to conclude that the motion is considerably more incoherent than predicted by the spin-echo results, but not so slow as to be entirely capture-limited. Thus, even in this one-dimensional system, time-resolved sensitized-luminescence experiments do not lead to a unique picture of exciton motion because of the additional problem of the uncertainty in the degree of coherence. It is not possible, on the basis of the sensitized-luminescence experiments alone, to distinguish between capture and motion as the limiting process, nor between coherent or incoherent transport in this system. Also, we emphasize that, if the degree of coherence in triplet motion in TCB is assumed to be as given by the spin-echo work,[42,43] the results of Ref. 40 indicate that in TCB we have another example of capture-limited sensitized luminescence.[45]

We thus see that time-resolved observations of sensitized luminescence fail to disentangle effects of capture from those of exciton motion for two different reasons in

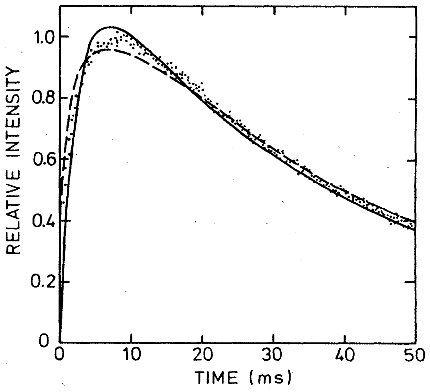

FIG. 2. Time dependence of the normalized X-trap phosphorescence in undoped TCB at 1.25 K from Ref. 41 along with theoretical fits. The solid curve corresponds to largely coherent motion (scattering rate $\alpha=3\times10^{5}$ s^{-1}) as suggested by the spin-echo experiments of Ref. 42, and represents the capture-limited case (resultant capture rate $c=6\times10^{3}$ s^{-1}). The dashed curve corresponds to completely incoherent motion with infinite capture rate ($c=\infty$), and represents the motion-limited case (resultant transfer rate $F=3.3\times10^{10}$ s^{-1}). Comparison with the data shows that the two extreme limits cannot be distinguished experimentally.

the systems studied. In the case of singlet motion in crystals such as anthracene, the high-dimensionality effect masks the time dependence of the energy-transfer rate. In the case of triplet motion in crystals such as TCB, where the motion is effectively one dimensional, the coherence question prevents the disentangling of capture and motion. In all cases the observations are compatible with an interpretation based on the *capture*-controlled limit.

III. DISCUSSION AND SUGGESTED EXPERIMENTS

The analysis presented in the preceding sections leads to the inescapable conclusion that sensitized-luminescence experiments of the usual variety are, as a result of the general lack of information available regarding the capture process, incapable of extracting the magnitude of exciton motion in pure[46] molecular crystals. Thus, in order to obtain information concerning exciton transport other experimental methods which by-pass the capture process are necessary. We discuss briefly several such methods: the spin-echo technique, the method of Ronchi rulings, the transient-grating technique, sensitized luminescence with surface quenching, and sensitized luminescence in which the initial placement of excitons is varied.

The spin-echo technique, perfected by Schmidt and collaborators,[42,43] relies on creating and probing a coherent spin state via the application of a sequence of coherent pulses and leads to a direct measurement of the Boltzmannization, i.e., of the redistribution of exciton population to a thermal state, within the band of exciton (momentum) states of the crystal. Being spin-based, this technique can be employed for the investigation of the motion of triplets but not of singlets and has been so employed for TCB. It is hoped that a larger number of triplet systems will be studied with the help of this technique.

