

## COMMENTS ON THE EXCITON ANNIHILATION CONSTANT AND THE ENERGY TRANSFER RATE IN NAPHTHALENE AND ANTHRACENE \*

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Observations of the annihilation constant and the energy transfer rate of singlet excitons in naphthalene and anthracene are analyzed in terms of a recent theoretical framework. Problems that arise in traditional interpretations of the temperature dependence are resolved. It is shown that in certain temperature ranges the observables contain little information about exciton motion. Lower bounds for motion rates and diffusion constants are obtained.

### 1. Introduction

A primary transport quantity of interest in energy transfer in molecular solids [1–3] is the diffusion constant of excitons. Among the experimental methods of arriving at the value of this quantity are sensitized luminescence [4–8] and the observations of exciton annihilation [4,7–11]. In the former, the crystal under investigation, called the host, is doped with another substance, the guest, and after selective illumination of the host or the guest, the quantum yield and/or luminescence intensities are observed. The usual procedure of interpreting these observations has consisted of first deducing the so-called "energy transfer rate"  $k$  and then obtaining from it the diffusion constant  $D$ . The observations of exciton annihilation are carried out on the host without any doping but with illumination intensities which are large enough to result in exciton densities high enough to

cause mutual annihilation of the excitons. The result shows up again in the quantum yield and the luminescence-intensities. The usual interpretation scheme in this kind of experiment consists of deducing the "annihilation constant"  $\gamma$  and then from it the diffusion constant  $D$ . The commonly used relations between the transport quantity  $D$  and the observables  $k$ ,  $\gamma$  lead to an apparent paradox in the light of available experimental data in aromatic hydrocarbon crystals. We provide a simple resolution of that paradox and comment on what information about exciton motion can be really extracted from those experiments. We use for this purpose a recently developed theory [12,13] of exciton trapping and annihilation.

The present note is laid out as follows. In section 2 we describe the usual theoretical schemes and the experimental observations and show that they lead to the apparent puzzle. We resolve the problem in section 3 and present in section 4 a discussion of what information can be obtained from these observations and of the source of the observed time-dependence of energy transfer rates.

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## 2. Statement of the problem

The expressions normally used to deduce the exciton diffusion constant  $D$  from measurables  $\gamma$  and  $k$  are:

$$\gamma = v\gamma' = 8\pi R_d D, \quad (1)$$

$$k = \rho v k' = 4\pi R_c D. \quad (2)$$

Here the annihilation constant  $\gamma$  and the transfer rate  $k$  are quantities appearing in the phenomenological equations

$$dn/dt = -n/\tau - \gamma n^2, \quad (3)$$

$$dn/dt = -n/\tau - kn, \quad (4)$$

which describe the evolution of the exciton density  $n$ . The first term on the right-hand sides of (3) or (4) describes exciton decay,  $\tau$  being the lifetime. The last term represents (mutual) annihilation in (3) and energy transfer in (4). In the latter equation  $n$  refers to the *host* exciton density. The other quantities in (1) and (2) are:  $v$ , the volume per molecule of the host crystal;  $\rho$ , the relative guest concentration, i.e. the ratio of the number of the guest molecules to that of the host molecules;  $R_d$ ,  $R_c$ , the radii of influence over which the elementary processes of mutual destruction and capture (respectively) occur. The quantities  $\gamma'$  and  $k'$  are rate constants measured e.g. in  $s^{-1}$ .

It is generally believed that expressions (1) and (2), and the corresponding kinetic schemes (3) and (4) follow from the coagulation analysis [14] of Smoluchowski and Chandrasekhar. They are used [4] extensively to deduce diffusion constants for excitons in molecular crystals through what are considered reasonable assumptions concerning  $R_d$  and  $R_c$ . Such ways of interpreting experimental data have sometimes led to rather alarming values of the diffusion constant for "reasonable" values of the  $R$  and vice versa. Some authors have therefore abandoned the expressions in favor of others giving *time-dependent* [4] energy transfer rates  $k(t)$ . While recent observations [7-9] in aromatic hydrocarbon crystals do not show  $k(t)$  to have a time dependence, they do force us to abandon prescriptions such as (1) and (2) because they present an apparent paradox. It has been found [7,8,15-17] that in naphthalene and anthracene the annihilation con-

