Production and Annihilation of Triplet Excitons in Organic Materials near Absorbing Surfaces

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The theory of delayed fluorescence produced in an organic material by singlet excitation through an absorbing layer is given. It is shown, that it will be reduced by a factor $l_a^2/(l_a+l_s)^2$ due to the singlet energy transfer to such a layer, where l_a the penetration depth of the exciting irradiation and l_s the diffusion lenght of the singlets. Further reduction of delayed fluorescence should be observed, when also triplet excitons transfer energy to the absorbing layer. Assuming this triplet transfer probalitity to be of the same order of magnitude as that for triplet energy transfer between neighbouring molecules, it should lead to quenching of delayed fluorescence proportional to l_a^2/l_t^2. The exponential portion of the decay of delayed fluorescence should become faster only if triplet energy transfer to the layer takes place. Further, the triplet induced hole-current produced at an absorbing electrode under singlet excitation should display a dependence on the wavelength of the exciting radiation as $l_a/(l_a+l_s)$. Its maximum should not occur at the wavelength of strongest absorption but at much larger penetration depths of the exciting radiation.

I. Introduction

It was shown by KALLMANN, VAUBEL and BAESSLER [1], that singlet excitons are quenched at absorbing surface layers due to energy transfer from the excitons to the absorbing layer [2]. The transfer probability was estimated to be about 10^{11} to 10^{12} sec^{-1} at the surface. Quenching results in a flux of excitons towards the surface, and a reduction of exciton density. As a consequence, their fluorescence is decreased by a factor of about $l_a/(l_a+l_s)$. l_a is the penetration depth of the exciting radiation and l_s the diffusionlength of the singlet exciton. Such a decrease of singlet density near the surface will also reduce the production rate of triplet exciton via singlets. Further reduction of triplet density may occur, if the triplets themselves are quenched at the absorbing surface. Such reductions by surface reactions and their consequences for fluorescence, lifetimes, and hole injection are theoretically treated in this paper.

Surface reactions will alter triplet densities noticeably only if the triplets are produced via singlet excitation, since the influence of surfaces becomes rather small, when the peneration depth of excitation is larger than the respective diffusionlength which is the case if triplet excitons are produced by $S_0 \rightarrow T_1$ excitation. Information about changes in triplet densities can be obtained by comparing the delayed fluorescence [3] (DF) obtained with and without an absorbing layer at the surface. Under steady state conditions fluoresecence displays a non linear increase with the intensity of excitation (proportional to the square of the triplet density), caused by the recombination of triplets. This nonlinear portion of fluorescence should be reduced with an absorbing layer at the surface. The same should be true for the delayed fluorescence observed immediately after turning off the exciting radiation. Also the decay of DF should be changed under such condition. The exponential portion of the decay curve should become steeper, if triplets themselves are quenched at the surface than without such quenching. This would not occur, when only the production rate of triplets is reduced by singlet quenching.

II. Calculation of Triplet Densities near Absorbing Surfaces

The triplet density in the neighbourhood of an absorbing layer is computed from the normal dif-

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[1] H. KALLMANN, G. VAUBEL, and H. BÄSSLER, to be published.

[2] H. KUHN, J. Chem. Phys. **53**, 101 [1970].

[3] C. A. PARKER and C. G. HATCHARD, Proc. Chem. Soc. **1962**, 147; Proc. Roy. Soc. London A **269**, 574 [1962]. — C. A. PARKER, The Triplet State, Cambridge University Press **1967**, 353. — S. P. MCGLYNN et al., Chem. Phys. **47**, 5090 [1967]. — T. AZUMI and S. P. MCGLYNN, J. Chem. Phys. **39**, 1186 [1963]. — E. C. SWENBERG, J. Chem. Phys. **51**, 1753 [1969].