The method of Ronchi rulings, developed by Ern and collaborators,[47,48] consists of creating a periodic spatial inhomogeneity of triplet excitons in the crystal by illuminating it through a mask of alternating opaque and transparent strips and of monitoring the evolution of the spatial inhomogeneity by measuring the total time-dependent delayed fluorescence resulting from the mutual annihilation of the triplet excitons. The wide difference in the frequencies of the illumination and of the signal is one of the notable experimental virtues of this method. Since the signal is based on delayed fluorescence, this method is also restricted to triplets. It has been used for a variety of triplet systems but only for temperatures larger than 100 K. This method is excellently suited to the investigation not only of the magnitude of triplet exciton motion but also—and particularly—of the degree of coherence. The basic theory and predictions have been given by Kenkre *et al.*,[49] and coherence parameters for the systems already studied ($T > 100$ K) have been extracted by Kenkre and Schmid.[50] It is hoped that this method will be used for low-temperature triplet systems including those, such as TCB, which have been studied by other methods such as the spin-echo technique.

The transient-grating method of Fayer and collaborators[6,24] is similar to the Ronchi ruling method[47,48] in that the time evolution of a periodic spatial inhomogeneity of excitons is monitored in order to study exciton motion. However, the experimental procedure and the systems to which it can be applied are quite different. This is a picosecond technique in which two time-coincident laser beams are crossed at a definite but variable angle. A sinusoidal spatial inhomogeneity is created as a result of interference in the crystal and its evolution is studied via the diffraction of a probe laser beam from the exciton grating. This method is useful for the study of singlets but not for triplets and the only pure crystal studied so far is anthracene at low temperatures. The method is especially suited to the study of coherence in singlet exciton motion.

The basic theory has been given by Kenkre *et al.*[12,15,50,51] (see also Fayer,[6] and Garrity and Skinner[52]). Explicit extraction of the mean free path and degree of coherence has been given in Ref. 50, where it was shown on the basis of the reported observations of Rose *et al.*[24] that singlet excitons in pure anthracene appear to have mean free paths larger than 1700 intersite distances at 1.8 K and 100 intersite distances at 20 K. Clear manifestations of coherence such as oscillations have been shown to be expected for fringe spacings as large as 1 μm (at 1.8 K) and explicit predicted signals have been provided. We believe that it is very important to carry out such transient-grating experiments in other aromatic hydrocarbon crystals such as naphthalene and produce a new compilation of exciton diffusion constants for the various systems.

We have seen in Sec. II that the effectively two- or three-dimensional nature of singlet exciton motion defeats the idea of using time-resolved spectroscopy to separate capture effects from motion effects. Surface-quenched sensitized-luminescence experiments pioneered by Simpson,[16] and performed also by Gallus and Wolf,[53] Kurik,[17] and Tomura and Takahashi[18] could be of help in this regard, particularly when extended with time-resolved techniques. Such experiments probe motion along one dimension only, i.e., they represent an *effectively* one-dimensional trapping problem, even when the exciton migration is of higher dimensionality. The problems mentioned earlier associated with higher-dimensional systems might thus be avoided. Another desirable feature of these experiments is the introduction of a well-defined relationship between the initial exciton position and the trap. This eliminates the averages associated with the random trap placement which can tend to obscure information about the exciton motion. Theoretical considerations for surface-quenching observations have been given by Kenkre and Wong[19] in the steady-state case and by Parris and Kenkre[54] in the time-resolved domain. To our knowledge no attempts have yet been made to perform such experiments with time-resolved methods. Admittedly, such experiments are extremely difficult to carry out and to interpret. Prominent among the reasons for the difficulty is the fact that the sample thickness must be comparable to the exciton-transport length, and therefore small enough to introduce undesirable effects of surface defects and trap states in a pronounced fashion. These effects could well mask the intrinsic transport properties of the crystal.

