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Effect of dimensionality and size on triplet–triplet annihilation

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Abstract

A statistical approach and Monte Carlo simulations in regular lattices were used to study the dynamics of triplet–triplet annihilation (TTA) in 1D, 2D and 3D nanodomains. It was shown that the phosphorescence and triplet–triplet absorption decays can generally be fitted with a sum of two exponentials. The first exponential corresponds to domains containing initially one triplet and the second exponential to domains initially with two triplets. The triplet survival probability and the dependence of the annihilation rate constant on the energy migration rate, *W*, annihilation rate, *V*, and size of the domain, *M*, was obtained by Monte Carlo simulations in the diffusion-influenced limit ($V \gg W$).

Keywords: Triplet–triplet annihilation; Phosphorescence; Delayed fluorescence; Monte Carlo simulations

1. Introduction

The spectral properties of multichromophoric nanosystems, as well as their excited state time and space evolution, are critically dependent on their size and topology. This has been observed for singlet excitation energy migration and trapping in multichromophoric rings [1], linear polymer chains [2,3], small regular lattices [4], dendrimers [5,6] and photosynthetic systems [7]. More recently, this was also observed for singlet–singlet annihilation [8–12] and triplet–triplet annihilation (TTA) [13,14] in multichromophoric systems.

Triplet–triplet annihilation is an important process at relatively high excitation intensities that strongly influences the optical and optoelectronic properties of homogeneous liquid solutions [15,16], micellar solutions [13], molecular crystals [17], polymers [14,18,19] and Langmuir–Blodgett films [20].

TTA corresponds to the short-range energy transfer process $T_1 + T_1 \rightarrow S_1 + S_0$, whereby two molecules in the lowest excited triplet state yield a molecule in the singlet ground state an the other in the first excited singlet state [21]. Several processes can then follow, namely unimolecular ones, $S_1 \rightarrow S_0$ (including delayed fluorescence and internal conversion), and $S_1 \rightarrow T_1$ (intersystem crossing). A bimolecular process is also possible, namely excimer formation $S_1 + S_0 \rightarrow S_1'$, where the prime denotes an excimer electronic state. The singlet excimer can then dissociate according to unimolecular processes: $S_1' \rightarrow S_0 + S_0$ (delayed fluorescence, internal conversion), and $S_1' \rightarrow T_1 + S_0$ (intersystem crossing).

TTA thus generates one excited singlet that yields a ground state singlet either by internal conversion or by delayed fluorescence, or reverts back into a triplet, directly by intersystem crossing or indirectly via excimer formation–dissociation. As a result, either zero or one triplet can result from the annihilation of two triplets [21].

In systems with a high density of chromophores, the motion of the excitation occurs not only by molecular

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displacement (molecular diffusion), but also by migration due to the short-range triplet–triplet energy hopping [17,21], $T_1 + S_0 \rightarrow S_0 + T_1$.

The aim of this work is the study of TTA and of the associated delayed fluorescence in 1D, 2D and 3D nanosystems (linear chains and particles) with efficient triplet–triplet energy migration. The standard and statistical formalisms of TTA are presented in Sections 2 and 3. In Section 4, the survival probability for an annihilating pair of triplets is calculated for 1D nanosystems. In Section 5, Monte Carlo simulations in 1D, 2D and 3D nanosystems were performed and the survival probability for the annihilation of a pair of triplets was calculated. The delayed fluorescence kinetics are discussed in Section 6 and the main results are summarized in Section 7.

2. Standard approach to TTA

The standard approach used to describe TTA, assumes that the annihilation is a bimolecular process with rate proportional to the density of triplet excitations. Then, the rate equation can be written as [7,18,19,21]

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -kN - \gamma_0 N^2, \tag{1}$$

where N represents the average triplet excitation density, understood here as the number of excitations per closed domain (a linear polymer chain, micelle, nanoparticle, etc.), k is the reciprocal lifetime of the triplet, and γ_0 is the so-called annihilation rate constant, with dimensions of reciprocal time. For a time-independent γ_0 the solution of Eq. (1) is well known

$$N(t) = \frac{kN_0}{k\mathrm{e}^{kt} + \gamma_0 N_0(\mathrm{e}^{kt} - 1)} = \frac{N_0\mathrm{e}^{-kt}}{(1+\gamma_0 N_0/k) - (\gamma_0 N_0/k)\mathrm{e}^{-kt}}, \tag{2}$$

