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Delayed Fluorescence Quenching by Charge Carriers in Anthracene Crystals. A Quartet State Model,†‡

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Abstract—Previous observations of delayed fluorescence quenching by carriers in anthracene crystals are reanalyzed. It had been observed that this quenching was caused by two different mechanisms, namely the well-known triplet annihilation by carriers together with a hitherto unobserved annihilation process that is linear in the carrier concentration but quadratic in the concentration of triplet excitons. Two kinetic models for the latter process are considered and compared: (i) annihilation of triplet pairs by carriers and (ii) triplet–carrier interaction leading to quartet-excited carriers which are assumed to interact more strongly than unexcited carriers with triplet excitons. Triplet pairs have been observed in magnetic field experiments but their lifetime is much too short to explain the observed quenching. Quartet states are expected to have the required long lifetime, since their decay is spin-forbidden, although no independent evidence for their participation has been obtained so far.

1. Introduction

In a recent paper we have reported the results of an experimental study of the quenching of delayed fluorescence by injected charge carriers in anthracene crystals.[1] Since delayed fluorescence is due to triplet–triplet annihilation and since carriers are known to quench triplet excitons,[2] quenching of delayed fluorescence by charge carriers is not an unexpected phenomenon. It turns out, however,

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that for high excitation intensities the observed fluorescence quenching is stronger than that predicted on the basis of triplet quenching.[1] This is not due to direct singlet exciton quenching, since prompt fluorescence is not quenched. To explain the results we need a state intermediate between two independent triplet excitons and one singlet exciton, which can either return to a pair of independent triplets or proceeed to form a singlet. Such a triplet pair state can only explain the fluorescence quenching by carriers if it has a long lifetime, i.e., long compared to the lifetime of the fluorescent state, and thus very long compared to the lifetime of higher excited singlet states. Magnetic field experiments have indicated however, that this triplet pair state has a lifetime that is very short compared to the lifetime of the fluorescent state.[3] Hence the intermediate state introduced to explain the kinetics of delayed fluorescence quenching by carriers cannot be comfortably identified with the triplet–pair state of magnetic field repute or indeed with any other known state of solid anthracene. Yet claims for the existence of hitherto unknown long-lived excited states in anthracene have been made before,[4] although none of these states has been identified to date.

In this paper we discuss two approaches to this problem: The triplet–pair model introduced in the previous paper[1] and an alternative quartet-state model based on the concept that triplet-carrier interactions may lead to the formation of quartet-excited charge carriers.

2. Kinetic Preliminaries

Delayed fluorescence is produced by the mutual annihilation of two triplet excitons. The time dependence of the triplet exciton population density T in the absence of carriers is given by

$$dT/dt = \alpha I - \beta T - \gamma_e T^2 \tag{1}$$

where α is the absorption coefficient, I the intensity of the excitation source, β the unimolecular triplet decay-rate constant and γ_e the over-all triplet–triplet annihilation rate constant. For times long compared to the prompt fluorescence decay time, the steady-state delayed fluorescence intensity F is given by $F = \frac{1}{2}\gamma_s T^2$, where γ_s is the part of γ_e leading to a singlet state.

Under low-excitation intensity ($\beta \gg \gamma_e T$), and steady-state

$(dT/dt = 0)$ conditions we have $T = \alpha I/\beta$ and $F = \frac{1}{2}\gamma_s \alpha^2 I^2/\beta^2$. If we now introduce charge carriers with a population density N, triplets will be quenched, and this quenching can be reproduced kinetically by adding a term $-\phi(N)T$ to Eq. (1). Under low intensity, steady-state conditions this term modifies the delayed fluorescence intensity as follows

$$F = \tfrac{1}{2}\gamma_s \alpha^2 I^2 [\beta + \phi(N)]^{-2}, \tag{2}$$

On switching off the excitation source, F will decay with a unimolecular rate constant given by $\frac{1}{2}[\beta + \phi(N)]$. This is indeed observed experimentally.[1,2]

