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Photochemical reactions on the surface of a circular disk: a theoretical approach to kinetics in restricted two-dimensional space

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Abstract

Kinetics of decay of excited donor molecules B* by static and diffusion-induced electron and energy transfer to acceptors (A) in restricted two-dimensional space, as described by the surface of a circular disk (circle), have been examined. In the first instance, an analytical solution is given to outline the decay of B* by a static distance-dependent electron and energy transfer process to some random acceptors. Results show that luminescence decay of B* on a restricted two-dimensional surface is slower than a similar decay on an infinite surface, with the difference between the kinetics in restricted space and infinite space increasing with increasing observation time. The decay of B* molecules on diffusion approach of reagents along the two-dimensional disk surface is exponential at sufficiently long times, a kinetic behavior that contrasts with the long-time behavior of diffusion-limited decay processes taking place on an infinite surface where the rate constant does not achieve an asymptotic value even for long times. Decay processes of excited triplet molecules of B* by triplet–triplet (T–T) annihilation on the restricted circle were also examined. These differ principally from those of luminescence quenching by the fact that the concentrations of surface-reacting species are equal. An approximate solution to T–T annihilation by static interactions is described on the basis of the average reagent concentration approximation and with the assumption that, in the course of the annihilation process, the triplet molecules are always randomly distributed at the prevalent mean surface concentration. The decay kinetics described by the analytical expressions derived agree fairly well with the results from Monte Carlo simulations. Kinetic expressions for diffusion-induced annihilation on the two-dimensional restricted surface are also described using an infinite space approximation for the rate constant; Monte Carlo simulations indicate that the resulting kinetic solution is useful to analyse the decay process on the circular disk provided that the effective radius of the annihilation event does not exceed one tenth the disk radius.

Keywords: Electron transfer; Energy transfer; Restricted geometry; Triplet–triplet annihilation; Monte Carlo method; Diffusion

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1. Introduction

The kinetics of chemical reactions in restricted spaces have been the subject of several investigations in the last few years [1–12]. Various experimental situations exist in which a chemical reaction occurs when the reaction volume is too small to allow usage of theories of kinetics that apply to processes in infinite space. These types of system are known as restricted geometries. They are systems that are not spatially infinite and do no involve an infinite number of reacting molecules. Amongst these systems, micellar and vesicular systems, membranes, polymer solutions and porous systems have been examined [3,7,11–15]. The kinetic behavior of chemical reactions in such systems differs from that in infinite space. The partition of reacting species over the small volumes and the small number of species present in each volume preclude application of classical chemical kinetics to describe the temporal course of reactions in such restricted systems. A study of the kinetic peculiarities of chemical processes in restricted systems provides important information on their structures and dynamics.

The mathematical description of chemical reactions in restricted geometries is based on the use of the stochastic approach that provides a well-defined method for the analysis of statistical fluctuations in the number of reacting species. The principal basis of the stochastic approach is to treat the concentration as a time-varying discrete random variable being influenced at different times by probability effects. The problem is to determine the probability that the system is at the specified state (concentration) at time *t*. The stochastic approach is applicable to all types of reaction system. In many cases, however, the resulting differential equation that defines

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the stochastic model cannot be solved exactly. Alternatively, an explicit analytical solution of the problem can be found only under some special simplified assumptions about the system. Monte Carlo simulation methods can validate simplified analytical equations for the analysis of chemical reactions in real and more complicated restricted systems.

Quantized semiconductor colloidal particles, whose dimensions range from nanometers to several tens of nanometers, represent a new class of systems with restricted geometry. These particular systems show some unusual photophysical and photochemical properties: (i) non-linear optical response, (ii) blue shifts in the optical spectra, (iii) increase in the redox power with a decrease of the quantized particle dimensions and (iv) unusual catalytic properties, among others [16–19]. Efforts to use quantized particles in waste-water detoxification systems [20] and in the sensitization of large-band-gap semiconductors for solar energy conversion systems are relevant [21,22]. Surface reactions play a decisive role in the properties of quantized materials in such systems.

The kinetics of triplet–triplet (T–T) annihilation and luminescence quenching of excited donor molecules by acceptors on the surface of quantized layered MoS_2 particle were recently examined experimentally [6]. Quantized particles of metal dichalcogenide layered semiconductors possess excellent characteristics for studying surface processes. They are characterized by weak van der Waals interactions between the layers, while strong chemical forces hold molecules together inside the layers. This makes it possible to form highly ordered interfaces, avoiding problems of surface structure heterogeneity and adsorbed molecules mismatch that are characteristic of three-dimensional materials [20]. Moreover, the shape of quantized particles of metal dichalcogenide layered semiconductors can be approximated to a circular disk [23,24]; this facilitates modeling chemical reaction kinetics on its surface.

In this study, we describe the kinetics of electron and energy transfer processes on the surface of a restricted two-dimensional circular disk whose dimension is so small that only a small number of reagent molecules can be adsorbed on it. Three cases are considered: (1) electron transfer quenching of an excited donor molecule B* by an acceptor(s) A when both are adsorbed on the surface of the disk (henceforth also referred to as circle); (2) quenching of B* by energy transfer to acceptors via an exchange mechanism; (3) T–T annihilation of adsorbed excited B* molecules. All these processes are characterized by the exponential dependence of the rate constant on the distance r between the reagents. The principal goals of this paper are then twofold: (i) to describe kinetic equations for luminescence quenching and for T–T annihilation on a flat two-dimensional restricted surface and (ii) to compare the results from the consequent analytical expressions with those from Monte Carlo calculations if only approximate equations can be derived. Utilization of the binary approximation avoided complications of multiparticle correlations and permitted conventional methods for treating the reaction kinetics [25–28]. Comparison of results from the approximate analytical equations with results from Monte Carlo calculations yielded estimates of their limits of validity. In addition, we evaluated the influence of surface dimension restriction on the decay kinetics of excited molecules.

2. Kinetics of luminescence quenching in restricted two-dimensional space (circular disk)

Relaxation kinetics of excited donor molecules in infinite space by distant interactions with acceptors are a well-known problem [25,29–34]. When more than two molecules are present in the reaction volume, the problem reduces to the summation of the excited donor molecule decay rates over all the acceptor molecules. The necessity to account for multiparticle correlations make this a difficult problem to analyse quantitatively. A two-particle approximation is commonly used to avoid complications of multiparticle corrections. Therefore the decay of an excited donor molecule by electron or energy transfer to an acceptor molecule is assumed to be unaffected by the presence of another acceptor molecule. The assumption of a low concentration of acceptors allows us to replace the summation of the decay rates over all acceptor sites by an integration over all space. Under this assumption, a number of approximate analytical expressions for the decay of an excited donor have been derived using a variety of different procedures [27–36].

After pulse excitation, the decay kinetics of excited donor molecules that follow the reactions

$$\left.\begin{array}{l} B^* + A \longrightarrow B^+ + A^- \\ B^* + A \longrightarrow B + A \end{array}\right\} \quad \text{with rate constant } w(r) \qquad \begin{array}{r} (1a) \\ (1b) \end{array}$$

$$B^* \longrightarrow h\nu \qquad \text{with rate constant } \frac{1}{\tau} \qquad (2)$$

obey the differential equation of the non-Markovian encounter theory [25,33,37]:

$$\frac{\mathrm{d}N(t)}{\mathrm{d}t} = -k(t)cN(t) - \frac{1}{\tau}N(t) \qquad (3)$$

where $N(t)$ is the density of excited donors, c is the concentration of the acceptor species and $k(t)$ is the time-dependent rate constant for the quenching of the excited donor by an acceptor in binary approximation and is given by

$$k(t) = \int w(r)p(r,t)\,\mathrm{d}r \qquad (4)$$

The term $w(r)$ is a distance-dependent rate constant that depends on the electronic coupling between donor and acceptor which in turn depends exponentially on the intermolecular distance r, both for luminescence quenching via electron transfer from B* to A and for emission quenching of B* by energy transfer via an exchange mechanism (see for example [31,34]); it is given by

$$w(r) = \nu \exp\left(-2\frac{r-d}{a}\right) \tag{5}$$

where r is the distance between centers of the reagent molecules, d is the sum of radii of the molecules, ν is the frequency factor, a is a factor that takes into account the decrease in $w(r)$ with increasing distance, and $p(r, t)$ is the distribution function for the pair (B^*...A) at time t in which the donor and acceptor are separated by the distance r. Integration of Eq. (4) is carried out over all space, and $p(r, t)$ satisfies the kinetic equation [25,32]

$$\frac{\partial p(r,t)}{\partial t} = D\nabla^2 p(r,t) - w(r)p(r,t) - \frac{1}{\tau}p(r,t) \tag{6a}$$

and the initial conditions defined by

$$p(r, 0) = 1 \tag{6b}$$

where D is the sum of the diffusion coefficients of donor and acceptor species.

