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Time-dependent fluorescence depolarization arising from exciton annihilation in confined molecular domains

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A theory of fluorescence depolarization arising from singlet–singlet exciton annihilation is presented for an ensemble of randomly oriented molecular domains. This paper extends our prevịous work including the effects of the orientational distribution of chromophores forming a domain. The orientational order of the domain is described by the distribution function $f(\theta)$ depending on one angle θ, the angle between the transition dipoles of chromophores (or their aggregates) and the symmetry axis of the domain. By using a kinetic equation of a continuous model for exciton annihilation, the time evolution of the fluorescence anisotropy is investigated. For large $t<\tau$, the anisotropy was shown to decrease as $t^{-1/2}$, t^{-1} $(\ln t+\text{const.})$ and t^{-1} for $S=1$, $S=-\frac{1}{2}$ and $-\frac{1}{2}<S<1$ $(S\neq 0)$, respectively, τ being the excited - state lifetime and $S=\bar{P}_2=(3\cos^2\theta-1)/2$ being the order parameter of the domain. The residual anisotropy at long times is analysed using both continuous and discrete models of exciton annihilation. It is shown that from the residual anisotropy against intensity curves one can estimate both the domain size and the order parameter S. The theory accounts for the intensity-dependent depolarization observed recently in the *J*-aggregated pseudoisocyanine dye (PIC) solution. Applications to photosynthetic systems are also discussed.

1. Introduction

The excitation energy transfer in condensed molecular systems together with the related high-density effect of exciton–exciton annihilation has been the subject of many investigations [1–11]. Experimentally, singlet–singlet exciton annihilation manifests itself by a decrease in the integrated fluorescence quantum yield and also by a decrease in the fluorescence lifetime, as the intensity of the excitation laser pulses is increased. This paper considers another possible manifestation of exciton annihilation. The object of this paper is to treat the time-dependent fluorescence depolarization arising from exciton annihilation. This phenomenon is sensitive to the intensity of the excitation pulses, whereas the usual depolarization arising from energy transfer [2,12–15] or the rotational motion [16,17] is independent of intensity. Our previous study [18] is extended here, taking account of the orientational distribution of the transition moments of the chromophores forming a domain. It is shown that the present depolarization can provide information not only about the domain size, as pointed out in ref. [18], but also about the orientational distribution of the chromophores forming the domain.

The paper is organized as follows. In section 2 the problem is formulated. In section 3 the continuous model of exciton annihilation is employed to investigate the time evolution of the fluorescence depolarization. In section 4 the residual fluorescence anisotropy at long times is analysed using both the continuous and discrete descriptions of the annihilation. In section 5 some final remarks are presented, as well as applications to J-aggregated dye solutions and photosynthetic systems being discussed.

2. Formulation of the problem

2.1. The system

The system of interest, shown schematically in fig. 1a, consists of a large number of molecular domains embedded in a three-dimensional medium. An individual domain is composed of many identical chro-

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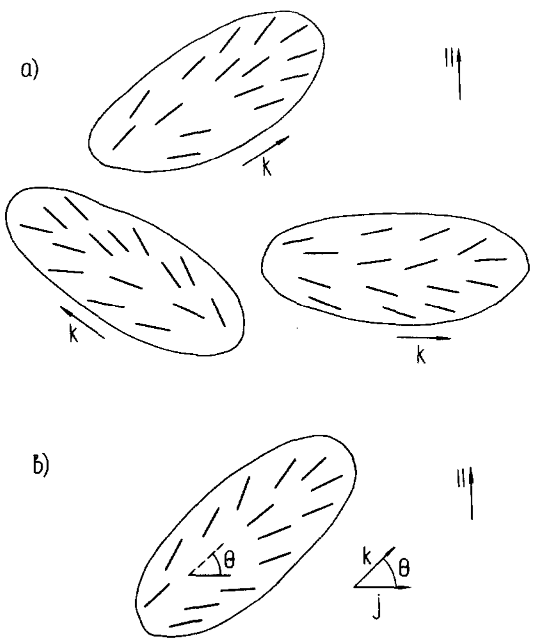

Fig. 1. Schematic representation of the ensemble of molecular domains (a) and an individual domain (b). Here **k** and **j** are the unit vectors parallel to the symmetry axis of the domain and to the transition moment of a chromophore (or an aggregate) forming the domain, respectively, and ∥ is the vector indicating the polarization of the excitation pulse.

mophores (or their aggregates), and all domains are assumed to be of the same size. The orientational order of molecules forming the domain is described by a normalized probability distribution function depending on one angle θ, the angle between the transition dipoles of chromophores (or their aggregates) and the symmetry axis of the domain (fig. 1b). This function can be expanded in a series of even Legendre polynomials as follows:

$$f(\theta)=\sum_{L=0,2,\dots}\tfrac{1}{2}(2L+1)\bar{P}_L P_L(\cos\theta)\,, \qquad (2.1)$$

where $\bar{P}_L$ are the order parameters of the domain defined as the moments of the distribution,

$$\bar{P}_L=\int_0^{\pi} P_L(\cos\theta)\,f(\theta)\,\sin\theta\,\mathrm{d}\theta\,. \qquad (2.2)$$

An isotropic probability density for the orientations of the domains is assumed. Both the interdomain excitation energy transfer and the changes in orientation due to rotational motion are considered to be negligible. No barriers for energy transfer within a domain exist. The fraction of initially excited chromophores is considered to be sufficiently low to avoid saturation effects.