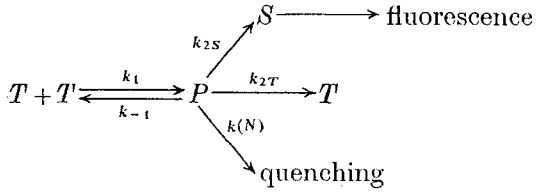
Similarly, under high-intensity steady-state conditions, $\beta \ll \gamma_e T$, we have $T = (\alpha I/\gamma_e)^{1/2}$ and $F = \frac{1}{2}(\gamma_s/\gamma_e)\alpha I$. On switching off the light at a time $t = 0$ where $T = T_0$, the delayed fluorescence decays initially (i.e. for $t \ll (\beta + \phi)^{-1}$) according to

$$F(t) = \tfrac{1}{2}\gamma_s T_0 (1 + \gamma_e T_0 t)^{-2}. \tag{3}$$

Neither $F(0)$ nor $F(t)$ depends on β in this limit. Thus when, upon the introduction of carriers, β changes into $\beta + \phi(N)$, this change cannot affect $F(0)$ or $F(t)$. Yet it is observed that $F(0)$ and $F(t)$ decrease with increasing N and that this decrease can be represented formally by a term $-\xi(N)T^2$ in Eq. (1); that is by replacing γ_e by $\gamma_e + \xi(N)$. It follows that in addition to the well-known triplet quenching term $-\phi(N)T$ which is bilinear in N and T, there is a thus far unidentified term $-\xi(N)T^2$ which is linear in N but quadratic in T. Physically this term can be interpreted either as quenching of a pair of correlated (bound) triplets (or any state produced from them) by a carrier, or as quenching of a correlated triplet-carrier pair by another triplet.

3. A Triplet–Pair Model

Correlated triplet pairs are known to exist in anthracene crystals and their properties are reasonably well understood through the study of delayed fluorescence in a magnetic field.[3] Denoting the triplet pair population density by P and the singlet exciton density by S, we arrive at the following kinetic scheme applicable in the high-intensity region



(4)

Here the term $-k(N)P$ replaces the term $-\xi(N)T^2$ introduced above. An analysis of the experimental results in terms of this scheme leads to the following values for the rate parameters: $k_1 \simeq 1.4 \times 10^{-10}\,\mathrm{cm^3\,sec^{-1}}$ and $(2k_{-1}+k_{2T})/(2k_{2S}+k_{2T}) \simeq 2$. These values agree well with those obtained for triplet pairs in magnetic-field experiments. However, a more detailed analysis indicates the necessity to refine the model: P has to be separated into its three spin components (singlet, triplet and quintet) and it has to be assumed that only the singlet component is quenched by the carriers. This can be rationalized if it is assumed that the pair is so tightly bound that the dipole moment associated with the singlet character is strong enough to govern the transport of the pair. If the triplet–pair with singlet character travels faster than pairs with triplet or quintet character, namely as fast as or faster than the charge carriers, then its larger quenching rate can be understood. Although this explanation is perhaps not entirely satisfactory, a much more severe difficulty arises when the magnitude of the quenching is assessed, since the product of the pair lifetime $\tau_p = (k_{-1}+k_{2S}+k_{2T})^{-1}$, and the pair quenching rate constant by carriers, $k_q = k(N)/N$, is found to be of the order of $10^{-13}\,\mathrm{cm^3}$. According to the magnetic-field experiments,[3] $\tau_p \simeq 10^{-10}\,\mathrm{sec}$. Although k_q is not immediately known, the fact that the electron-hole recombination rate constant[5] is of order $10^{-6}\,\mathrm{cm^3\,sec^{-1}}$ implies that $k_q \lesssim 10^{-8}\,\mathrm{cm^3\,sec^{-1}}$. Hence the observed value of the product $\tau_p k_q$ is at least 5 orders of magnitude larger than the predicted value. Since it seems impossible to increase k_q beyond the limit given, the model requires an intermediate state with a lifetime of the order of $10^{-5}\,\mathrm{sec}$ or longer. Such long lifetimes are normally associated with states that are the lowest in energy of a given multiplicity, all other states being subject to very rapid radiationless relaxation.