Eqs. (3)–(6) have been used in several studies to formulate the kinetics of energy and electron transfer reactions in infinite spaces. An analogous procedure for the decay of an excited donor molecule can be used in the analyses of processes in restricted spaces [28]. We now examine the decay kinetics of excited molecules on the surface of a circular disk (circle) using, where possible, appropriate results obtained previously for related objects.

We consider first the concentration and the time dependences of the direct electron or energy transfer from a single excited donor to acceptors randomly distributed on the surface of the circle. In accordance with a typical condition that is valid in luminescence quenching experiments in restricted systems, we assume that only one donor is present on the two-dimensional surface. This assumption avoids donor–donor interactions and possible saturation of acceptors by electron or energy transfer from other excited donors. We also neglect any possibility of back electron transfer or back energy transfer. Only two-body interactions between the donor and each acceptor are taken into account; also any interaction between acceptors is excluded. The transfer of excited donor or acceptor molecules from one circle to another and any interaction between species from different circles in solution are also excluded.

2.1. Static quenching: approximate analytical solution

We examine here the deactivation of an excited state molecule B^* by electron and energy transfer to some random acceptors A that are restricted on the surface of a circle, in competition with the B^* spontaneous transition to the ground state.

We first consider the round flat restricted surface of radius R with an immobile excited donor B^* and acceptor A molecules randomly distributed on the circle, so that the center of each molecule is placed on the surface (Fig. 1). The sum of radii of B^* and A is denoted d. The space restriction will necessarily result in a different initial distribution function of (B^*...A) pairs with different positions of B^* on the disk surface. Accordingly, the time-dependent rate constant $k(t)$ in Eq. (3) will differ for different excited donor molecules. For this reason, averaging over different positions of the excited donor is necessary in the calculations of the decay law.

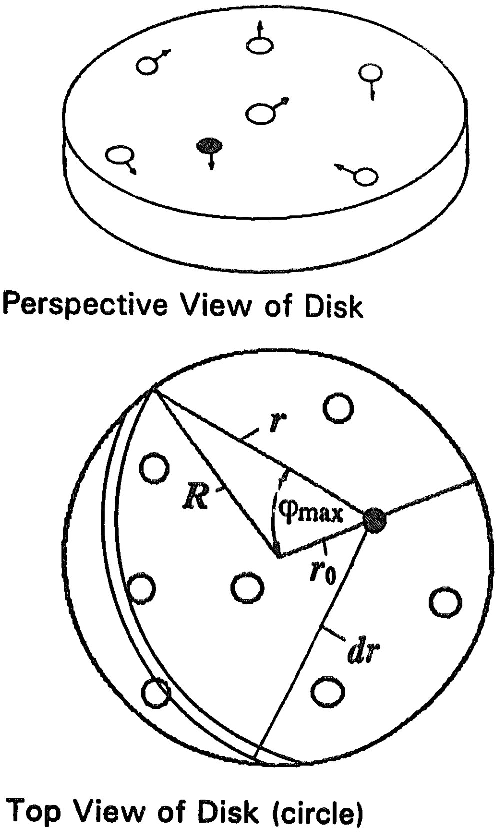

Fig. 1. Schematic picture of the spatial confinements of the donor (●) and of the acceptors (○) on the surface of the circle.

Consider next the excited donor molecule B^* positioned at a distance r_0 from the center of the circle. The concentration $N(t, r_0)$ of excited donor molecules is given by

$$\frac{dN(t,r_0)}{dt} = -k(t,r_0)cN(t,r_0) - \frac{1}{\tau}N(t,r_0) \tag{7}$$

Note the similarity between Eq. (7) and Eq. (3); however, the rate of quenching of excited donor B^* by acceptor A now depends on the position of the donor:

$$k(t, r_0) = \int w(r)g_0(r)p(r,t)\,dr \tag{8}$$

where $g_0(r)$ is a site-density function [1,4], and the index zero is a reminder that the integral is evaluated for the donor located at r_0. Integration of Eq. (8) is taken over the surface of the disk.

Integration of Eq. (7) with $k(t, r_0)$ as defined by Eq. (8) results in

$$\frac{N(t,r_0)}{N(0,r_0)}=\exp\left(-\frac{t}{\tau}-c\int\int_0^t w(r)g_0(r)p(r,t')\,\mathrm{d}r\,\mathrm{d}t'\right) \tag{9}$$

The distribution function $p(r,t')$ is given by Eq. (6a). Subsequent integration of Eq. (6a) in the absence of diffusion of reagent, $D=0$, and with the initial condition given by Eq. (6b) yields

$$p(r,t)=\exp\left[-\left(w(r)+\frac{1}{\tau}\right)t\right] \tag{10}$$

Integration of Eq. (9) over time t' with $p(r,t)$ from Eq. (10) gives

$$\frac{N(t,r_0)}{N(0,r_0)}=\exp\left(-\frac{t}{\tau}-c\int g_0(r)\,\frac{w(r)}{w(r)+1/\tau}\times\left\{1-\exp\left[-\left(w(r)+\frac{1}{\tau}\right)t\right]\right\}\mathrm{d}r\right) \tag{11}$$

In calculating the integral in Eq. (11) it is necessary to evaluate the normalized area $g_0(r)$ dr of three circles (Fig. 1) on the disk; the first main circle centered at $r_0=0$ with radius R and two others centered at the position of B* (full circle in Fig. 1) with radii r and $r+\mathrm{d}r$. Thus

$$g_0(r)\,\mathrm{d}r=\frac{r\,\mathrm{d}r\,2\varphi_{\max}}{\pi(R^2-d^2)} \tag{12}$$

where

$$\varphi_{\max}=\arccos\left(\frac{R^2-r^2-r_0^2}{2rr_0}\right)\qquad \text{if } r>R-r_0 \tag{13}$$

and

$$\varphi_{\max}=\pi\qquad \text{if } r\leqslant R-r_0 \tag{14}$$

Substituting Eq. (12) into Eq. (11) and averaging $N(t, r_0)$ over the surface of the circle results in

$$\frac{N(t)}{N(0)}=\exp\left(-\frac{t}{\tau}\right)\frac{2}{R^2-d^2}\int_d^R r_0\,\mathrm{d}r_0\times\exp\left(-c\int_d^{R+r_0}\frac{w(r)}{w(r)+1/\tau}\times\left\{1-\exp\left[-\left(w(r)+\frac{1}{\tau}\right)t\right]\right\}2r\varphi_{\max}\,\mathrm{d}r\right) \tag{15}$$

It is readily seen that, at $R\to\infty$, at almost all values of r, $\varphi_{\max}=\pi$. Eq. (15) then reduces to

$$\frac{N(t)}{N(0)}=\exp\left(-\frac{t}{\tau}-c\int_d^{\infty}\frac{w(r)}{w(r)+1/\tau}\times\left\{1-\exp\left[-\left(w(r)+\frac{1}{\tau}\right)t\right]\right\}2\pi r\,\mathrm{d}r\right) \tag{16}$$

Where the lifetime of excited donor molecules is very large, $\tau\to\infty$, and at $\nu t\gg 1$ (note that $w(r)$ is defined by Eq. (5)) we have from Eq. (16) that

$$\frac{N(t)}{N(0)}=\exp\left(-c\,\frac{\pi a^2}{4}\ln^2(\nu t)\right) \tag{16a}$$

which is indeed the equation that describes the kinetics of a static reaction in infinite two-dimensional space [34].

Comparison of Eq. (15) with Eq. (16) shows that geometrical restriction in two-dimensional space leads to a slower decay of the excited donor molecule B* by static distance-dependent electron and energy transfer.

It is instructive to consider now a sample that contains a large number of restricted circles. For this sample, Eq. (15) is valid only if the surface concentrations of acceptor molecules A are the same for all circles. However, fluctuations in the number of reactant species are inherent in the reactions that occur in restricted systems containing a small number of interacting species. Thus one needs to average the decay kinetics (Eq. (16)) over a distribution of the number of acceptor molecules on the disk. The actual form of the decay kinetics will depend on the distribution function chosen; amongst the various reasonable distribution functions, the kinetics will have the simplest form if the Poisson distribution were employed.