2.2. Fluorescence anisotropy

The quantity of interest is the time-dependent fluorescence anisotropy given by

$$r=(I_\parallel-I_\perp)/(I_\parallel+2I_\perp)\,, \qquad (2.3)$$

where $I_\parallel$ and $I_\perp$ are the intensities of the emitted light polarized parallel and perpendicular, respectively, to the polarization of the excitation pulse.

We shall consider the anisotropy at relatively long times, $t>\tau_r$, after the electronic excitations have already redistributed within the domains, $\tau_r\approx R^2/D$ being the redistribution time, R being the domain radius, and D being the coefficient of exciton diffusion. Under the assumption that the incoherent excitation energy transfer (hopping) among the chromophores forming the domains takes place, the diffusion coefficient can be evaluated as $D=wa^2$, where w is the rate of the excitation transfer between the adjacent chromophores and a is the interchromophore distance. This means that, for example, in case $a=10$ Å, $w^{-1}=0.25$ ps and $R=200$ Å, the redistribution time τ_r is about 100 ps.

For $t>\tau_r$, the emission intensities of the individual domains are given by [#1]

$$I_\parallel^{\mathrm{dom}}\propto\overline{j_\parallel^2}\,N_{k_\parallel}(t)\,, \qquad I_\perp^{\mathrm{dom}}\propto\overline{j_\perp^2}\,N_{k_\parallel}(t)\,, \qquad (2.4)$$

where the unit vector $\boldsymbol{k}$ indicates the orientation of the domain, $k_\parallel$ is its parallel component, $j_\parallel$ and $j_\perp$ are the components of the unit vector $\boldsymbol{j}$ parallel to the transition moment of an individual chromophore forming a domain (see fig. 1b), and $N_{k_\parallel}(t)$ is the exciton-number density, which depends on the domain orientation. The overscribed bar denotes the average over the different orientations of the chromophores forming a domain:

[#1] The present theory is valid for $t<\tau_r$ as well, providing the domain is composed of chromophores with parallel transition moments ($S=1$) [18].

$$\overline{j^2_{\|(\perp)}}=(2\pi)^{-1}\int_0^{2\pi}\int_0^{\pi} j^2_{\|(\perp)}f(\theta)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,, \qquad (2.5)$$

where φ is the azimuthal angle (see fig. 2).

The averaging of $I_{\|}^{\mathrm{dom}}$ and $I_{\perp}^{\mathrm{dom}}$ over the orientations of the domains ($I_{\|}\propto\langle I_{\|}^{\mathrm{dom}}\rangle, I_{\perp}\propto\langle I_{\perp}^{\mathrm{dom}}\rangle$) and the subsequent use of eq. (2.3) yield

$$r=[3\langle\overline{j^2_{\|}}N_{k_\|}(t)\rangle/\langle N_{k_\|}(t)\rangle-1]/2\,, \qquad (2.6)$$

where the brackets $\langle\ \rangle$ denote the average over all possible orientations of the domains.

Relative to $\boldsymbol{k}$, $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ the unit vector $\boldsymbol{j}$ can be defined by the polar coordinates θ and φ (see fig. 2):

$$\boldsymbol{j}=\boldsymbol{k}\cos\theta+\boldsymbol{e}_1\sin\theta\cos\varphi+\boldsymbol{e}_2\sin\theta\sin\varphi\,. \qquad (2.7)$$

Using eqs. (2.5) and (2.7) one finds

$$\overline{j^2_{\|}}=Sk^2_{\|}+(1-S)/3\,, \qquad (2.8)$$

where S is the order parameter of the domain, $S=\bar{P}_2=(3\overline{\cos^2\theta}-1)/2$. The model presented includes two limiting cases, $S=1$ and $S=-\frac{1}{2}$. For $S=1$ the domain is composed of chromophores with parallel transition dipoles. This situation has been investigated in our previous paper [18]. For $S=-\frac{1}{2}$, the transition moments of the chromophores forming the domain are perpendicular to the orientational vector $\boldsymbol{k}$.

