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B. Nickel [a]
[a] Max-Planck-Institut für Biophysikalische Chemie Abteilung, Spektroskopie, 34, Göttingen-Nikolausberg, Am Fassberg
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Intensity Dependence of the Sensitized Delayed Fluorescence of Anthracene Single Crystals

B. NICKEL

Max-Planck-Institut für Biophysikalische Chemie
Abteilung Spektroskopie
34 Göttingen–Nikolausberg, Am Fassberg

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Abstract—The intensity I_2 of the sensitized delayed fluorescence (SDF) of an anthracene single crystal depends in the simplest case on four quantities: The generation rate $k_0 \propto I_0$ of triplet excitons (I_0 = excitation intensity), the rate of surface quenching of triplet excitons and the rates of monomolecular and bimolecular decay of triplet excitons. For this case the intensity dependence $I_2 = I_2(I_0)$ is derived for the stationary state and compared with experimental results obtained with erythrosin as a sensitizer. The agreement between theory and experiment is satisfactory.

1. Introduction

In a preceding publication[1] the connection between sensitized photoconduction and sensitized delayed fluorescence (SDF) of anthracene single crystals was investigated. A simple reaction scheme was proposed for the dependence of the intensity I_2 of the SDF on the surface generation of triplet excitons and on the decay processes, competing with triplet–triplet-annihilation. This reaction scheme is shown once more in Fig. 1.

In the present paper the quantitative consequences of this model are derived and compared with experimental data.

2. Spatial Distribution $n(x)$ of Triplet Excitons in the Stationary State

2.1. Production and Decay of Triplet Excitons

Triplet excitons are generated at the crystal surface with the rate k_0:

$$k_0 = I_0 \epsilon_n c \eta_{ET} = I_0 \eta_{sens} \propto I_0 \tag{1}$$

I_0 = excitation intensity in photons $cm^{-2}\ s^{-1}$,

ϵ_n = natural molar extinction coefficient in $cm^2\ mol^{-1}$,

c = concentration of adsorbed dye in $mol\ cm^{-2}$,

η_{ET} = quantum yield of the energy transfer
$^1D^* + A \rightarrow \ldots \rightarrow D + {}^3A^*$

η_{sens} = yield of triplet excitons with respect to I_0

$k_0 \propto \epsilon_n \cdot c$ is justified because only a small fraction of the light is absorbed.

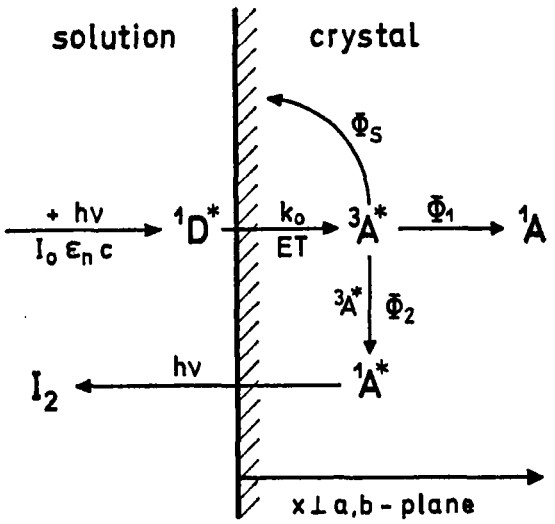

Figure 1. The simplest reaction scheme for the sensitized generation of triplet excitons $^3A^*$ with the rate $k_0 \propto I_0$ and the decay of triplet excitons by surface quenching Φ_s, monomolecular decay Φ_1 and bimolecular decay Φ_2.

Triplet excitons are consumed by three processes:

1. Quenching of triplet excitons at the surface with the rate Φ_s:

$$\Phi_s = k_s n(0) \qquad (2)$$

(k_s = surface quenching rate constant; $n(x)$ = concentration of triplet excitons at a distance x from the surface).

2. Monomolecular decay of triplet excitons in the bulk of the crystal with the rate Φ_1:

$$\Phi_1 = \beta \int_0^\infty n(x)\mathrm{d}x \tag{3}$$

(β = monomolecular decay constant).

3. Bimolecular decay of triplet excitons by T–T-annihilation with the rate Φ_2:

$$\Phi_2 = \gamma \int_0^\infty n(x)^2\mathrm{d}x \tag{4}$$

(γ = T–T-annihilation rate constant).

