

FLUORESCENCE DEPOLARIZATION DUE TO EXCITON ANNIHILATION IN MOLECULAR DOMAINS

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A theory of time-resolved fluorescence depolarization due to singlet–singlet exciton annihilation is presented for the ensemble of randomly oriented molecular domains formed of chromophores (or their associates) with parallel transition moments. For large $t < \tau$, the fluorescence anisotropy induced by the delta pulse excitation is shown to decrease as $t^{-1/2}$, while the anisotropy after the long-pulse excitation decreases as $t^{-1}(\text{const} + \ln t)$, τ being the excited-state lifetime. The residual fluorescence anisotropy at long times is estimated. The results obtained are applied to J-aggregated pseudoisocyanine dye (PIC) solutions to account for the intensity-dependent depolarization recently observed. From the comparison of the theory with the experiment, the number of PIC molecules forming a domain was evaluated to be more than 10^4 .

1. Introduction

The transfer of electronic excitations in condensed molecular systems [1–3] together with the related high-density effect of exciton–exciton annihilation [4–11] has provided an interesting field of research for many years. Experimentally, singlet–singlet exciton annihilation manifests itself by a decrease in the fluorescence lifetime and also by a decrease in the integrated quantum yield of fluorescence, as the intensity of the excitation pulses is increased. In this paper we consider another possible experimental manifestation of exciton annihilation, viz., intensity-dependent fluorescence depolarization. To our knowledge, all theoretical studies so far have been limited to the intensity-independent fluorescence depolarization, such as the depolarization due to the excitation transfer [2,12–15].

The time-resolved fluorescence depolarization technique has proved to be extremely useful for obtaining information both on the transfer of electronic excitation between identical molecules and on their mutual orientations [16–19]. Here we show that from the intensity dependence of time-resolved fluorescence depolarization one can also

get information on the number of chromophores forming a domain. The results obtained can be applied to systems in which excitation transfer within the domain occurs between highly oriented chromophores (or their associates), an example of such a system being the J-aggregated pseudoisocyanine dye (PIC) solution [10].

The paper is organized as follows. In section 2 the problem is formulated. In section 3 the continuous model of exciton annihilation is used to derive the fluorescence anisotropy considered both as a function of time and intensity. In section 4 the influence of the fluctuations of the initial exciton number in domains on the residual anisotropy at long times is investigated by using the discrete model of exciton annihilation. In section 5 some final remarks are given, as well as the application to highly concentrated PIC solutions is considered.

2. Formulation

The system under investigation consists of a large number of molecular domains embedded in a three-dimensional medium. The excitation en-

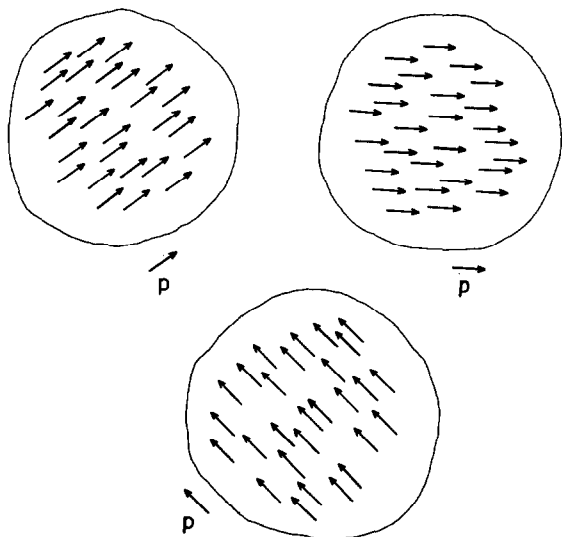


Fig. 1. Schematic representation of the system of molecular domains. Arrows indicate the transition moments of chromophores (or their associates) forming domains.