stant  $\gamma$  is essentially temperature independent in the range of observation (4-300 K), but that the energy transfer rate  $k$  has a strong dependence. Unless one follows the quite unsatisfactory procedure of attaching to  $R_d$  and  $R_c$  temperature dependences invented ad hoc to produce precisely the observed result, one is therefore faced with a paradox. Furthermore, the observed value of  $\gamma$  is  $4 \times 10^{-11} \text{ cm}^3/\text{s}$  but that of  $k$  varies from  $3 \times 10^{12} \text{ s}^{-1}$  at 4 K to  $2 \times 10^{11} \text{ s}^{-1}$  at 300 K in naphthalene. In anthracene  $\gamma$  is  $1 \times 10^{-8} \text{ cm}^3/\text{s}$  but  $k$  varies from  $1.7 \times 10^{13} \text{ s}^{-1}$  at 4 K to  $3 \times 10^{12} \text{ s}^{-1}$  at 300 K. One can, no doubt, "deduce" values of  $D$  by assigning values as well as temperature dependences of one's choice to  $R_d$  and  $R_c$ . But, as is well known, expressions (1) and (2) were derived [14] to be valid in the motion-controlled limit wherein characteristics of the elementary processes of mutual destruction and/or capture drop out. We shall see below that this limit is far from being generally applicable to the observations under discussion.

## 3. Resolution

The resolution of the paradox is quite straightforward in terms of a first-principles theory of annihilation [12] and of energy transfer [13], which gives for the rates  $\gamma'$  and  $k'$  appearing in (1) and (2) the following expressions:

$$\gamma' = (1/b + 1/M)^{-1}, \quad (5)$$

$$k' = (1/c + 1/M)^{-1}. \quad (6)$$

Here  $2b$  is the rate at which the elementary process of annihilation (mutual destruction) occurs,  $c$  is the rate at which the elementary capture process occurs, and  $M$  is the motion rate defined as

$$M = \left[ \int_0^\infty \exp(-t/\tau) \psi_0(t) dt \right]^{-1}, \quad (7)$$

where  $\psi_0(t)$  is the exciton self-propagator, i.e. the probability that an exciton initially placed at a site is at that site at a later time  $t$ , in the pure capture-less and annihilation-less host crystal. If the trap concentration is very high or the capture or destruction processes are long range,  $\psi_0$  is replaced in (7) by a suitable weighted sum over propagators. Details may be found elsewhere [12,13].

The form implicit in (5) and (6) has been recognized and commented on, in more or less detail, by a number of workers earlier including Suna [18] for the annihilation case. In a loose way (6) may be said to represent the fact that the overall observed trapping time  $1/k'$  equals the sum of the motion time, i.e. the time to get the exciton within the trapping influence of a guest molecule, and the elementary capture time  $1/c$ , i.e. the time to get the exciton into the guest molecule from the guest-influenced host molecule. Similarly (5) may be said to express the overall annihilation time  $1/\gamma'$  as the sum of the motion time and the mutual destruction time  $1/b$ , the latter being a measure of the time for the actual destruction process to occur once the two mutually annihilating excitons are within each other's region of influence. Useful as they are, these statements should be taken to be associated only with very rough pictures and not to represent the situation accurately:  $1/M$  is not really the time to arrive at a trapping site or near another exciton.

We stress that the form of eqs. (5) and (6), relating the observables  $\gamma'$  and  $k'$  to the elementary quantities  $b$ ,  $c$ , and  $M$ , is expected even on simple physical grounds. The two processes, viz. mutual destruction or capture on one hand and motion on the other, act together to present the same kind of formal situation as the one encountered in the passage of current through two conductances in series. As is well known, the slower process is the limiting one. Thus, if  $b \gg M$  in (5), the annihilation rate  $\gamma'$  is identical to the motion rate  $M$ . This is the situation that corresponds to (1). However, (1) is quite inapplicable if  $b$  is not much larger than  $M$ . In fact, if  $b \ll M$  in (5),  $\gamma'$  equals  $b$  and contains no information about motion. Identical comments apply to  $k'$  and to (6).

While the forms (5) and (6) are well known, it is not generally recognized that they are not mere phenomenological constructs. The theory in refs. [12, 13] results in (5) and (6) in a well-defined analytic way starting from a generalized-master-equation description of exciton dynamics which is valid under a large class of conditions including arbitrary dimensionality of the crystal and arbitrary degree of coherence. Furthermore, that theory gives a specific expression for the motion rate  $M$ , viz. (7). It contains microscopic motion parameters such as the hopping rates or bandwidth and also the decay time  $\tau$ . It has

been calculated [13] for various lattices and for various degrees of coherence. Although it is tempting to call  $1/M$  the time taken by the exciton to arrive at the location of a capture or destruction event, (7) shows that it is more closely associated with the lifetime of the exciton *at the site* at which it is put initially, in the absence of capture or destruction but in the presence of motion and decay. It is helpful to represent the self-propagator  $\psi_0(t)$  by the simple single exponential  $\exp(-ft)$  and examine (7), and (5) and (6) in this case. The motion rate  $M$  is then the sum  $f + 1/\tau$  and (5) takes the form

$$\gamma' = [1/b + 1/(f + \tau^{-1})]^{-1}, \quad (8)$$

a similar equation being obtained in place of (6). Notice that the electrical network analogy mentioned above continues to be applicable: the motion and decay processes may be said to occur "in parallel" with each other but "in series" with the destruction process. Notice also that the motion rate  $M$  equals  $1/\tau$  if exciton motion is much slower than its decay but that in the opposite limit (which is, without doubt, applicable to aromatic hydrocarbon crystals)  $M$  is given entirely by the effective rate  $f$  at which the exciton moves away from a site. These comments may make the meaning of  $M$  more clear.