where N_0 is the initial number of triplet states in the domain. When modeling TTA by Eq. (1), it is usually assumed that: (i) the triplet excitations are molecular excitations as a result of strong disorder and/or high temperatures; (ii) the excitations move by diffusion within the system. If the diffusion rate is large compared to the nearest-neighbor annihilation rate, V (with dimensions of reciprocal time), the decay is annihilation-controlled, and $\gamma_0 = V/2$. However, when the annihilation dominates over diffusion, the process is diffusion-influenced and the global annihilation rate constant γ_0 is determined not only by the annihilation rate, V, but also by the time-evolution of the triplets pair correlation function. In this case the annihilation rate can be time-dependent, this dependence being determined by the dimensionality of the domains [7,22–27].

Using the expansion $1/(1-x) = 1 + x + x^2 + \cdots$ $(x < 1)$, it follows from Eq. (2) that the phosphorescence intensity, normalized to unity at $t = 0$, $I_\mathrm{P}(t) = N(t)/N_0$, can be written as a series:

$$\begin{aligned} I_\mathrm{P}(t) &= \frac{\mathrm{e}^{-kt}}{1+\gamma_0 N_0/k}\left(\frac{1}{1 - \frac{\gamma_0 N_0/k}{1+\gamma_0 N_0/k}\mathrm{e}^{-kt}}\right) \\ &= \frac{1}{1+\gamma_0 N_0/k}\mathrm{e}^{-kt} + \frac{\gamma_0 N_0/k}{(1+\gamma_0 N_0/k)^2}\mathrm{e}^{-2kt} \\ &\quad + \frac{(\gamma_0 N_0/k)^2}{(1+\gamma_0 N_0/k)^3}\mathrm{e}^{-3kt} + \cdots \end{aligned} \tag{3}$$

Each term of the series decays exponentially with time, the time dependence being determined by the intrinsic relaxation rate of the triplet, k. The annihilation constant, γ_0 only appears in the pre-exponential factors of the decay components.

The above description has limitations, which can become rather important at very low temperatures, where triplet excitations can be delocalized over several molecules and form excitons [28,29].

3. Statistical approach to TTA

A more general approach for the description of TTA is the so-called statistical approach proposed by Paillotin et al. [30] (see also [7,10]). In this approach, ensembles of closed domains (e.g., non-interacting polymer chains, micelles, or nanoparticles) are considered. After a pulse of excitation light, followed by singlet–triplet conversion, each domain contains N_0 triplets. Considering that: (i) excitations in different domains do not interact with each other; (ii) the distribution of excitations over domains follows a Poisson distribution; (iii) The annihilation occurs by two bimolecular processes with constants, $\gamma^{(1)}$ and $\gamma^{(2)}$ corresponding to the disappearance of one or two triplets, respectively, the phosphorescence intensity, $I_\mathrm{P}(t)$, is given by [30]

$$\begin{aligned} I_P(t) &= \sum_{p=0}^{\infty} b_{p+1}\exp\left[-(p+1)(p+r)\gamma t/2\right] \\ &= b_1\mathrm{e}^{-kt} + b_2\mathrm{e}^{-\gamma t-2kt} + b_3\mathrm{e}^{-3\gamma t-3kt} + b_4\mathrm{e}^{-6\gamma t-4kt} \\ &\quad + b_5\mathrm{e}^{-10\gamma t-5kt} + \cdots, \end{aligned} \tag{4}$$

where

$$b_{p+1} = \sum_{m=0}^{\infty}\frac{(-1)^m(p+m)!Z^{p+m}(r+1+2p)}{p!m!(r+p+1)(r+p+2)\ldots(r+p+1+p+m)}. \tag{5}$$

and $\gamma = \gamma^{(1)} + \gamma^{(2)}$; $r = 2k/\gamma$ and $Z = N_0(1 + \gamma^{(2)}/\gamma)$.

Both approaches (Eqs. (3) and (4)) predict that the time resolved phosphorescence intensity decay as a sum of exponentials. However, the corresponding relaxation constants and the pre-exponential factors in each model are different.

Fig. 1 shows the dependence of coefficients b_p on r for two different values of the parameter Z that measures the average number of triplet excitations per domain. The plot shows that the first two or three terms of Eq. (4) are enough to describe the overall decay.