ergy transfer within an individual domain is assumed to occur among chromophores (or their strongly coupled associates) with parallel transition moments, and the unit vector $\mathbf{p}$ parallel to them indicates the orientation of the domain (fig. 1). An isotropic probability density for the orientations of domains is assumed. Both the interdomain excitation transfer and the changes in orientation of domains due to rotational motion are considered to be negligible. The quantity of interest is the time-dependent fluorescence anisotropy given by

$$r = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp}), \quad (1)$$

with

$$I_{\parallel} \sim \langle p_{\parallel}^2 N_{p_{\parallel}} \rangle, \quad I_{\perp} \sim \langle p_{\perp}^2 N_{p_{\parallel}} \rangle. \quad (2)$$

Here $I_{\parallel}$ and $I_{\perp}$ are the intensities of the emitted light polarized parallel and perpendicular to the polarization of the excitation pulse, $p_{\parallel}$ and $p_{\perp}$ are components of the unit vector $\mathbf{p}$. $N_{p_{\parallel}}$ is the exciton-number density in domains depending on the domain orientation. For example, for strictly perpendicular orientation ($p_{\parallel} = 0$) it equals zero, while for the parallel one ($p_{\parallel} = 1$) $N_{p_{\parallel}}$ reaches its maximum value. The brackets $\langle \rangle$ denote an aver-

age over all possible orientations of the domains. The density $N_{p_{\parallel}}$ is supposed to be independent of space variables. Equations (1) and (2) can be easily rewritten as follows:

$$r = (3L_2/L_0 - 1)/2, \quad (3)$$

where

$$L_n = \langle p_{\parallel}^n N_{p_{\parallel}} \rangle = \int_0^1 p_{\parallel}^n N_{p_{\parallel}} dp_{\parallel}. \quad (4)$$

Equations (2)–(4) implicitly assume that the absorption and fluorescence transition dipole moments are polarized along the same axis. If a different electronic level than that from which emission occurs is excited and its transition moment is at some angle α to that of the latter, the anisotropy (3) should be reduced by the factor

$$(3 \cos^2 \alpha - 1)/2.$$

At low pumping intensity only one exciton can be created per domain, so the exciton-number density of all domains decreases with the same exponential decay rate. Under this condition no depolarization is possible. When several excitons are created simultaneously in a given domain, bimolecular singlet–singlet annihilation can take place. The rate of exciton annihilation is known to increase with the increase of the density of excitons, i.e., more excited domains decay faster than less excited ones. Thus, the annihilation tends to reduce the initial anisotropy induced in the sample by the polarized excitation pulse. In the next two sections concrete annihilation models will be considered to investigate the peculiarities of the depolarization due to singlet–singlet exciton annihilation.

3. Continuous model

In this section the mean number of excitons per domain is considered to be sufficiently large, so that the fluctuations of the exciton number would be of no importance. The exciton-number density $N_{p_{\parallel}}$ is supposed to satisfy the standard bimolecular annihilation equation [4–6,20]

$$dN_{p_{\parallel}}/dt = -\tau^{-1}N_{p_{\parallel}} - \gamma N_{p_{\parallel}}^2, \quad (5)$$

where τ^{-1} is the unimolecular decay rate and γ is the exciton annihilation coefficient. The solution of eq. (5) is given by

$$N_{p\parallel}(t) = N_{p\parallel}(0) \left[1 + N_{p\parallel}(0) \gamma T \right]^{-1} \exp(-t/\tau), \quad (6)$$

with

$$T = [1 - \exp(-t/\tau)] \tau, \quad (7)$$

$$T \approx t, \quad \text{if } t \ll \tau. \quad (8)$$

Here the annihilation coefficient γ is taken to be a constant. The time dependence of γ can be easily taken into account in eq. (6) and the subsequent equations simply by replacing γT by $\int_0^T \gamma(t') \exp(-t'/\tau) dt'$. It is necessary to do this at short times when the annihilation radius exceeds the diffusion length [4,20] and $\gamma(t)$ does not reach its limiting value.

The initial condition $N_{p\parallel}(0)$ depends on the temporal profile of the excitation pulse. Two limiting cases will be discussed below.

