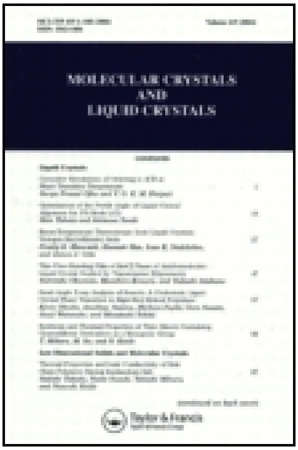

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Delayed luminescence of organic mixed Crystals. IV. Triplet-Triplet Annihilation Phenomena†

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Abstract—The phenomenon of triplet-triplet annihilation in the following mixed crystal systems is discussed: phenanthrene-h_{10} in biphenyl, phenanthrene-d_{10} in biphenyl, naphthalene-h_8 in biphenyl, naphthalene-d_8 in biphenyl and chrysene in biphenyl. The kinetics of the phenomenon are elaborated, particular attention being paid to the effects of (i) host-guest triplet energy gaps; (ii) random walk of triplet host excitons; and (iii) the influence of adventitious impurity or host crystalline defects. The topics discussed and concerning which experimental information is presented are: (a) the decay behavior of phosphorescence and delayed fluorescence; (b) the temperature dependence of the above decays; (c) the growth characteristics of phosphorescence and delayed fluorescence; (d) the temperature dependence of phosphorescence and delayed fluorescence intensities; (e) the concentration dependence of delayed fluorescence intensity; and (f) the incident intensity dependence of phosphorescence and delayed fluorescence intensities. It is shown that all data, with the single exception of delayed fluorescence decay at $T \sim 77°K$, are in accord with the kinetic model developed. The decay behavior of delayed fluorescence at 77°K is interpreted in terms of a crystal defect model. Exception is taken to the model of Hadley, Rast and Keller for the temperature dependence of phosphorescence decay; it is shown that the annihilative model is in better accord with fact.

1. Introduction

Of the several different types of fluorescence of organic materials which have been discovered in recent years, delayed fluorescence seems to be a rather general phenomenon which may very well be of crucial importance to the understanding of other seemingly unrelated physical events. Delayed fluorescence can be observed in a variety of liquid solutions, in

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so-called "pure" crystals,[1] in mixed crystals, and in rigid glassy solutions. Several types of interpretation seem to be required; these have been reviewed in an earlier paper by Azumi and McGlynn[2] which was primarily concerned with the fluid and vapor phases. The present work is restricted to triplet-triplet annihilations in organic mixed crystal systems.

Although the phenomenon of delayed fluorescence in aromatic crystals has probably been known since 1958[3], a satisfactory interpretation was first given by Robinson *et al.*[4] in 1962. According to Robinson *et al.*[5], triplet exciton interactions are much larger than previously supposed, and when coupled with the long lifetime of the triplet state, these interactions lead to significant trap-to-trap migration of triplet excitation energy in organic crystals; a substantial probability of annihilation of two triplet excitons is also supposed to result, one molecule being degraded to the ground state and the other further excited to a higher energy singlet, triplet or quintet state. The higher excited state is then partially and non-radiatively degraded to the lowest singlet excited state, whence delayed fluorescence occurs.

Most investigations have been concerned with mixed crystals of different guest-host chemical species (e.g., phenanthrene as a guest in biphenyl host), where the guest triplet states are located 1000 ~ 3000 cm^1 lower energetically than the host triplet states[6-11]. The results obtained are interpretable more or less satisfactorily in the manner proposed.[5] However, the nature of delayed fluorescence in the vicinity of 77°K for these mixed crystals has not yet been satisfactorily elucidated.

Our experiments were made on the following mixed crystals over a wide temperature range above 77°K; phenanthrene-h$_{10}$ in biphenyl; phenanthrene-d$_{10}$ in biphenyl; naphthalene-h$_8$ in biphenyl; naphthalene-d$_8$ in biphenyl; and chrysene in biphenyl. These systems were chosen in order to emphasize the effects of phosphorescence lifetimes and host-guest triplet energy gaps (see Table 1) on delayed luminescence behavior.

TABLE 1 Energy levels

Substance	S_1 (cm^{-1})	T_1 (cm^{-1})
Biphenyl (host)	32,480	23,010
Phenanthrene	28,620	21,380
Naphthalene-h_8	31,440	21,070
Naphthalene-d_8	31,480	21,180
Chrysene	27,200	19,660

We have presented other data relative to these same question in a number of other publications.[7-9]

2. Kinetic considerations

The kinetic model used here has been discussed by Sternlicht, Nieman and Robinson[8] and by us.[2] In the case of mixed crystals with a certain minimal energy separation between host and guest triplet states, however, modification and extension of the model are required.[8, 10] We will, therefore, describe in this section the kinetic model in brief and its generalization in some detail. We will use a similar symbolization to that of Sternlicht *et al.*[5] The rate parameters used are identified in Table 2.

TABLE 2

Process	Rate Constant	Remarks
(0) $S_0 + h\nu \rightarrow S_1$	R_0	Over-all rate constant
(1) $S_1 \rightarrow S_0 + h\nu$	k_1^*	Radiative $\}$ $K_1 \equiv k_1 + k_1^*$
(1') $S_1 \rightarrow S_0$	k_1	Non-radiative
(2) $S_1 \rightarrow T_1$	k_2	Intersystem crossing
(3) $T_1 \rightarrow S_0 + h\nu$	k_3^*	Radiative $\}$ $K_3 \equiv k_3 + k_3^*$
(3') $T_1 \rightarrow S_0$	k_3	Non-radiative
(4) $T_1 + T_1 \rightarrow S_1 + S_0$	K_4	Annihilation
(5) $T_1 + T_1 \rightarrow T_1 + S_0$	K_5	Annihilation