In the stationary state the production of triplet excitons equals the decay of triplet excitons:

$$k_0 = k_s n(0) + \beta \int_0^\infty n(x)\mathrm{d}x + \gamma \int_0^\infty n(x)^2\mathrm{d}x \tag{5}$$

$$k_0 = \Phi_s + \Phi_1 + \Phi_2 \tag{5a}$$

and in the bulk of the crystal ($x > 0$) the equation

$$D\frac{d^2n(x)}{\mathrm{d}x^2} - \beta n(x) - \gamma n(x)^2 = 0 \tag{6}$$

holds (D = diffusion constant of triplet excitons for the direction $x \perp$ crystal surface).

2.2. Simplifying Assumptions Contained in Eqs. (5) and (6)

The equations (5) and (6) contain several simplifying assumptions:

(a) The crystal surface is illuminated homogeneously and the diameter of the illuminated area is large compared to the diffusion length of triplet excitons in a plane parallel to the surface (see Sec. 4).

(b) The surface is an ideal plane surface.

(c) The direct generation of triplet excitons by $^1A \rightarrow {}^3A^*$ absorption is neglected. This assumption is easily justified experimentally by the measurement of the delayed fluorescence I_{20} in a blank experiment when no dye is adsorbed on the surface. For thin crystals ($d < 100\ \mu$m) the condition $I_{20} < 10^{-3} I_2$ was usually fulfilled.

(d) The finite thickness d of the crystal is not taken into account. This is justified if for the diffusion length $L = \sqrt{D\tau}$ of the triplet

excitons $d > 5L$. $\tau \sim 10^{-2}$ sec and $D = D_{c'} \sim 10^{-6}$ cm^2 s^{-1}[2] gives $L \sim 10^{-4}$ cm $= 1\ \mu$m. The crystal thickness was usually between 10 and 100 μm.

(e) The constants k_s, β, γ do not depend on the excitation intensity I_0. At least for k_s this is not a trivial assumption. If for the triplet energies $E(^3A^*)$ and $E(^3D^*)$

$$E(^3A^*) \approx E(^3D^*), \tag{7}$$

triplet excitons can be quenched at the surface by T–T–ET and deactivation of $^3D^*$:

$$^3A^* \ldots {}^1D \underset{k_{DA}}{\overset{k_{AD}}{\rightleftharpoons}} {}^1A \ldots {}^3D^* \tag{8}$$

$$^3D^* \xrightarrow{k_D} {}^1D \tag{9}$$

In homogeneous solution the reverse energy transfer (8) has been observed, e.g. with D = eosin or erythrosin.[3] In the stationary state k_s can be written as

$$k_s = k_{s0} + k_{AD}\frac{k_D}{k_D + k_{DA}} \cdot c' = k_{s0} + k_{s1} \tag{10}$$

c' is a constant with the dimension of a length (see Sec. 5.3). A consequence of (8) is the possibility of mixed T–T-annihilation (11):

$$^3D^* + {}^3A^* \rightarrow ({}^1D^* + A) \rightarrow D^- + A^+ \tag{11}$$

i.e., to the balance equation (5) a second surface quenching term $k_{s2}n(0)^2$ should be added. Thus, the simplifying assumption contained in (5) is

$$k_{s2}n(0) \ll k_{s0} + k_{s1}.$$

(f) β does not depend on x. It should be noted that the intensity dependence $I_2 \propto I_0^2$, derived in Sec. 3.1 for low excitation intensities, does not depend on this assumption. For $I_2 \propto I_0^2$ it is sufficient that $n(x) = n(0) \cdot f(x)$—with $n(0) \propto I_0$ and $f(x)$ independent of I_0.

2.3. Solution of the Differential Equation (6).

With the boundary conditions

$$\lim_{x\to\infty} n(x) = 0; \quad \lim_{x\to\infty} \frac{dn(x)}{dx} = 0 \tag{12}$$

one obtains from (6):

$$n(x) = n_0 \exp(-x/L)\{g/[1 - (1-g)\exp(-x/L)]\}^2 \tag{13}$$

with $n_0 = n(0)$ and

$$L = (D/\beta)^{1/2} = (D\tau)^{1/2} \tag{14}$$

$$g = \frac{3\beta}{\gamma n_0}\left[\left(1 + \frac{2\gamma n_0}{3\beta}\right)^{1/2} - 1\right] \tag{15}$$

With (13) one gets for the integrals Φ_1 and Φ_2 in Eq. (5a):

$$\Phi_1 = \beta \int_0^\infty n(x)\mathrm{d}x = \beta n_0 L g \tag{16}$$

$$\Phi_2 = \gamma \int_0^\infty n(x)^2 \mathrm{d}x = \tfrac{1}{2}\gamma n_0^2 L \frac{g(2+g)}{3} \tag{17}$$