Moreover, if such a long-lived triplet–pair state would exist, it

would itself be subject to quenching by triplet excitons. In the high-intensity limit, under the experimental conditions given, T exceeds N by at least three orders of magnitude.[1] Even allowing for the larger velocity of carriers relative to triplets, this means that T–P encounters should be more numerous than N–P encounters. However, there is every indication that under zero-electric field conditions, triplet decay remains a strictly bimolecular process, not only at the highest intensities used in the present work, but even at intensities that are orders of magnitude higher.[6] This indicates that the triplet pair concentration remains well below the triplet concentration under the experimental conditions, of Ref. 1, which in turn implies that pair quenching by carriers should be a much less efficient quenching process than triplet quenching by carriers. Hence it appears that the efficient quenching of delayed fluorescence observed at high intensities cannot be explained in terms of a triplet–pair intermediate state. The same arguments apply to a charge-transfer state or any other state formed from a pair of triplets.

The concept that the triplet pairs may be trapped in "cages" resulting from boundaries in the crystals is open to similar objections.[7] This model would also conflict with the evidence that a random-walk hopping motion is the dominant mode of triplet exciton transport near room temperature, so that triplet excitons are unlikely to be reflected by grain boundaries etc. Moreover, substantially the same quenching of delayed fluorescence is observed in crystals of widely varying purity and perfection.[1]

For these reasons the triplet–pair model seems unable to give a physically cogent explanation of the experimental results obtained earlier. In the next section we consider therefore a model not based on triplet pairs.

4. A Quartet-State Model

We now consider the possibility that the third-order quenching term $-\xi(N)T^2$ refers to quenching of a correlated triplet-carrier pair by a triplet. A triplet-carrier pair can exist in either a doublet or a quartet state. The former state will rapidly relax to the carrier ground state. Since we need a long-lived intermediate state we consider only the quartet component which is expected to have a

long lifetime since it is the lowest state of its multiplicity. This involves the assumption that there is such a state in anthracene within thermal range of the triplet state. Quartet–triplet annihilation will then produce a doublet (i.e., an unexcited charge carrier), or a quartet state, if we rule out sextet states on energetic grounds. If we denote the quartet population density by Q, we have the following kinetic equations

$$dT/dt = \alpha I - \beta T - \gamma_e T^2 - \phi(N)T - \zeta QT \tag{5}$$

$$dQ/dt = \phi_Q(N)T - \psi Q - \zeta_Q QT, \tag{6}$$

where ψ is the unimolecular quartet decay rate constant and ζ the bimolecular triplet–quartet annihilation rate constant. Since charge is conserved under the experimental conditions, i.e., $N = D + Q$ where D is the doublet (unexcited carrier) population density, the total triplet-carrier annihilation rate is governed by a term $-\xi DT$ and a term $-\sigma QT$. where ξ and σ represent the doublet–triplet and quartet–triplet interaction rate constants. However since N rather than D is experimentally observed, it is convenient to rewrite $-\xi DT$ in the form $-\xi(N-Q)T = -\phi(N)T - \xi QT$ and to combine $+\xi QT$ and $-\sigma QT$ into $-\zeta QT$, where $\zeta = \sigma - \xi$. In the same way we have $\zeta_Q = \sigma_Q - \xi_Q$. Since not all of the triplet-carrier encounters leading to triplet destruction will produce quartets, $\phi_Q(N)$ is smaller than $\phi(N)$. On the basis of spin statistics there are two quartets produced for every doublet, so that $\phi_Q(N) = \frac{2}{3}\phi(N)$. Similarly, not all of the triplet–quartet encounters leading to triplet destruction also destroy quartets since on the basis of spin statistics only one of every three such encounters leads to a doublet state so that $\sigma_Q = \frac{1}{3}\sigma$. Thus we have $\zeta = \sigma - \xi$ and $\xi_Q = \frac{1}{3}(\sigma - 2\xi)$, so that the ratio of ζ and ζ_Q depends on the relative magnitudes of σ and ξ. The experimental results require that $\sigma \gtrsim 2\xi$, as follows from the fact that fluorescence quenching takes place even for high intensities. If we write $\zeta_Q = \zeta/R$, we would have $R = 1/3$ for $\sigma \gg \xi$ and $R \gg 1$ for $\sigma \simeq 2\xi$, according to spin statistics. In the following both limiting cases will be considered. It should be pointed out, however, that the statistical argument is not rigorous, since other properties of the (quasi-) particles may affect the relative rate constants.