The rate equations for guest singlet and triplet states are given by

$$\frac{d[S_1]}{dt} = R_0 - (K_1 + k_2)\,[S_1] + K_4[T_1]^2 \tag{1}$$

$$\frac{d[T_1]}{dt} = k_2[S_1] - K_3[T_1] - (2K_4 + K_5)\,[T_1]^2 \tag{2}$$

Straightforward manipulation yields the expressions for the steady-state intensities and the decays of phosphorescence and delayed fluorescence. The results are:

$$(I_0)_P = k_3^* K_3[(4K + 1)^{1/2} - 1]/2k_6 \tag{3}$$

$$(I_0)_{DF} = k_1^* K_4 K_3^2[(4K + 1)^{1/2} - 1]^2/[4(K_1 + k_2)\,k_6^2] \tag{4}$$

$$(I/I_0)_P = (1 - A)/[\exp\,(K_3 t) - A] \tag{5}$$

$$(I/I_0)_{DF} = (1 - A)^2/[\exp\,(K_3 t) - A]^2 \tag{6}$$

where

$$k_6 \equiv K_4(2K_1 + k_2)/(K_1 + k_2) + K_5 \tag{7}$$

$$K \equiv k_2 k_6 R_0/[(K_1 + k_2)\, K_3^2] = A/(1 - A)^2 \tag{8}$$

$$A \equiv \frac{k_6[T_1]_0}{K_3 + k_6[T_1]_0} = \frac{[(1 + 4K)^{1/2} - 1]}{[(1 + 4K)^{1/2} + 1]} \tag{9}$$

The quantity K [or A] is a most important parameter in triplet-triplet annihiation kinetics because it gauges the relative annihilative contribution to triplet guest decay.†

Assuming that there is no significant long range direct interaction between guest triplet states, the annihilative processes (4) and (5) in Table 2 require a guest triplet state to migrate and to encounter another triplet state. We will assume, as is usually dictated by experiment, that this other triplet state is also a guest triplet state. This process may be realized as follows:

$$\begin{array}{lll}
T_1 \rightleftarrows T_1^* & & [T_1^*] = [T_1] \exp(-\Delta E/kT) \\
T_1^* + S'_{0H} \rightleftarrows S_0 + T'_{1H} & & \overrightarrow{\varkappa}_1,\ \overleftarrow{\varkappa}_1 \\
T'_{1H} + S_{0H} \rightleftarrows S'_{0H} + T_{1H} & & \overrightarrow{\varkappa}_2,\ \overleftarrow{\varkappa}_2 \\
T_{1H} + S_{0H} \rightleftarrows S_{0H} + T_{1H} & & \overrightarrow{\varkappa}_3,\ \overleftarrow{\varkappa}_3 \\
 & & \\
T_{1H} + S''_{0H} \rightleftarrows S_{0H} + T''_{1H} & & \overrightarrow{\varkappa}_n,\ \overleftarrow{\varkappa}_n \\
T''_{1H} + T_1 \rightarrow S''_{0H} + S_1 \text{ (or } T_1) & & \varkappa
\end{array}$$

where the subscript H identifies the host species; the primed symbols identify host molecules which are adjacent to guest molecules; ΔE is the energy separation between guest and host triplet states; and T_1^* is a vibrationally excited triplet state of the guest of comparable energy to the host triplet exciton band. There are, of course, other possible processes, which might occur, for example:

$$T'''_{1H} + S_0 \rightarrow S'''_{0H} + T_1$$

or

$$T_{1H} + T_{1H} \rightarrow S_{0H} + T_{1H} \text{ (or } S_{1H})$$

However, these are unimportant: the former cannot be distinguished from the main reaction, and the probability of the latter is usually small. Using the rate constants given above, the expression for singlet state

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† Note that $K \lesseqqgtr 2$ or $A \lesseqqgtr 1/2$ corresponds to (the 2*nd* order term) $\lesseqqgtr$ (the 1*st* order term).

generation by these processes is:

$$\frac{d[S_1]}{dt} = \varkappa \frac{\prod_{i=1}^{n} \overrightarrow{\varkappa}_i}{\prod_{i=1}^{n} \overleftarrow{\varkappa}_i} \frac{[S''_{\mathrm{OH}}]}{[S_{\mathrm{O}}]} \exp\,(-\varDelta E/kT)\,[T_1]^2 \equiv K_4[T_1]^2$$

where the rate constant K_4 of Table 2 has now been properly identified. Here it may be noted that the concentration $[S''_{\mathrm{OH}}]$ is different from the concentration $[S_{\mathrm{OH}}]$; the former represents host molecules adjacent to guest molecules whereas the latter may very well not be. Therefore, it is reasonable to set $[S''_{\mathrm{OH}}]$ proportional to $[S_{\mathrm{O}}]$, and as a result, K_4 does not include any explicit concentration dependence whatever. As has been suggested,[8] however, it does contain an implicit guest concentration dependence because the exciton migration rate between guest molecules through the intervening host crystal lattice is dependent on the average distance between guest species (i.e., on the cubic root of guest concentration when the assumption of a random walk of excitons and a random distribution of guest molecules is made). Similar consideration is applicable to K_5. The general results are as follows:

$$K_4,\, K_5,\, k_6 \propto C^{1/3} \exp\,(-\varDelta E/kT)$$

and consequently

$$K \propto C^{4/3} \exp\,(-\varDelta E/kT)\, I_{\mathrm{exc}}$$

where $C = [S_0]$, and I_{exc} is the exciting light intensity.

From these properties of the quantities K_4, K_5, k_6 and K, we may predict the dependencies of delayed luminescence intensities, $(I_0)_P$ and $(I_0)_{DF}$, on exciting light intensity, guest concentration, and temperature (assuming all other rate constants to be independent of these same quantities). These dependencies are given in Table 3. Among the listed quantities, however, the concentration dependence of $(I_0)_P$ or $(I_0)_{DF}$ is not readily accessible experimentally, because the geometrical conditions of the experimental set-up are quite difficult to maintain constant from one sample to another of different guest concentration.

