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CONDENSED-MATTER SPECTROSCOPY

Size Effects in Triplet–Triplet Annihilation: II. Monte Carlo Simulations[1]

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Abstract—The dynamics of triplet–triplet annihilation (TTA) is theoretically studied in linear chains and nanoparticles, modeled as 1D, 2D, and 3D regular lattices, as a function of size *M*, of the rate of excitation migration *W*, and of the rate of excitation annihilation *V* in the diffusion-influenced limit ($V \gg W$). It is shown that a sum of two exponentials is usually sufficient for fitting experimental phosphorescence and triplet–triplet absorption decays. The first term describes the decay of domains containing initially one triplet, while the second one reflects the disappearance of domains containing initially two triplets. Monte Carlo calculations were carried out to compute the survival probability of an annihilating pair of triplets, yielding expressions for the dependence of the rate constant of TTA on the parameters *M*, *W*, and *V* in one, two, and three dimensions.

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1. INTRODUCTION

The size and topology of multichromophoric nanosystems critically affect their spectral properties, as well as excited state time and space evolution. In particular, singlet excitation energy migration and trapping have been studied in detail in multichromophoric rings [1], linear chain polymers [2, 3], small regular lattices [4], dendrimers [5, 6], and photosynthetic systems [7]. Recently, attention has also been paid to multiphoton processes in nanosystems, including singlet–singlet annihilation [8–10] and triplet–triplet annihilation (TTA) [11, 12].

TTA is an important process that strongly influences the optical and optoelectronic properties of a multitude of systems at relatively high excitation intensities, such as homogeneous liquid solutions [13, 14], micellar solutions [11], molecular crystals [15], polymers [12, 16, 17], and Langmuir–Blodgett films [18].

TTA corresponds to the energy transfer process $T_1 + T_1 \longrightarrow S_1 + S_0$, whereby two excited molecules in the lowest triplet state yield, upon their close proximity, a ground state molecule and an excited molecule in the singlet state [19]. TTA thus generates one excited singlet S_1, which yields a ground state singlet S_0 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 excitation can result from the annihilation of two triplets [19]. In systems with a high density of chromophores, triplet motion is possible not only by molecular displacement (molecular diffusion) but also by triplet–triplet energy hopping [15, 19], $T_1 + S_0 \longrightarrow S_0 + T_1$. Like TTA, this process of energy transfer is short-range and takes place only between nearest neighbors.

The aim of this work is the study of the kinetics of TTA and of the associated delayed fluorescence in nanosystems (linear chains and particles) with efficient triplet–triplet energy migration, with special attention paid to the size dependence. In the previous paper [20], two formalisms for the description of TTA were presented in some detail: the standard [7, 16, 17, 19] and statistical [21] (see also [7, 11]) approaches. In the standard approach, the TTA kinetics is based on the bimolecular rate equation, in which it is assumed that the effective annihilation rate is proportional to the density of triplet excitations. This rate equation can be written as [7, 16, 17, 19]

$$\frac{dN}{dt} = -kN - \gamma_0 N^2, \qquad (1)$$

where *N* represents the average triplet excitation density, understood here as the number of excitations per closed domain (linear polymer chain, micelle, nanoparticle, etc.); *k* is the relaxation constant of triplet excitation ($1/k$ being thus the intrinsic lifetime of the triplet state); and γ_0 is the so-called annihilation constant, having the dimension of 1/time. The solution of Eq. (1) is well known, and the phosphorescence intensity, nor-

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[1] The text was submitted by the authors in English.

malized to unity at $t = 0$, $I_P(t) = N(t)/N_0$, can be written as a series:

$$I_P(t) = \frac{1}{1+\gamma_0 N_0/k}e^{-kt} + \frac{\gamma_0 N_0/k}{(1+\gamma_0 N_0/k)^2}e^{-2kt} + \frac{(\gamma_0 N_0/k)^2}{(1+\gamma_0 N_0/k)^3}e^{-3kt} + \dots \quad (2)$$