The apparent paradox arising from the observations of  $\gamma$  and  $k$  in naphthalene as well as anthracene resolves itself when we use (5) and (6) instead of (1) and (2). The latter are the  $M \ll b$  and  $M \ll c$  limit of (5) and (6). As there is no reason to believe this limit applies, the paradox disappears:  $b$  and  $c$  make different contributions to  $\gamma'$  and  $k'$  although the same  $M$  appears in both of the latter.

#### 4. Extraction of motion information

Expressions (5) and (6) resolve the "paradox" by recognizing that the observables  $\gamma'$  and  $k'$  contain  $b$  and  $c$  (respectively) in addition to the motion rate  $M$ . An inevitable consequence of this feature is that complete information about the motion rate  $M$  (and hence about transfer rates, diffusion constants, etc.) *cannot* be obtained from  $\gamma'$  and  $k'$  unless  $b$  and  $c$  are known a priori. We now address the question of what information about motion, if any, can be extracted from the available observations without such a priori

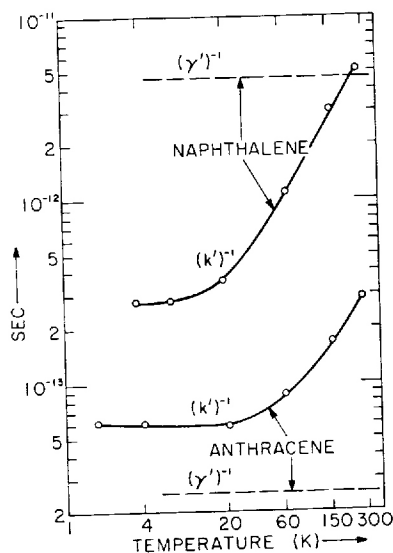


Fig. 1. The reciprocals of the rates  $\gamma'$  (annihilation) and  $k'$  (energy transfer) (see text for definition) plotted logarithmically as functions of temperature  $T$  for anthracene as well as for naphthalene.

knowledge. We find that, although  $\gamma'$  and  $k'$  would each, by itself, yield little information, together they do allow one to draw some definite and useful conclusions.

In fig. 1 we have plotted the reciprocals of the rates  $\gamma'$  and  $k'$  for naphthalene as well as for anthracene. While, as a result of experimental error, the absolute values of  $\gamma'$  are uncertain within a factor of two, its temperature independence is certain within  $\pm 30\%$ . We have used the volume  $v$  to be  $2.37 \times 10^{-22} \text{ cm}^3$  for anthracene and  $1.80 \times 10^{-22} \text{ cm}^3$  for naphthalene. The limits of error in  $k'$  increase from  $\approx 10\%$  at 4 K to  $\approx 50\%$  at 300 K.

Two pieces of information emerge from a study of fig. 1. First we see from (5) and (6) that  $1/M$  is smaller than  $1/\gamma'$  as well as  $1/k'$ . The observations lead us therefore to place lower bounds on the motion rate  $M$  and hence on the transfer rates or the diffusion constant. In anthracene it is the annihilation observations that yield the bound ( $M > \gamma'$ ):

$$M > 4.2 \times 10^{13} \text{ s}^{-1} . \quad (9)$$

On the other hand, in naphthalene, it is the energy transfer observations that place the bound ( $M > k'$ ):

$$M > 3 \times 10^{12} \text{ s}^{-1} \quad \text{for } T = 4 \text{ K} , \quad (10)$$

$$M > 2 \times 10^{11} \text{ s}^{-1} \quad \text{for } T = 300 \text{ K} . \quad (11)$$

Here the bound is dependent on the temperature  $T$  because  $k'$  depends on  $T$ .

The second piece of information that can be obtained from fig. 1 is as follows. For anthracene, for  $T > 60 \text{ K}$  we see that  $1/k'$  is considerably larger than  $1/\gamma'$ . Thus,  $1/k'$  is considerably larger than  $1/M$  (since  $1/\gamma' > 1/M$ ), leading one to the conclusion that  $1/k'$  is given almost entirely by  $1/c$ . In other words, the energy transfer rate in anthracene is definitely capture-limited at least from 60 to 300 K. In this temperature range the energy transfer range thus contains practically no information about exciton motion. Note that one can draw no definite conclusion for  $T < 60 \text{ K}$  because  $\gamma'$  and  $k'$  are comparable in that range.