Decay behaviors are best treated separately, because they are expected to yield quantitative information concerning K[or A][9]. Equations (5) and (6) are therefore approximated as follows: In the short time region

TABLE 3

Quantity	Expression	Range of $K_{(a)}$	Approximate expression	I_{exc} dependence	Temp. (T) dependence	Concentration (C) dependence
$(I_0)_P$	$\frac{k_3^* K_3}{2k_6}[(1+4K)^{1/2}-1]$	$K \ll 2$	$k_3^* k_2 R_0/(K_1+k_2)\,K_3$	I_{exc}^1	independent	C^1
		$K \gg 2$	$k_3^*[k_2 R_0/(K_1+k_2)k_6]^{1/2}$	$I_{\text{exc}}^{1/2}$	$\exp(+\Delta E/2kT)$	$C^{1/3}$
$(I_0)_{DF}$	$\frac{k_1^* K_4}{K_1+k_2}\,\frac{K_3}{2k_6}[(1+4K)^{1/2}-1]$	$K \ll 2$	$k_1^* k_2 K_4 R_0^2/(K_1+k_2)^3 K_3^2$	I_{exc}^2	$\exp(-\Delta E/kT)$	$C^{7/3}$
		$K \gg 2$	$k_1^* k_2 K_4 R_0/(K_1+k_2)^2\,k_6$	I_{exc}^1	independent	C^1
$(I_0)_{DF}/(I_0)_P^2$	$\frac{k_1^* K_4}{(K_1+k_2)\,k_3^{*2}}$		independent of K	Independent or log $(I_0)_{DF}$ vs. log $(I_0)_P$ plot gives slope of 2	$\exp(-\Delta E/kT)$	$C^{1/3}$

(a) When $K = 2$, the contributions from 1st- and 2nd-order terms become equal.

($t \ll K_3^{-1}$), we find

$$I(I/I_0)_P = 1/(I/I_0)_{DF}^{1/2} \cong K_3 t(1 - A) + 1, \tag{10}$$

while in the long time region ($t \gg K_3^{-1}$), we find

$$(I/I_0)_P = (I/I_{DF})^{1/2} \cong (1 - A)\exp(-K_3 t) \tag{11}$$

Therefore the quantity A, and consequently K, can be obtained from the analyses of decay curves in the short and long time regions.

3. Comparison with Experiment

Decay behaviors

Since the quantity K is proportional to $\exp(-\Delta E/kT)$, K is negligible at sufficiently low temperatures. In order to see whether 77°K is sufficiently low or not for the systems studied here, we will consider, in the first place, the temperature dependence of delayed luminescence decays. In Figure 1, the phosphorescence decays at various temperatures are plotted for systems of chrysene and naphthalene-h_8 in biphenyl host. At low temperatures, below 190°K for chrysene and below 140°K for naphthalene-h_8, the decays are solely exponential. Above these temperatures, however, the decay curves deviate from exponential behavior at fairly short times after excitation cut-off; the longer time region behavior, however, remains exponential, whence we can obtain the phosphorescence lifetime $1/K_3$ (Fig. 8). These features of phosphorescence decay are quite general for a number of mixed crystals. For the other systems studied, the characteristic temperatures (i.e., the temperature at which deviations from exponentiality begin to occur) are listed in Table 4. If K is sufficiently small, then we have $A \cong 0$, and the phosphorescence decay can be approximated as $(I/I_0)_P \cong \exp(-K_3 t)$. Therefore, we may conclude that the second order annihilative contribution is sufficiently small at 77°K, and that it becomes important only at temperatures higher than the characteristic temperatures. Indeed, using Eq. (10) [Fig. 2(a)], we obtain $K = 2$ at temperatures between 205 and 230°K for chrysene in biphenyl. Such temperature ranges evaluated for other systems are also listed in Table 4; they compare favorably with the experimental characteristic temperatures.

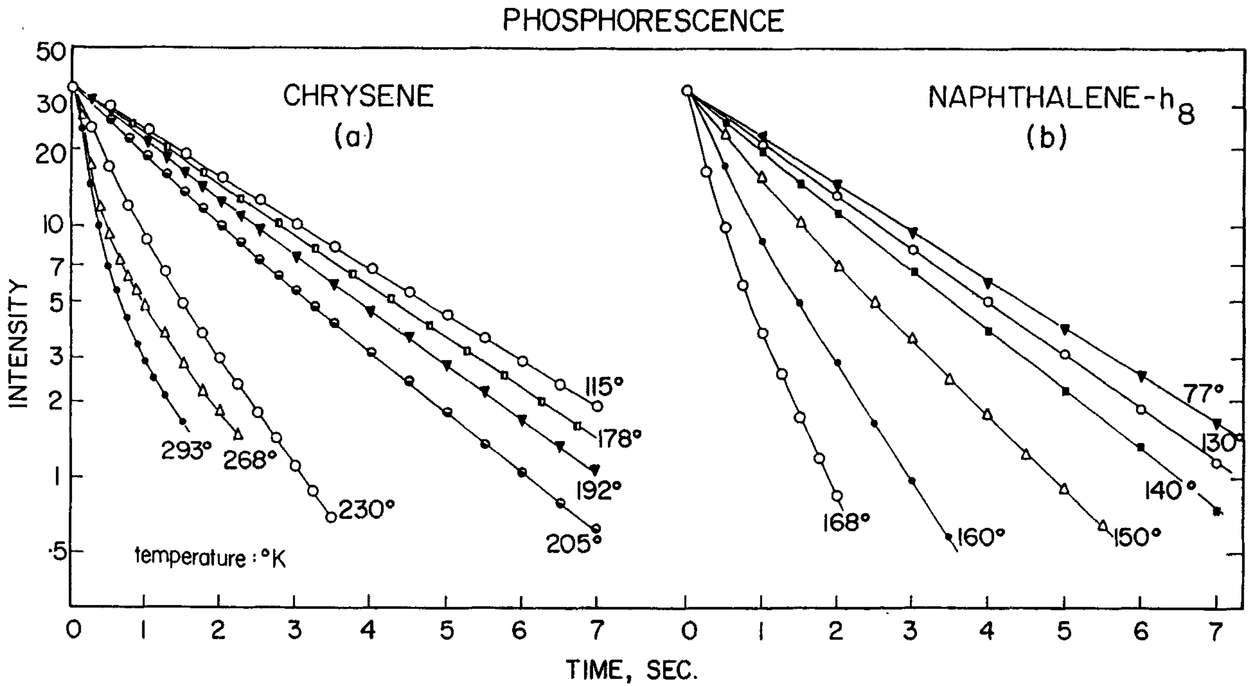

Figure 1. Phosphorescence decays at various temperatures. The initial intensities are arbitrarily normalized to 35.0. (a) 1 mole % chrysene in biphenyl, and (b) 0.3 mole % naphthalene-h_8 in biphenyl.