The Poisson distribution

$$P(n)=\frac{1}{n!}\bar{n}^n\exp(-\bar{n}) \tag{17}$$

of acceptor molecules on the surface of the disks yields the luminescence decay

$$\frac{N(t)}{N(0)}=\exp\left(-\frac{t}{\tau}\right)\frac{2}{R^2-d^2}\sum_{n=1}^{\infty}\frac{1}{n!}\bar{n}^n\times\exp(-\bar{n})\int_d^R r_0\,\mathrm{d}r_0\exp\left(-\frac{n}{\pi(R^2-d^2)}f(r_0,t)\right) \tag{18}$$

where $\bar{n}$ is the average number of acceptor molecules per disk, and $f(r_0,t)$ is given by

$$f(r_0,t)=\int_d^{R+r_0}\frac{w(r)}{w(r)+1/\tau}\times\left\{1-\exp\left[-\left(w(r)+\frac{1}{\tau}\right)t\right]\right\}2r\varphi_{\max}\,\mathrm{d}r \tag{19}$$

If we interchange the order of summation and integration in Eq. (18) and consider that the surface of the disk is sufficiently large that the maximal possible number of acceptor molecules on this surface is infinite, then summing over all values of n affords

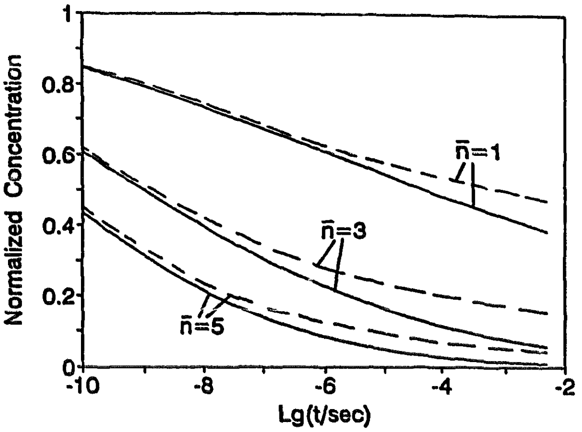

Fig. 2. Decay kinetics of static luminescence quenching on the restricted circle obtained from Eq. (20) (– – –) for the following set of parameters: $R=20$ Å, $d=4$ Å, $\nu=10^{12}$ s^{-1}, $a=1$ Å and $\tau=10^2$ s. The numbers over the curves refer to the average numbers of acceptors per circle. The full curves show the decay kinetics of static emission quenching on the infinite surface calculated with Eq. (16a), for equal values of ν, a and the same average surface concentrations of the acceptor.

$$\frac{N(t)}{N(0)}=\exp\left(-\frac{t}{\tau}\right)\frac{2}{R^2-d^2}\int_d^R r_0\,dr_0 \times\exp\left\{-\bar{n}\left[1-\exp\left(-\frac{1}{\pi(R^2-d^2)}f(r_0,t)\right)\right]\right\} \tag{20}$$

The decay kinetics of excited donor molecules can be obtained by numerical integration of Eq. (20). The same averaging procedure can be performed on another type of distribution function of acceptors over the surface of the disk; however, the final decay equation will take a more complex form than Eq. (20). As an example, Fig. 2 shows the decay kinetics of the static luminescence quenching obtained from Eq. (20) (broken curves) for several surface concentrations of acceptor species and for the following set of parameters: $R=20$ Å, $d=4$ Å, $\nu=10^{12}$ s^{-1} and $a=1$. Å. The emission lifetime was chosen to be 1 s so that almost no intrinsic decay of excited donor molecules occurred during the time of observation ($t\leqslant 10^{-2}$ s). The full curves in Fig. 2 show the decay kinetics of the static emission quenching on an infinite surface calculated with Eq. (16a) for identical values of ν and a, and for the same surface concentrations of acceptor molecules. Note how the geometrical restriction in two-dimensional space slows down the decay of excited donors (broken curve) in comparison with the decay seen on an infinite surface (full curve).

2.2. Non-static quenching: analytical solution

We now examine the case of the diffusion-induced quenching of B* molecules by the acceptor A species by electron and energy transfer processes. However, it is first relevant to consider the kinetics of non-static quenching in infinite space for comparison.

The pair probability function $p(r,t)$ satisfies Eq. (6a) and the initial condition of Eq. (6b) [25,32]. As noted earlier, $p(r,t)$ represents the radial distribution of excited donors around a single acceptor. Electron or energy transfer burns a hole in the center of the distribution, with the hole becoming deeper and wider with time. For diffusion-controlled reactions, the spread of the hole terminates when its radius reaches the maximal value of the effective radius R_{eff} of the reaction circle

$$R_{\mathrm{eff}}=d+\frac{a}{2}\ln(\nu\tau_{\mathrm{d}}) \tag{21}$$

where a and ν are the same parameters as in Eq. (5)and τ_{d} is the average time of diffusion of the reagent molecules.

The decay behavior of B* (Eqs. (1) and (2)) strongly depends on the value of the diffusion coefficient D [33,38]. The limit at very low diffusion ($D\approx 0$) was treated earlier (see above). In the limit of very fast diffusion ($D\to\infty$), $p(r,t)$ is approximately 1 for any value of r and quenching is then kinetically controlled. In the intermediate region of moderate diffusion when the quenching reaction is diffusion controlled, the effective radius R_{eff} exceeds the contact distance d between the donor and acceptor centers. Three stages of the process may be established.

(1) In the first stage at which $t\ll\tau_{\mathrm{d}}$, the process kinetics are described by equations characteristic of static quenching discussed previously.

(2) When $t\approx\tau_{\mathrm{d}}$, the quenching decay kinetics are represented by an infinite series and are characterized by a non-exponential time dependence of the donor concentration. During these two stages, all the donor–acceptor pairs with $r<R_{\mathrm{eff}}$ have already decayed and the remaining donors decay at the moment that the acceptor reaches the perimeter of the reaction circle in the course of the diffusion encounter.

(3) The majority of donors are quenched when $t\gg\tau_{\mathrm{d}}$; under this condition, if the acceptor concentration strongly exceeded that of the excited donor, the quenching kinetics in three dimensional space would then be described by the exponential time-dependent equation

$$\frac{N(t)}{N(0)}=\exp\left(-\frac{t}{\tau}-k_{\mathrm{q}}ct\right) \tag{22}$$

where k_{q} is the time-independent rate constant: $k_{\mathrm{q}}=4\pi R_{\mathrm{eff}}D$.

For diffusion-controlled reactions on the infinite surface, the reaction rate constant does not achieve an asymptotic value even at long times [39–42]. For short times, however, $t<\tau_{\mathrm{d}}$ and k_{q} is defined by

$$k_{\mathrm{q}}=\pi D[1+2R_{\mathrm{eff}}(Dt\pi)^{-1/2}] \tag{23a}$$

For long times, $t>\tau_{\mathrm{d}}$ and k_{q} is then given by

$$k_{\mathrm{q}}=\pi D\frac{4}{\ln(4Dt/R_{\mathrm{eff}}^2)-1.15} \tag{23b}$$

The above notwithstanding, it is common to neglect the time dependence of the rate constant for long times and replace it by a mean value [41].

Equations (22)–(23b) are good approximations of the quenching kinetics for sufficiently large surfaces. For small surfaces, however, the applicability of these equations requires special analysis. We describe below a decay equation for the luminescence quenching of an excited donor B* on the surface of the restricted circle.

The general case of emission quenching on the restricted circle on which both the donor and the acceptor are permitted to diffuse is a difficult task. We assume therefore that the excited donor B* is fixed at the center of the circle whereas the acceptor can diffuse with the diffusion coefficient D. We further assume that all other decay processes are slow relative to the quenching of B* by a quencher A and are therefore neglected on the time scale of observation. We also restrict the present treatment by assuming that, within a circle (radius R_{eff}) around each excited donor molecule, the reaction occurs immediately; outside the reaction (space) circle, one species diffuse freely. A general case can be considered using the Monte Carlo method. In this instance, the distribution function $p(r, t)$ will satisfy the kinetic expression

$$\frac{\partial p(r, t)}{\partial t} = D\nabla^2 p(r, t) \tag{24a}$$

and the initial and boundary conditions [25,33]

$$p(r, 0) = 1 \tag{24b}$$

$$p(R_{\text{eff}}, t) = 0 \tag{24c}$$

$$\left(\frac{\partial p(r, t)}{\partial r}\right)_{r=R} = 0 \tag{24d}$$

Eqs. (3), (4) and (24a), together with the initial and boundary conditions of Eqs. (24b)–(24d), describe the kinetics of emission quenching of excited molecules by acceptors on the surface of the disk. The term on the right-hand side in Eq. (24a) describes the random stochastic motion of the acceptor A with respect to B*. Eq. (24d) takes into account the reflection of the acceptor when it reaches the periphery of the circle.