It was shown previously [30] that Eq. (4) simplifies into Eq. (3) in the limit of $r \to \infty$ (i.e., $2k/\gamma \to \infty$), with $Z = N_0$ and $\gamma = 2\gamma_0$. This means that both approaches are similar when the rate of bimolecular annihilation is much smaller than the intrinsic decay rate. Nevertheless, the statistical approach is more general and can be used to describe the TTA in both small and large domains, whatever the value of the annihilation constant.

The statistical approach allows a simple interpretation of each term in Eq. (4). The first term corresponds to domains containing initially only one triplet that decays with the intrinsic rate constant k. The second term considers the domains containing two excitations and that therefore decay individually with rate constant k or by annihilation with rate constant, γ. The third term takes into account the decay of domains containing three excitations and therefore the excitation decays individually or by annihilation with rate constant, 3γ.

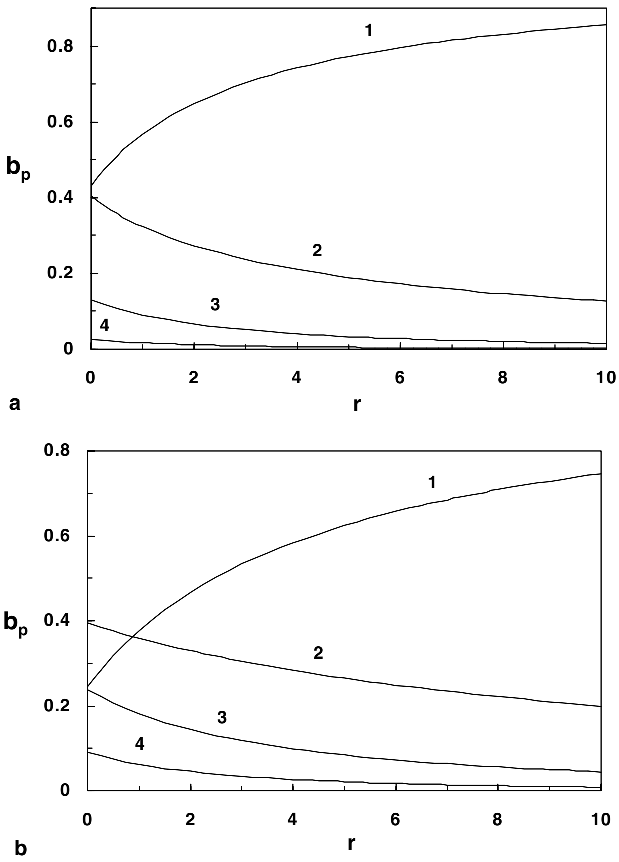

Fig. 1. Dependence of coefficients b_p on r for two different values of Z (proportional to the average number of triplet excitations per domain): $Z = 2$ (a) and $Z = 4$ (b). Values of parameter p are indicated next to each curve.

The coefficient 3 in γ is the number of ways (in two or three-dimensional cases) by which three excitations can meet in pairs. Analogously, the nth term considers domains containing n excitations that decay by the intrinsic process or by annihilation with the rate constant $C_n^2\gamma$, where $C_n^2 = n(n-1)/2$ is the number of pairs that can be formed from n elements (the binomial coefficient C_n^2).

Both the standard and the statistical approaches do not show the dependence of the annihilation constant on the rate of excitation diffusion, W (i.e., the frequency of hops between nearest-neighbor chromophores in the domain), the rate of nearest-neighbor annihilation, V, and on the size and dimension of the domain. To our knowledge, the first and single attempt to answer some of these questions was done by Onipko and Zozulenko [31], for the case of a one-dimensional lattice and $V = \infty$.

4. Survival probability for an annihilating pair of triplets

The survival probability for an annihilating pair of triplets, $\rho_M^{(2)}(t)$, diffusing in one-dimensional domain (e.g., a polymer chain with M chromophores) was obtained by Onipko and Zozulenko [31], after solving the corresponding master equation for a one-dimensional lattice. It was assumed that the excitation jumps between neighboring lattice sites with a unit time probability W; when two excitations meet at the same site, the annihilation occurs with unit efficiency, i.e., the annihilation rate is infinite, $V = \infty$. The solution for an initial uniform excitation and, $M \gg 1$; $Wt \gg 1$, is

$$\rho_M^{(2)}(t) = \exp(-2kt)\frac{2^6}{\pi^4}\times\left\{\sum_{l=1}^{\infty}\frac{1}{(2l-1)^4}\exp\left(-(2l-1)^2\frac{\pi^2 Wt}{M^2}\right)\right. + 2\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\frac{1}{\left((2m)^2-(2l-1)^2\right)^2} \left.\times\exp\left(-\left((2m)^2+(2l-1)^2\right)\frac{\pi^2 Wt}{M^2}\right)\right\}. \qquad (6)$$