3.1. Delta pulse excitation

The pulse duration τ_{puls} is assumed to be sufficiently short so that both exciton annihilation and unimolecular decay can be neglected during the excitation, i.e.,

$$3\gamma N_0 \tau_{\text{puls}} \ll 1, \quad \tau_{\text{puls}}/\tau \ll 1, \quad (9)$$

where N_0 is the average density of excitons created by the pulse. Under these conditions the initial exciton concentration is

$$N_{p\parallel}(0) = 3N_0 p_{\parallel}^2, \quad \langle N_{p\parallel}(0) \rangle = N_0. \quad (10)$$

Using eqs. (3), (4), (6) and (10) we obtain

$$r = \left[(1 - \phi_1^{-1/2} \arctg \phi_1^{1/2})^{-1} - 3\phi_1^{-1} - 1 \right] / 2, \quad (11)$$

with

$$\phi_1 = 3\gamma N_0 T. \quad (12)$$

For $\phi_1 \ll 1$ the anisotropy is close to its theoretical maximum of 0.4:

$$r = 0.4 - (35/360) \phi_1. \quad (13)$$

In the opposite case, when $\phi_1 \gg 1$, we have

$$r = (\pi/4) \phi_1^{-1/2}, \quad (14)$$

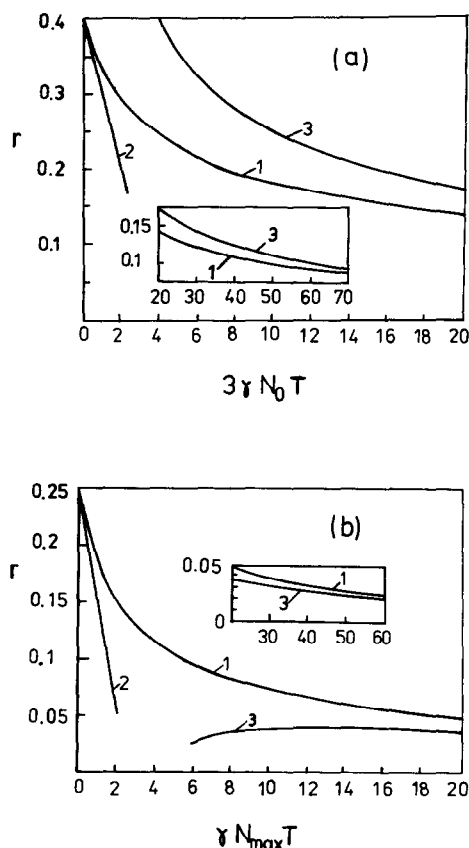


Fig. 2. The anisotropy as a function of reduced time T . (a) Delta pulse excitation. Curves 1–3 are calculated from eqs. (11), (13) and (14) respectively. (b) Long pulse excitation. Curves 1–3 are calculated from eqs. (18), (20) and (21) respectively.

$r \sim t^{-1/2}$, if $t \ll \tau$. Thus, the fluorescence anisotropy decreases more slowly than the average exciton-number density ($\langle N_{p\parallel} \rangle \sim t^{-1}$, as $\phi_1 \gg 1$ and $t \ll \tau$). Equations (11), (13) and (14) are plotted in fig. 2(a).

It should be noticed that for $\exp(-t/\tau) \ll 1$ the annihilation rate becomes negligible compared to the monomolecular decay rate and the reduced time T approaches τ . Therefore, a finite residual anisotropy r_∞ exists at long times. It is obtained from eqs. (11)–(14) [or eqs. (18)–(21), see below], substituting τ for T . For example, using eqs. (14) and (12) we find

$$r_\infty^{\text{cont}} = (\pi/4) (3N_0 \gamma \tau)^{-1/2}, \quad 3N_0 \gamma \tau \gg 1. \quad (15)$$

Here the superscript “cont” refers to the continuous model.