TABLE 4 Comparison of Characteristic Temperature with the Temperature Range in which $K \sim 2$

Guest	Temperature Range (°K)	Characteristic Temperature (°K)
Phenanthrene	125–135	120
Naphthalene-h_8	148–150	145
Naphthalene-d_8	120–132	100
Chrysene	205–230	190

Delayed fluorescence decays are analysable similarly, but using $(I/I_0)_{DF}$ instead of $(I/I_0)_P$. This mode of analysis, however, is correct only in the higher temperature regions. Decay curves at high and low temperatures are separately shown in Fig. 3. In the vicinity of the characteristic temperature the decay is nearly exponential, and the lifetimes obtained from the long time region give the expected relationship of $\tau_P = 2\tau_{DF}$ (Fig. 8). Above the characteristic temperature, delayed fluorescence decays deviate from exponentiality at short times. The second-order analysis according to Eq. (10) is applicable for these curves and we can obtain K-values similar to those obtained from phosphorescence decay [Fig. 2(b)]. Although they are not strictly coincident with each other, their temperature dependencies yield more or less identical activation energies, as shown in Table 5.

On the other hand, in the lower temperature regions where the phosphorescence decay enhibits an exponential behavior, the delayed fluorescence decay deviates considerably from exponentiality. Similar observations have been reported by Hirota[11] and by us.[8] In order to explain this, Hirota suggested that there are two different types of energy transfer mechanisms: one dominant at high guest concentration and due to direct exchange interaction similar to that apparently found in rigid glass solutions, and the other independent of guest concentration and due to a spin-forbidden intermolecular energy transfer similar to that discussed by Bennett, Schwenker and Kellogg.[12] On the other hand, we suggested that some kinds of traps, probably imperfections in the host crystal lattice, might be responsible for this decay behavior.[8] Both sets of suggestions seem to be reasonable. The close resemblance between decay behaviors at 77°K in mixed crystal and in rigid glass solutions may

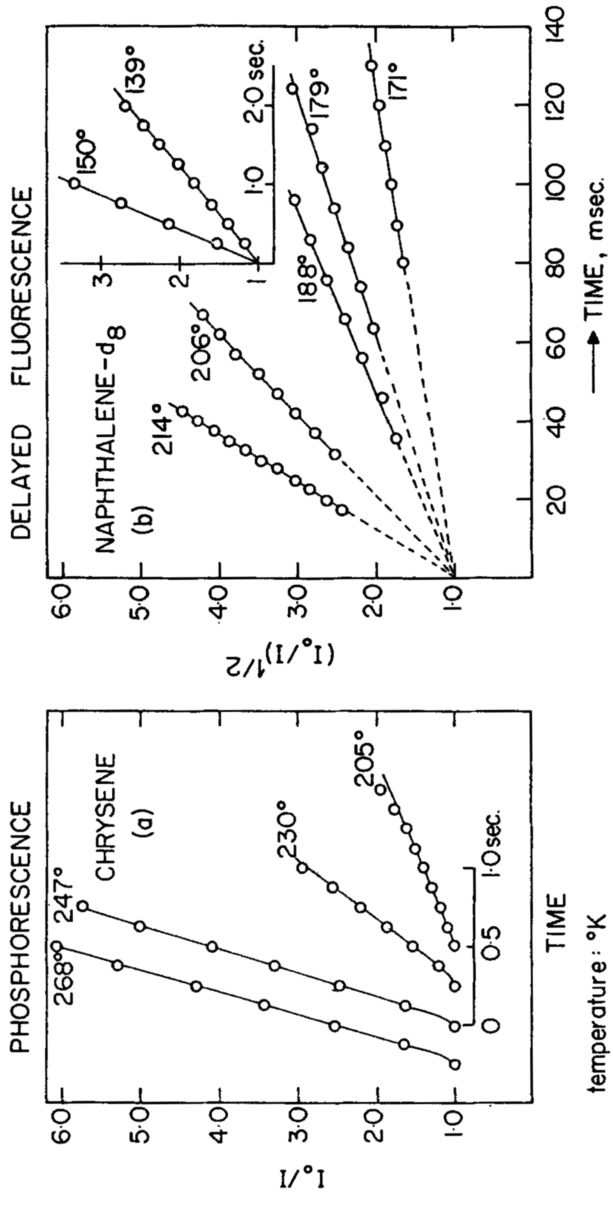

Figure 2. Second-order analyses for (a) phosphorescence decays of chrysene (1mole% and (b) delayed fluorescence decays of naphthalene-d$_8$ (0.34 mole %).

TABLE 5 Activation Energies (cm^{-1}) obtained from the Second-Order Analysis

Guest	Spectroscopic Energy Difference[a] ($T_{1H} - T_{1G}$)	Activation Energy Obtained from Temperature Dependence of Intensity[a]	Activation Energy Obtained from the Second-order decay analysis				Activation Energy Obtained from the First-order decay analysis of three Component System[c]
			Present	Results	Our analysis of data from Ref's 10 and 11		
			Phosphorescence	Delayed Fluorescence	Phosphorescence	Delayed Fluorescence	
Naphthalene-h_8	1940	1760	2820	1960	—	—	—
Naphthalene-d_8	1830	2000	2420	2420	—	2090[c]	1670 ~ 1900[d]
Chrysene	3350	2650	3560	3020	—	—	—
Phenanthrene-h_{10}	1630	1850	2460	2320	—	—	—
Phenanthrene-d_{10}	1600	1550	—	—	1570[b]	2500[c]	1390 ~ 1480[d]

a From ref. 8.
b After ref. 10.
c After ref. 11.
d Several values between these figures are reported, depending on the acceptor used.