fusion equation for triplets introducing the singlet density as triplet producing agent rather than the exciting radiation. This density is taken from the solution of the singlet diffusion equation and contains two exponential terms: $\exp\{-x/l_a\}$ and $\exp\{-x/l_s\}$. Both enter the diffusion equation for triplets. In order to obtain the required solutions, boundary conditions for singlets and triplets must be given. At the surface through which the sample is excited, the boundary condition for singlets is[1]:

$$v_s \, n_s(0) = D_s (\mathrm{d}n_s/\mathrm{d}x)_0 \, .$$

The index s refers to singlets; zero indicates values taken at the absorbing layer ($x=0$). v_s is the surface recombination velocity for singlets as described in Ref.[1] and equals c/τ_{qs}, where $1/\tau_{qs}$ is the energy transfer probability from a singlet exiton to the absorbing layer; c is the lattice constant. A respective relation holds for triplets, where now the index t refers to triplets:

$$v_t \, n_t(0) = D_t (\mathrm{d}n_t/\mathrm{d}x)_0 \quad \text{and} \quad v_t = c/\tau_{qt}$$

with $1/\tau_{qt}$ the probability that a triplet is quenched at the absorbing surface. The boundary condition at the nonirradiated surface is that the densities of triplets and of singlets are negligible.

In the diffusion equation for triplets a term $\beta_{tot} \, n_t^2$ occurs which describes the triplet annihilation by collision of two triplets. Only the portion $\beta_r \, n_t^2$ results in formation of singlets and leads thus to fluorescence. To simplify the problem it is first assumed that $\beta_{tot} \, n_t$ is small compared to $1/\tau_t$, where τ_t is the natural lifetime of the triplet exciton. The case $\beta_{tot} \, n_t$ larger than $1/\tau_t$ will be discussed below. The following expression for $n_t(x)$ is obtained.

$$n_t(x) = \frac{I_0 \, \tau_s \, \tau_t}{\tau_{st}} \cdot \frac{l_a}{(l_a^2 - l_s^2)} \cdot \left[\left(\frac{l_a^2 (v_t + D_t/l_a)}{(l_t^2 - l_a^2)(v_t + D_t/l_t)} - \frac{l_s^2 (v_t + D_t/l_s)(v_s + D_s/l_a)}{(l_t^2 - l_a^2)(v_t + D_t/l_t)(v_s + D_s/l_s)} \right) \cdot e^{-x/l_t} + \frac{l_s^2 (v_s + D_s/l_a)}{(l_t^2 - l_s^2)(v_s + D_s/l_s)} \cdot e^{-x/l_s} - \frac{l_a^2}{(l_t^2 - l_a^2)} \cdot e^{-x/l_a} \right] . \tag{1}$$

The indices a, s, t, refer to the absorbed radiation, singlets and triplets respectively (l_a is the penetration depth of the exciting radiation and l_s, l_t the respective diffusionslengths). $1/\tau_{st}$ is the probability per sec that a singlet produces a triplet and τ_s/τ_{st} is the singlet-triplet conversion factor. The triplet density for the case of neither singlet nor triplet quenching is given in Eq. (1 a)

$$n_t(x) = \frac{I_0 \, \tau_s \, \tau_t}{\tau_{st}} \, \frac{l_a}{(l_a^2 - l_s^2)} \left[\frac{l_t (l_a^2 - l_s^2)}{(l_t^2 - l_a^2) \, l_a} \cdot e^{-x/l_t} + \frac{l_s^3 \cdot e^{-x/l_s}}{l_a (l_t^2 - l_s^2)} - \frac{l_a^2 \cdot e^{-x/l_a}}{(l_t^2 - l_a^2)} \right] . \tag{1 a}$$

Usually the diffusionlength of triplets is much larger than l_a and l_s. Therefore the first term in (1) is the essential one. It gives the total number of triplets.

III. Delayed Fluorescence

Delayed fluorescence is given by the integral $\int \beta_r \, n_t^2(x) \, \mathrm{d}x$. For its evaluation several approximations are made. l_a and l_s are neglected compared to l_t and the second and third terms in (1) are omitted, because they depend on $1/l_t$ with a higher power than the first term. PF and DF stand for prompt and delayed fluorescence.