From the viewpoint of a mathematical decision, the problem of luminescence decay kinetics on the surface of the restricted circle in the above formulation is analogous to the problem of the heat flow in a hollow cylinder at some appropriate initial and boundary conditions. The solution to this problem is well known [43]; we use the results obtained by Carslaw and Jaeger [43] to treat the emission decay kinetics on the surface of the circle. Using the results from the two-dimensional heat flow distribution function, $p(r, t)$ can be calculated from

$$p(r, t) = \frac{\pi^2}{2} \sum_{i=1}^{\infty} \frac{\alpha_i^2 [J_1(R\alpha_i)]^2}{[J_0(R_{\text{eff}}\alpha_i]^2 - [J_1(R\alpha_i)]^2} \times \exp(-\alpha_i^2 Dt) C(r, \alpha_i) \int_{R_{\text{eff}}}^{R} r' C(r', \alpha_i)\, \mathrm{d}r' \tag{25}$$

where α_i are the positive roots of

$$J_0(R_{\text{eff}}\alpha) Y_1(R\alpha) - J_1(R\alpha) Y_0(R_{\text{eff}}\alpha) = 0 \tag{26}$$

J_0 and J_1 are the zero- and first-order Bessel functions, Y_0 and Y_1 are the zero- and first-order Neumann functions, and $C(r, \alpha_i)$ is given by

$$C(r, \alpha_i) = J_0(r\alpha_i) Y_0(R_{\text{eff}}\alpha_i) - Y_0(r\alpha_i) J_0(R_{\text{eff}}\alpha_i) \tag{27}$$

If we denote the initial probability of an acceptor being placed at distance r by $u(r)$ *the survival probability* $p(t)$ of the donor molecule at time t can then be expressed as

$$p(t) = \frac{N(t)}{N(0)} = \int_{R_{\text{eff}}}^{R} u(r) p(r, t)\, \mathrm{d}r \tag{28}$$

Now, if the circle contained n acceptor molecules that diffused mutually independent of one another, the probability that the excited donor would survive would then be given by

$$\frac{N(t)}{N(0)} = \left(\int_{R_{\text{eff}}}^{R} u(r) p(r, t)\, \mathrm{d}r\right)^n \tag{29}$$

For a random distribution, $u(r) = 2\pi r/(\pi R^2 - \pi R_{\text{eff}}^2)$ and from Eqs. (25) and (29) we obtain

$$\frac{N(t)}{N(0)} = \left(\sum_{i=1}^{\infty} A_i(R, R_{\text{eff}}, \alpha_i) \exp(-\alpha_i^2 Dt)\right)^n \tag{30}$$

where

$$A_i(R, R_{\text{eff}}, \alpha_i) = \frac{\pi^2}{R^2 - R_{\text{eff}}^2} \frac{\alpha_i^2 [J_1(R\alpha_i)]^2}{[J_0(R_{\text{eff}}\alpha_i)]^2 - [J_1(R\alpha_i)]^2} \times \left(\int_{R_{\text{eff}}}^{R} r C(r, \alpha_i)\, \mathrm{d}r\right)^2 \tag{31}$$

Eq. (30) provides an analytical solution to Eqs. (24a)–(24d) on the surface of the restricted circle. It is relevant to note that $N(t)$ decays exponentially at sufficiently long times. The limiting value of the rate constant is $k_1 = \alpha_1^2 D$. This behavior of the decay kinetics on the restricted surface contrasts with the long-time behavior of the decay of excited molecules on an infinite surface, where the reaction rate constant does not achieve any asymptotic value even at long times (see Eq. (23b)) [41].

Another point is worth noting. In deriving Eq. (30), the donor molecule was assumed to be fixed at the center of the circle. We take Eq. (30) to remain approximately correct when both the donor and the acceptor species move freely on the circle surface. In this case, the diffusion coefficient D stands for the sum of the diffusion coefficients of donor and acceptor. Consequently, taking into account that acceptor and donor molecules cannot leave the circle during the reaction and a Poisson distribution applies for acceptor molecules in the circle, we have

$$\frac{N(t)}{N(0)}=\sum_{n=0}^{\infty}\left(\sum_{i=1}^{\infty}A_i(R,\,R_{\mathrm{eff}},\,\alpha_i)\right.$$
$$\left.\times\exp(-\alpha_i^2Dt)\right)^n\frac{1}{n!}\bar{n}^n\exp(-\bar{n}) \tag{32}$$

which after evaluation yields

$$\frac{N(t)}{N(0)}=\exp\left[-\bar{n}\left(1-\sum_{i=1}^{\infty}A_i(R,\,R_{\mathrm{eff}},\,\alpha_i)\exp(-\alpha_i^2Dt)\right)\right] \tag{33}$$

When t is sufficiently large, the decay kinetics approach the description

$$\frac{N(t)}{N(0)}=\exp\{-\bar{n}[1-A_i(R,\,R_{\mathrm{eff}},\,\alpha_1)$$
$$\times\exp(-\alpha_1^2Dt)+A_0]\} \tag{34}$$

where α_1 is the smallest positive root of Eq. (26); the factor A_0 takes into account the initial decay of excited donors at short times. Eq. (34) can be used to analyse the long-time portion of the decay curves and permits an evaluation of the diffusion coefficient D of the molecules. For shorter decay times, other members of the infinite series in Eq. (33) must be taken into account.

2.3. Monte Carlo calculations

The above treatments of non-static emission quenching are the results of approximate considerations of the problem of a bimolecular reaction on the surface of a restricted circle. To understand the extent of their applicability, Monte Carlo simulations were performed for the kinetics of luminescence quenching.

In carrying out calculations with the Monte Carlo model, the excited donor and acceptor molecules were modeled as circles with radii R_{B^*} and R_{A} respectively. The initial state was prepared by assuming that the reagent molecules are flat bodies and are randomly distributed on the surface of the disk with radius R, such that the center of each molecule is inside the plane and that no molecule intersects another.

As a first step, we filled the disk surface with small circles representing the acceptors to achieve maximal density. We also assumed hexagonal packing of acceptor molecules. Subsequently, the smaller circles were sorted using a random number F between 0 and 1, that is $0<F<1$, and a given number of the surface filling φ which denotes the ratio of the given average number $\bar{n}$ of acceptor molecules to its maximal value $n_{\max}$ that can be placed on the surface of the circle; thus $\varphi=\bar{n}/n_{\max}$. For $F<\varphi$, the acceptor molecule is left on the surface of the circle; for $F>\varphi$, the acceptor molecule is deleted from the circle.

As the third step, one donor molecule was placed randomly on the surface of the circle so that it did not overlap an acceptor molecule. After this step, there was one donor molecule and a random number of acceptor molecules on the surface of the circle with the given average density. However, their positions are not random. To randomize, all molecules were then moved randomly with the limitation that no movements resulting in overlap were accepted. These movements are carried out to destroy the particle correlation arising from the initial placement requirements. Typically, the number of movement steps was 500, sufficient to randomize the initial positions of the molecules at the average number of acceptors used per circle: $\bar{n}\leqslant 7$.

After preparation of the initial state at $t=0$, Monte Carlo moves were made at time intervals Δt on the excited donor molecule and for each acceptor molecule in the system. At every move, the donor molecule and every acceptor molecule were permitted to shift randomly in any direction for a distance $\Delta\lambda_{\mathrm{B}^*}$ and $\Delta\lambda_{\mathrm{A}}$ respectively. The values of Δt, $\Delta\lambda_{\mathrm{B}^*}$ and $\Delta\lambda_{\mathrm{A}}$ change randomly from one move to another in the interval 0 to τ_{d}, 0 to λ_{B^*} and 0 to λ_{A} respectively. Neither intersection of the molecules nor exit of the center of the molecule out of the disk plane were permitted. Appropriate diffusion trials were rejected.

The excited donor molecule was allowed to emit a light quantum with the probability per unit time τ^{-1}. Any pair of excited donor and acceptor molecules were permitted to undergo reaction (1a) or (1b) at each Monte Carlo move with the probability $w(r)$ per unit time given by Eq. (5).

The spontaneous decay of excited molecules was taken into account in the following manner. If at a diffusion step a random number is lower than $\Delta\tau/\tau$, then the donor molecule was decayed at this step. Similarly for quenching by an acceptor molecule, if at a diffusion step a random number is lower than the probability of the reaction during the time interval Δt, that is for

$$F<1-\exp\left[-\Delta t\,\nu\exp\left(-2\frac{r-d}{a}\right)\right] \tag{35}$$

then, the excited donor molecule is quenched at this step.

The algorithm of Marsaglia and Zaman [44] was chosen to select random numbers. Moreover, λ_{d} was chosen to be zero to treat the static reaction.

Most of the simulations were carried out with the number of trials exceeding 3000 for each decay curve. The final emission decay curves were obtained by averaging all the trial emission decay kinetics.

2.4. Comparison of simulation results with analytical equations

It is important to examine the accuracy of the description of the luminescence decay kinetics embodied by the approximate Eq. (30). It is not clear, a priori, at which time intervals and/or to what reaction extents Eq. (30) can be used to fit the experimental decay data.