A more general approach to the description of TTA is the so-called statistical approach, used by Paillotin et al. [21] (see also [7, 11]). In this approach, ensembles of closed domains (e.g., noninteracting polymer chains, micelles, or nanoparticles) are considered. After pulse excitation and singlet–triplet conversion, each domain contains, on the average, N_0 triplet excitations. The distribution of excitations over domains is given by the Poisson distribution. There are two bimolecular excitation annihilation constants, $\gamma^{(1)}$ and $\gamma^{(2)}$, corresponding to the disappearance of one or two triplets in the annihilation event. It is assumed that excitations in different domains cannot interact with each other. The overall annihilation constant is $\gamma = \gamma^{(1)} + \gamma^{(2)}$. After introducing the parameters $r = 2k/\gamma$ and $Z = N_0(1 + \gamma^{(2)}/\gamma)$, the phosphorescence intensity $I_P(t)$ is given by [21]

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

where

$$b_{p+1} = \sum_{m=0}^{\infty} \frac{(-1)^m (p+m)! Z^{p+m}(r+1+2p)}{p!m!(r+p+1)(r+p+2)\dots(r+p+1+p+m)}. \quad (4)$$

Note that parameters b_p are always positive.

Both Eqs. (2) and (3) are sums of exponentials in time; however, the arguments of the exponentials in Eq. (2) do not depend on the TTA constant γ, while the arguments of the exponentials in Eq. (3) are also functions of the TTA constant.

The dependence of coefficients b_p on r (a measure of the average number of triplet excitations per domain) was investigated in [20]. It was shown that the first two or three terms in Eq. (3) suffice to describe the experimental decay of phosphorescence. In general the series in Eq. (3) is rapidly convergent.

It was shown previously [21] that Eq. (3) is reduced to Eq. (2) in the limit $r \longrightarrow \infty$ (i.e., $2k/\gamma \longrightarrow \infty$) by putting $Z = N_0$ and $\gamma = 2\gamma_0$. This means that Eq. (1) is valid when the rate of bimolecular annihilation is much smaller than the unimolecular decay rate.

In comparison with the standard approach, the statistical approach is valid even for domains with small dimensions and large annihilation constants, which explains the dependence on γ of the decay constants in Eq. (3).

It was shown in the previous paper [20] that the form of the phosphorescence decay given by Eq. (3) has a simple interpretation. The first term corresponds to domains containing initially only one triplet, which therefore decay exponentially with the rate constant k. The second term reflects the disappearance of domains containing exactly two excitations. Each excitation decays individually with the rate constant k and they decay together with the rate constant γ. The third term is the decay of domains containing exactly three excitations. Each excitation decays individually with the rate constant k and they decay together with the rate constant 3γ. The numerical coefficient 3 before γ is the number of ways (in two- or three-dimensional cases) by which three excitations can meet in pair collisions. This number is equal to the number of pairs that can be formed from three elements (the binomial coefficient), C_3^2. The nth term in the series in Eq. (3) is the decay of domains containing exactly n excitations. Each excitation decays individually with the rate constant k and they decay together with the rate constant $C_n^2\gamma$, where $C_n^2 = n(n-1)/2$ is equal to the number of pairs that can be formed from n elements.

Like the standard approach, the statistical approach does not give any information on how the annihilation constant in a domain (polymer chain, nanoparticle, etc.) depends on the rate of excitation diffusion (i.e., the frequency of hops between nearest neighbor chromophores in the domain W), on the rate of nearest neighbor annihilation V, and on the size (for example, the number of segments M in a polymer chain) and dimension of the domain. To our knowledge, the first and only attempt to answer some of these questions was made in [22], for the case of a one-dimensional lattice and $V = \infty$. In the previous paper [20], the survival probability for an annihilating pair of triplets $\rho_M^{(2)}(t)$ was introduced and a simple equation for its time dependence in 1D systems was derived. Based on the interpretation of the series in Eq. (3) and comparing the long time asymptote of $\rho_M^{(2)}(t)$ with the second term of the series in Eq. (3), the dependence of the annihilation rate constant γ on the unit time probability of a jump between nearest neighbor sites W and on the size of a one-dimensional lattice (a chain) M was obtained,

$$\gamma = \pi^2 W/M^2. \quad (5)$$

In this paper, Monte Carlo calculations of the survival probability for an annihilating pair of triplets are carried out in 1D, 2D, and 3D cases (in Section 2). For the 1D case, the survival probability for an annihilating trio of triplets is also obtained. In Section 3, TTA delayed fluorescence kinetics are discussed. Finally, the main results are summarized in Section 4.