This equation has asymptotes for short and long times

$$\rho_M^{(2)}(t) = \exp(-2kt)\times\begin{cases} 1-\frac{4\sqrt{2}}{\sqrt{\pi}}\sqrt{\frac{Wt}{M^2}}, & \text{if } \frac{Wt}{M^2}\ll 1 \qquad \text{(a)}\\ \frac{2^6}{\pi^4}\exp\left(-\pi^2\frac{Wt}{M^2}\right), & \text{if } \frac{Wt}{M^2}\gg 1 \qquad \text{(b)}\end{cases} \qquad (7)$$

The asymptote for long times can simply be obtained by considering that on the average, each of the two excitations can freely move in half of the chain and that annihilation occurs when both excitations encounter in the middle of the chain. Therefore, to a first approximation, the behavior of each excitation is equivalent to the migration along a chain of length $M/2$ that contains a quencher at one end. The long-time asymptote for large M, $(8/\pi^2)\exp(-\pi^2 Wt/M^2)$, was obtained before [32] and coincides, apart from a numerical factor, with the long-time asymptote in Eq. (7b).

Based on this interpretation, it is possible to obtain the annihilation rate constant, γ, by comparing the asymptote (Eq. (7b)) with the second term of Eq. (4)

$$\gamma = \pi^2 W/M^2. \tag{8}$$

As expected, γ, decreases when the size of the domain increases.

An approximate equation for $\rho_M^{(2)}(t)$, more adequate for the analysis of experimental results, was obtained from the numerical computation of Eq. (6) and from its asymptotic behavior, Eq. (7), and is

$$\rho_M^{(2)}(t) = \exp(-2kt) \times \left\{ \left(1 - \frac{2^6}{\pi^4}\right) \exp\left[-\frac{4\sqrt{2}}{(1-2^6/\pi^4)\sqrt{\pi}} \sqrt{\frac{Wt}{M^2}} - \left(30\frac{Wt}{M^2}\right)^{3/2} \right] + \frac{2^6}{\pi^4} \exp\left[-\pi^2 \frac{Wt}{M^2}\right] \right\}, \tag{9}$$

Fig. 2 shows that this equation is a very good approximation to the exact solution (Eq. (6)), with a precision better than 2% for all times.

5. Monte Carlo simulations

Monte Carlo (MC) simulations were carried out on 1D, 2D and 3D nanodomains of several sizes. The simulations were performed following the procedure of Pearlstein [32], considering that the rate of energy hopping between lattice sites is W, and that the annihilation occurs with rate V when two excitations encounter in neighboring sites. The initial distribution of the excitation in the domain is uniform. The final results are averages over 50000 (1D and 2D) and 20000 (3D) trajectories.

5.1. One dimensional domain

The survival probability over a small polymer chain of size $M = 25$, 50, and 100 was obtained considering the procedure outlined before. There are initial configurations for which the two excitations exist at nearest-neighbor sites. Their relative number is $(M-1)/C_M^2 = 2/M$ and then the decay begins at $1-2/M$ instead of 1 for $V = \infty$.

For sufficiently long times ($\rho_M^{(2)}(t)\exp(2kt) < 0.4$), the pair survival probability $\rho_M^{(2)}(t)$ is, irrespective of size, very similar to the long-time asymptote (Eq. (7b)). The accuracy between the asymptote and MC simulations improves with the number of sites M. The simulations were carried out also for finite values of the V/W ratio. It was found that for $V/W \geqslant 0.5$, $\rho_M^{(2)}(t)$ is independent of V/W and very similar to the case with $V = \infty$.

In order to verify the accuracy of the third term in Eq. (4) the survival probability for an annihilating triplet of excitations, $\rho_M^{(3)}(t)$ was calculated. There are initial configurations for which two or even three excitations exist initially at nearest-neighbor sites. Their relative number is $(M-1)(M-2)/C_M^3 = 6/M$, and as these configurations decay instantaneously ($V = \infty$), the overall decay begins at $1-6/M$ instead of 1. Fig. 3 shows the survival probability $\rho_M^{(3)}(t)\exp(3kt)$ for $M = 25$, 50, 100.