We compare below the simulated emission decay kinetics obtained from Eq. (33) with those calculated by the Monte Carlo method. The data from the latter method are taken as the "experimental" data for this purpose. To study the influence of the restricted geometry on the decay kinetics, calculations were performed for several values of the disk plane radius R for different distances d of maximal approach of the excited donor and of the acceptor and for different number of reagent molecules on the disk plane surface.

The quenching decay kinetics of the excited donor molecules B^* on the surface of the circular disk was determined by Eq. (33) which contains an infinite series with parameters α_i that are the roots of Eq. (26). However, this equation cannot be used to analyze the experimental decay kinetics without further simplification.

Our calculations revealed that for the dimensions of the circle and for the reagents examined, $R=20$–50 Å and, for $R_{\text{eff}}=4$–12 Å, the first coefficient $A_1(R, R_{\text{eff}}, \alpha_1)$ that corresponds to the minimal root α_1 of Eq. (26) exceeds all other coefficients, i.e. $A_1(R, R_{\text{eff}}, \alpha_1) > A_i(R, R_{\text{eff}}, \alpha_i)$ for $i \geqslant 2$, and is greater than 0.5. We found that for several first members of the infinite series, the coefficients $A_i(R, R_{\text{eff}}, \alpha_i)$ monotonically decrease with increase in i, $A_{i+1}(R, R_{\text{eff}}, \alpha_{i+1}) < A_i(R, R_{\text{eff}}, \alpha_i)$. The reverse relation of the coefficients $A_{i+1}(R, R_{\text{eff}}, \alpha_{i+1}) > A_i(R, R_{\text{eff}}, \alpha_i)$ was found for the next few values of i. Such a non-monotonic change in $A_i(R, R_{\text{eff}}, \alpha_i)$ precludes usage of only the first members of the series in Eq. (32) to fit the "experimental" decay kinetics. Therefore, in the infinite series of Eq. (33), we retain the first (i.e. the most significant) member of the series and substitute the sum of the rest of the members by a sum of several (two or three) exponents with parameters that can be found from a fitting of the "experimental" decay kinetics.

Accordingly, to fit the decay curves of luminescence quenching on the surface of the disk we use the following equation instead of Eq. (33):

$$\frac{N(t)}{N(0)}=\exp\left[-\bar{n}\left(1-\sum_{i=1}^{3}B_i\exp(-k_it)\right)\right] \tag{36}$$

By such a procedure the lowest coefficient k_1 coincides with the first time coefficient in the infinite series in Eq. (33): $k_1=\alpha_1^2D$.

To verify the above approximation we used Eq. (36) to analyze the Monte Carlo decay kinetics. Monte Carlo calculations were performed using the following set of parameters: $R=20$–50 Å, $d=2$–10 Å, $\tau_d=10^{-10}$–10^{-11} s, $\lambda_{B*}=\lambda_A=\lambda_d=0.1$–$0.5$ Å, $\nu=10^{12}$ s^{-1} and $a=0.1$–1 Å. The emission lifetime was chosen to be 10^{-4} s so that almost no intrinsic decay of the excited donor molecules occurred during the time of observation ($t \leqslant 10^{-6}$ s). The fitting procedure consisted in varying all the parameters B_i and k_i in Eq. (36) to minimize the difference between the "theoretical" (Eq. (36)) and the "experimental" (Monte Carlo calculations) decay curves.

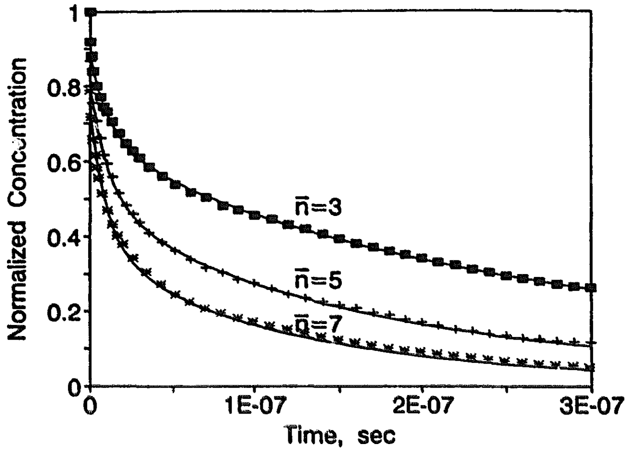

Fig. 3. Non-static luminescence quenching decay curves on the surface of the restricted circle obtained from Eq. (36) (——) and from Monte Carlo calculations ("experimental" points) for $R=20$ Å, $d=2$ Å, $\nu=10^{12}$ s^{-1} and $a=0.1$ Å. The numbers over the curves denote the average number of acceptor species per circle. The best fit to Eq. (36) and Monte Carlo decay curves corresponds to $B_1=0.859$, $k_1=1.49\times10^6$ s^{-1}, $B_2=0.101$, $k_2=7.67\times10^7$ s^{-1}, $B_3=0.04$ and $k_3=1.4\times10^{10}$ s^{-1}.

Our calculations showed that Eq. (36) provides a good fit to Monte Carlo decay kinetics with k_1 that coincides with α_1^2D if D were related to the microscopic parameters of the reagents movement on the surface by

$$D=\gamma\frac{\lambda_d^2}{4\tau_d} \tag{37}$$

with $\gamma \approx 0.5$.

Fig. 3 shows an example of the decay curves of emission quenching obtained by the Monte Carlo calculations (symbols) and by Eq. (36) (full curves) for a circle of radius $R=20$ Å; the radii of the donor and acceptor molecules were taken to be 2 Å and $a=0.1$ Å, so that $R_{\text{eff}}=4.2$ Å. The different curves in Fig. 3 correspond to a different average number of acceptor molecules per circle. The best fit of Eq. (36) and Monte Carlo decay curves corresponds to $B_1=0.859$, $k_1=1.49\times10^6$ s^{-1}, $B_2=0.101$, $k_2=7.67\times10^7$ s^{-1}, $B_3=0.04$ and $k_3=1.4\times10^{10}$ s^{-1}. The first root of Eq. (26) at $R=20$ Å and $R_{\text{eff}}=4.2$ Å is $\alpha_1=7.3\times10^6$ cm^{-1}. This set of parameters corresponds to $\gamma=0.45$ in Eq. (37). It is worth noting that the same value of γ was obtained from the analysis of the Monte Carlo decay curves at large t with the help of the simplified Eq. (34).

Examinations of actual experimental results on the kinetics of quenching of excited singlet and triplet molecules by acceptors on the surface of quantized layered MoS_2 particles using equations described above have been reported elsewhere [6,45].

3. Triplet–triplet annihilation in restricted two-dimensional space (surface of circular disk)

Interaction of two triplet excited molecules gives rise to T–T annihilation. Confinement of triplet excited molecules on the surface of particles that provide a restricted two-dimensional reaction space considerably enhances T–T annihilation [6]; the rate constant depends on the electronic coupling between the two excited molecules and exponentially on the intermolecular distance r in the same manner as in luminescence quenching reactions noted above. Two diametrically opposite mechanisms may be responsible for T–T annihilation of excited molecules: (i) annihilation occurs by diffusional approach of two excited molecules towards each other and (ii) annihilation occurs by static interaction of two triplet molecules. Both limiting cases of T–T annihilation on the surface of the restricted circle are considered below.

We conceive a round flat restricted surface of radius R with triplet excited molecules B^* of diameter d randomly adsorbed on the surface. We then examine the kinetics of deactivation of the molecule B^* which might occur by T–T annihilation with another excited molecule B^* and/or by spontaneous transition to the ground state. Only two-body interactions between the excited molecules are taken into account. Transfer of an excited triplet molecule from one circle to another and any interaction between triplet molecules from different circles in solution are excluded in the present analysis.

Two limiting situations exist concerning the products of T–T annihilation: (1) annihilation leads to the decay of two triplet molecules and (2) annihilation results in the formation of a triplet and a ground-state molecule. In our considerations we assumed that no triplets are formed in any of the steps that follow a T–T annihilation event.

3.1. Static triplet–triplet annihilation: analytical solution

We use the following equations for the decay of excited triplet molecules:

$$B^* + B^* \longrightarrow B + B \qquad \text{with rate constant } w(r) \tag{38}$$

$$B^* \longrightarrow B + h\nu \qquad \text{with rate constant } \frac{1}{\tau} \tag{39}$$

From a quantitative analysis viewpoint, the principal difference between T–T annihilation and luminescence quenching by acceptors considered previously is the difference between the relative concentrations of donors and between the concentrations of donors and acceptors respectively. The concentration of acceptor molecules strongly exceeds the concentration of excited donor molecules in emission quenching, whereas the concentrations of reagents are obviously identical in the case of T–T annihilation.