2. MONTE CARLO SIMULATIONS

A Linear Chain: Survival Probability for an Annihilating Pair of Triplets

To confirm the obtained dependences, we carried out Monte Carlo (MC) simulations of the survival probability for an annihilating pair of excitations in the case of polymer chains of small sizes: $M = 25$, 50, and 100. Following the simulation procedure of Pearlstein [23], it was assumed that an excitation jumps between neighboring lattice sites with a rate W and that neighboring excitations annihilate with a rate V. The initial distribution of excitations in the chain was supposed to be homogeneous. The obtained kinetics is the result of averaging over 50000 trajectories of excitation motion in the one-dimensional lattice.

There are initial configurations for which the two excitations exist initially at nearest neighbor sites. Their relative number is $(M-1)/C_M^2 = 2/M$. If $V = \infty$, these configurations decay instantaneously, so the overall decay begins not at unity but at $1 - 2/M$.

From the MC simulations (Fig. 1a), it was obtained that, for sufficiently long times ($\rho_M^{(2)}(t)\exp(2kt) < 0.4$) and in the case of an infinite rate of annihilation $V = \infty$, the function $\rho_M^{(2)}(t)$ ($M = 25$, 50, 100) is exponential and is approximately equal to the long time asymptote

$$\rho_M^{(2)}(t)\exp(2kt) = \frac{2^6}{\pi^4}\exp\left[-\pi^2\frac{Wt}{M^2}\right], \quad \text{if} \quad \frac{Wt}{M^2} \gg 1, \quad (6)$$

obtained in [22]. The agreement between asymptote (6) and the MC simulations improves with increasing number of sites M.

MC simulations were also carried out for situations with $V/W < \infty$. It was found that, if $V/W > 0.5$, the decay function $\rho_M^{(2)}(t)$ is approximately equal to that for $V = \infty$ (Fig. 1b). Therefore, Eq. (5) is generally valid if $V/W \geq 0.5$.