3.2. Long pulse excitation

The pulse is supposed to be sufficiently long and intense, so that during the excitation a steady-state exciton concentration would be formed in the domains due to annihilation, i.e.,

$$3\gamma N_0 \tau_{\text{puls}} \gg 1, \quad \tau_{\text{puls}} < \tau, \quad (16)$$

where N_0 corresponds to the density of excitons created per pulse in the absence of annihilation. N_0 is considerably higher than the average exciton concentration just after the pulse since most of the excitons annihilate during the excitation. For simplicity, the pulse is supposed to have a constant intensity for the duration τ_{puls} (a square pulse). With these assumptions the initial concentration just after the excitation is given by

$$N_{p_{\parallel}}(0) = N_{\text{max}} |p_{\parallel}|, \quad (17)$$

$$N_{\text{max}} = (3N_0/\gamma\tau_{\text{puls}})^{1/2}. \quad (17)$$

Using eqs. (3), (4), (6) and (17) we obtain

$$r = 0.5 \left\{ (1 - 1.5\phi_2^{-1}) [1 - \phi_2^{-1} \ln(1 + \phi_2)]^{-1} + 3\phi_2^{-2} - 1 \right\}, \quad (18)$$

with

$$\phi_2 = \gamma N_{\text{max}} T. \quad (19)$$

In the limit of short times, $\phi_2 \ll 1$, we can write

$$r = 0.25 - 0.1\phi_2, \quad (20)$$

i.e., the maximum anisotropy after long pulse excitation is 0.25. It is lower than the theoretical maximum of 0.4 after delta pulse excitation, since a certain depolarization due to annihilation occurs at the beginning of the excitation before the steady-state concentration distribution ($N_{p_{\parallel}} \sim |p_{\parallel}|$) is formed in most of the domains.

For long times, $\phi_2 \gg 1$, eq. (18) simplifies to

$$r = (2\phi_2)^{-1} (\ln \phi_2 - 1.5), \quad (21)$$

$r \sim t^{-1}(\text{const} + \ln t)$, if $t \ll \tau$. That is, after the long pulse excitation the fluorescence anisotropy decreases faster than that after the delta pulse excitation.

Fig. 2(b) shows curves obtained from eqs. (18), (20) and (21).

It is to be noted that the initial condition (17) holds as long as

$$|p_{\parallel}| \geq p_{\text{lim}}, \quad p_{\text{lim}} = (3\gamma N_0 \tau_{\text{puls}})^{-1/2} \ll 1. \quad (22)$$

For domains with $|p_{\parallel}| \leq p_{\text{lim}}$ the annihilation rate is not sufficiently high to form a steady-state exciton concentration during the excitation, and in the case that $|p_{\parallel}| \ll p_{\text{lim}}$ the initial condition (10) of the delta pulse excitation should be used. Since at long times the main contribution to the anisotropy is due to domains with small $|p_{\parallel}|$, the asymptotic behaviour (21) holds only for intermediate times, i.e., as long as $T^{1/2} \ll \tau_{\text{puls}}^{1/2} \ln \phi_2$. For extremely long times, $T^{1/2} \gg \tau_{\text{puls}}^{1/2} \ln \phi_2$, the anisotropy obeys the asymptotic decay law (14) corresponding to the delta pulse excitation.

4. Discrete model

In this section we investigate the residual anisotropy at long times, $r_{\infty}^{\text{fluct}}$, due to the fluctuations of the initial number of excitons in domains. The unimolecular decay time is supposed to be much greater than the decay time due to the annihilation ($\tau \gg t_{\text{anni}}$), i.e., only the last remaining exciton in a domain may decay via fluorescence. The pulse duration is taken to be sufficiently short compared to the unimolecular decay time. With these assumptions the exciton concentration at sufficiently long times is proportional to the probability for at least one photon to be absorbed per domain (this situation corresponds to that treated by Mauzerall [21]):

$$N_{p_{\parallel}}(t) \sim [1 - \exp(-y)] \exp(-t/\tau), \quad (23)$$

$$y = 3n_0 p_{\parallel}^2, \quad t \gg t_{\text{anni}},$$

where y is the mean number of excitons created in a domain, and n_0 is its average over all possible orientations of domains. Here the Poisson distribution of photon hits per domain is utilized. After making use of eqs. (3), (4) and (23), we find

$$r_{\infty}^{\text{fluct}} = 0.25 [2A - A/n_0 + n_0^{-1} \exp(-3n_0)] \times 1/(1 - A), \quad (24)$$