A rigorous analysis of the kinetics of distant reactions at comparable reagent concentrations is unavailable. The problem is that under these conditions it is somewhat evident that correlation effects in the decay of different donors cannot be disregarded; that is, one must account for the fact that the spatial distribution of acceptors near a given donor can be changed as a result of the decay of the acceptors in the reactions with other donors in the vicinity of the given donor.

The approximate analytical description of the kinetics of a distant reaction in infinite space at comparable reagents concentrations has been reported earlier by Khairutdinov et al. [34] and by Parmon et al. [46]. The suggested approximation replaces the constant concentration c in Eq. (3) by a time-dependent concentration from an equation somewhat similar to Eq. (3). For reaction (38), such an approximation indirectly assumes the triplet molecules are always randomly distributed at the mean prevalent concentration. However, it does not account for possible fluctuations of the local distribution of triplet molecules around a given triplet molecule (denoted B_g^*) because of competition between different B_g^* species for recombination with a chosen triplet molecule. This approximation is expected to be valid only for relatively small reaction extents as it overestimates the real recombination rate for large reaction extents at long times.

Calculations [47] from the Monte Carlo method have shown that for equal reagents concentrations and for an exponential dependence of $w(r)$ on the distance between donor and acceptor species the above approximation is valid for about 80% of the B^* decay with the error being 4% or less (i.e. less than almost 4% of the initial concentration of the species). In analyzing further the static T–T annihilation kinetics on the surface of the restricted circle, we employ the approximation suggested by Parmon et al. [46]. Thus, in lieu of Eq. (7), we consider the relationship

$$\frac{\mathrm{d}N(t, r_0)}{\mathrm{d}t} = -k(t, r_0)\left[N(t, r_0)\right]^2 - \frac{1}{\tau}N(t, r_0) \tag{40}$$

which following integration over time t with $k(t, r_0)$ given by Eq. (8) and subsequent averaging over the different positions of triplet molecules on the surface of the circle gives

$$\frac{N(t)}{N(0)} = \exp\left(-\frac{t}{\tau}\right)\frac{2}{R^2-d^2}\int_d^R r_0\,\mathrm{d}r_0$$
$$\times\left(1+N(0)\int_d^{R+r_0} r\,\mathrm{d}r\,2\varphi_{\max}\frac{w(r)}{w(r)+1/\tau}\right.$$
$$\left.\times\left[1-\exp\left\{-\left(w(r)+\frac{1}{\tau}\right)t\right\}\right]\right)^{-1} \tag{41}$$

For a very large circle such that $R \to \infty$, $\varphi_{\max} = \pi$ and Eq. (41) reduces to Eq. (42)

$$\frac{N(t)}{N(0)} = \exp\left(-\frac{t}{\tau}\right)\left(1+N(0)\int_d^{\infty} 2\pi r\,\mathrm{d}r\,\frac{w(r)}{w(r)+1/\tau}\right.$$
$$\left.\times\left\{1-\exp\left[-\left(w(r)+\frac{1}{\tau}\right)t\right]\right\}\right)^{-1} \tag{42}$$

This is the equation for a static reaction on an infinite surface. As in the case of emission quenching, geometrical restriction yields slower excited-state decay kinetics at the longer times.

Eq. (41) does not take into account the distribution of an initial concentration of triplet molecules on the circles in real solutions. If we thus assume an initial (at time zero) Poisson distribution for the number of triplet molecules on the circles, then, instead of Eq. (41), one obtains the equation

$$\frac{N(t)}{N(0)}=\exp\left(-\frac{t}{\tau}\right)\frac{2}{R^2-d^2}\sum_n\frac{1}{n!}(\bar{n})^n\exp(-\bar{n})\int_d^R r_0\,\mathrm{d}r_0$$
$$\times\left(1+\frac{n}{\pi(R^2-d^2)}\int_d^{R+r_0}r\,\mathrm{d}r\,2\varphi_{\max}\frac{w(r)}{w(r)+1/\tau}\right.$$
$$\left.\times\left[1-\exp\left\{-\left(w(r)+\frac{1}{\tau}\right)t\right\}\right]\right)^{-1} \tag{43}$$

where $\bar{n}$ is the average number of "acceptor" molecules per circle. Thus the decay kinetics of excited triplet molecules can be obtained by numerical integration of Eq. (43).

3.2. *Non-static triplet–triplet annihilation: analytical solution*

For this case, we consider excited triplet molecules confined on the surface of a restricted circle in which the triplets can approach each other by diffusion along the surface. The problem of kinetics of non-static T–T annihilation on the surface of the circle is germane to that considered by McQuarrie and coworkers [48,49]. These workers solved the stochastic model for the second-order reaction A + A → C for molecules restricted in a single volume. Later, a similar approach was used by Rothenberger et al. [50] to examine T–T annihilation in micelles. A similar model is equally adequate to describe the present situation. Following the earlier reports [48–50], we restrict our treatment of the kinetics of diffusion-induced T–T annihilation by assuming that annihilation of two triplet molecules on the surface of the restricted circle obeys pseudo-first-order kinetics with rate constant k_{TT}. This assumption is based on the conclusion of Carslow and Jaeger [51] that surface diffusion-controlled reactions can be described fairly well by simple kinetic equations with a time-dependent rate constant (see below). A more rigorous description of T–T annihilation on the surface of a restricted circle should take into account a more complex behavior than a simple pseudo-first-order character of the decay kinetics (see Section 2.2. above)

The scheme for T–T annihilation when n excited molecules are on the surface of the circle is described by [48–50]

$$\mathrm{T}_n\longrightarrow\mathrm{T}_{n-2}\qquad n=2,3,4,\ldots$$
$$\text{with rate constant }\tfrac{1}{2}n(n-1)k_{\mathrm{TT}} \tag{44}$$

$$\mathrm{T}_n\longrightarrow\mathrm{T}_0\qquad n=1,2,3,4,\ldots$$
$$\text{with rate constant }\frac{1}{\tau} \tag{45}$$

where T_n stands for the circle containing n triplet molecules; the factor $\frac{1}{2}n(n-1)$ in the rate constant of Eq. (44) denotes the number of ways of choosing a pair of triplets in a circle containing n triplet molecules. From Eqs. (44) and (45), the concentration $[\mathrm{T}_n]$ of circles containing n triplet molecules is given by

$$\frac{\mathrm{d}[\mathrm{T}_n](t)}{\mathrm{d}t}=-\tfrac{1}{2}n(n-1)k_{\mathrm{TT}}[\mathrm{T}_n](t)-\frac{1}{\tau}[\mathrm{T}_n](t)$$
$$+\tfrac{1}{2}(n+2)(n+1)k_{\mathrm{TT}}[\mathrm{T}_{n+2}](t) \tag{46}$$

The initial distribution of the number of triplet molecules on the circles must be known to solve Eq. (46). The resulting equation for the decay of triplet molecules has the simplest form if the initial distribution of the triplet molecules amongst the circles were given by the Poison distribution

$$[\mathrm{T}_n](0)=C_c\frac{1}{n!}\bar{n}^n\exp(-\bar{n}) \tag{47}$$

where C_c is the total concentration of circles in solution.

The series of Eq. (46) with the boundary condition defined by Eq. (47) can be solved by generating function techniques [52]. Then, if the total concentration of triplet molecules in solution were given by $N(t)=\sum_{n=1}^{\infty}n[\mathrm{T}_n](t)$, one would obtain [48–50]

$$\frac{N(t)}{N(0)}=\exp\left(-\frac{t}{\tau}\right)\sum_{n=1}^{\infty}B_n\exp[-\tfrac{1}{2}n(n-1)k_{\mathrm{TT}}t] \tag{48}$$

where

$$B_n=\frac{2n-1}{2^n}\frac{\exp(-\bar{n})}{\bar{n}}\sum_{j=n}^{\infty}\frac{\bar{n}^j}{(j-n)!}\frac{\Gamma((j-n+1)/2)}{\Gamma((j+n+1)/2)}$$

with $j=n, n+2, n+4,\ldots$ and Γ is the gamma function [53].

We consider next the final distribution of triplet molecules amongst the circles after completion of T–T annihilation. We assume that all other decay processes are slow compared with T–T annihilation and thus neglect them on the time scale of observation. Since triplet molecules react in a pairwise fashion, only those circles that initially contained an odd number of triplet molecules will contain one triplet molecule after completion of the T–T annihilation process. Consequently, for the total concentration of triplet molecules after completion of T–T annihilation we have [50]

$$\frac{N(\infty)}{N(0)}=B_1=\frac{1-\exp(-2\bar{n})}{2\bar{n}} \tag{49}$$

In practice, one takes into account only a few members of the sum in Eq. (48). Our calculations have shown that $\sum_{n=5}^{\infty}B_n\leqslant10^{-2}$ (for $\bar{n}=3$), $\sum_{n=7}^{\infty}B_n\leqslant10^{-2}$ (for $\bar{n}=5$) and $\sum_{n=9}^{\infty}B_n\leqslant10^{-2}$ (for $\bar{n}=7$). Thus the difference between the explicit decision of Eqs. (46) and (47) and the approximate one (Eq. (43)) does not exceed 1% of the initial triplet concentration if one takes into account in Eq. (48) only four members of the sum at $\bar{n}=3$, six members of the sum at $\bar{n}=5$ and eight members of the sum at $\bar{n}=7$. The total concentration of triplet molecules after completion of T–T annihilation is $B_1\approx0.17$ (for $\bar{n}=3$), $B_1\approx0.10$ (for $\bar{n}=5$) and $B_1\approx0.07$ (for $\bar{n}=7$).