The long-time survival probability ($\rho_M^{(3)}(t)\exp(3kt) < 0.4$) for both $V/W = \infty$ and 1, is well described by

$$\rho_M^{(3)}(t)\exp(3kt) \approx 0.5\exp\left(-52\frac{Wt}{M^2}\right). \tag{10}$$

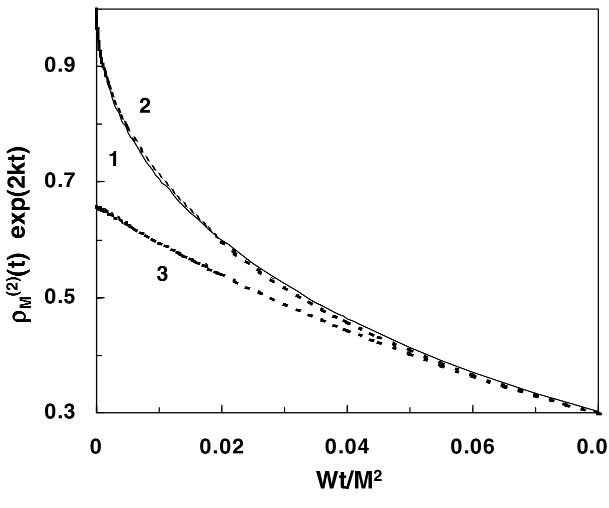

Fig. 2. Survival probability for an annihilating pair of excitations in a linear lattice, $\rho_M^{(2)}(t)$, for $V/W = \infty$. (solid line 1) Exact solution from Eq. (6); (dotted line 2) approximate decay from Eq. (9); (dotted line 3) Long time 2 asymptote from Eq. (7b).

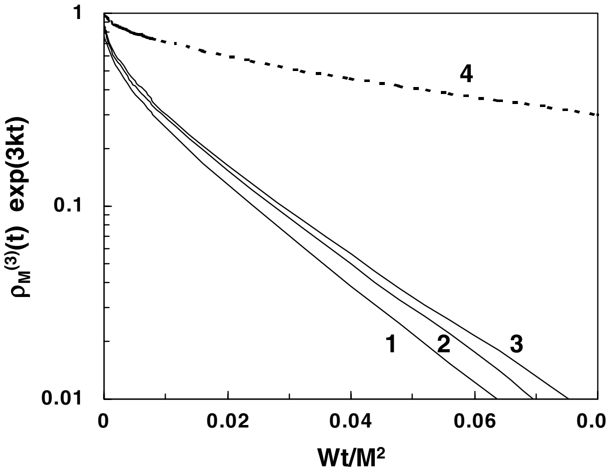

Fig. 3. Survival probability for an annihilating triplet of excitations on a linear lattice, $\rho_M^{(3)}(t)$, for $V/W = \infty$ and 1. (Lines 1–3) $\rho_M^{(3)}(t)$, with $V/W = \infty$ and $M = 25$, 50, and 100, respectively. For $V/W = 1$ and $M = 25$ or 50, the corresponding curves practically coincide with line 3; (line 4) $\rho_M^{(2)}(t)\exp(2kt)$ values for comparison ($V/W = \infty$, $M = 50$).

In comparison with Eq. (7b) the same type of dependence was observed, apart from the numerical coefficient of the exponent that changes by more than 5 times, from π^2 to 52. This is expected, because, on the average, each of the three excitations can freely move along a section of the chain of size $M/3$. Upon an encounter, one or two excitations disappear and therefore, the motion of every excitation is to a first approximation equivalent to a motion along a chain of length, $M/3$. Two of these chains have a quencher at one end and the third has quenchers at both ends.

The decay function, $\rho_M^{(3)}(t)$ decreases very fast with time, and this explains why only the two first terms of the series in Eq. (4) are generally needed to fit phosphorescence decays in linear polymer chains.

5.2. Square lattice

In the case of a square lattice having $L = M \times M$ sites (e.g., a polymer monolayer), there are initial configurations for which two excitations exist at nearest-neighbor sites. Their relative number is $2M(M-1)/C_{M^2}^2 = 4/[M(M-1)]$, and the overall decay ($V = \infty$), begins at $1 - 4/[M(M-1)]$ instead of 1. The MC simulations were performed on square lattices of several sizes ($M = 5, 10, 20, 40$). The survival probability for an annihilating pair of excitations, $\rho_M^{(2)}(t)$, for $10 < V/W < \infty$ can be expressed by

$$\rho_M^{(2)}(t)\exp(2kt) = A_{\rm sq}\exp\left[-B_{\rm sq}\frac{Wt}{M^2\left(2\ln M - 1 + 1/\sqrt{M}\right)}\right], \tag{11}$$

with $A_{\rm sq} = 0.86 \pm 0.01$. The $B_{\rm sq}$ parameter depends on the V/W ratio as shown in Fig. 4.