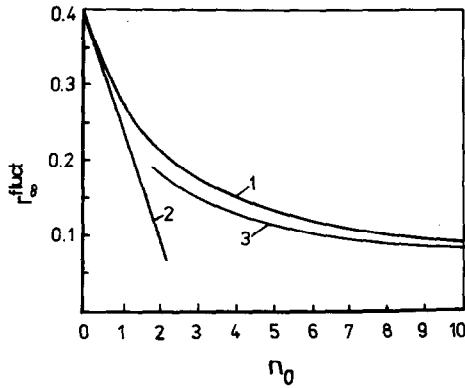


Fig. 3. The residual anisotropy $r_{\infty}^{\text{fluct}}$ as a function of the initial exciton number in domains n_0 . Curves 1–3 are calculated from eqs. (24), (26) and (27) respectively.

where

$$A = 0.5\pi^{1/2}(3n_0)^{-1/2} \text{erf}(3n_0)^{1/2}, \quad (25)$$

with erf being the error function [22].

For low intensities of the excitation pulse (when the probability of creating more than one exciton per domain is small) the residual anisotropy is close to the theoretical maximum of 0.4:

$$r_{\infty}^{\text{fluct}} = 0.4 - (54/350)n_0, \quad n_0 \ll 1. \quad (26)$$

For relatively high intensities $r_{\infty}^{\text{fluct}}$ goes as $n_0^{-1/2}$:

$$r_{\infty}^{\text{fluct}} = 0.25\pi^{1/2}(3n_0)^{-1/2}, \quad n_0 \gg 1. \quad (27)$$

In fig. 3 we have plotted $r_{\infty}^{\text{fluct}}$ against n_0 .

The discrete model considered above yields the lower limit to the residual anisotropy, since in this model there is a complete annihilation of excitons as long as there is more than one exciton in a domain. For the continuous model discussed in section 3, the anisotropy reaches its limiting value r_{∞}^{cont} before the mean number of excitons per domain decreases to unity. So, the following inequality must hold: $r_{\infty}^{\text{cont}} > r_{\infty}^{\text{fluct}}$. To compare both cases quantitatively, we will rewrite eq. (15). Expressing the exciton-number density as excitons per domain ($N_0 \rightarrow n_0$) and using eq. (27), for $n_0 \gg (\Gamma\tau)^{-1}$ we find

$$\begin{aligned} r_{\infty}^{\text{cont}} &= (\pi/4)(3n_0\Gamma\tau/2)^{-1/2} \\ &= (2\pi)^{1/2}(\Gamma\tau)^{-1/2}r_{\infty}^{\text{fluct}}, \end{aligned} \quad (28)$$

where Γ is the bimolecular decay rate of a pair of excitons in a domain ($\Gamma = 2\gamma N_d$, N_d being the exciton-number density corresponding to one exciton per domain). The anisotropy r_{∞}^{cont} is seen to increase with the increase of the ratio of the monomolecular and bimolecular decay rate constants τ^{-1}/Γ . The application of the continuous model is justified as long as $\tau^{-1} \gg \Gamma$ [7]. Therefore, it follows from eq. (28) that $r_{\infty}^{\text{cont}} \gg r_{\infty}^{\text{fluct}}$.

5. Concluding remarks

In this paper we have presented a theoretical analysis of time-resolved fluorescence depolarization due to singlet–singlet exciton annihilation in molecular domains of highly oriented chromophores. By using both continuous and discrete descriptions of exciton annihilation, we have investigated the time and intensity dependence of fluorescence anisotropy. For the continuous model, the fluorescence anisotropy after the delta pulse excitation was shown to be a universal function of $\gamma N_0 T$, where γ is the annihilation constant, T is the reduced time [defined in eq. (7)], and N_0 is the average density of excitons created by the pulse. For large $t < \tau$, the fluorescence anisotropy after the delta pulse excitation goes as $t^{-1/2}$ and that after the long pulse excitation goes as t^{-1} ($\text{const} + \ln t$), τ being the excited-state lifetime. Both continuous and discrete models give a finite value of the residual anisotropy at long times ($r_{\infty} \neq 0$). The discrete model discussed in section 4, yields the lower limit to the residual anisotropy. Thus, using eq. (24) or eqs. (26) and (27), the lower limit to the domain size may be obtained from the intensity dependence of the residual anisotropy.