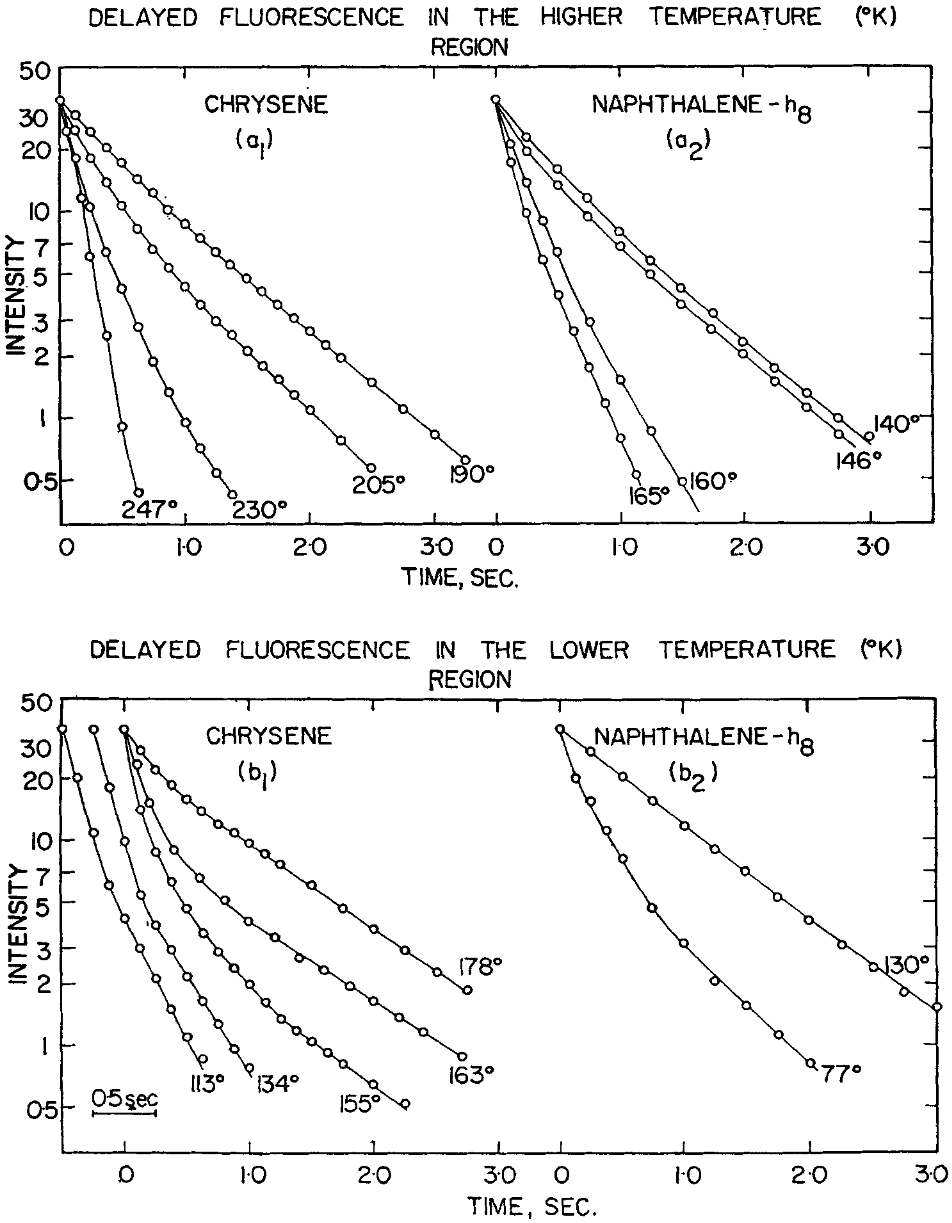

Figure 3. Delayed fluorescence decays (a) in the higher temperature region and (b) in the lower temperature region. (1) chrysene and (2) naphthalene-h_8 in biphenyl host. Initial intensities are obtained by extrapolation.

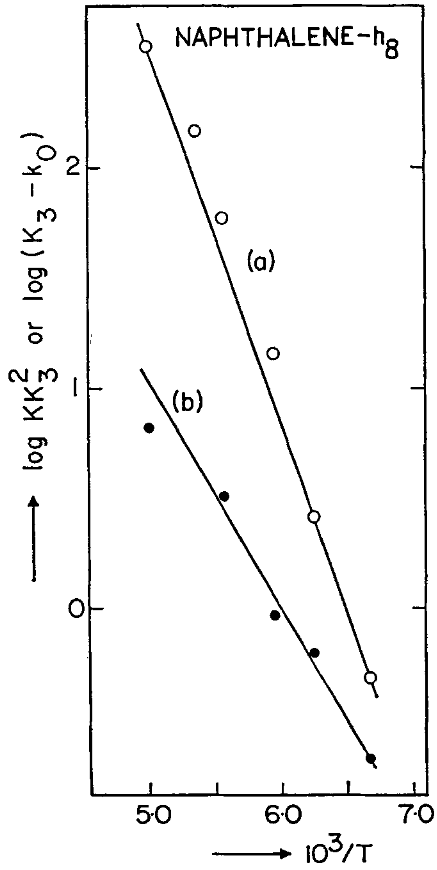

Figure 4. Plots of (a) log KK$_3^2$ *vs.* 1/T and (b) log (K_3 — k_0) *vs.* 1/T for naphthalene-h$_8$ in biphenyl, where k_0 is the K_3 at 77°K.

possibly support Hirota's interpretation. However, the observation of defect fluorescence in pure aromatic crystals by Helfrich and Lipsett[13] and by Zima and Faidysh[14] may support our point of view. Misra and McGlynn themselves observed a defect phosphorescence of durene.[8] Furthermore, we have also observed two different phosphorescences, depending on the preparation of specimens, from purified biphenyl crystals; these phosphorescences are red-shifted considerably from the spectrum observed in a rigid glass solution.[18] In any event, further detailed experiments are required to clarify this question fully.

Apart from the single difficulty discussed above, we may conclude that below and above the characteristic temperature the conditions $K \ll 2$ and $K \gg 2$ are satisfied, respectively, for the systems studied here. We will now proceed to examine other properties, keeping this conclusion in mind.