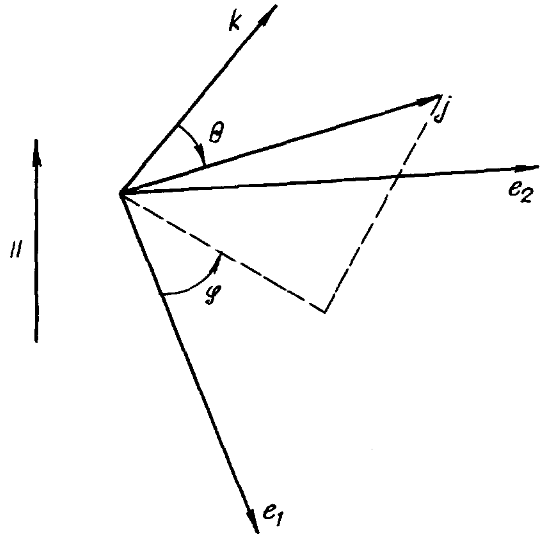

Fig. 2. Relation between the unit vectors $\boldsymbol{j}$, $\boldsymbol{k}$ and the polar coordinates θ and φ. Here $\boldsymbol{k}$, $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ is the set of the orthogonal basis vectors, $\boldsymbol{e}_2$ being perpendicular to the polarization of the excitation pulse ($e_{2\|}=0$).

Using eqs. (2.6) and (2.8) the anisotropy becomes

$$r=S(3G_2/G_0-1)/2\,, \qquad (2.9)$$

with

$$G_m=\langle k^m_{\|}N_{k_\|}(t)\rangle=\int_0^1 k^m_{\|}N_{k_\|}(t)\,\mathrm{d}k_{\|}\,. \qquad (2.10)$$

Equations (2.4), (2.9) and (2.10) implicitly assume that the absorption and emission transition dipoles are directed along the same axis. In case 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 (2.9) should be reduced by the factor $d=(3\cos^2\alpha-1)/2$.

2.3. Intensity-dependent depolarization

At low pumping intensity only one excitation can be created per domain, so the exciton-number density of all domains decreases exponentially with the same decay rate. Under this condition the anisotropy (at $t>\tau_r$) is equal to $0.4S^2$. It is lower than the theoretical maximum of 0.4, since a certain depolarization arising from the energy transfer takes place just after the excitation (at $t<\tau_r$), before the homogeneous distribution of the excited states is formed within the domains.

When several excitons are created simultaneously in a given domain, a bimolecular singlet–singlet annihilation is possible. The annihilation rate is known to increase with the density of the excitons. In other words, more excited domains decay faster than less excited ones [the number of excitons created in an individual domain depends on the domain orientation, see eqs. (3.2) and (4.2)]. Thus, the annihilation tends to reduce the initial anisotropy induced in the sample by the polarized excitation pulse. It leads to the intensity-dependent fluorescence depolarization.

For large molecular domains, the annihilation persists down to very low intensity, provided the energy transfer within a domain is fast enough. This means that the present depolarization is possible even when the fraction of excited chromophores, p, is relatively low, for example, $p=1/3000$ [11]. The usual intensity-dependent depolarization arising from saturation effects (because of the ground-state depletion) [19] occurs at considerably higher intensities when p is comparable with unity.

3. Kinetics of depolarization

In this section the continuous model of exciton annihilation is employed to investigate the kinetics of the depolarization. That is the mean number of excitons per domain is considered to be sufficiently large, so that the fluctuations of the exciton number would be negligible. The time evolution of the exciton-number density, $N_{k_\parallel}(t)$, is assumed to obey the standard kinetic equation of exciton annihilation [3–6,20]:

$$\mathrm{d}N_{k_\parallel}/\mathrm{d}t=-\tau^{-1}N_{k_\parallel}-\gamma N_{k_\parallel}^2\,, \tag{3.1}$$

where τ^{-1} is the unimolecular decay rate, γ is the exciton annihilation coefficient, and the subscript $k_\parallel$ indicates the domain orientation. The initial exciton-number density, $N_{k_\parallel}(0)$, depends on the intensity of the excitation pulse as well as on the domain orientation. The pulse duration is assumed to be sufficiently short, so that both exciton annihilation and unimolecular decay could be neglected during the pumping (delta pulse excitation). Under this condition the initial density of excitons is proportional to the absorption probability in a given domain ($\propto \overline{j_\parallel^2}$, see eq. (2.8)):

$$N_{k_\parallel}(0)=3N_0[Sk_\parallel^2+(1-S)/3]\,, \tag{3.2}$$

where $N_0=\langle N_{k_\parallel}(0)\rangle$ is the average density of excitons created by the pulse.

Eq. (3.1) has a solution

$$N_{k_\parallel}(t)=N_{k_\parallel}(0)[1+N_{k_\parallel}(0)\gamma T]^{-1}\exp(-t/\tau)\,, \tag{3.3}$$

where

$$T=[1-\exp(-t/\tau)]\tau\,, \tag{3.4}$$

$$T\approx t\,,\quad \text{for}\quad t\ll\tau\,. \tag{3.5}$$

In eq. (3.3) the annihilation coefficient is assumed to be a constant. If γ wre a time-dependent function, γT should be replaced by

$$\int_0^t \gamma(t')\exp(-t'/\tau)\,\mathrm{d}t'\,.$$

This is the case at short times when the diffusion length is less than the annihilation radius and thereby $\gamma(t)$ does not reach its limiting value. Moreover, if the energy transfer within a domain is low dimensional, no annihilation constant exists, for example, for a two-dimensional energy transfer $\gamma(t)\sim(\ln t)^{-1}\to 0$, as $t\to\infty$ [20].