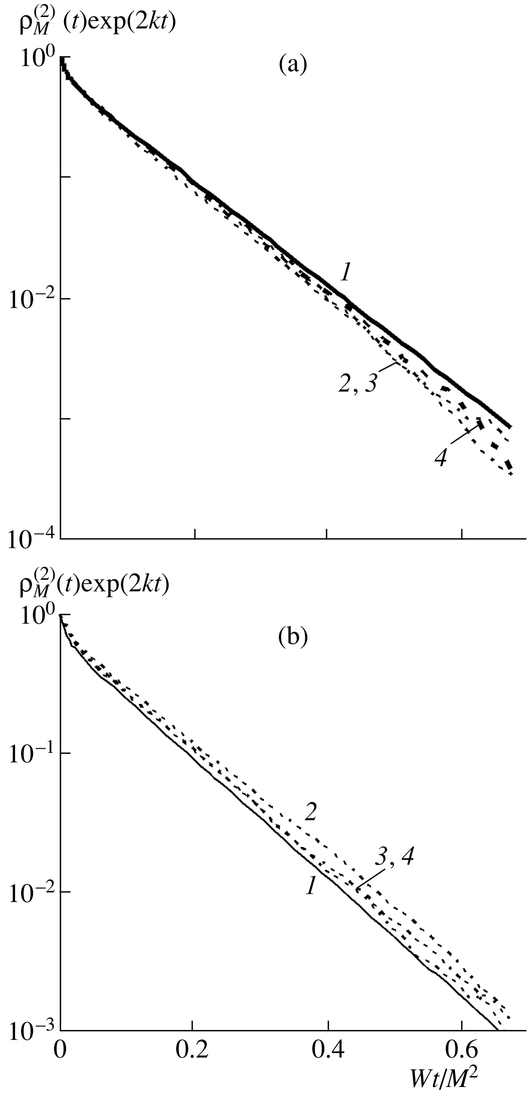

Fig. 1. Survival probability for an annihilating pair of excitations in a linear lattice $\rho_M^{(2)}(t)$ for $V/W = \infty$ (a) and 0.5 (b). Exact solution [20, 22] (*1*) and Monte Carlo simulations: (*2–4*) $N = 25$, 50, and 100, respectively. Curves *2*, *3* in (a) and *3*, *4* in (b) practically coincide.

A Linear Chain: Survival Probability for an Annihilating Trio of Triplets

To obtain the correct time dependence of the third term in Eq. (3), the survival probability for an annihilating triplet of excitations $\rho_M^{(3)}(t)$ was numerically obtained by MC simulation.

There are initial configurations for which two or even three excitations exist initially at nearest neighbor sites. Their relative number is $(M-1)(M-2)/C_M^2 = 6/M$. If $V = \infty$, these configurations decay instantaneously, so the overall decay begins not at unity but at $1 - 6/M$.

Using MC simulations, it was obtained that, at long times (when $\rho_M^{(3)}(t)\exp(3kt) < 0.4$) and in the cases where $V/W = \infty$ and 1, the function $\rho_M^{(3)}(t)$ ($M = 25$, 50, 100) is exponential and is approximately equal to the asymptote (Fig. 2)

$$\rho_M^{(3)}(t)\exp(3kt) \approx 0.5\exp\left(-52\frac{Wt}{M^2}\right). \quad (7)$$

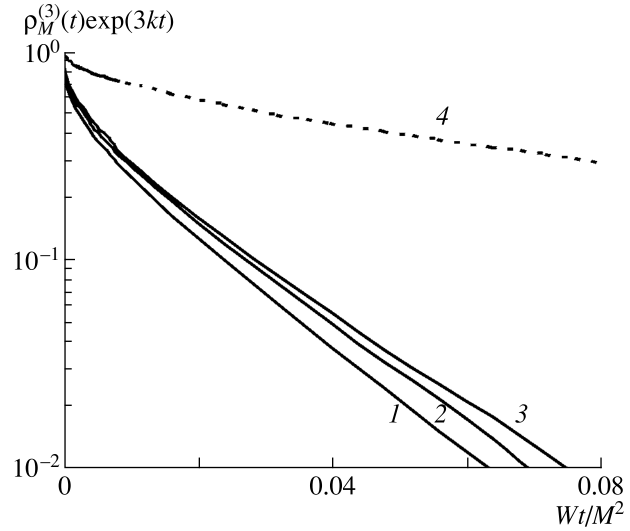

Fig. 2. Survival probability for an annihilating triplet of excitations on a linear lattice $\rho_M^{(3)}(t)$ for $V/W = \infty$ and 1. (*1*–*3*) $\rho_M^{(3)}(t)$ with $V/W = \infty$ and $N = 25$, 50, and 100, respectively. For $V/W = 1$ and $N = 25$, 50, and 100, the corresponding curves practically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

In comparison with Eq. (6), the numerical coefficient near Wt/M^2 has increased by more than five times (from π^2 to 52). This is understandable as, on the average, each of the three excitations can freely move along a section of the chain of size $M/3$. After collision, one or two excitations disappear and therefore, to a first approximation, the motion of every excitation is equivalent to motion along a chain of smaller length, $M/3$. Two such chains contain a quencher at one end and the third chain contains quenchers at both ends. Since trio decay function (7) decreases very rapidly with time, only the two first terms of the series in Eq. (3) are needed for fitting TTA observables in linear polymer chains.

A Square Lattice: Survival Probability for an Annihilating Pair of Triplets

The TTA rate constant should also be influenced by the dimensionality of the domain. Let the domain be a square lattice (e.g., a polymer monolayer) having L sites ($L = M \times M$). It is assumed that (i) excitation motion occurs by jumps between neighboring lattice sites with a unit time probability W, (ii) when two excitations are at neighboring sites they annihilate with a unit time probability V, and (iii) the initial distribution of excitations in the lattice is homogeneous.