In the case where $R \gg 1$, we expect that $\zeta_Q T \ll \psi$, except at the

highest intensities, so that the steady-state quartet density is given by $Q \simeq \phi_Q(N)T/\psi$. Substitution into (5) and (6) yields the steady-state results

$$dT/dt = 0 \simeq \alpha I - [\beta + \phi(N)]T - [\gamma_e + \zeta\phi_Q(N)/\psi]T^2 \tag{7}$$

Thus in the high-intensity region this modification of Eq. (1) will have the effect of apparently increasing the triplet–triplet annihilation rate constant. Since $F \propto \gamma_e^{-1}$ in this region, the characteristic decrease of F by a factor of two for $N \simeq 10^{11}\,\mathrm{cm}^{-3}$ implies that[6] $\gamma_e \simeq \xi\phi_Q(N)/\psi = \gamma_Q\gamma_N N/\psi \simeq 10^{-11}\,\mathrm{cm}^3\,\mathrm{sec}^{-1}$ where γ_Q and γ_N represent the quartet–triplet and doublet–triplet interaction rate constants respectively. Since the overall carrier–triplet annihilation rate constant $\gamma_Q \simeq 10^{-9}\,\mathrm{cm}^3\,\mathrm{sec}^{-1}$,[1,2] it follows that $\gamma_Q/\psi \simeq 10^{-13}$ cm^3. This could for example correspond to $\gamma_Q \simeq 10^{-9}\,\mathrm{cm}^3\,\mathrm{sec}^{-1}$ and $\psi \simeq 10^4\,\mathrm{sec}^{-1}$, both of which values are close to expectations. This magnitude of ψ may not be due to the natural decay of Q to a ground state carrier, but the transit time of the excited carrier which is of the order of $10^{-4}\,\mathrm{sec}^1$ under the experimental conditions used.

These rough estimates indicate that the quartet model merits a more detailed investigation. We therefore remove the assumption that $\zeta_Q T \ll \psi$ and solve the coupled Eqs. (5) and (6) under steady-state conditions:

$$\gamma_e\zeta_Q T^3 + [\gamma_e\psi + \beta\zeta_Q + \zeta\phi_Q(N) + \zeta_Q\phi(N)]T^2 + [\beta\psi + \psi\phi(N) - \alpha I\zeta_Q]T - \alpha I\psi = 0. \tag{8}$$