3.3. Monte Carlo treatment

To express the validity of the aforementioned analytical expression, we have carried out calculations (to simulate experiments) of T–T annihilation kinetics using the Monte Carlo model similar to that described earlier when discussing emission quenching of an excited donor molecule by acceptors. Excited triplet molecules were modeled by a round circle of diameter d. Each triplet molecule was permitted to undergo intrinsic decay with lifetime τ. Also, any two triplet excited molecules were allowed to undergo annihilation at each Monte Carlo move with the probability w per unit time given by Eq. (5). We have further assumed that all other processes were slow compared with T–T annihilation and thus neglected them on the time scale of observation.

3.4. Comparison of simulation ("experimental") results with analytical equations

We now verify the validity of the approximate equations derived above by comparing the "experimental" results of Monte Carlo calculations with decay curves obtained using Eqs. (43) and (48).

3.4.1. Static quenching. We first test for the accuracy of the description of T–T annihilation decay kinetics by Eq. (43). As in the earlier treatment of luminescence quenching, our theoretical treatment of the decay of triplet molecules is approximate, and it is not clear a priori at which time intervals and/or to what reaction extent Eq. (38) can be used to fit the "experimental" decay kinetics of T–T annihilation. To clarify, we contrast the decay kinetics of T–T annihilation obtained with Eq. (43) with those determined by the Monte Carlo method.

Fig. 4 shows the decay kinetics of static T–T annihilation obtained using Eq. (43) (full curves) and the results of Monte Carlo calculations (symbols) for several surface concentrations of triplet molecules and for $R = 20$ Å and $d = 4$ Å. The same values of the parameters ν and a were used in calculations of the decay kinetics by Eq. (43) and by the Monte Carlo method. As seen in Fig. 4, the decay kinetics obtained from Eq. (43) agree reasonably well with the Monte Carlo decay curves. Also Eq. (43) describes the kinetics of the decay at about 90% of reagent decay with an accuracy of approximately 5% of the initial concentration. These data indicate that the approximate Eq. (43) can be used to analyse the "experimental" data for static T–T annihilation on the surface of a restricted circle; use of Eq. (43) is complicated by the need for numerical integration.

3.4.2. Non-static quenching. Eq. (48) describes the kinetics of T–T annihilation in terms of the pseudo-first-order rate constant k_{TT}. To analyze the validity of Eq. (48) for a treatment of non-static diffusion-induced T–T annihilation decay kinetics, we first examine how the rate constant k_{TT} is related to the parameters of the above Monte Carlo calculations; k_{TT} is defined as

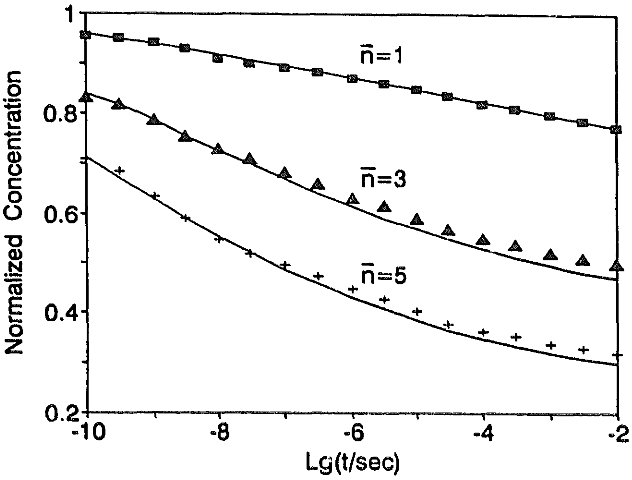

Fig. 4. Decay kinetics of static T–T annihilation obtained by using Eq. (43) (——) and results of Monte Carlo calculations ("experimental" points) for $R = 20$ Å, $d = 4$ Å, $\nu = 10^{12}$ s^{-1} and $a = 1$ Å. The numbers over the curves show the average number of acceptors per circle. The same values of the parameters ν and a were used in the calculations of the decay kinetics by Eq. (43) and by the Monte Carlo method.

$$k_{TT} = k_c \frac{1}{\pi R^2} \tag{50}$$

where $1/\pi R^2$ is the surface concentration of triplet molecules when one of these is placed on the surface of the circle and k_c is the bimolecular rate constant for T–T annihilation. Typically T–T annihilation is a diffusion-controlled reaction. Therefore

$$k_c = k_D \tag{51}$$

where k_D is the bimolecular rate constant of the surface diffusion-controlled reaction. According to Carslaw and Jaeger [51] (see also [39–42]), for surface reaction k_D is a weakly dependent function of time that can frequently be replaced, to a good approximation, by its suitably averaged value that is related to the surface diffusion coefficient D by

$$k_D = \bar{\alpha} \pi D \tag{52}$$

For diffusion-controlled reactions on the infinite surface, the parameter $\bar{\alpha}$ typically assumes values between 0.3 and 0.6 [40–42].

To verify the validity of Eq. (48) and the possibility of using the time-independent value of the bimolecular rate constant for T–T annihilation on the surface of the restricted circle we compared the results of Monte Carlo calculations of the kinetics of T–T annihilation with those predicted by Eq. (48).

Fig. 5 depicts the series of decay curves for non-static T–T annihilation obtained by Monte Carlo simulations ("experimental" points) and the best fit of these decay data by Eq. (48) (full curves) for different dimensions of the circle and of the triplet molecule, and several average number of triplet

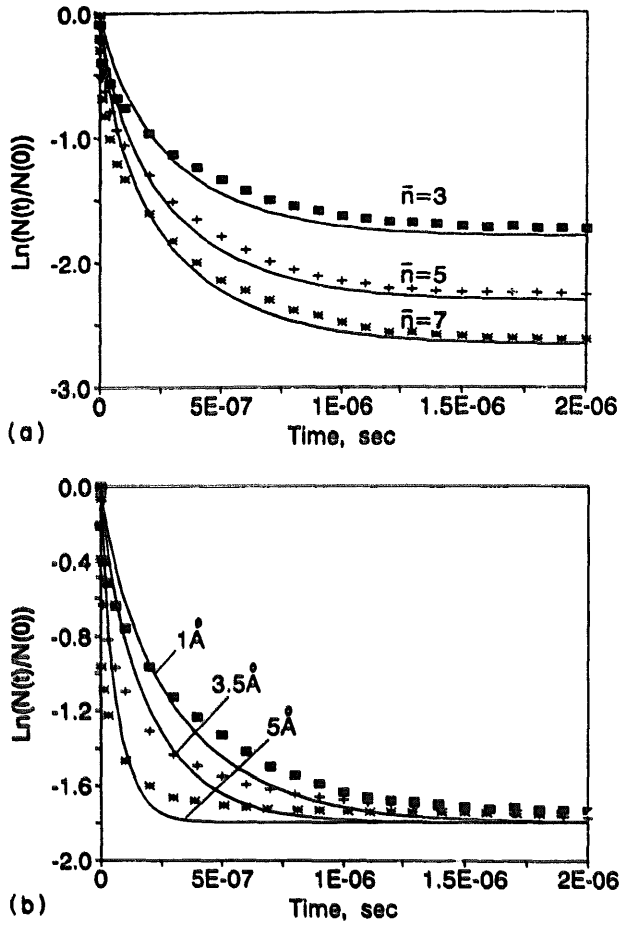

Fig. 5. Decay kinetics of diffusion-induced (non-static) T–T annihilation on the surface of the circle calculated with the help of Eq. (48) (——) and by Monte Carlo calculations (''experimental'' points). (a) The circle radius $R=20$ Å, the triplet molecule diameter $d=2$ Å, $\nu=10^{12}$ s^{-1}, $a=1$ Å and $k_{TT}=3.5\pm0.3\times10^{6}$ s^{-1}. The numbers over the curves show the average number of acceptors per circle. (b) The circle radius $R=20$ Å, $\nu=10^{12}$ s^{-1} and $a=1$ Å. The numbers for the decay curves correspond to the diameters of the triplet molecule.

molecules on the circle. Typically, Monte Carlo calculations were performed using a set of parameters for diffusion of triplet molecules and for T–T annihilation; $\tau_d=10^{-10}$ s, $\lambda_d=0.5$ Å, $\nu=10^{12}$ s^{-1}, $a=0.1$–1 Å, and the average number of triplet molecule per circle varied from $\bar{n}=3$ to $\bar{n}=7$. The emission lifetime was chosen to be 3×10^{-4} s so that almost no intrinsic decay of triplet molecules occurred during the time of observation ($t\leqslant3\times10^{-6}$ s).