There are initial configurations for which two excitations exist initially at nearest neighbor sites. Their relative number is $2M(M-1)/C_{M^2}^2 = 4/[M(M-1)]$. If $V = \infty$, these configurations decay instantaneously, so the overall decay begins not at unity but at $1 - 4/[M(M-1)]$.

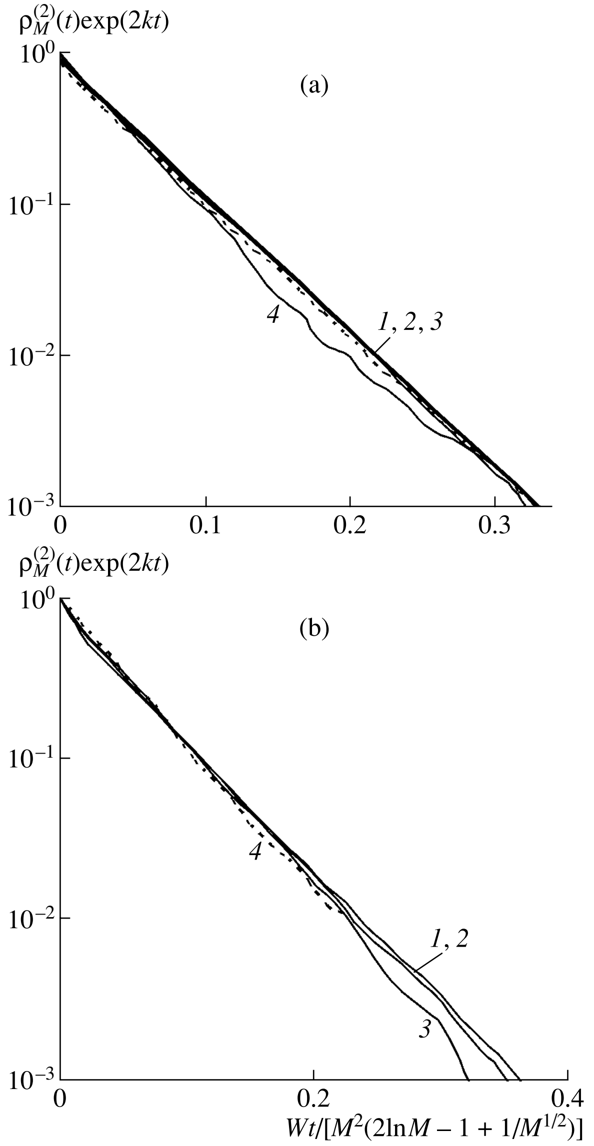

Fig. 3. Survival probability for an annihilating pair of excitations in a square lattice $\rho_M^{(2)}(t)$ for $V/W = \infty$ (a) and 10 (b). Monte Carlo simulations: (*1*–*4*) $N = 5$, 10, 20, and 40, respectively. Curves *1*, *2*, *3* (a) and *1*, *2* (b) practically coincide.

The kinetics obtained by MC simulation (for $M = 5$, 10, 20, and 40) are a result of averaging over 50000 trajectories of excitation motion over the lattice sites. Simulations show (Fig. 3) that the survival probability for an annihilating pair of excitations on a square lattice $\rho_M^2(t)$ is exponential and can be written as

$$\rho_M^{(2)}(t)\exp(2kt) = A_{\mathrm{sq}}\exp\left[-B_{\mathrm{sq}}\frac{Wt}{M^2(2\ln M - 1 + 1/\sqrt{M})}\right] \tag{8}$$

for $10 < V/W < \infty$. The parameter A_{sq} is

$$A_{\mathrm{sq}} = 0.86 \pm 0.01. \qquad (9)$$

The dependence of the parameter B_{sq} on V/W is shown in Fig. 4 and can be approximated by

$$B_{\mathrm{sq}} = \frac{20.7(V/W)^{1.5}}{2.65 + (V/W)^{1.5}} \pm 0.2. \qquad (10)$$