Turning to naphthalene one observes for  $T < 60 \text{ K}$  that  $1/k'$  is considerably smaller than  $1/\gamma'$ . Using identical reasoning as above, we conclude that  $1/\gamma'$  is definitely destruction-limited at least from 4 to 60 K and that in this temperature range the annihilation constant of naphthalene contains practically no information about exciton motion. Note again that no definite conclusions can be obtained in naphthalene for  $T > 60 \text{ K}$  because  $\gamma'$  and  $k'$  do not have widely different values in that range.

It is important to realize the futility of attempting to obtain the diffusion constant (or other motion information) by equating the anthracene energy transfer rate  $k$  to  $4\pi R_c D$  particularly for temperatures larger than 60 K or by equating the naphthalene annihilation constant  $\gamma$  to  $8\pi R_d D$  particularly for temperatures smaller than 60 K. There happens to be no information about exciton motion in those observables in the stated temperature ranges.

It is possible to convert the lower bounds for the motion rate  $M$  given above into lower bounds for the hopping rate, or for the diffusion constant, or for related quantities by calculating the propagator  $\psi_0(t)$  for a specific lattice and model of motion and obtaining  $M$  from (7). Thus, for nearest-neighbor incoherent motion with hopping rates  $F$ , the rate  $M$  is given [13] by

$$M = (1 + F\tau)^{1/2} / \tau \quad (12)$$

for one-dimensional motion, by

$$M = \frac{1 + F\tau}{2\tau/\pi} \left[ K \left( \frac{4F\tau}{1 + 4F\tau} \right) \right]^{-1} \quad (13)$$

for two-dimensional motion, and by

$$M = 2F [I(0, 0, 0; 1; 1 + 1/6F\tau)]^{-1} \quad (14)$$

for three-dimensional motion, where  $K$  is the complete elliptical integral of the first kind and where

$$I(a, b, c; \alpha; \beta) = \int_0^\infty \exp[-(2 + \alpha)\beta t] I_a(t) I_b(t) I_c(\alpha t) dt \quad (15)$$

in terms of modified Bessel functions  $I_a$ ,  $I_b$  and  $I_c$ . Although singlet motion is not nearest-neighbor in character, we have calculated bounds for the hopping rate  $F$  and for the diffusion constant  $D$  through (13) and (14) to illustrate the analysis. We use the limit  $F\tau \gg 1$  which certainly applies for naphthalene and anthracene. Then (4.5) and (4.6) simplify considerably. For two-dimensional motion

$$M \approx \pi F / \ln(32F\tau) \quad (16)$$

and for three-dimensional motion

$$M \approx 3.956776F [1 + 0.315(F\tau)^{1/2}] \approx 4F. \quad (17)$$

Writing the diffusion constant as equal to  $\frac{1}{4}Fa^2$  and  $\frac{1}{8}Fa^2$  respectively for two- and three-dimensional motion and taking the nearest-neighbor distance  $a$  as 5 Å, we obtain from the above bounds for  $M$  the bounds for the diffusion constants given in table 1.

We conclude this note with a summary. We have shown how the traditional expressions (5) and (6) used to extract information about exciton motion from annihilation and sensitized luminescence observations lead one to a paradox in the light of existing ob-

servations. We have shown how the paradox may be resolved and we have extracted quantitative information in the form of lower bounds for the motion rates and the diffusion constants in naphthalene and anthracene. We have also shown that the naphthalene  $\gamma$  for low temperatures ( $T < 60$  K) and the anthracene  $k$  for high temperatures ( $T > 60$  K) contain practically no information about exciton motion. The lower bounds on the motion rates that we obtain are compatible with the experimental findings in these systems of the lack of a time dependence in the energy transfer rate  $k$ . The question of the time dependence of  $k$  has been analyzed in ref. [13] where it has been shown that, while  $k$  should be generally time dependent, fast motion could make present-day spectroscopy incapable of observing that time dependence.

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Table 1  
Bounds for the diffusion constants  $D$  (in  $\text{cm}^2/\text{s}$ )

	Naphthalene		Anthracene
two-dimensional motion	$> 6 \times 10^{-4}$	(300 K)	$> 1.6 \times 10^{-1}$
	$> 1.1 \times 10^{-2}$	(4 K)	
three-dimensional motion	$> 2.1 \times 10^{-5}$	(300 K)	$> 4.3 \times 10^{-3}$
	$> 3.1 \times 10^{-4}$	(4 K)	

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