Temperature dependence of intensity

Typical examples of temperature dependence[8] are reproduced in Fig. 5(a). Phosphorescence intensity usually shows a plateau in the lower temperature region and then decreases rather sharply in the intermediate temperature region. At still higher temperatures the intensity is found to decrease exponentially with increase in temperature, and the plot against $1/T$ yields a straight line;[9] an activation energy $\Delta E = 2420\ \mathrm{cm}^{-1}$ is obtained for phenanthrene in biphenyl mixed crystal in accordance with the result of decay analysis (see Table 5). This behavior of phosphorescence agrees, at least qualitatively, with prediction.

On the other hand, the temperature dependence of delayed fluorescence intensity is rather peculiar. In the lower temperature region where an exponential dependence is expected, the delayed fluorescence intensity of virtually all systems studied passes through a minimum. Assuming that the kinetic model described above holds over the whole range of temperature, this peculiarity may be correlated to the decay behavior of delayed fluorescence at the same low temperatures. If there are shallow traps for migrating triplet excitons as suggested by us,[8] then we may explain this minimum in the same manner as has been pointed out by Siebrand[16] for the delayed fluorescence of anthracene crystal.[17]

In the intermediate temperature region, the delayed luminescence intensities depend on temperature in a somewhat complicated manner. It is most convenient to use the ratio $(I_0)_{DF}/(I_0)_P^2$, which is expected to depend exponentially on reciprocal temperature as is given in Table 3. The plots of $\log (I_0)_{DF}/(I_0)_P^2$ *vs.* $1/T$ are shown in Fig. 5(b) for naphthalene-h_8 and naphthalene-d_8 in biphenyl as examples. All these plots give good straight lines, yielding the activation energies given in Table 5. In Fig. 5(b), the same plots for lower temperature region are also shown. On subtraction of the extrapolated higher temperature region, we find very small (sometimes a continuum of) activation energies in the vicinity of 77°K; this observation supports the suggestion of shallow traps.

At higher temperatures the delayed fluorescence intensity, contrary to

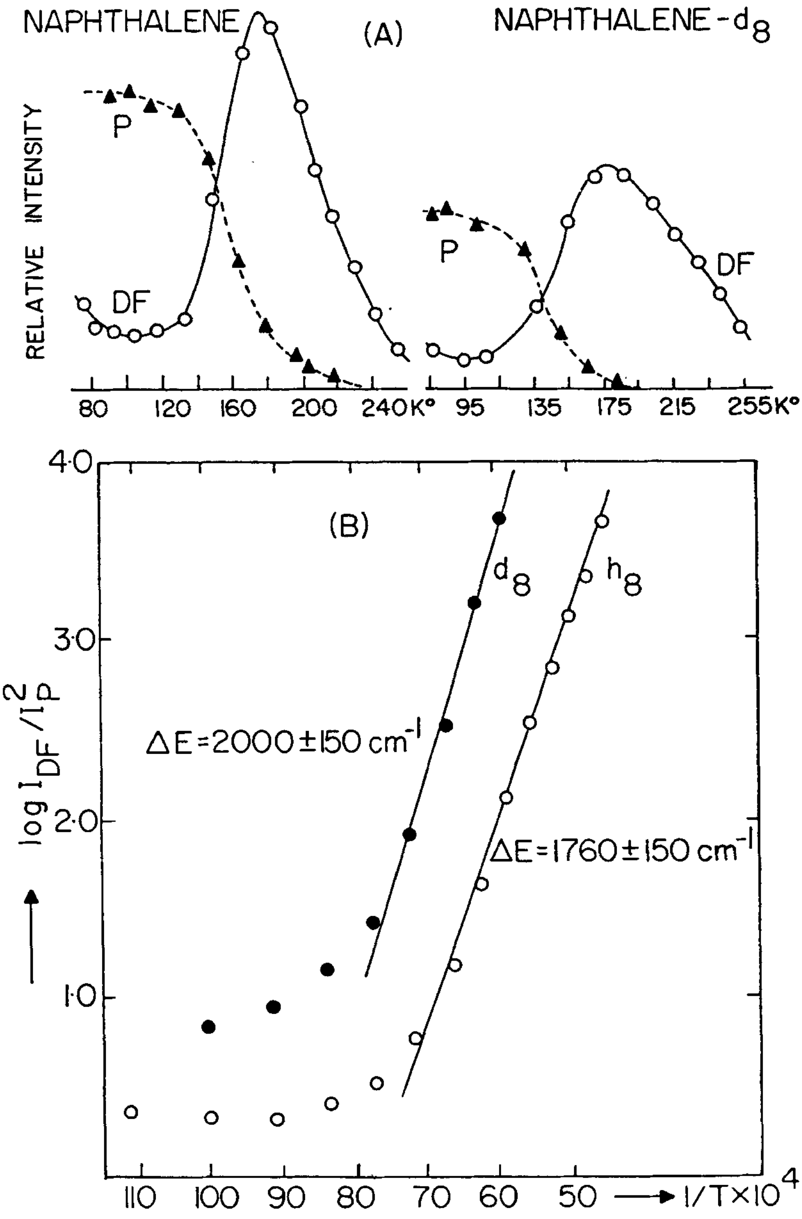

Figure 5. (a) Temperature dependence of delayed luminescence of mixed crystals of naphthalene-h_8 and naphthalene-d_8 in biphenyl host; the solid curves denote delayed fluorescence intensity and the broken lines denote phosphorescence intensity. (b) Plots of $\log (I_0)_{DF}/(I_0)_P^2$ as a function of 1/T for (d_8) naphthalene-d_8 in biphenyl and (h_8) naphthalene-h_8 in biphenyl.

prediction, drops sharply with increasing temperature. This behavior may be attributed, at least partially, to experimental difficulty. Since we are using a phosphoroscope in order to separate delayed fluorescence from normal fluorescence, we are unable to observe, in any strict sense, the true value of $(I_0)_{DF}$. This causes significant discrepancy at large values of K. Delayed fluorescence decay for large K and for $t \ll K_3^{-1}$ is given by

$$(I/I_0)_{DF} = (1 + K^{1/2}K_3t)^{-2} \tag{12}$$

Consequently when observing delayed fluorescence intensity a few milliseconds after excitation cut-off, $K^{1/2}K_3t$ cannot be negligible compared to unity for large K (say $K \geqq 10^4$) and since K is proportional to $\exp(-\Delta E/kT)$, the apparent intensity decreases with increasing temperature. Furthermore, other triplet quenching processes may also become operative at high temperatures; these also increase the decay constant K_3 (Fig. 8) and cause further enhancement of the discrepancy.