After making use of eqs. (2.9), (2.10) (3.2), and (3.3), we find

$$r=0.5[(1-R)^{-1}-3\phi^{-1}-1]\,, \tag{3.6}$$

$$\langle N_{k_\parallel}\rangle=3N_0\phi^{-1}(1-R)\exp(-t/\tau)\,, \tag{3.7}$$

where

$$\phi=3\gamma N_0T\,, \tag{3.8}$$

$$R=(S\phi)^{-1}M\tan^{-1}M\,,\quad 0<S\leqslant 1\,, \tag{3.9}$$

$$\quad=(|S|\phi)^{-1}M\tanh^{-1}M\,,\quad -\tfrac{1}{2}\leqslant S<0\,, \tag{3.10}$$

$$M=[|S|\phi/(b\phi+1)]^{1/2}\,, \tag{3.11}$$

$$b=(1-S)/3\,, \tag{3.12}$$

that is, the fluorescence anisotropy is a function of $\phi=3\gamma N_0T$, N_0 being proportional to the intensity of the excitation pulse. In other words, information about the large (small) reduced time behaviour of the anisotropy is the same as information about its high-(low-) intensity behaviour. The analysis of the limiting cases of small and large reduced times (low and high intensities) is presented in the appendix. It should be noted that for $t\ll\tau$, the reduced time T coincides with the ordinary time t [see eq. (3.5)], whereas for $t>\tau$, $T\to\tau$. Moreover, one must remember that in case $S\neq 1$, the theoretical analysis of the depolarization presented here holds only for $t<\tau_r$, τ_r being the redistribution time of excitons within a domain (see section 2).

Examples of decay curves calculated according to eq. (3.6) using various values of S are shown in fig. 3. For $1-S\ll 1$, the differences between the curves are more distinguishable if one plots $\phi^{1/2}r/r(0)$ against $\log\phi$ (fig. 4). As seen in fig. 4, the curves differ from each other in shape and in position with respect to the abscissa. As the value of S increases, the

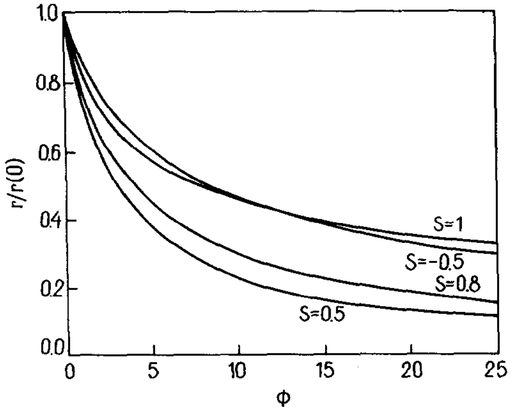

Fig. 3. Normalized anisotropy, $r/r(0)$, plotted as a function of $\phi = 3\gamma N_0 T$.

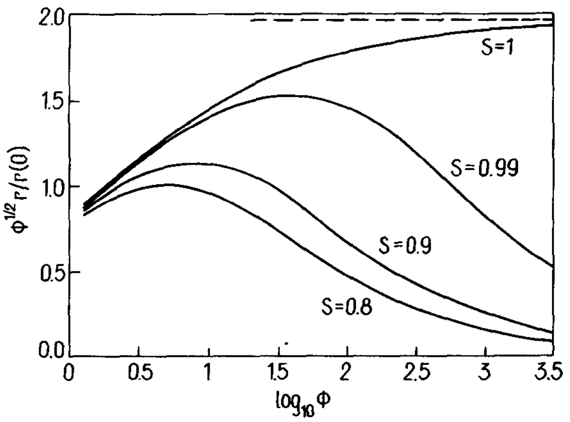

Fig. 4. Plot of $\phi^{1/2}\, r/r(0)$ as a function of $\log_{10}\phi$.

curves decrease more slowly and are shifted to the right on the horizontal $\log\phi$ scale. Thus, it is possible to determine S from the anisotropy decay curves. All curves in fig. 4, except that for $S=1$, approach zero as $\phi\to\infty$. The asymptotic solution for $S=1$ is shown by the horizontal dashed line.