Fig. 5(a) shows an example of the decay curves for the different average number of triplet molecules on the circle, for a circle radius $R=20$ Å and for a diameter of triplet molecule $d=2$ Å. Eq. (48) gives a reasonably good fit to the ''experimental'' results of Monte Carlo calculations with k_{TT} identical for all three decay curves, $3.5\pm0.3\times10^{6}$ s^{-1}, the corresponding value of k_c is $4.9\pm0.4\times10^{-7}$ cm^{-2} s^{-1}.

Calculations show that a decisive factor for the kinetics of T–T annihilation is the value of R_{eff}/R, where R_{eff} given by Eq. (21) is the radius of the T–T annihilation event; R_{eff} is the radius of the circle around the triplet molecule, intrusion into which causes a reaction with the other triplet molecule resulting in their mutual annihilation during time τ_d [34]. This is clearly seen from the decay curves presented in Fig. 5(b) obtained for a fixed radius of the circle, $R=20$ Å, and for different radii of the triplet molecules indicated in Fig. 5(b) by the numbers on the decay curves.

Fig. 6(a) shows the k_c dependence on the radius of T–T annihilation at three different values of a ($a=1$ Å (full squares), $a=0.4$ Å (asterisks) and at $a=0.1$ Å (pluses)) and for different diameters of the triplet molecule.

The rate constant for T–T annihilation also depends on the radius R of the circle. This dependence is shown in Fig. 6(b) for three different values of the radius of T–T annihilation, $R_{eff}=4.3$ Å, $R_{eff}=2.9$ Å and $R_{eff}=2.2$ Å, for a fixed value of the diameter of triplet molecules, $d=2$ Å, and for different values of a. The full squares in Fig. 6(b) show the result of the calculations at $a=1$ Å ($R_{eff}=4.3$ Å), the pluses correspond to $a=0.4$ Å ($R_{eff}=2.9$ Å) and the asterisks refer to $a=0.1$ Å ($R_{eff}=2.2$ Å).

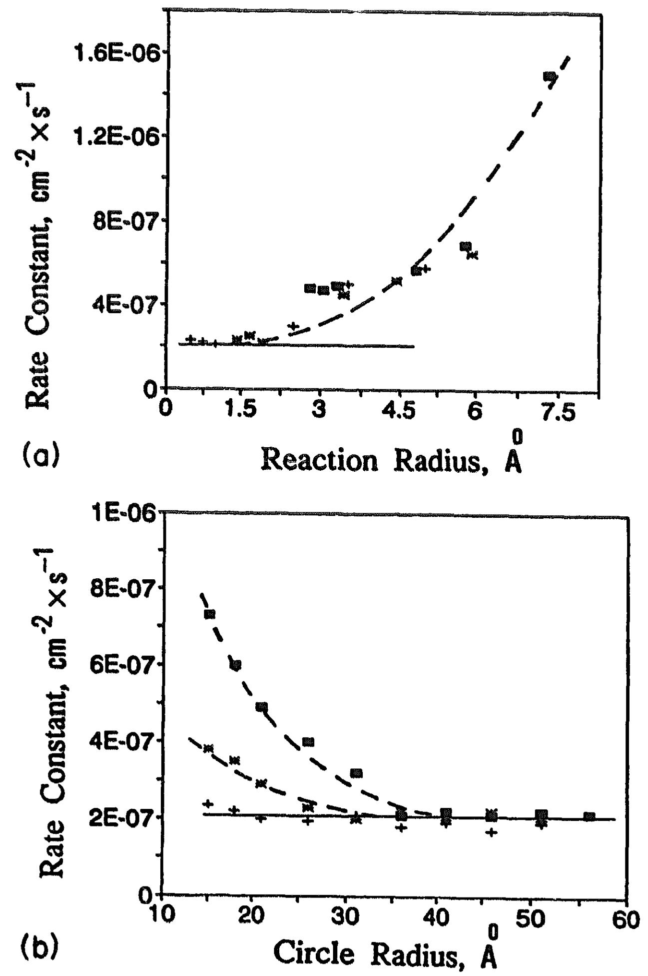

Fig. 6. (a) Dependence of the rate constant of T–T annihilation on the effective radius of the reaction for different values of a: ■, $a=1$ Å; *, $a=0.4$ Å; +, $a=0.1$ Å. (b) Dependence of the rate constant of T–T annihilation on the radius of the circle for different values of the T–T annihilation radius: ■, $R_{eff}=4.3$ Å; +, $R_{eff}=2.9$ Å; *, $R_{eff}=2.2$ Å.

As noted in Figs. 6(a) and 6(b), the ratio R_{eff}/R has a decisive influence on the k_c value. An increase of k_c is observed with an increase in R_{eff}/R at $R_{eff}/R > 0.1$, whereas the notion that there is almost no dependence of k_c on the circle radius is characteristic for values of $R_{eff}/R < 0.1$.

The data presented in Figs. 5(b) and 6(b) show that for a diffusion controlled T–T annihilation, a restricted circle may be considered as an infinite surface only if $R_{eff}/R < 0.1$. An appropriate value of the bimolecular rate constant $k_c^\infty = 2.0 \pm 0.2 \times 10^{-7}$ cm ^{2} s^{-1} may be considered therefore as that which corresponds to the rate constant of T–T annihilation on the infinite surface.

The values of τ_d (10^{-10} s) and λ_d (0.5 Å) above correspond to the value of the diffusion coefficient of triplet molecules $D \approx \lambda_d^2/4\tau_d = 6.2 \times 10^{-8}$ cm^{-2} s^{-1}. Then, from Eqs. (51) and (52) we have $k_D \approx 2\bar{\alpha} \times 10^{-7}$ cm^{-2} s^{-1}. This value of k_D is in good agreement with the above value of k_c^∞ at $\bar{\alpha} \approx 1$. These data indicate that at $R_{eff}/R < 0.1$ we can use Eqs. (48), (50), (51) and (52) to estimate the value of the surface diffusion coefficient D. For $R_{eff}/R \gg 0.1$ the use of Eqs. (48), (50), (51) and (52) results in an overestimation of k_c and D while a seemingly good fit of the "experimental" data can be obtained by use of Eq. (48). For $R_{eff}/R \geqslant 0.1$, the Monte Carlo fitting procedure of T–T decay kinetics can be used to get adequate values of the parameters of the annihilation reaction [6].

4. Conclusions

Four problems of the kinetics of static and non-static electron and energy transfer from excited donor molecules to acceptors on the surface of the restricted circle were considered in the present article. The analytical Eq. (20) allows the decay kinetics of an excited donor molecule B* by static distance-dependent electron and energy transfer to random acceptors to be described. Luminescence decay kinetics on the surface of the restricted circle are slower than those on the infinite surface and the difference between them increases with an increase in the time of observation. Decay kinetics of excited molecules originating from diffusion approach of reagents on the surface of the circle obey Eq. (33); they are exponential at sufficiently long times. This long-time behavior of the kinetics contrasts with the long-time behavior of diffusion-limited reactions on an infinite surface, where the reaction rate constant does not achieve an asymptotic value even at long times. To fit the "experimental" decay kinetics, one can use the phenomenological expression (35); the minimal time coefficient in this equation can be used to evaluate the diffusion coefficient of the reagent molecules on the surface of the circle. These two problems of emission decay quenching for such systems are typically solved by assuming that only one excited donor molecule and a number of acceptor species are placed on the surface of the circle.

The problem of the decay of excited triplet molecule by T–T annihilation on the surface of the restricted circle has also been examined. This problem differs principally from that of emission quenching since the concentrations of the reagent molecules on the surface are equal to each other. An approximate solution of this problem for the static interaction is given on the basis of the average reagent concentration approximation, when one assumes that in the course of the reaction the triplet molecules are always randomly distributed at a given mean concentration. Monte Carlo simulations ("experiments") show that the decay kinetics obtained with the aid of derived equations agree fairly well with the results of simulations. Diffusion-induced annihilation kinetics on the surface of a restricted surface have been considered using the infinite space approach. In this case, Monte Carlo simulations show that Eq. (48) derived under this approximation can be used to analyse the reaction(s) on the circle until the effective radius of the annihilation R_{eff} does not exceed one tenth of the circle radius R, i.e. when $R_{eff} < 0.1R$.

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