The dependence of the pair survival probability $\rho_M^{(2)}(t)$ on W and M is confirmed by simple analytical considerations. For this purpose, let us replace the square lattice by a continuous two-dimensional circle with radius $R \approx Ma$, where a is the distance between nearest neighbor sites in the lattice. Excitations move diffusively over this medium with a diffusion constant $D \approx Wa^2$. Let the first excitation be immobile and located at the center of the circle. The evolution of the second excitation obeys the diffusion equation

$$\frac{\partial}{\partial t}\rho(r, t) = D\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\rho(r, t) \qquad (11)$$

with initial and boundary conditions $\rho(r, t) = 1/S$ (S being the area of the circle), $\rho(a, t) = 0$ ($V = \infty$), and $\partial\rho/\partial r|_{r = R} = 0$. Let us look for a solution of Eq. (11) in the form $\rho(r, t) = \exp(-C_{\mathrm{sq}}t)\rho_{\mathrm{st}}(r)$, where C_{sq} is a constant. This function gives an exponential decay $\rho_M^{(2)}(t)$, $\rho_M^{(2)}(t) = 2\pi\int_S \rho(r, t)rdr \propto \exp(-C_{\mathrm{sq}}t)$, and describes the survival probability at long times. After introducing the function $\rho(r, t)$ into Eq. (19), we get

$$-C_{\mathrm{sq}}\rho_{\mathrm{st}}(r) = D\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\rho_{\mathrm{st}}(r). \qquad (12)$$

The integration of the left- and right-hand sides of this equation over r gives

$$C_{\mathrm{sq}} = \frac{2\pi aD\frac{\partial}{\partial r}\rho_{\mathrm{st}}(r)|_{r = a}}{2\pi\int\limits_a^R \rho_{\mathrm{st}}(r)rdr}. \qquad (13)$$

One can check that the solution of Eq. (12) for small r (near a) is $\rho_{\mathrm{st}}(r) \propto \ln(r/a)$. To a first approximation, this solution can be used for all possible values of r ($a < r < R$). Inserting this solution into Eq. (13), we get

$$C_{\mathrm{sq}} = \frac{4D}{a^2 - R^2 + 2R^2\ln(R/a)}. \qquad (14)$$

Taking into account that $a \ll R$ and $R \approx Ma$, $D \approx Wa^2$, we obtain

$$C_{\mathrm{sq}} \approx \frac{4W}{M^2(2\ln M - 1)}. \qquad (15)$$

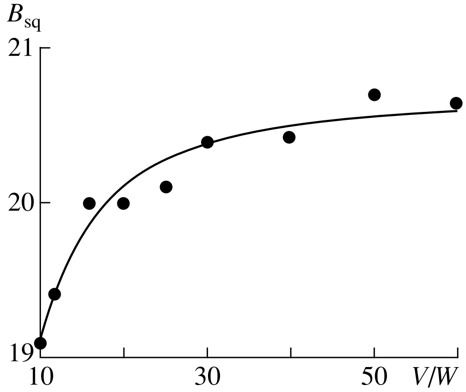

Fig. 4. Survival probability for an annihilating pair of excitations in a square lattice. Dependence of the parameter B_{sq} on V/W. Circles correspond to Monte Carlo simulations, and the solid line is the approximation given by Eq. (10).

Comparison of Eqs. (8) and (15) shows an almost identical dependence on M. The last term in the denominator of Eq. (8) was added for better precision.

Thus, in a two-dimensional lattice, the dependence of the pair TTA constant γ_{sq} on M, W, and V ($10 < V/W < \infty$) is, according to Eqs. (8) and (10),

$$\gamma_{\mathrm{sq}} = \frac{20.7(V/W)^{1.5}}{2.65 + (V/W)^{1.5}}\frac{W}{M^2(2\ln M - 1 + 1/\sqrt{M})}. \qquad (16)$$

A Cubic Lattice: Survival Probability for an Annihilating Pair of Triplets

Consider now TTA in three-dimensional domains. Let the domain be a cubic lattice having L sites ($L = M \times M \times M$). As before, it is assumed that (i) excitation motion occurs by jumps between neighboring lattice sites with a unit time probability W, (ii) when two excitations are at neighboring sites they annihilate with a unit time probability F, and (iii) the initial distribution of excitations in the lattice is homogeneous.