Concentration dependence

For the system of phenanthrene-h_{10} in biphenyl, the ratio of the delayed fluorescence intensity to the square of phosphorescence intensity at 77°K at various guest concentrations[8] is reproduced in Fig. 6. A line of

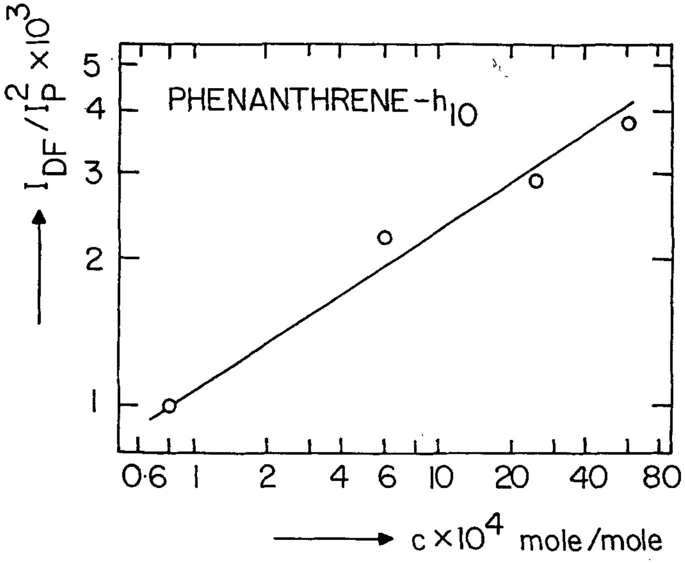

Figure 6. Plot of $(I_0)_{DF}/(I_0)_P^2$ as a function of concentration for phenanthrene-h_{10} in biphenyl at 77°K.

slope 1/3 is also drawn for comparison. The experimental points are fitted well within experimental error. The random walk processes of triplet excitons are thereby validated.

Excitation light intensity dependence

An example of the interdependence of delayed fluorescence, phosphorescence and exciting light intensities at 77°K is shown in Fig. 7 for phenanthrene-d_{10} in biphenyl (2.7 × 10^{-3} mole/mole). As seen in Table 3, this behavior corresponds to the case $K \ll 2$. Slight deviations from predictions may be due to experimental error or the peculiarity of delayed fluorescence at this temperature. In the case of phenanthrene-h_{10} in biphenyl (2.1 × 10^{-3} mole/mole), indeed, the following results are obtained: $I_P \propto I_{\text{exc}}^{0.8}$, $I_{DF} \propto I_{\text{exc}}^{1.5}$, and $I_{DF} \propto I_P^{1.9}$; these deviations are greater than the experimental error. It is indicated that some other kinds of processes not discussed here are operative at this temperature.

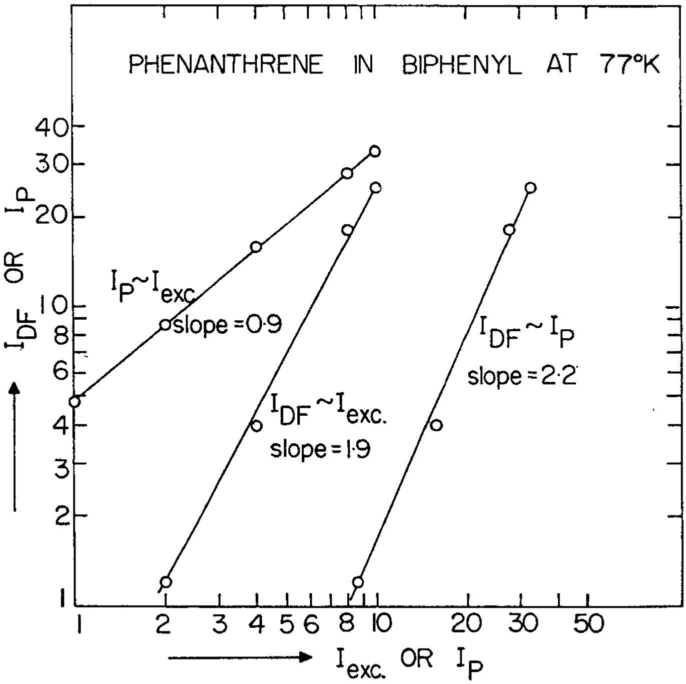

Figure 7. Interdependencies of phosphorescence, delayed fluorescence and exciting light intensities for the system of 0.27 mole % phenanthrene-d_{10} in biphenyl at 77°K.

4. Concluding remarks

In the higher temperature region, although many triplet quenching processes may be possible, the main process must be considered to be the triplet-triplet annihilation mechanism discussed here; indeed, the behavior of both phosphorescence and delayed fluorescence at temperatures greater than the characteristic temperature, can be explained satisfactorily using only the kinetics described above. The characteristic temperature is determined essentially by the competition between the first- and the second-order decay processes. The second-order annihilative contribution is, in turn, determined by the energy difference between host and guest triplet states and, consequently, by temperature. This situation is particularly manifest by the dependence of the characteristic temperature on the phosphorescence lifetime and the triplet host-guest energy difference. When the first-order triplet decay rates, K_3, of the guests are comparable (e.g., phenanthrene-h_{10}, naphthalene-h_8 and chrysene), the characteristic temperatures follow the order of the host-guest triplet gaps, ΔE. On the other hand, when the host-guest triplet gaps are comparable (e.g., naphthalene-h_8 and naphthalene-d_8), then the sequence of characteristic temperatures is determined by the size of the first order triplet decay constants.