A remark should be made concerning the behaviour of the anisotropy at large reduced times (or high intensities). As is shown in the appendix, both for $0<S<1$ and $-\frac{1}{2}<S<0$, the anisotropy is hyperbolic in reduced time, while for $S=1$ and $S=-\frac{1}{2}$, the anisotropy decreases more slowly. The differences in asymptotic behaviour arise from the different types of initial conditions. That is, for $-\frac{1}{2}<S<1$ the excitation of all domains is possible $[N_{k_\parallel}(0)\neq 0]$, whereas for $S=1$ and $S=-\frac{1}{2}$, the domains with $k_\parallel=0$ and $k_\parallel=\pm 1$, respectively, cannot be excited and thereby the asymptotic decay law depends on the behaviour of the initial density of excitons near $N_{k_\parallel}(0)=0$. For $S=1$, $N_{k_\parallel}(0)\sim k_\parallel^2$ and for $S=-\frac{1}{2}$, the initial density goes linearly around $k_\parallel=\pm 1$. As a result, the anisotropy decreases as $T^{-1/2}$ and $T^{-1}(\ln T+\text{const.})$, respectively. For $-\frac{1}{2}<S<0$ and $0<S<1$, all domains make a significant contribution to the fluorescence anisotropy at large reduced times. The relative difference of the exciton-number density of two initially excited domains, $[N_{k_\parallel}(t)-N_{k'_\parallel}(t)]/N_{k_\parallel}(t)$, decreases as $(\gamma T)^{-1}$. This leads to the hyperbolic decay of the anisotropy.

4. Residual anisotropy

Firstly, let us consider the continuous model of the annihilation discussed in the previous section. At long times, $\exp(-t/\tau)\ll 1$, the annihilation rate becomes negligible compared to the monomolecular decay rate. As a result, the excited-state decay of all domains becomes exponential and thus the depolarization ceases. The residual anisotropy at long times, r_∞^{cont}, is obtained from eq. (3.6) or fig. 3 by substituting τ for T. Here the superscript "cont" refers to the continuous model considered. The residual anisotropy r_∞^{cont} becomes small compared to its low-intensity value of $0.4S^2$, as $N_0\gg(\gamma\tau)^{-1}$.

The second model to be discussed includes the fact that the annihilation ceases when the number of excitons in the domain decreases to unity. That is, we shall investigate the residual anisotropy, r_∞^{fluct}, arising from the fluctuations of the initial number of excitons in the domains. The annihilation time, t_{annih}, is supposed to be short enough as compared with the unimolecular decay time τ, so that only the last remaining exciton in a domain could decay via fluorescence. The duration of the excitation pulse is assumed to be sufficiently short compared to the unimolecular decay time. With these assumptions the exciton-number density at sufficiently long times is proportional to the probability for at least one photon to be absorbed per domain (such a situation corresponds to the case treated by Mauzerall [21]):

$$\mathrm{N}_{k_\parallel}\propto[1-\exp(-y)]\exp(-t/\tau)\,, \quad t\gg t_{\text{annih}}\,, \tag{4.1}$$

$$y=3n_0[Sk_\parallel^2+(1-S)/3]\,, \tag{4.2}$$

where y is the mean number of excitons created in a domain and n_0 is its average over all possible orientations of the domains. Here the Poisson distribution of the number of excitons generated in the domain is taken. Using eqs. (2.9), (2.10), (4.1), and (4.2), we obtain

$$r_\infty^{\text{fluct}}=0.25\{2SA-n_0^{-1}A+n_0^{-1}\exp[-(g+h)]\}/(1-A)\,, \tag{4.3}$$

where

$$A=\exp(-h)\int_0^1\exp(-gk_\parallel^2)\,\mathrm{d}k_\parallel\,, \tag{4.4}$$

$$g=3Sn_0\,, \qquad h=(1-S)n_0\,. \tag{4.5}$$

Eq. (4.4) can be rewritten as follows:

$$A=0.5(\pi/g)^{1/2}\operatorname{erf}(g^{1/2})\exp(-h)\,, \quad 0<S\leqslant 1\,, \tag{4.6}$$

and

$$A=|g|^{-1/2}F(|g|^{1/2})\exp[-(g+h)]\,, \quad -\tfrac{1}{2}\leqslant S<0\,, \tag{4.7}$$

with erf(...) being the error function and $F(\ldots)$ being the Dawson function (see section 7.1 of ref. [22]).

For low intensities of the excitation pulse, $n_0\ll 1$, the residual anisotropy is close to its maximum of $0.4S^2$:

$$r_\infty^{\text{fluct}}=0.4S^2[1-\tfrac{1}{2}(1+\tfrac{4}{7}S-\tfrac{4}{5}S^2)n_0]\,. \tag{4.8}$$