MC simulations averaged over 20000 trajectories for $M = 5$, 10, and 15 and carried out for different values of V show (Fig. 5) that the survival probability for an annihilating pair of triplets in a cubic lattice $\rho_M^2(t)$ is exponential and can be written as

$$\rho_M^{(2)}(t)\exp(2kt) = A_{\mathrm{cub}}\exp\left[-B_{\mathrm{cub}}\frac{Wt}{M^3}\right] \qquad (17)$$

for $1 < V/W < \infty$. The parameter A_{cub} is almost constant for the values of the parameter V tried and is

$$A_{\mathrm{cub}} = 0.96 \pm 0.02. \qquad (18)$$

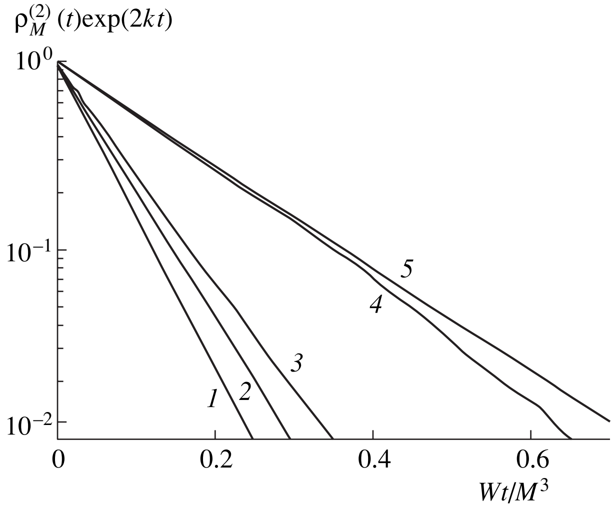

Fig. 5. Survival probability for an annihilating pair of excitations in a cubic lattice $\rho_M^{(2)}(t)$: (a) $V/W = \infty$, $M = 5$ (*1*), 10 (*2*), and 15 (*3*); (b) $V/W = \infty$ (*1*), 10 (*2*), 5 (*3*), and 1 (*4*, *5*) (curve *4*, $M = 10$ and 15; curve *5*, $M = 5$).

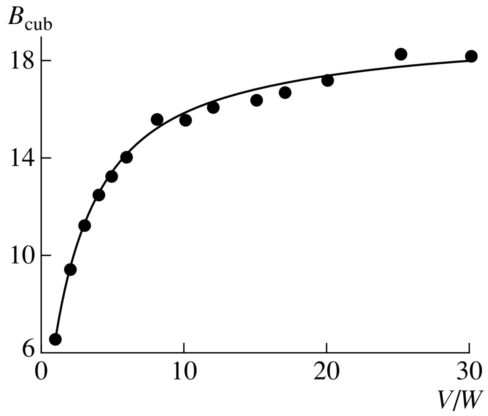

Fig. 6. Survival probability for an annihilating pair of triplet excitations on a cubic lattice. Dependence of the parameter B_{cub} on V/W. Circles correspond to Monte Carlo simulations and the solid line is the approximation given by Eq. (19).

The dependence of the parameter B_{cub} on the rate of TTA is shown in Fig. 6. Its values can be approximated by the equation

$$B_{\text{cub}} = \frac{19.5(V/W)^{0.93}}{2 + (V/W)^{0.93}} \pm 0.5. \tag{19}$$

The dependence of the survival probability $\rho_M^{(2)}(t)$ on W and M is confirmed by simple analytical considerations. For this purpose, let us replace the square lattice by a continuous three-dimensional sphere with a radius $R \approx (La^3)^{1/3} = Ma$, where a is the distance between nearest neighbor sites in the lattice. Excitations are allowed to diffuse over this medium with a diffusion constant $D \approx Wa^2$. Let the first excitation be immobile and located at the center of the sphere. The evolution of the second excitation obeys the diffusion equation

$$\frac{\partial}{\partial t}\rho(r, t) = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\rho(r, t), \tag{20}$$

with initial and boundary conditions $\rho(r, t) = 1/V_0$ (V_0 being the volume of the sphere), $\rho(a, t) = 0$ ($V = \infty$), and $d\rho/dr|_{r=R} = 0$.