It is useful to define two other quantities: The average distance of T–T-annihilation from the surface, $\overline{x_{TT}}$, is defined by

$$\overline{x_{TT}} = \int_0^\infty n(x)^2 x\,\mathrm{d}x \Big/ \int_0^\infty n(x)^2 \mathrm{d}x \tag{18}$$

$$\overline{x_{TT}} = \tfrac{1}{2}L \frac{2g(1-g+g^2\ln g)}{(1-g)^2(2+g)} \tag{19}$$

The average decay constant $\bar{\beta}$ of triplet excitons in the bulk of the crystal is defined by

$$\bar{\beta} = \int_0^\infty (\beta + \gamma n(x)) \cdot n(x)\,\mathrm{d}x \Big/ \int_0^\infty n(x)\,\mathrm{d}x \tag{20}$$

$$\bar{\beta} = \beta(1 + \Phi_2/\Phi_1) = \beta + \tfrac{1}{2}\gamma n_0 \frac{2+g}{3} \tag{21}$$

3. Connection Between Φ_2 and the Measurable SDF I_2

3.1. Limiting Case $\Phi_2 \ll \Phi_1$

For small excitation intensities I_0 the T–T-annihilation can be neglected as a process leading to the decay of triplet excitons, i.e. $\gamma n_0 \ll \beta$, $g \approx 1$ and $\Phi_2 \ll \Phi_1$. In this case the following equations are obtained:

$$n(x) = n_0 \exp(-x/L) \tag{13a}$$

$$\Phi_1 = \beta n_0 L \tag{16a}$$

$$\Phi_2 = \tfrac{1}{2}\gamma n_0^2 L \tag{17a}$$

$$\overline{x_{TT}} = \tfrac{1}{2}L \tag{19a}$$

$$\bar{\beta} = \beta \tag{21a}$$

$n(x)$ is an exponential function of x. The rate $v_2(x)$ of generation of singlet excitons by T–T-annihilation is then also an exponential function:

$$v_2(x) = \tfrac{1}{2}\gamma f n_0^2 \exp(-2x/L) \tag{22}$$

(f is the probability of formation of a singlet exciton by a T–T-annihilation; $f \approx 0.4$[4]. The exponential dependence of $v_2(x)$ on x has been used for the determination of the diffusion constant $D = D_{c'}$[2]. $v_2(x)$ can be compared with the rate $v_{pr.}(x)$ of prompt generation of singlet excitons by direct excitation in the near UV:

$$v_{pr.}(x) = I_0 \alpha \exp(-\alpha x) \tag{23}$$

(α = absorption constant of anthracene). The exponential functions in (22) and (23) are identical if $2/L = \alpha$. In Fig. 2(a) fluorescence spectra of an anthracene single crystal are shown for different penetration depths $1/\alpha$ of the excitation light. With increasing $1/\alpha$ the first maximum at 400 nm decreases because of increasing reabsorption of the short wavelength fluorescence. Figure 2(b) shows identical spectra of prompt fluorescence and sensitized delayed fluorescence.

The exponential function in (22) is independent of the excitation intensity. Therefore the fraction of singlet excitons which are quenched at the surface is constant, and

$$I_2 \propto \Phi_2 \tag{24}$$

holds. The balance equation (5) reduces to

$$I_0 \eta_{sens} = k_0 = k_s n_0 + \beta n_0 L \tag{25}$$

or

$$n_0 \propto I_0 \tag{26}$$

and with (17a)

$$I_2 \propto \Phi_2 = \tfrac{1}{2}\gamma n_0^2 L = \tfrac{1}{2}\gamma \left(\frac{I_0 \eta_{sens}}{k_s + \beta L}\right)^2 \propto I_0^2 \tag{27}$$

3.2. General Case

In the general case I_2 is only approximately proportional to Φ_2 for two reasons:

(a) With increasing excitation intensity $\overline{x_{TT}}$ decreases, i.e. the quenching of singlet excitons at the surface increases. Let $P_f(\overline{x_{TT}})$ be the probability that a singlet exciton is not quenched at the