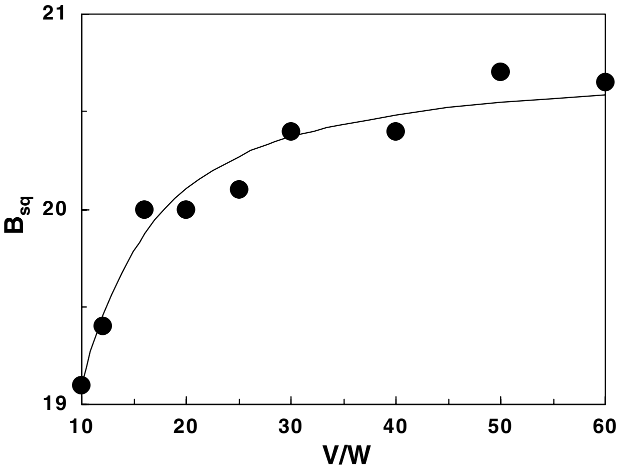

Fig. 4. Dependence of parameter $B_{\rm sq}$ on V/W. Circles correspond to Monte Carlo simulations, and the solid line are the values given by Eq. (12).

This dependence is well described by

$$B_{\rm sq} = \frac{20.7(V/W)^{1.5}}{2.65 + (V/W)^{1.5}} \pm 0.2. \tag{12}$$

The choice of the form of the empirical function Eq. (11) is motivated by a simple analytical calculation for a circle with radius $R \approx Ma$, where a is a distance between neighboring sites in the lattice. The excitations move in the circle with a diffusion constant $D \approx Wa^2$. Let us consider that one triplet is immobile and located at the center of the circle, while the motion of the other obeys the diffusion equation

$$\frac{\partial}{\partial t}\rho(r,t) = D\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\rho(r,t) \tag{13}$$

with initial and boundary conditions: $\rho(r,t) = 1/S$ (S being the area of the circle); $\rho(a,t) = 0$ ($V = \infty$); $\partial\rho/\partial r|_{r=R} = 0$.

Let us look for a solution of Eq. (13) in the form $\rho(r,t) = \exp(-C_{\rm sq}t)\rho_{\rm st}(r)$, where $C_{\rm sq}$ is a constant. The pair survival probability for long times is $\rho_M^{(2)}(t) = 2\pi\int_V \rho(r,t)r\,\mathrm{d}r \propto \exp(-C_{\rm sq}t)$. After introducing $\rho(r,t)$ into Eq. (13), we obtain

$$-C_{\rm sq}\rho_{\rm st}(r) = D\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\rho_{\rm st}(r). \tag{14}$$

That by integration over r gives

$$C_{\rm sq} = \frac{2\pi a D\frac{\partial}{\partial r}\rho_{\rm st}(r)|_{r=a}}{2\pi\int_a^R \rho_{\rm st}(r)r\,\mathrm{d}r}. \tag{15}$$

The solution of Eq. (14) for small r (near a) is $\rho_{\rm st}(r)\ \ln(r/a)$, as can be checked by integrating Eq. (14) using $\rho_{\rm st}(r) \approx \rho_{\rm st}(a) = 0$ on its right-hand side. To a first approximation, this solution can be used for $a \leqslant r \leqslant R$. Inserting this into Eq. (15),

$$C_{\rm sq} = \frac{4D}{a^2 - R^2 + 2R^2\ln(R/a)} \tag{16}$$

and as $a \ll R$; $R \approx Ma$ and $D \approx Wa^2$, we obtain

$$C_{\rm sq} \approx \frac{4W}{M^2(2\ln M - 1)}. \tag{17}$$

The expression for $C_{\rm sq}$ shows that the dependence on M is practically equal to the dependence obtained by simulation (Eq. (11)).