Let us look for a solution of Eq. (20) in the form $\rho(r, t) = \exp(-C_{\text{cub}}t)\rho_{\text{st}}(r)$, where C_{cub} is a constant. This function gives an exponential decay of $\rho_M^2(t)$, $\rho_M^2(t) = 4\pi\int\rho(r, t)r^2dr \propto \exp(-C_{\text{cub}}t)$, and describes the asymptote of the survival probability at long times. After introducing the function $\rho(r, t)$ into Eq. (20), we get

$$-C_{\text{cub}}\rho_{\text{st}}(r) = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\rho_{\text{st}}(r). \tag{21}$$

The integration of the left- and right-hand sides of this equation over distances gives

$$C_{\text{cub}} = \frac{4\pi a^2 D\frac{\partial}{\partial r}\rho_{\text{st}}(r)|_{r=a}}{4\pi\int_a^R \rho_{\text{st}}(r)r^2dr}. \tag{22}$$

One can check that the solution of Eq. (21) for small r (near a) is $\rho_{\text{st}}(r) \propto F(1 - a/r)$, where F is a constant. To a first approximation, this solution can be used for all values of r ($a < r < R$). Inserting this solution into Eq. (22), we get

$$C_{\text{cub}} \approx \frac{3Da}{R^3}, \tag{23}$$

where we took into account that $a \ll R$. In this way, as $R \approx Ma$, $D \approx Wa^2$, we obtain

$$C_{\text{cub}} \approx \frac{3W}{M^3}. \tag{24}$$

Comparison of Eqs. (17) and (24) shows an identical dependence on M and W.

Thus, in a three-dimensional lattice, the dependence of the TTA constant γ_{cub} on N, W, and V ($1 < V/W < \infty$) is given by the equation

$$\gamma_{\text{cub}} = \frac{19.5(V/W)^{0.93}}{2 + (V/W)^{0.93}}\frac{W}{M^3}. \tag{25}$$

3. DELAYED FLUORESCENCE

Only domains containing two or more excitations contribute to the kinetics of delayed fluorescence. As the kinetics of disappearance of domains with three or more excitations is very fast and the singlet lifetime is much shorter than the triplet lifetime, the kinetics of delayed fluorescence is well described by the survival probability of an annihilating pair of excitations, especially in the case of relatively low excitation. Thus, for long times, the normalized decay of delayed fluorescence $I_{DF}(t)$ is

$$I_{DF}(t) \approx \exp(-2kt - \gamma t), \qquad (26)$$

where the annihilation constant γ is given by Eqs. (5), (16), or (25) according to the dimensionality of the domains under consideration.

4. CONCLUSIONS

In this paper, we studied triplet–triplet annihilation in one-, two-, and three-dimensional lattices, which can be considered simple models of nanosystems. In particular, the dependences on size M, on the rate of excitation migration W, and on the rate of excitation annihilation V were studied.

We showed that the usual TTA observables (delayed fluorescence, phosphorescence, and triplet–triplet absorption) are well described by a single exponential decay (delayed fluorescence) or by a sum of two exponentials (phosphorescence and triplet–triplet absorption). In the latter 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 omitted (especially in the case of relatively low-intensity excitation).

In this paper, 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 annihilation-controlled limit, $W \gg V$), the diffusion rate is large compared to the rate of nearest neighbor annihilation and the distribution of excitations over the domains is homogeneous (the diffusion displacement of triplet excitation during the lifetime $\sqrt{D/k}$ is large compared to the size of the domains Ma; i.e., $\sqrt{W/k} > M$). The statistical approach is in such a case valid; $\gamma = V$ and Eq. (3) applies.

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