As another proposed candidate for experiments which might by-pass the capture problem, we suggest one wherein *bulk* sensitized luminescence is involved but the initial placement of the excitons within the host crystal is varied. A closely related experiment was proposed in the surface-quenching context in Ref. 55, where it was suggested that the measurement of the quantum yield in the Simpson geometry for different wavelengths of the exciting light—consequently, different penetration lengths of the excitons into the crystal—might allow one to determine the exciton diffusion constant even in the absence of information about the capture process. In order to understand our proposal in the bulk-quenching context, it is necessary to begin with a result from the general theory of sensitized luminescence,[12,35] viz.,

$$\phi_G=\frac{\sum_r{}'\tilde{\eta}_r(1/\tau)}{(1/c)+\tilde{\nu}(1/\tau)}\ . \tag{3.1}$$

There ϕ_G is the quantum yield of the impurities (i.e., traps), the ν function is given, as usual,[32,35] by the sum of exciton propagators in the trap-influenced region, and η_r is the exciton occupation probability at site r, *in the absence* of traps. The primed summation goes only over the sites r which are trap-influenced, i.e., which feed the traps via the capture rate c. The details of the derivation of (3.1) are not necessary here. Suffice it to point out the essential physical meaning of (3.1). The numerator of the right-hand side of (3.1), i.e., the primed sum, describes the time spent by the exciton in the trap-influenced region (assuming the capture rate c were zero), during the exciton lifetime τ. This is so since the numerator can be written as the product of τ and the probability of occupation of that region, viz.,

$$(1/\tau)\int_0^\infty dt\, e^{-t/\tau}\sum_r{}'\eta_r(t)\ .$$

The denominator of (3.1) may be interpreted as the total trapping time composed of the sum of the capture time $1/c$ and the motion time

$$\int_0^\infty dt\, e^{-t/\tau}\nu(t)\ .$$

The general result (3.1) thus expresses the yield, quite naturally, as the product of the total trapping rate (the reciprocal of the total trapping time) and the average time the exciton would spend in the trap-influenced region (although in the absence of c).

The particular case of (3.1) for the usual bulk sensitized-luminescence situation,[1,2,4,7,8] wherein the initial exciton population is homogeneous over the entire crystal is the familiar

$$\phi_G^1=\frac{\rho\tau}{(1/c)+\tilde{\nu}(1/\tau)}\ , \tag{3.2}$$

which may also be obtained by replacing ϵ' by $1/\tau$ in (2.1). The numerator of (3.2) which, as in (3.1), is the average time spent by the exciton in the trap-influenced region is, in this case, simply the product of the lifetime τ and the probability that the homogeneously distributed exciton may find itself in the vicinity of a trap.

Consider now a situation wherein the exciton initially occupies only the trap-influenced host sites. In such a case the numerator in (3.1) equals $\tilde{\nu}(1/\tau)$ from the definition of the ν function,[35] and

$$\phi_G^2=\frac{\tilde{\nu}(1/\tau)}{(1/c)+\tilde{\nu}(1/\tau)}\ . \tag{3.3}$$

What is to be noted in (3.2) and (3.3) is that the denominator, i.e., the total trapping time, contains capture information but the numerators do not. Therefore, the *ratio* of the two yields, given by

$$\frac{\phi_G^1}{\phi_G^2}=\frac{\rho\tau}{\tilde{\nu}(1/\tau)}\ , \tag{3.4}$$

contains no contribution from the capture rate c! Therefore, the experiment we propose consists of measuring the yields ϕ'_G and ϕ_G^2 for the two different initial placements of the excitons for the same doped sample, and of extracting motion parameters directly from their ratio. Information about exciton motion is present in $\nu(1/\tau)$, which is given as[35]

$$\tilde{\nu}(1/\tau)=\rho\tau+(1-\rho)/M\ , \tag{3.5}$$

where

$$M\equiv\int_0^\infty dt\, e^{-t/\tau}\psi_0(t)$$

is the motion rate[12,21] of the exciton appearing in (1.5) and (1.6). Expressions for M are known[12] from calculations of the self-propagator. Equation (3.5) results in

$$\phi_G^2/\phi_G^1=1+(1-\rho)(M\rho\tau)^{-1}\approx 1+(M\rho\tau)^{-1} \tag{3.6}$$

for the yield ratio described in the suggested experiment. The approximate equality in (3.6) holds for a large number of sensitized-luminescence experiments on aromatic hydrocarbon crystals as a result of solubility restrictions since the mole-per-mole guest concentration ρ cannot exceed 10^{-4}. For such systems, using the additional fact that the condition $F\tau\gg 1$ is valid, and assuming for simplicity that the excitons execute simple incoherent motion via identical nearest-neighbor transfer rates F in mutually perpendicular directions, it is straightforward to obtain the particular results (1D denotes one dimensional, etc.)