The results of the paper can be applied not only to the fluorescence depolarization, but to the decay of the induced absorption anisotropy in polarized pump-probe experiments as well, provided the changes of the absorption spectrum, ΔA , are a linear function of the exciton density. That is, the intensity of the excitation pulse should be sufficiently low to avoid nonlinear spectral changes. Moreover, both the stationary absorption band A and the spectrum of its changes ΔA should be polarized along the same direction. In

case A and ΔA are polarized at some angle α to each other, the anisotropy must be reduced by the factor $(3 \cos^2 \alpha - 1)/2$. For thread-like J-aggregates discussed below, the single-photon excitation of the aggregate induces a blue shift of the excitonic J-band without any changes of its polarization [23], so both the J-band and the spectrum of its changes are polarized along this the same axis *.

During the last decade the J-aggregated PIC solution has been intensively studied using time-resolved spectroscopy [10,26–31]. In ref. [10] the excited-state dynamics of PIC J-aggregates in aqueous solution was investigated by means of picosecond and subpicosecond absorption spectroscopy. At very low excitation intensity, where there was almost no annihilation, a high value of the induced absorption anisotropy was obtained at long times. It suggests a high order of J-aggregates forming a domain. Moreover, the residual anisotropy at long times, r_∞ , was shown to decrease with the increase of the excitation intensity. The theory developed here accounts for such intensity-dependent depolarization. To estimate the domain size, we will make use of eq. (24). At $I_{\text{ex}} = 1.4 \times 10^{12}$ ph cm⁻² pulse⁻¹ and $\lambda_{\text{ex}} = 569$ nm (under these conditions the fraction of initially excited PIC molecules is about 1 : 3000) the residual anisotropy r_∞ is 2.5 times lower than that for almost annihilation-free conditions [10]. Thus, a domain should contain more than $\sim 10^4$ PIC molecules. This is in agreement with the earlier evaluations obtained from both the kinetic data and the fluorescence quantum yield curves [10].

It is our hope that the theoretical results presented here can be applied to other systems, such as photosynthetic antennae. The domain size of photosynthetic systems is usually estimated by comparing theoretical calculated and experimentally obtained fluorescence quantum yield versus intensity curves [7,32,33]. Here we have shown that the domain size can be also evaluated from the intensity dependence of the residual anisotropy. In other words, the present technique could be used as an alternative way for estimating

the domain size in photosynthetic antennae. It should be pointed out, that the method presented can be applied only to systems in which excitation transfer within the domain occurs between highly oriented chromophores. For example, it seems to be not applicable to photosynthetic antenna systems of purple bacteria, since the depolarization measurements suggest the absence of the long-range orientational order of chromophores forming a domain [34]. On the other hand, in living cells of green bacteria the excitation energy transfer within the bacteriochlorophyll *c* antenna occurs between chromophores (or their aggregates) with parallel transition moments [19].

Our theoretical investigation can be extended taking into account the orientational distribution of chromophores forming a domain [35]. For example, in case the transition moments of the molecules forming a domain are distributed within a cone of small half-angle β , the residual anisotropy, r_∞^{fluct} , goes as $n_0^{-1/2} \exp(-0.75 \beta^2 n_0)$, $n_0 \gg 1$ [compare to eq. (27)]. That is, whereas for relatively low intensities ($1 \ll n_0 < \beta^{-2}$) the $n_0^{-1/2}$ dependence is preserved, for $n_0 > \beta^{-2}$ an exponential decrease takes place. Thus from the intensity dependence of the residual anisotropy one can get information not only on a domain size, but on the orientational distribution of chromophores forming the domain as well [35].

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* The J-band is known to be polarized parallel to the aggregate axis [24,25].

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