$$\mathrm{PF} = \frac{I_0 \, \tau_s}{\tau_e} \; ; \quad v_s \to 0 ; \tag{2 a}$$

$$\mathrm{PF} \cong \frac{I_0 \, \tau_s}{\tau_e} \, \frac{l_a}{(l_a + l_s)} \; ; \quad v_s > \frac{D_s}{l_s} \; ; \tag{2 b}$$

$$\mathrm{DF} = \beta_r \left(\frac{I_0 \, \tau_s}{\tau_{st}} \, \tau_t \right)^2 \frac{1}{2 \, l_t} \; ; \quad v_s \to 0 ; \quad v_t \to 0 ; \tag{2 c}$$

$$\mathrm{DF} = \beta_r \left(\frac{I_0 \, \tau_s}{\tau_{st}} \, \tau_t \right)^2 \frac{l_a^2}{(l_a + l_s)^2} \, \frac{1}{2 \, l_t} \; ; \qquad v_t = 0 ; \quad v_s > D_s/l_s ; \tag{2 d}$$

$$\begin{aligned} \mathrm{DF} &= \beta_r \cdot \frac{I_0 \, \tau_s}{\tau_{st}} \, \tau_t \Big)^2 \, \frac{(1 + D_t/v_t (l_a + l_s))^2}{(1 + D_t/v_t \, l_t)^2} \, \frac{1}{2} \, \frac{l_a^2}{l_t^3} \\ &= \beta_r \left(\frac{I_0 \, \tau_s}{\tau_{st}} \, \tau_t \right)^2 \frac{(1 + l_t^2/c \, (l_a + l_s) \, \tau_{qt}/\tau_t)^2}{(1 + l_t/c \, \tau_{qt}/\tau)^2} \, \frac{l_a^2}{2 \, l_t^3} \; ; \\ & \qquad v \# 0 ; \quad v_s > D_s/l_s \, . \end{aligned} \tag{2 e}$$

τ_s, τ_e is the singlet natural and radiative lifetime. Even if no special triplet quenching occurs at the surface, DF is reduced by a factor $l_a^2/(l_a + l_s)^2$ and the ratio DF/PF is reduced by a factor $l_a/(l_a + l_s)$ due to singlet quenching. For anthracene DF would be quenched by about 90% for $l_a = l_s$. For the same penetration depth l_a the quenching effect for tetracene would be much smaller since l_s in tetracene is very small. For quenching of triplet excitons themselves the reduction of DF can become as large as l_a^2/l_t^2 according to (2 a), if $v_t > D_t/l_a$, which is about 10 for anthracene. For $l_a \approx 3 \cdot 10^{-6}$ cm DF would be reduced by a factor of 10^{+5}. Only for values of v_t smaller than $5 \cdot 10^{-2}$ DF would reach the value (2 d).

In order to quantitatively evaluate the quenching effect for triplets at the surface, it is convenient to express v by c/τ_{qt}, as in the last term of (2 e) and to introduce transfer probabilities for $1/\tau_{qt}$ which are known from other transfer experiments with triplets. For intersystem crossing, values of $5 \cdot 10^7 \exp\{-\Delta E/E_0\}$ are given for the respective transition probability, and for triplet energy transfer between neighbouring molecules, values of $10^{11} \exp\{-\Delta E/E_0\}$ are given as transfer probability. One would like to compare the latter with the energy transfer to an absorbing layer, since in both cases, no change of angular momentum is involved. ΔE in the above expressions refers to the amount of energy which is transferred into vibrational energy, and E_0 is a constant of the order 0.1 eV. Since in the energy transfer process triplet – metal all the triplet energy can be transferred to the metal electrons, one would expect that the values of transfer probabilities given above also hold for triplet transfer to an absorbing layer, particularly if the latter is a metal. Introducing these probabilities into Eq. (2 e) one sees that the terms containing τ_{qt} are small compared to one for anthracene as well as for tetracene. Thus one may conjecture that strong quenching of DF takes place in these crystals. To this conjecture one is also led by the fact that for singlet quenching at an absorbing layer similar transfer probabilities are observed as for singlet transfer between neighbouring molecules. According to (2) DF decreases with decreasing penetrationsdepth of the exciting radiation, although the density of triplet production increases with decreasing l_a. This comes about by the diffusion of triplets across l_t under steady state excitation. Thus $n(x)$ decreases rather slowly with x in Eq. (1 a) (no quenching). With quenching, however, the density across the range l_a is reduced [Eq. (1)] because of the diffusion flux towards the surface. This reduction increases with decreasing l_a, the range in which the excitons are produced.