$$\phi_G^2/\phi_G^1=1+(1/2\rho\tau)(\tau/F)^{1/2}\ \text{ for 1D}\ , \tag{3.7}$$

$$\phi_G^2/\phi_G^1=1+[\ln(32F\tau)/4\pi\rho F\tau]\ \text{ for 2D}\ , \tag{3.8}$$

$$\phi_G^2/\phi_G^1=1+(1/4\rho F\tau)\ \text{ for 3D}\ . \tag{3.9}$$

The measured ratio of the yields and known values of ρ and τ would thus allow one to deduce the value of the transfer rate F and thus the exciton diffusion constant *without* knowledge of capture parameters.

We suggest two different ways of realizing this experiment which might be feasible. One would be to excite X traps, which have been known for some time[56] to exist in the neighborhood of guest molecules, and whose absorption has also been observed recently.[57] This would require a light source with a narrow spectral bandwidth in addition to the condition that the overlap between the exciton and the X-trap absorption band be small, and would force one to confront serious problems arising from the wide disparity in the values of the absorption coefficient of the X trap and the host lattice—which differ typically by a factor of ρ, i.e., by about 10^{-6}. Another way would consist of exciting the guest molecules themselves selectively using a laser pulse and then promoting the excitation to the host molecules in the neighborhood of the guest by using heat pulses[58] (for triplet states) or a second laser pulse of appropriate wavelength (for singlets).

For the experiment to work, even in principle, it is necessary that $M\rho\tau$ is not too much larger than 1, so that the yields in the two different initial setups are different from each other. Furthermore, for the yields to be measurable under both setups their values should not be too disparate. This means that M and $\rho\tau$ should be of the order of each other. For experiments on anthracene[8] the concentration ρ lies between 10^{-4} and 10^{-6}, $\tau \approx 10^{-8}$ s, and traditional considerations along with quoted values of the diffusion constant of the order of 10^{-2} cm^2/s would indicate that M is of the order of 10^{13} s^{-1}. It would appear possible therefore to satisfy the condition $M\rho\tau \approx 1$, if the traditional estimate of the motion rate M ("hopping rate") were accurate. The lower bound for M obtained in Ref. 21 from the simultaneous consideration of energy transfer and annihilation is 4.2×10^{13} s^{-1}, with the consequence that one would be driven to the lowest possible value of the concentration, viz., 10^{-6}. In naphthalene, the corresponding bound[21] is 3×10^{12} s^{-1} at 4 K and 2×10^{11} s^{-1} at 300 K. Although M is lower for naphthalene, τ is larger by an order of magnitude and therefore one would still have to work at the lower limit of ρ. At 300 K these particular problems are alleviated for naphthalene since M could be smaller by another order of magnitude.[21] However, selective population of the guest-influenced region of the host necessary for the measurement of ϕ_G^2 presents nontrivial problems since, at 300 K, the absorption bands of X traps (which could be excited for the purposes of selective population) disappear in the wings of the absorption band of the host.

The actual realization of the suggested experiment may be quite difficult, therefore, at least for the systems discussed above. However, it is hoped that the essential idea behind the experiment, which is the elimination of the need for capture information by varying the initial spatial population of the excitons,[55] can be developed into a feasible observational scheme.