Below the characteristic temperature, the triplet state population is controlled predominantly by first-order processes, and the phosphorescence behavior are explained satisfactorily by the given kinetics. Nevertheless, the delayed fluorescence behaves in an anomalous fashion. It is, therefore, immediately suggested that the main part of the observed delayed fluorescence at 77°K does not arise from the triplet state of the guest. For example, the decay of phosphorescence is solely exponential at 77°K, even though there is a very much faster delayed fluorescence decay. However, these attitudes are not conclusive, because the delayed fluorescence at 77°K is too weak to affect the phosphorescence decay appreciably. In order to resolve this anomaly, more information is needed, particularly at low temperatures.

Recently, we have found that the growth characteristics of delayed luminescence are also relevant to investigations of the kinetic behavior of triplet-triplet annihilation.[18] Because of the biexcitonic nature of delayed fluorescence, the growth curve shows distinctive features not found in the decay curves, and is more sensitive to smaller contributions from the annihilative processes than are the decay curves. According to the results obtained, the suggestion of shallow traps in host crystal lattices seems to be the preferable interpretation of the delayed fluorescence in the lower temperature region.[8]

5. The temperature dependence model of phosphorescence decay due to Hadley, Rast and Keller

It is pertinent to discuss the temperature dependence of phosphorescence lifetime further. In Fig. 8, the phosphorescence lifetime obtained from the long-time decay region (i.e., first-order decay) is shown as a function of temperature for the system of naphthalene in biphenyl host. In general, rather sharp decreases in lifetime occur in the proximity of the characteristic temperature of all the mixed-crystal systems investigated. Therefore, it may be suggested that, when the triplet-triplet annihilation process becomes predominant, some radiationless deactivation of the triplet state is simultaneously enhanced. A similar temperature dependence of lifetime has been reported for naphthalene-h_8 and -d_8 in

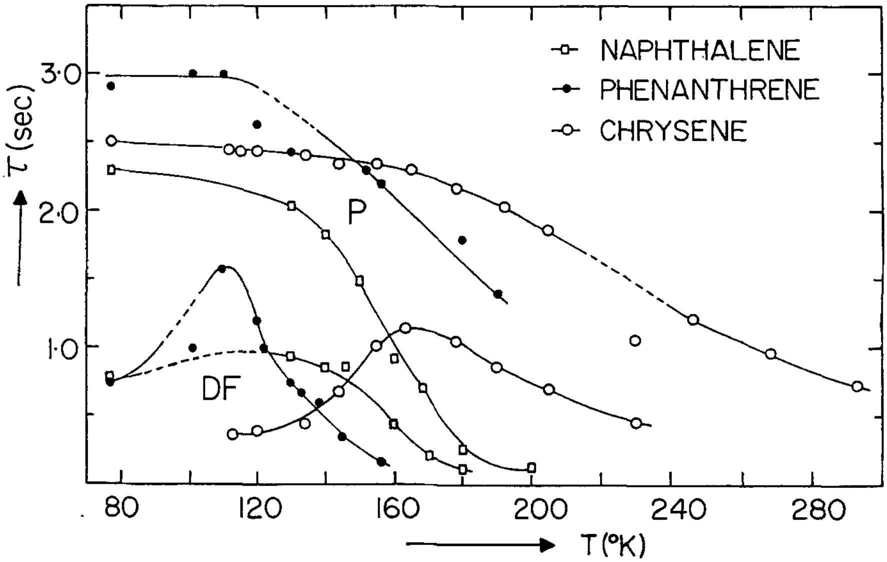

Figure 8. Temperature dependence of the lifetimes obtained from the long-time decay region of 1 mole % chrysene in biphenyl, 0.3 mole % naphthalene-h_8 in biphenyl and 0.2 mole % phenanthrene-h_{10} in biphenyl.

durene by Hadley, Rast and Keller.[19] They have observed the same sharp decrease of phosphorescence lifetime above 220°K, and they interpreted it in terms of an *intramolecular* intersystem radiationless deactivation of the triplet state directly to the ground singlet state (namely, $T_1 \rightarrow T_1^* \rightarrow S_0^* \rightarrow S_0$). They have obtained activation energies of 3558 and 3362 cm^{-1}† for the process $T_1 \rightarrow T_1^*$ for naphthalene-h_8 and -d_8, respectively, in durene; these intervals are supposed to correspond to a combination of two C-C stretching fundamentals. If this be the case, the activation energy and the temperature range where the steep lifetime decrease is observed should not be significantly dependent on environment. However, a large shift of this temperature range is observed when the host matrix is changed from durene to biphenyl; the steep lifetime decrease occurs in the temperature ranges 130 ~ 180°K for naphthalene-h_8 in biphenyl (Fig. 8) and 100 ~ 150°K for naphthalene-d_8 in biphenyl. Furthermore, if we use the same method of analysis as theirs, the activation energy obtained for the system of naphthalene-h_8 in biphenyl, as is shown in Fig. 4, is approximately 1660 cm^{-1}, which is in disagreement with their results for naphthalene in durene. These facts suggest that their interpretation, which is self-consistent within their phenomenological observation range, is not correct in the case of biphenyl host systems.

It seems to us that the host triplet state plays an important role in the deactivation process of the guest triplet state. Two more experimental results supporting this surmise are as follows:

(1) The steep lifetime decrease in chrysene-in-biphenyl system occurs at rather higher temperature (above 180° as shown in Fig. 8), and close to the corresponding temperature for naphthalene-in-durene system. This fact may be explained by the closeness of the triplet energy gaps for both systems.

(2) Delayed fluorescence of naphthalene-h_8 and -d_8 has been observed in durene host mixed crystals by us,[8] indicating that the host triplet state is thermally accessible for the guest triplet state in these systems. According to our results, the delayed fluorescence at room temperature is expected to be very weak. This may be the reason why Hadley *et al.*[19] did not detect any delayed fluorescence in spite of their attempt to observe an α-phosphorescence at room temperature. In any case, the results of Hadley, Rast and Keller may be re-interpreted as due to triplet-triplet annihilation.

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