Eq. (2) holds under the assumption $\beta_{tot} \cdot n_t(x) < 1/\tau_t$. If this condition is not fulfilled, DF becomes larger and approaches $l_0 (\tau_s/\tau_{st}) (\beta_r/\beta_{tot})$ eventually at very high intensities, if neither singlet nor triplet quenching at the surface takes place. If only singlets get quenched, DF is reduced again by the factor $l_a^2/(l_a + l_s)^2$. If also triplet quenching occurs, DF is further reduced. But in this case, very large intensities are required to bring about $\beta_{tot} \cdot n_t(x) > 1/\tau_t$. In the absence of quenching, the conditions for $\beta \cdot n(x) > 1/\tau_t$ is: $(I_0 \, \tau_s/\tau_{st}) > l_t/(\beta_t \, \tau_t^2)$, for singlet quenching:

$$> \frac{l_t}{\beta_t \, \tau_t^2} \cdot \frac{(l_a + l_s)}{l_a},$$

and for triplet quenching:

$$> \frac{l_t}{\beta_t \, \tau_t^2} \cdot \frac{l_t}{l_a}.$$

This is equivalent to 10^{16} or 10^{17} quanta per cm^2 and sec for anthracene and tetracene respectively.

IV. Decay of Delayed Fluorescence

The reduction of triplet densities near absorbing any surface quenching, the decay curve consists of surfaces influences also the decay of DF. Without an hyperbolic part and an exponential one with a time-constant one half of the triplet lifetime[4]. The hyperbolic part stems from those regions, where $\beta_{tot} \cdot n(x) > 1/\tau_t$. It is reduced by a factor $l_a^2/(l_a + l_s)^2$ by singlet quenching. Triplet quenching brings about a further reduction. The time-constant of the exponential part is only changed, if triplet quenching occurs, because only under this condition additional removal of excitons from the sample arises. The change is not more than a factor of two.

V. Hole Injection by Excitons[5] at Absorbing Electrodes

The efficiency of hole injection by triplet excitons at surfaces is also strongly modified, when quenching of singlets or triplets occurs at these surface. The respective formulae are given for various quenching cases. They are derived from (1) forming the diffusion-flux $D_t \cdot (\mathrm{d}n_t/\mathrm{d}x)_0$ and expressing D_t

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[4] H. Bässler, G. Vaubel, and H. Kallmann, J. Chem. Phys. **53**, 370, 375 [1970].

[5] G. Vaubel, Phys. Stat. Sol. **38**, 217 [1970]. — N. E. Geacintov, M. Pope, and H. Kallmann, J. Chem. Phys. **45**, 2639 [1966]. — M. Pope and H. Kallmann, Symposium on Electrical Conductivity in Organic Solids, Interscience Publishers 1960, p. 83 and 1.

by l_t^2/τ_t and separating the transfer probability into two parts, $1/\tau_{qt}(\text{total})$ and $1/\tau_{qt}(\text{hole})$. The latter is the probability for hole injection alone whereas the former comprises energy transfer and hole injection.

$$\dot{i}_h = \frac{I_0\,\tau_s}{\tau_{st}}\,\frac{\tau_t}{\tau_{qt}(\text{hole})}\,\frac{c}{l_t}\,; \quad v_s = 0; \quad v_t \to 0\,, \tag{3 a}$$

$$\dot{i}_h = \frac{I_0\,\tau_s}{\tau_{st}}\,\frac{\tau_{qt}(\text{total})}{\tau_{qt}(\text{hole})}\,; \quad v_s = 0; \quad v_t > \frac{l_t}{\tau_t}\,\frac{l_t}{l_a}\,, \tag{3 b}$$

$$\dot{i}_h = \frac{I_0\,\tau_s}{\tau_{st}}\,\frac{\tau_t}{\tau_{qt}(\text{hole})}\,\frac{c}{l_t}\,\frac{l_a}{(l_a+l_s)}\,v_s\,\frac{l_s}{\tau_s}\,; \quad v_t \to 0\,, \tag{3 c}$$

$$\dot{i}_h = \frac{I_0\,\tau_s}{\tau_{st}}\,\frac{\tau_{qt}(\text{total})}{\tau_{qt}(\text{hole})}\,\frac{l_a}{(l_a+l_s)}\,; \quad v_t > \frac{l_s}{\tau_s}\,; \qquad v_s > \frac{l_t}{\tau_t}\,\frac{l_t}{(l_a+l_s)}\,. \tag{3 d}$$