We assume that $\phi_Q(N) = \frac{2}{3}\phi(N)$ and introduce the following notation $\zeta = R\zeta_Q$; $\phi(N) = \beta v$; $\zeta_Q/\psi = n\gamma_e/\beta$; $p = 4\alpha I\gamma_e\beta^{-2}$; $y = (2\gamma/\beta)T$. (9) Then Eq. (8) reduces to

$$\tfrac{1}{2}ny^3 + [1 + n + nv + \tfrac{2}{3}Rnv]y^2 + 2\left[1 + v - \frac{np}{4}\right]y - p = 0 \tag{10}$$

which for numerical computation is more conveniently transformed into

$$p = y^2 + 2(1+v)y + \tfrac{1}{4}Rnvy^2/(2+ny) \tag{11}$$

In the special case where $\psi \gg \zeta_Q T$, as considered above, we have

$$y = -\frac{1+v}{1+\frac{2}{3}Rvn}\left[\left(\frac{1+v}{1+\frac{2}{3}Rvn}\right)^2 + \frac{p}{1+\frac{2}{3}Rvn}\right]^{1/2} \tag{12}$$

which for very small p further reduces to

$$y = p/(1+v) \tag{13}$$

The alternative limit where $\psi \ll \zeta_Q T$ leads to the equation

$$y = -(1+v+\tfrac{2}{3}Rv) + [(1+v+\tfrac{2}{3}Rv)^2 + p]^{1/2}. \tag{14}$$

For $v = 0$ we have the standard result

$$y(0) = -1 + (1+p)^{1/2} \tag{15}$$

In general we shall express the results in the form

$$F(v)/F(0) = [y(v)/y(0)]^2.$$

For $p \to 0$ we thus have

$$F(v)/F(0) \to (1+v)^{-2}.$$

The maximum quenching experimentally observed at low intensities amounts to $F(v)/F(0) \simeq \frac{1}{4}$, corresponding to $v \simeq 1$.

In Figs. 1 and 2 we have plotted $F(v)/F(0)$ against p for $v = 0.3$ and 1 and different values of n and R. Quenching via quartets is largest for large n and R. Note that in the limit $n = 0$ no quenching

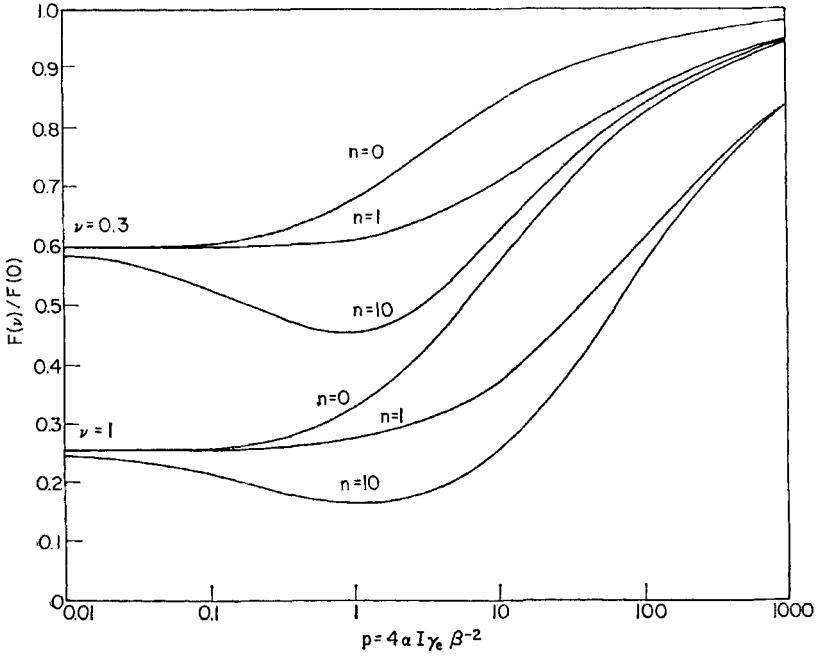


Figure 1 Delayed fluorescence quenching predicted for increasing excitation intensities, taking $\zeta.\zeta_Q^{-1} = R = 3$ and different values of $v = \phi(N)\beta^{-1}$ and $n = \zeta_Q\beta/\gamma e\psi$.