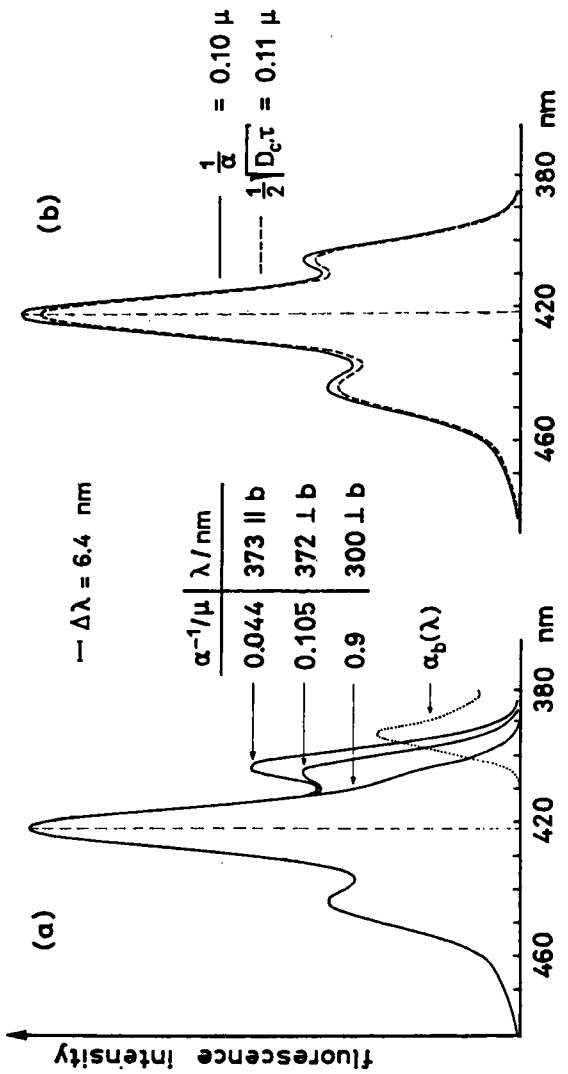

Figure 2. Fluorescence spectra of an anthracene single crystal with rhodamine B adsorbed on the surface. (*a*) Uncorrected spectra of the prompt fluorescence for different penetration depth $1/\alpha$ of the exciting light. $\parallel b$ and $\perp b$ indicate polarization of the exciting light parallel or perpendicular to the crystallographic *b*-axis. $\alpha_b(\lambda)$ = absorption spectrum for *b*-polarized light in relative units; (*b*) Identical spectra of prompt and sensitized delayed fluorescence. Lifetime of triplet excitons: $\tau = 1/\beta \approx 1$ ms (experimental value).

surface. For a pure anthracene crystal $P_f(\overline{x_{TT}})$ is approximately the quantum yield of the primary fluorescence. In the general case the rate $v_2(x)$ of generation of singlet excitons by T–T-annihilation is a non-exponential function of x. Approximating $v_2(x)$ by $v_2(x) \propto \exp(-x/\overline{x_{TT}})$ and assuming that every singlet exciton that contacts the surface is quenched, one gets[5]:

$$P_f(\overline{x_{TT}}) = \frac{\overline{x_{TT}}}{\overline{x_{TT}} + L_s} \tag{28}$$

(L_s = diffusion length of singlet excitons; $L_s \approx 400$ Å for the direction $c' \perp a,b$-plane[5]).

(b) With decreasing $\overline{x_{TT}}$ the fluorescence reabsorption also decreases. The average wavelength of the observable fluorescence is shifted to shorter wavelengths. $I_2 \propto \Phi_2 P_f(\overline{x_{TT}})$ is still valid, if the spectral sensitivity $\vartheta(\lambda)$ of the measuring system is constant in the spectral region of the anthracene fluorescence and if the increase of total reflection of fluorescence light with decreasing λ is neglected. With the used combination, Schott blue filter BG 12 (8 mm) + RCA photomultiplier 1 P 21, the maximum of $\vartheta(\lambda)$ was at 400 nm; at 450 nm $\vartheta(\lambda)$ was only $\frac{1}{4}$ of the maximum. Thus $\vartheta(\lambda)$ was far from being constant. The probability that the emitted fluorescence is measured, P_3, increases with decreasing $\overline{x_{TT}}$. Thus generally

$$I_2 \propto \Phi_2 \cdot P_f(\overline{x_{TT}}) \cdot P_3(\overline{x_{TT}}) = \Phi_2 f(\overline{x_{TT}}). \tag{29}$$

4. Experimental

For details of the experimental technique see Ref. 1.

The SDF of anthracene was measured with erythrosin as a sensitizer. Erythrosin was chosen for three reasons:

1. With erythrosin a higher intensity I_2 of the SDF was found than with eosin Y or rhodamine B.
2. The properties of the heterogeneous system anthracene single crystal/adsorbed dye/aqueous dye solution were constant for hours in the case of erythrosin.
3. With erythrosin a practically normal time dependence $I_2(t)$ was found.[1] Thus a necessary condition for the applicability of the model in Fig. 1 was fulfilled.