In the limit of high intensities, $n_0|S|\gg 1$, the behaviour of the anisotropy depends on the sign of the order parameter:

$$r_\infty^{\text{fluct}}=\frac{1}{4}\left(\frac{S\pi}{3n_0}\right)^{1/2}\exp[-(1-S)n_0]\,, \quad 0<S\leqslant 1\,, \tag{4.9}$$

and

$$\tau_\infty^{\text{fluct}}=(6n_0)^{-1}\exp[-(2S+1)n_0]\,, \quad -\tfrac{1}{2}\leqslant S<0\,, \tag{4.10}$$

that is, for $S=1$, the anisotropy goes as $n_0^{-1/2}$ [18] and for $S=-\frac{1}{2}$, it goes as n_0^{-1}. In case the transition moments of chromophores forming a domain are neither parallel ($S\neq 1$) nor perpendicular to the orientational vector $\boldsymbol{k}$ ($S\neq -\frac{1}{2}$), the excitation of all domains becomes possible. This leads to the exponential decay of the anisotropy at high intensities. The exponential factors in eqs. (4.9) and (4.10) are equal to the probabilities that domains with $k_\parallel=0$ $(S>0)$ or $k_\parallel=\pm 1$ $(S<0)$ were not initially excited. The behaviour of pre-exponential factors depends on the sign of the order parameter. At intermediate intensities, $1\ll n_0\ll(1-S)^{-1}$ $[(1-S)\ll 1]$ or $1\ll n_0\ll(2S+1)^{-1}$ $[(2S+1)\ll 1]$, the exponential factors are of no importance, and the decrease of the residual anisotropy is algebraic ($\sim n_0^{-1/2}$ and $\sim n_0^{-1}$, as for $S=1$ and $S=-1/2$, respectively).

In fig. 5 we have plotted $r_\infty^{\text{fluct}}/r(0)$ against n_0 for different order parameters.

The discrete model considered above gives a lower bound 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 the domain. For the continuous model, the anisotropy reaches its limiting value before the mean number of excitons per domain, n_0, decreases to unity, so the following inequality must hold: $r_\infty^{\text{cont}}\geqslant r_\infty^{\text{fluct}}$.

To compare the two models quantitatively, one should express the exciton density N_0 as the number of excitons per domain: $N_0\to n_0$ and $\gamma\to\Gamma/2$, where $\Gamma=2\gamma N^{(\mathrm{D})}$ is the bimolecular decay rate of a pair of excitons in a domain, $N^{(\mathrm{D})}$ being the exciton number

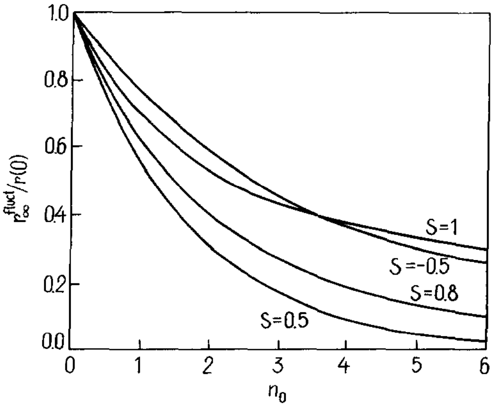

Fig. 5. Normalized residual anisotropy, $r_\infty^{\text{fluct}}/r(0)$, plotted against the initial number of excitons per domain n_0, calculated according to eq. (4.3).

density corresponding to one exciton per domain. The application of the continuous model is justified as long as $\tau^{-1} \gg \Gamma$ [6]. Therefore, writing $T = \tau$ and comparing eq. (3.6) with eq. (4.3) or fig. 3 with fig. 5, for

$$N_0 > (\gamma\tau)^{-1} \quad [n_0 > 2(\Gamma\tau)^{-1} \gg 1]$$

we find that $r_\infty^{\text{cont}} \gg r_\infty^{\text{fluct}}$. Moreover, in case $S \neq 1$ and $S \neq -\frac{1}{2}$, the residual anisotropy r_∞^{fluct} falls to zero faster than r_∞^{cont}, as the initial density of excitons increases. That is, the high-intensity dependence of r_∞^{fluct} is exponential and that of r_∞^{cont} is hyperbolic. For $S = 1$, both r_∞^{cont} and r_∞^{fluct} go as $n_0^{-1/2}$ [18]. The relation between the two approaches will be discussed in more detail elsewhere [23] using the annihilation model, which incorporates both continuous and discrete models [6].