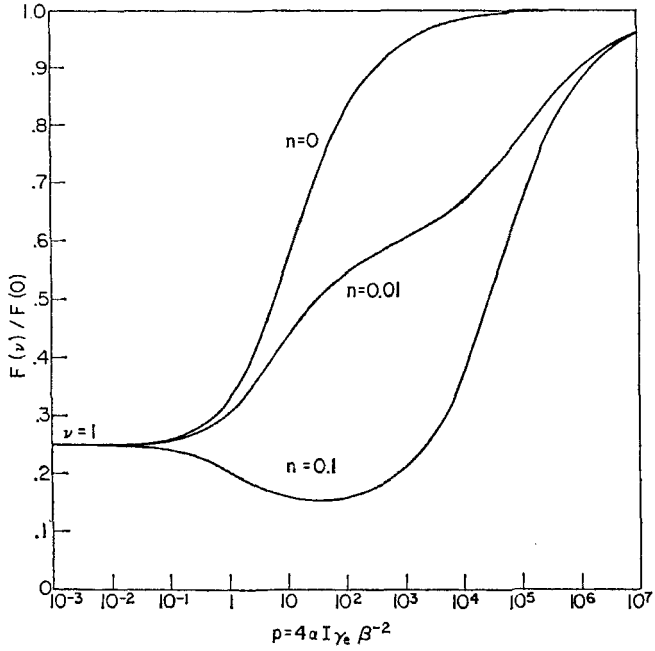


Figure 2. The same plot as in Fig. 1, for $R = 100$, $v = 1$ and different values of n.

via quartets occurs. For certain large parameter values the curves may show a minimum, indicating that quenching is strongest for intermediate light levels. It does not mean, of course, that F itself decreases with increasing I. Unfortunately, the data are not precise enough to allow determination of R and n from a comparison with published experimental results.[1] The "reasonable" choice $R = 3$, $n = 1$ is not bad, but somewhat better agreement is obtained by taking $R \gg 3$ and $n \ll 1$.

We have also studied the dependence of $[F(0) - F(v)]/F(v)$ on v for several values of p and R. Experimentally it is found that $[F(0) - F(v)]/F(v)$ increases about linearly with the free carrier concentration in the low and medium intensity region.[1] It follows from Eq. (13) that in the low intensity region we have

$$[F(0) - F(v)]/F(v) = 2v + v^2 \tag{16}$$

which is quadratic rather than linear. However for $v < 1$ the curve is not too different from a straight line. Similarly curved functions

are obtained in the intermediate intensity region, although there the curvature tends to be slightly less. It is not easy to decide whether Eq. (16) contradicts the experimental observations. Since trapping plays a role in the experiments, it seems possible that the agreement between the model and the experiment is within the experimental error.

Also, according to the kinetic model the quartet concentration should be of the same order of magnitude as the doublet concentration at the highest intensities. One might expect quartets to have (slightly) different mobility components than doublets, so that carrier mobilities should be sensitive to intense radiation in the triplet absorption region. This remains to be investigated.

Summing up we conclude that the quartet model has the following advantages over the triplet–pair model: (i) it does not require the introduction of a new state in the zero-field case, where such a state has not been detected; (ii) it identifies the long-lived intermediate state apparently involved in the quenching as the lowest state of a particular multiplicity. On the other hand there is as yet no independent evidence for the involvement of quartet excited carriers. The energy of the quartet state in anthracene is not known. We have carried out crude Pariser–Parr type calculations involving only one- and two-center integrals and obtained values of about 3.3 eV for the quartet energy relative to the doublet ground state energy of the anthracene ion. Since the triplet energy is only 1.8 eV, this result, when confirmed, would rule out the quartet model. However, the calculation is very crude and may well yield a high energy value. This is indeed suggested by the observation[8] that in decacylene (the only aromatic hydrocarbon ion for which a quartet state has been observed to date), the quartet state has an energy which is lower than the triplet energy of the parent molecule. Finally the model requires quartet–triplet quenching to be at least twice as fast as doublet–triplet quenching.

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