IV. CONCLUSION

This paper is the result of a series of theoretical attempts[12,15,19,21,31–35,37,40] to understand what information concerning exciton motion in pure molecular crystals may be extracted from sensitized-luminescence observations and related experiments such as annihilation. Heeding a very appropriate statement[2] that had been made in the literature that a dialogue between experimentalists and theorists was largely lacking in this field, a detailed effort was undertaken to develop the required exciton-transport theory with specific sensitized-luminescence experiments in mind and to apply it to those observations. The formal apparatus of generalized master equations[12,59] was recast[34,35,60] to calculate experimental observables such as the quantum yield, energy-transfer rate, and luminescence intensities rather than formal theoretical constructs such as the first passage time and the number of sites visited by a random walker. A theory was constructed to address surface-quenching observations and experiments were proposed which would focus on wavelength dependence or time resolution of the observables.[19,54,55] The generalized master-equation analysis of sensitized luminescence was extended to finite trap concentrations[32,35] and brought to the point[33,35,37] where explicit predictions for time-resolved observables could be made through a combination of analytical and numerical methods. However, even after a practical theoretical framework for addressing experiments was readied in this way, attempts to extract motion information failed repeatedly as a result of an inability to separate the effects of capture and motion from the observations. A comparison[21] of annihilation and sensitized-luminescence experiments on anthracene led to a strong indication that the sensitized-luminescence observations might be capture-limited. While that study was highly suggestive, it was based on the assumption that exciton capture and mutual destruction both occurred over a very short range. This assumption is, no doubt, the standard one, and is used almost universally in such contexts in the interpretation of experiment. However, it is possible, for instance, that annihilation in anthracene occurs via a long-range destruction process. In such a case, none of the conclusions in Ref. 21 would be applicable.[61] This would *not* mean that one would return to the previous belief that the sensitized-luminescence observations in anthracene are motion-limited. It would rather mean that no definite information could be extracted from those observations and that the situation was quite inconclusive.

The observed *lack* of time dependence in the energy-transfer rate was sometimes interpreted as signifying that exciton motion was diffusive. That such a conclusion cannot be drawn was pointed out[12] and it appeared that the absence of time dependence meant either very fast motion[12] or long-range capture.[61] These conclusions would reinforce the present tendency[4,10,21] towards considering sensitized luminescence for singlets in pure molecular crystals to be capture-controlled, and yet, a further throwback to the motion-controlled picture was the result of an explicit investigation[33,37] of the dimensionality effect on the time-dependent luminescence. We have reported the details of this investigation in Sec. II of the present paper. We see that, for the relevant experimental parameters, the departure from a time-independent energy-transfer rate would be practically indiscernible even in the case of *completely* motion-controlled trapping for systems which are effectively two dimensional or three dimensional. Although the curves in Fig. 1(a) were obtained under the assumption of nearest-neighbor transfer for calculational convenience, we believe that the essential conclusions would be unchanged under an analysis that would incorporate realistic dipole-dipole interactions responsible for singlet motion. Investigation of effectively one-dimensional systems also met with failure in the extraction of motion parameters[40] as a result of inadequate information concerning the transport coherence of the excitons.

The disentangling[62] of capture and motion from sensitized-luminescence observations is, thus, at least extremely difficult and perhaps practically impossible. We have suggested in Sec. III the idea of comparing observations under different initial conditions to extract motion information without prior knowledge concerning capture and have described the theory underlying the suggestion, but have noted that the actual experiments could well have insurmountable problems. We conclude this paper with three remarks. First, it should be clear by now that sensitized luminescence in pure molecular crystals has not demonstrated its usefulness for the investigation of exciton motion[46] and may well be inappropriate for that purpose in these systems. Second, the large body of data[1–4,7–10,27–30] collected over the past 25 years should be studied anew for the purpose of extracting the valuable information it contains about the *capture* process. Third, there is a pressing need at the moment to undertake a whole series of efforts along new experimental directions to deduce even the most basic information about transport quantities concerning excitons in molecular crystals.

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[45] It should go without saying that phosphorescence from X traps is certainly a case of sensitized luminescence even though the traps are not introduced as external guest molecules.

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