The excitation intensity of an argon-ion-laser beam was varied with calibrated neutral density filters. In addition the relative excitation intensity was monitored by measuring the fluorescence intensity of the dissolved erythrosin. At the end of the experiments I_2 was for a given I_0 less than 10% lower than at the beginning. The maximum deviation of $I_0(y,z)$ from the average $\overline{I_0(y,z)}$ was estimated to be less than 20% (y,z-plane perpendicular to the beam direction x).

Spectra of the SDF were measured with a Bausch and Lomb high intensity monochromator with an additional Schott filter BG 12 (4 mm) for suppression of stray excitation light. For the selective measurement of the fluorescence intensity at 400 nm (first maximum) and 422 nm (second maximum) Schott double band interference filters DEPAL with an additional BG 12 (4 mm) were used.

Orientation of the crystal: The crystal was situated between two crossed polarizers. Visible linearly polarized light passes unchanged through the crystal if the crystallographic a-axis or b-axis is in the plane of polarization. Thus, if complete darkness occurs the polarization of the light is parallel to one of the two axes. For the differentiation between the two axes use was made of the fact that the fluorescence spectrum of crystalline anthracene depends on the penetration depth of the exciting light. The crystal was excited in the second absorption maximum at 373 nm with polarized light and the fluorescence intensity I was measured at 400 and 420 nm. The ratio $I(400)/I(420)$ is greater for polarization parallel to the b-axis.

The experiments reported in this paper were performed before the oriented adsorption of erythrosin[6] was known.

5. Results and Discussion

5.1. Intensity Dependence of the SDF

In Fig. 3 experimental values of the intensity I_2 of the SDF are shown in relative units as a function of the excitation intensity I_0 : $I_2 = I_2(I_0)$—full circles. The curve $\Phi_2 = \Phi_2(I_0)$ has been calculated. In the dashed curve Φ_2' the increasing surface quenching of singlet excitons has been taken into account (cf. Eq. (28)):