Then, it follows that for a two-dimensional lattice, the dependence of the long-time limit of the TTA rate constant is

$$\gamma_{\rm sq} = \frac{20.7(V/W)^{1.5}}{2.65 + (V/W)^{1.5}}\frac{W}{M^2\left(2\ln M - 1 + 1/\sqrt{M}\right)}. \tag{18}$$

5.3. Cubic lattice

Consider now TTA in three-dimensional domains described by a cubic lattice of $L = M \times M \times M$ sites. Fig. 5 shows the MC simulations for $M = 5$, 10, 15, and sev-

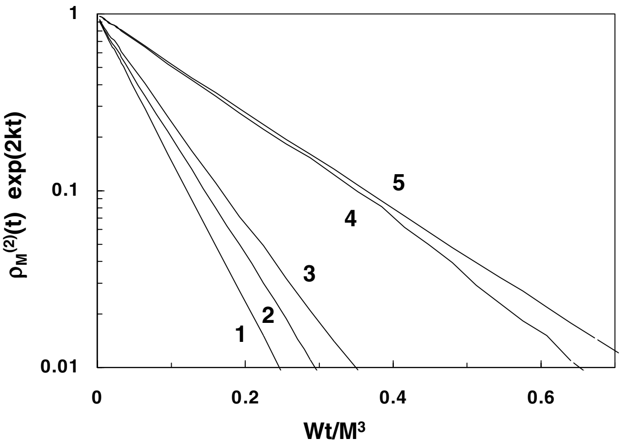

Fig. 5. Survival probability for an annihilating pair of excitations in a cubic lattice. $V/W = \infty$ (curve 1), 10 (curve 2), 5 (curve 3), and 1 (curve 4 for $M = 10$, 15 and curve 5 for $M = 5$).

eral values of V. The parameter M has no important effect except for $V/W = 1$.

The survival probability for an annihilating pair of triplets in a cubic lattice, $\rho_M^{(2)}(t)$, can be written as

$$\rho_M^{(2)}(t)\exp(2kt) = A_{\text{cub}}\exp\left[-B_{\text{cub}}\frac{Wt}{M^3}\right] \tag{19}$$

for $1 < V/W < \infty$. The parameter, $A_{\text{cub}} = 0.96 \pm 0.02$ for all values of V. The dependence of B_{cub} on the V/W ratio is shown in Fig. 6.

A good fit to these values can be obtained by

$$B_{\text{cub}} = \frac{19.5(V/W)^{0.93}}{2+(V/W)^{0.93}} \pm 0.5. \tag{20}$$

The dependence of the survival probability, $\rho_M^{(2)}(t)$, on W and M can be confirmed from the analytical results of TTA in a continuous three-dimensional sphere with a radius $R \approx (La^3)^{1/3} = Ma$, where a is a distance between nearest-neighbor sites in the lattice. Let us consider that one triplet is immobile and located in the center of the sphere, while the other moves in its interior with diffusion constant, $D = Wa^2$. The evolution of the mobile triplet is described by the diffusion equation

$$\frac{\partial}{\partial t}\rho(r,t) = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\rho(r,t) \tag{21}$$

with initial and boundary conditions: $\rho(r,t) = 1/V$ (V is the volume of the sphere); $\rho(a,t) = 0$ ($V = \infty$); $\partial\rho/\partial r|_{r=R} = 0$.

Let us look for a solution of Eq. (21) in the form of $\rho(r,t) = \exp(-C_{\text{cub}}t)\rho_{\text{st}}(r)$, where C_{cub} is a constant. The long-time behavior of the survival probability $\rho_M^{(2)}(t) = 4\pi\int_V \rho(r,t)r^2\,\mathrm{d}r \propto \exp(-C_{\text{cub}}t)$. After introducing $\rho(r,t)$ into Eq. (21), we obtain

$$-C_{\text{cub}}\rho_{\text{st}}(r) = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\rho_{\text{st}}(r). \tag{22}$$

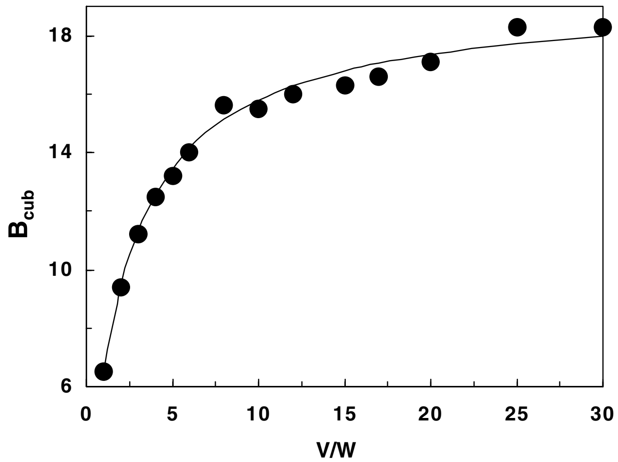

Fig. 6. Dependence of parameter B_{cub} on V/W. Circles correspond to Monte Carlo simulations and the solid line was computed with Eq. (20).