5. Concluding remarks

In this paper we have extended our previous work on fluorescence depolarization due to exciton annihilation [18] to include the effects of the orientational distribution of the transition dipoles of chromophores (or their aggregates) forming a domain. The depolarization was shown to be dependent on the order parameter of the domain, $S = \bar{P}_2$. By using both continuous and discrete models for exciton annihilation, the time and intensity dependence of the fluorescence anisotropy, r, has been investigated. For the continuous model, the anisotropy was shown to be a function of two variables, $\phi = 3\gamma N_0 T$ and S, where γ is the annihilation constant, N_0 is the average density of excitons created by the pulse, and T is the reduced time defined in eq. (3.4). For small reduced times (or low intensities), $T \ll (\gamma N_0)^{-1}$, the anisotropy is close to its low-intensity value of $0.4\,S^2$. In the limit of large reduced times, $T \gg (\gamma N_0)^{-1}$, the asymptotic decay law depends on the order parameter. That is, both for $-\frac{1}{2} < S < 0$ and $0 < S < 1$, the anisotropy is hyperbolic in reduced time, and for $S = 1$ and $S = -\frac{1}{2}$ it goes as $T^{-1/2}$ and $T^{-1}(\ln T + \text{const.})$, respectively. At long times, $\exp(-t/\tau) \ll 1$, $T \to \tau$, the anisotropy reaches a finite value, $r \to r_\infty^{\text{cont}} \neq 0$. The residual anisotropy r_∞^{cont} is obtained from eq. (3.6) (or fig. 3) by writing $\phi = \phi_0 = 3\gamma N_0 \tau$. Experimentally, γN_0 and τ can be determined from the isotropic excited-state decay kinetics using eq. (3.7). Thus, a comparison of the theoretical and experimental $r_\infty / r(0)$ plotted against ϕ_0 curves gives the value of S, $r(0) = 0.4\,S^2$ being the low-intensity residual anisotropy. In the case that the absorption and emission dipoles are at some angle α to each other, both r_∞ and $r(0)$ should be reduced by the same factor $d = (3\cos^2\alpha - 1)/2$. This means that $r_\infty / r(0)$ does not depend on α and thereby the present method gives the correct values of S for $\alpha \neq 0$ as well. After the order parameter is obtained from the intensity dependence of the residual anisotropy, the angle α can be estimated knowing the value of the low-intensity anisotropy since, in general, $r(0) = 0.4\,S^2 d$.

The discrete model discussed in section 4 gives a lower limit to the residual anisotropy, for in this model the annihilation is considered to be fast enough, so that only the last remaining exciton in a domain can decay via fluorescence. Thus, knowing the residual anisotropy at high intensities one can obtain the lower bound to the domain size using eqs. (4.3) or fig. 5.

The domain size of photosynthetic systems [6–8,24] and aggregated dye solutions [11] is usually estimated by comparing the theoretically calculated fluorescence quantum yield against intensity curves with the curves obtained experimentally. Here we have shown that, using the residual fluorescence anisotropy against intensity curves, one can obtain information not only about the domain size, but also about the orientational distribution of chromophores (or their aggregates) forming a domain as well. The present method, however, is applicable only to systems in which the transition moments of chromophores in domains are ordered ($S \neq 0$).

In this paper we have dealt with the fluorescence depolarization. The results presented can also be used to analyse the decay of the induced absorption anisotropy in polarized pump-probe experiments, provided the changes in the absorption spectrum, ΔA, are a linear function of the exciton density. In other words, the energy of the excitation pulses should be sufficiently low to avoid nonlinear spectral changes. The decay of the induced absorption anisotropy in the J-aggregated pseudoisocyanine (PIC) dye solution will be discussed below.

In aqueous solutions the highly concentrated PIC dye is known to form thread-like J aggregates having an unusually narrow excitonic J band at 573 nm [25–27]. The optical properties of J aggregates have been the subject of continuous interest for many years [11,25–35]. Recently, the excited-state dynamics of PIC J aggregates has been investigated by Sundström et al. using polarized picosecond and subpicosecond absorption spectroscopy method [11]. High values of the induced absorption anisotropy have been found at long times. This suggests a high orientational order of the J aggregates forming a domain. At very low excitation intensity (below the onset of the annihilation) the residual anisotropy at long times is $r(0)=0.25$ [11]. Theoretically, $r(0)=0.4S^2d$, with $d=(3\cos^2\alpha-1)/2$, α being the angle between the polarization of the J band and that of the spectrum of its changes. For PIC J aggregates $d=1$ $(\alpha=0)$, since the single-photon excitation of the J aggregate induces a blue shift of the excitonic J band without any change to its polarization [#2] [36]. In this way, we find the order parameter: $S\approx 0.8$. For instance, if the transition moments of aggregates forming a domain were distributed homogeneously within a cone of half-angle β, $S=0.8$ would correspond to $\beta=34°$. Moreover, the residual anisotropy was shown to decrease as the intensity of excitation pulses increases [11]. The present theory accounts for such a depolarization. At $I_{\mathrm{ex}}=1.4\times10^{12}$ photons cm^{-2} pulse^{-1} and $\lambda_{\mathrm{ex}}=569$ nm (under these conditions the fraction of initially excited PIC molecules is about 1/3000), the residual anisotropy is: $r_\infty=0.1$, that is $r_\infty/r(0)=0.4$. Since the discrete model presented in section 4 gives a lower limit to the residual anisotropy, using fig. 5 we find that the domain should contain more than 6×10^3 PIC molecules. The slightly higher value of the lower limit of the domain size ($N_{\mathrm{D}}>10^4$) has been obtained in our previous paper [18] using a simpler model in which $S=1$. The estimate $N_{\mathrm{D}}>6\times10^3$, is in agreement with earlier evaluations of the domain size obtained from both integrated fluorescence quantum yield curves and excited-state decay kinetics [11]. The lack of experimental data on the intensity dependence of the residual anisotropy of the PIC solution does not allow us to obtain information on the orientational distribution of J aggregates forming a domain using the present technique. Neither are we able to compare the experimental decay of the anisotropy at short times with the theoretical one, since the distribution time τ_{r} of excitons within PIC domains in solution is too large (about 100 ps) [11]. (For $S\neq1$, the present theory is applicable only for times greater than the redistribution time τ_{r}, see section 2.) The fit of $r(t)$ at short times is possible for systems where either the redistribution time is short enough or the transition dipoles of chromophores forming the domain are parallel ($S=1$).