$$\Phi_2' = \Phi_2 \cdot P_f(\overline{x_{TT}})/P_f(L/2) \tag{30}$$

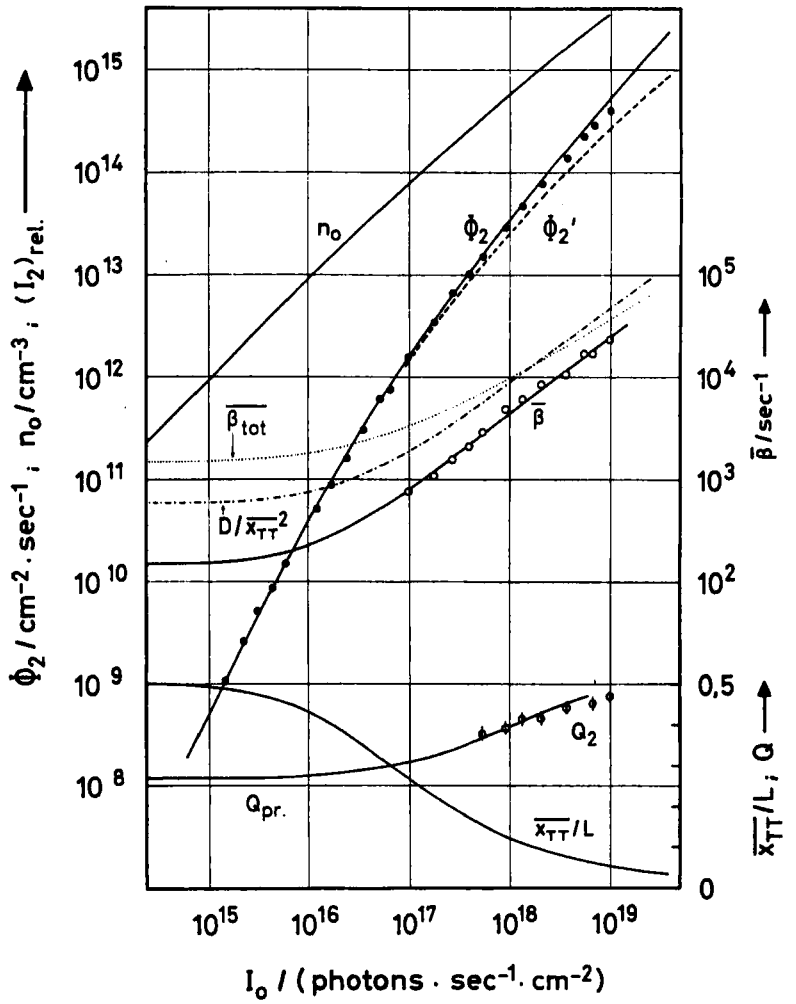

Figure 3. Intensity dependence of the SDF of an anthracene single crystal. *Experimental values*: $I_2(I_1)$—full circles; $(2.6 \cdot t_r)^{-1}$—empty circles (for the definition of t_r see Fig. 4); $Q_2 = I_2(400)/I_2(420)$—symbol ϕ. Calculated curves: n_0, Φ_2, Φ_2', $\bar{\beta}$, $\overline{\beta_{tot}}$, $D/\overline{x_{TT}}^2$ (the vertical scale of $\overline{\beta_{tot}}$ and $D/\overline{x_{TT}}^2$ is the same as for $\bar{\beta}$), $\overline{x_{TT}}/L$. The curve $Q_{pr.}$ has been calculated from experimental values. *Experimental conditions*: Aqueous solution with $1.6 \cdot 10^{-6}$ M erythrosin, 10^{-2} M NaOH, 1 M KCl in contact with the *a*,*b*-plane of an anthracene single crystal. Temperature: 22 °C. Excitation at 514 nm.

In the calculation of $\Phi_2 = \Phi_2(I_0)$ the triplet concentration n_0 was used as independent variable. Φ_s, Φ_1, Φ_2 were calculated for a given n_0 with Eqs. (2), (16), (17); k_0 was obtained from the balance Eq. (5a), and with η_{sens}, I_0 was obtained from Eq. (1). The following values of the constants were used:

$$\beta = 143\ \text{s}^{-1},\ D = 5 \cdot 10^{-7}\ \text{cm}^2\ \text{sec}^{-1},^{(2)}$$
$$\gamma = 2 \cdot 10^{-11}\ \text{cm}^3\ \text{sec}^{-1}.^{(4)}$$

The constants k_s and η_{sens} were used as adjustable parameters. The curves n_0, Φ_2, Φ_2', $\bar{\beta}$, $\overline{\beta_{\text{tot}}}$, $D/\overline{x_{\text{TT}}}^2$ and $\overline{x_{\text{TT}}}/L$ in Fig. 3 were calculated with

$$k_s = 0.08\ \text{cm s}^{-1};\ \eta_{\text{sens}} = 8.1 \cdot 10^{-5}.$$

Figure 3 shows that the experimentally found intensity dependence $I_2(I_0)$ can be described quantitatively by the model in Fig. 1. Especially at low excitation intensities the expected quadratic dependence $I_2 \propto I_0^2$ has been found. At high intensities the experimental values I_2 lie between the two calculated curves Φ_2 and Φ_2'.

The values of the constants k_s and η_{sens} are to some extent arbitrary for two reasons: Firstly because of the uncertainty introduced by the unknown function $f(\overline{x_{\text{TT}}})$ in Eq. (29), secondly because of the uncertainty of the constants γ and $D_{c'}$. For this reason possibly only the order of magnitude of k_s and η_{sens} is correct.

5.2. Time Dependence $I_2 = I_2(t)$

It has been pointed out[1] that at constant excitation intensity I_0 the intensity I_2 of the SDF should rise monotonously and finally attain a stationary value. Figure 4 shows that this is approximately the case even with the highest excitation intensities used.

The complete analysis of the time dependence $I_2(t)$ requires the calculation of $\Phi_2(t)$. In principle the rise of Φ_2 can be calculated from the partial differential equation

$$\frac{\partial n(x,t)}{\partial t} = D\frac{\partial^2 n(x,t)}{\partial x^2} - \beta n(x,t) - \gamma n(x,t)^2, \tag{31}$$

the balance equation

$$k_0(t) = k_s n(0,t) + \beta \int_0^\infty n(x,t)\,\mathrm{d}x + \gamma \int_0^\infty n(x,t)^2\,\mathrm{d}x + \frac{\partial}{\partial t}\int_0^\infty n(x,t)\,\mathrm{d}x, \tag{32}$$