The integration over r on both sides of this equation, gives

$$C_{\text{cub}} = \frac{4\pi a^2 D\frac{\partial}{\partial r}\rho_{\text{st}}(r)|_{r=a}}{4\pi\int_a^R \rho_{\text{st}}(r)r^2\,\mathrm{d}r}. \tag{23}$$

The solution of Eq. (22) for small r (near a) is $\rho_{\text{st}}(r) \propto F(1 - a/r)$, where F is a constant. This can be used to a first approximation as a solution for $a \leqslant r \leqslant R$ Inserting this solution into Eq. (23), and knowing that $a \ll R$, we get

$$C_{\text{cub}} \approx \frac{3Da}{R^3} \tag{24}$$

and as $R \approx Ma$ and $D \approx Wa^2$, we obtain

$$C_{\text{cub}} \approx \frac{3W}{M^3}. \tag{25}$$

The expression for C_{cub} (Eq. (25)) shows that the dependence observed by Monte Carlo is appropriate (see Eq. (19)).

Thus, in a three-dimensional lattice, the dependence of the long-time limit TTA rate constant, γ_{cub}, is given by

$$\gamma_{\text{cub}} = \frac{19.5(V/W)^{0.93}}{2+(V/W)^{0.93}}\frac{W}{M^3}. \tag{26}$$

6. Delayed fluorescence

The decay of domains containing more than two excitations is very fast, which means that the overall decay is determined by domains initially containing one and two excitations. As the singlet lifetime is orders of magnitude shorter than the triplet lifetime the delayed fluorescence is well described by the survival probability of an annihilating pair of triplets. Thus, for long times, the normalized decay of delayed fluorescence, $I_{\mathrm{DF}}(t)$, is

$$I_{\mathrm{DF}}(t) \approx \exp(-2kt - \gamma t), \tag{27}$$

where the annihilation constant γ is given by Eqs. (8), (18), or (26), according to the dimensionality of the domains under consideration.

7. Conclusions

In this paper, we showed that the usual TTA observables (delayed fluorescence, phosphorescence, triplet–triplet absorption), are well described by a single exponential decay (delayed fluorescence) or by a sum of two exponentials (phosphorescence, triplet–triplet absorption). In the last case, the first term describes the decay of domains containing exactly one excitation, while the second one reflects the disappearance of domains containing exactly two excitations. In the case of delayed fluorescence, the first term, describing the decay of domains containing exactly one excitation, is usually negligible (unless unimolecular thermally activated delayed fluorescence also occurs), and only the second term is important. In all cases, the higher terms of the infinite series expansion, describing domains containing three or more excitations, decay much faster and can be neglected for the intensities of excitation usually used.

From Monte Carlo calculations the survival probability for an annihilating pair of triplets was obtained and the dependence of the rate constant of TTA on the size of the domain, M, on the rate of excitation migration, W, and on the rate of excitation annihilation, V, for 1D, 2D and 3D nanodomains was obtained. It should be noted that an independent procedure for the determination of the rate of triplet migration, W, is the measurement of time-resolved phosphorescence anisotropy under conditions where rotational motion of the chromophores is negligible during the triplet lifetime, e.g., a low temperature glass, and for low excitation intensities. This approach will be adequate only when the chromophores are randomly oriented, so that transfer will result in depolarization.

We considered mainly the diffusion-influenced limit ($V \gg W$) where the rate of nearest-neighbor annihilation, V, dominates over the diffusion rate, W. In the opposite case, the diffusion rate is larger than the rate of nearest-neighbor annihilation, and the distribution of excitations over the domains is homogeneous (diffusion displacement of triplet excitation during the lifetime, $\sqrt{D/k}$, large compared to the size of the domains, Ma, i.e., $\sqrt{W/k} > M$) for all times. Then, $\gamma = V$ and the triplet survival probability is well described by Eq. (4) in the context of the statistical approach.

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