We hope that the theoretical results presented here can be applied to other systems, such as J aggregates adsorbed on colloid silica and photosynthetic antennae. For example, the absence of the depolarization suggests that in living cells of green bacteria the excitation transfer within a bacteriochlorophyll c antenna occurs between chromophores (or their aggregates) with parallel transition moments [37]. The absence of the depolarization also suggests a high orientational order of the J-aggregates of PIC on colloid silica [38]. However, although the laser intensities employed by Horng and Quitevis [38] have been comparable to those used by Sundström at al. [11], no intensity-dependent depolarization arising from exciton–exciton annihilation has been observed. This could be because of the fact that the domains of J aggregates on colloid silica are considerably smaller than those in the solution [38]. The present theoretical investigation seems to be not applicable to photosynthetic antenna systems of purple bacteria at $T_*=296$ K, because the complete decay of the induced absorption anisotropy indicates the absence of the long-range orientational order of chromophores forming a domain [39]. On the other hand, the high values of the residual anisotropy obtained at the longer wavelength region of the spectrum at $T_*=77$ K imply that either the bacteriochlorophyll Q_{y} transition moments are highly oriented or no energy transfer between BChl molecules occurs [40].

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[#2] The J band is polarized parallel to the aggregate axis [25,27].

Appendix: asymptotic behaviour of the fluorescence anisotropy

(i) For small reduced times (or low intensities), $T \ll (\gamma N_0)^{-1}$, only a small fraction of the initially created excitons has decayed via annihilation:

$$\langle N_{k_\parallel} \rangle = N_0[1-\tfrac{1}{3}(1+\tfrac{4}{5}S^2)\phi]\exp(-t/\tau) \approx N_0\exp(-t/\tau)\,. \tag{A.1}$$

As a result, the anisotropy is close to its low-intensity value of 0.4 S^2:

$$r=0.4S^2[1-\tfrac{1}{3}(1+\tfrac{4}{7}S-\tfrac{4}{5}S^2)\phi]\,. \tag{A.2}$$

(ii) For large reduced times, $T \gg (\gamma N_0)^{-1}$, eqs. (3.6) and (3.7) simplify to

$$r=0.5(R-3/\phi)\,, \tag{A.3}$$

$$\langle N_{k_\parallel} \rangle = (\gamma T)^{-1}\exp(-t/\tau) \ll N_0\,, \tag{A.4}$$

and the asymptotic behaviour of the anisotropy depends strongly on the value of the order parameter. For $0<S<1$, we have

$$r=B_1\phi^{-1}\,, \qquad T \gg [\gamma N_0(1-S)]^{-1}\,, \tag{A.5}$$

where

$$B_1=0.5[(Sb)^{-1/2}\tan^{-1}(S/b)^{1/2}-3]\,, \tag{A.6}$$

with b given by eq. (3.12). That is, the anisotropy goes as T^{-1}. For $S=1$, the anisotropy goes as $T^{-1/2}$ [18]. The present decay law is also preserved for $S \neq 1$ at intermediate times, provided the transition moments are nearly parallel:

$$r=0.25\pi\phi^{-1/2}\,, \qquad (\gamma N_0)^{-1} \ll T \ll [\gamma N_0(1-S)]^{-1}\,. \tag{A.7}$$

For negative order parameters, we find that

$$r=B_2\phi^{-1}\,, \qquad T \gg [\gamma N_0(\tfrac{1}{2}-|S|)]^{-1}\,, \tag{A.8}$$

$$r=(2\phi)^{-1}[\ln(2\phi)-3]\,, \qquad (\gamma N_0)^{-1} \ll T \ll [\gamma N_0(\tfrac{1}{2}-|S|)]^{-1}\,, \tag{A.9}$$

where

$$B_2=0.5[(|S|b)^{-1/2}\tanh^{-1}(|S|/b)^{1/2}-3]\,, \tag{A.10}$$

that is, at large reduced times the anisotropy goes as T^{-1} for $S \neq -\tfrac{1}{2}$, and for $S=-\tfrac{1}{2}$ (the transition moments of chromophores forming a domain are perpendicular to the orientational vector $\boldsymbol{k}$) it behaves as $T^{-1}(\ln T + \text{const.})$. The latter decay law also holds for $S \neq -\tfrac{1}{2}$ at intermediate times, provided $(\tfrac{1}{2}-|S|) \ll 1$.

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