and from the condition $n(x,t) = 0$, if the excitation begins at $t = 0$,

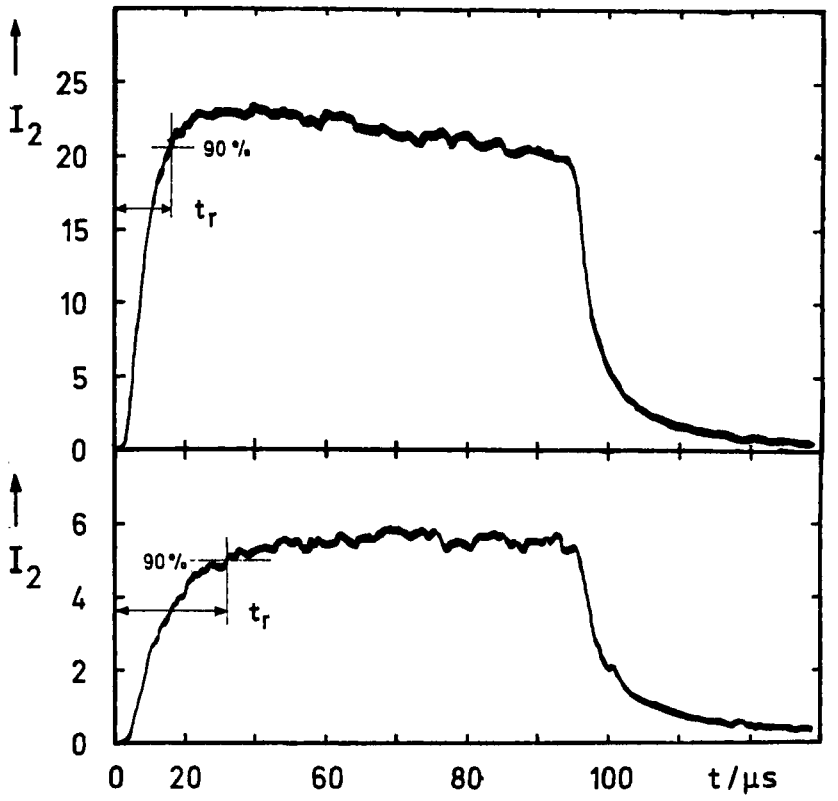

Figure 4. Definition of the rise time t_r of the intensity I_2 of the SDF. Excitation intensity for the upper curve: $I_0 \approx 1.0 \cdot 10^{19}$ photons cm^{-2} sec^{-1}; for the lower curve I_0 is by a factor 0.34 lower.

The decay of Φ_2 can be calculated from (31), from the boundary condition

$$k_s n(o,t) = D\left(\frac{\partial n(x,t)}{\partial x}\right)_{x=0}, \tag{33}$$

and from the stationary distribution $n(x)$ at $t = 0$, if the excitation ceases at $t = 0$. The numerical calculation of $\Phi_2(t)$ certainly constitutes a considerable computational task. However, for certain purposes a much simpler approach is sufficient.

The experimentally observable rise of the SDF can be characterized by the rise time t_r. t_r is arbitrarily defined by $I_2(t_r) = 0.9\,(I_2)_{max}$ (see Fig. 4). The intensity dependence of t_r can be estimated in two ways. The diffusion of triplet excitons into the bulk of the crystal is limited by monomolecular and bimolecular decay. The average decay constant for both processes is in the stationary state $\bar{\beta}$ (see Eq. (20)). Therefore one should find approximately $1/t_r \propto \bar{\beta}$. Figure 3 shows that in fact $(2.6 \cdot t_r)^{-1} = \bar{\beta}$. In view of the arbitrary definition of t_r and of the experimental uncertainty of $t_r(\pm 10\%)$, the close fit of the calculated curve to the experimental points has to be regarded as fortuitous. By analogy with a homogenous distribution of triplet excitons, one should expect for the absolute values: $t_r > \bar{\tau} = 1/\bar{\beta}$. In contrast to this $t_r = \bar{\tau}/2.6 < \bar{\tau}$ is found. This is certainly caused by the complete neglect of surface quenching of triplet excitons, which is the dominating decay process in nearly the whole intensity range.

Another approach to the estimation of the intensity dependence of t_r can be based on the fact that the average distance $\overline{x_{TT}}$ of triplet–triplet-annihilation from the surface decreases with increasing excitation intensity—see Fig. 3, $\overline{x_{TT}}/L$. The time required to attain, at $x = \overline{x_{TT}}$, a definite fraction of the stationary value $n(\overline{x_{TT}})_{stat}$ therefore decreases too, and one should expect approximately $t_r \propto \overline{x_{TT}}^2/D$. In fact the intensity dependence of t_r is nearly as well represented by $\overline{x_{TT}}^2/D$ as by $\bar{\tau}$.