All these formulae are derived neglecting l_a and l_s compared to l_t. The essential result is that a dependence on the penetration depth of the exciting radiation only occurs when singlets are strongly quenched at the surface. Then again the factor $l_a/(l_a+l_s)$ enters into the equations. That in the case of no quenching of singlets no dependence on l_a is found comes from neglecting l_a compared to l_t. Otherwise the current would be highest for small l_a, but only as $1/(l_t+l_a)$. With singlet quenching, however, the situation is quite different. The current has no maximum at strongest absorption but would be relatively weak at this wavelength and would increase with decreasing absorption and would have its maximum for l_a several times larger than l_s.

It may be difficult to observe this unusual behaviour of the current under singlet quenching condition, because in anthracene the hole current is mostly produced by singlets with a dependence as $l_s/(l_a+l_s)$ and the contribution of triplets to the hole current amounts only to a few percent. In tetracene where hole production by triplets is an efficient process, l_s is small. Thus even for strongest absorption, i. e. l_a small, $l_a/(l_a+l_s)$ is close to unity.

The effect of singlet quenching on the triplet hole production efficiency could, however, be evaluated from the decay of a current pulse. The singlet induced current decays with a time constant equal to the transit-time of charge transport through the crystal, which is about 10^{-5} sec with 10^4 V/cm and a one mm thick crystal. This is much smaller than the triplet decay time constant of $2 \cdot 10^{-2}$ sec. Since under light excitation the number of trapped charges in a crystal is small, their thermal release should be much smaller than the triplet induced component of the current. Thus the long time component of the current decay should display the effect of singlet quenching and its strength relatively to the steady state component should show the dependence $l_a/(l_a+l_s)$ at metal electrodes, but not at water electrodes.

The Eq. (3) a and b differ from each other in the value for $\tau_{qt}(\text{hole})$. If $1/\tau_{qt}(\text{total})$ is large because of energy transfer from triplet to the absorbing layer, and is for instance of the order $10^{10}\ \text{sec}^{-1}$, then $1/\tau_{qt}(\text{hole})$ must be several percent of the total transfer probability; that is of the order $10^8\ \text{sec}^{-1}$. In case of no triplet energytransfer to the electrode $1/\tau_{qt}(\text{total})$ equals $1/\tau_{qt}(\text{hole})$ and this probability can be of the order 10^3 to $10^4\ \text{sec}^{-1}$ to account for triplet induced hole production.

VI. Summary

Based on a paper by KALLMANN et al.[1] it is theoretically shown that delayed fluorescence, resulting from collisions of triplets which are produced via singlet excitons, must be quenched by a factor $l_a^2/(l_a+l_s)^2$, if the singlets are excited through an absorbing layer. This results from the observed energy transfer[1] singlet – absorbing layer. If also triplets transfer energy to an absorbing layer, delayed fluorescence should be reduced still further. Assuming that the transfer probability triplet-absorbing layer is of the same order of magnitude as the triplet transfer probability between neighbouring molecules, as it is the case for singlet exciton transfer, delayed fluorescence should be quenched by a factor l_a^2/l_t^2. The decay of delayed fluorescence, particularly its exponential part, should only be shortened by a factor of two, if triplets transfer energy to the absorbing layer. The quenching of singlet excitons at an absorbing layer introduces a strong dependence of the triplet induced hole current on the penetration depth of the exciting radiation, which would not be present without such singlet quenching. In the latter case its dependence on l_a would be proportional to $1/(l_a+l_t)$, in the case of singlet quenching it would be proportional to $l_a/(l_a+l_s)$. Thus the maximum current would not occur at strongest absorption, smallest l_a, but at considerably smaller absorption, when l_a is larger than the singlet diffusion length l_s.