The decrease of $\overline{x_{TT}}$ with increasing I_0 has been observed more directly by the measurement of the intensity I_2 at 400 and 420 nm, $I_2(400)$ and $I_2(420)$. With decreasing $\overline{x_{TT}}$ the ratio $Q_2 = I_2(400)/I_2(420)$ increases, because the fluorescence reabsorption decreases (see Fig. 3). The slope of Q_2 is of the right order of magnitude. This is shown by comparison of Q_2 with the corresponding ratio $Q_{pr.}$ of the prompt fluorescence. One should expect $Q_2 \approx Q_{pr.}$, if $\overline{x_{TT}} = 1/\alpha$. With this assumption the curve $Q_{pr.}$ has been calculated from the excitation spectrum[2] $Q_{pr.} = Q_{pr.}(\alpha(\tilde{\nu}))$.

The initial slope of the decay curve of I_2 can be estimated by including surface quenching in the average decay constant of triplet excitons:

$$\overline{\beta_{tot}} = \beta\left(1 + \frac{\Phi_2}{\Phi_1} + \frac{\Phi_s}{\Phi_1}\right) \tag{34}$$

If the excitation ends at $t = 0$, one should find

$$\left(\frac{d \ln I_2}{dt}\right)_{t=0} \approx \left(\frac{d \ln \Phi_2}{dt}\right)_{t=0} \sim -2\,\overline{\beta_{tot}} \tag{35}$$

I_2 is only approximately proportional to Φ_2 because $\overline{x_{TT}}$ increases monotonously for $t > 0$. Experimentally this can be demonstrated by measuring the decay of I_2 at 400 and 420 nm: $I_2(400)$ decays faster than $I_2(420)$. An example of the applicability of (35) is given by the lower curve in Fig. 4. One finds $(d \ln I_2/dt)_{t=0} \approx -9 \cdot 10^4\ s^{-1}$ and $2\,\overline{\beta_{tot}} = 4.0 \cdot 10^4\ s^{-1}$.

If the initial slope of the decay of I_2 is mainly determined by the surface quenching constant k_s, it can be used to decide whether the change of an external parameter leaves k_s unchanged or not; e.g. application of a voltage[1] decreases I_2. If the decrease of I_2 is only due to a decrease of k_0, then, for a given stationary value of I_2, the initial slope of the decay of I_2 should be independent of the applied voltage.

5.3. Interpretation of the Constant k_s

The dimension of k_s is cm s^{-1}. From k_s a first order rate constant k_s' can be obtained by the following consideration: Let the crystal surface be a pure (001) plane. Then it is reasonable to assume that triplet excitons are quenched by a surface reaction only if they are in the first monolayer of anthracene molecules. The thickness of this layer is $c' = 9.17 \cdot 10^{-8}$ cm.[7] Thus the rate of surface quenching, Φ_s, can be written as

$$\Phi_s = k_s n(0) = \frac{k_s}{c'} \int_0^{c'} n(x)\,dx = k_s' \int_0^{c'} n(x)\,dx$$

With $k_s = 0.08$ cm sec^{-1} one obtains $k_s' = k_s/c' \approx 1 \cdot 10^6\ sec^{-1}$. k_s' is the decay constant of the contact pair $D \ldots {}^3A^*$ with respect to surface quenching. D stands here for the total adsorption layer and not only for the adsorbed dye.

Concluding Remark

It should be possible to clarify the role of the reverse T–T–ET ${}^3A^* + D \rightarrow A + {}^3D^*$ by the measurement of the phosphorescence of the adsorbed dye. In this connection it is noteworthy, that the dye solution can be removed after sufficient dye has been adsorbed, and

that the SDF can be observed also at 77 °K: The absolute intensity and the excitation spectrum of the SDF are not very different at room temperature and at 77 °K.

In principle, some of the quantities occurring in the model can be determined independently. The absolute value of $\frac{1}{2}f\Phi_2$ can be determined by the comparison of the SDF I_2 with a prompt fluorescence $I_{pr.}$: If $\alpha(\tilde{\nu}) = 1/\overline{x_{TT}}$, and if the absorbed intensity $I_0(\tilde{\nu})$ is known, then $\frac{1}{2}f\Phi_2 = I_0(\tilde{\nu})$ follows from $I_2 = I_{pr.}(\tilde{\nu})$.

The rate of light absorption by the adsorbed dye, $I_0\epsilon_n c$, can be measured directly.[6] Thus, if k_0 is known from the intensity dependence $I_2(I_0)$, the quantum yield η_{ET} of energy transfer can also be determined. η_{ET} is the quantity needed for the comparison of different sensitizers.

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