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Effects of quencher concentration on bimolecular reaction rate in solution

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Abstract

Fluorescence decay curves of Coumarin 151 quenched by *N,N*-dimethylaniline in anisole for a wide range of quencher concentrations have been measured by using a time correlated single photon counting as well as a fluorescence up-conversion technique at room temperature. At low quencher concentrations the observed decay curves can be analyzed well by a simple diffusion model with the Smoluchowski equation. At higher quencher concentrations, however, both the simple diffusion model and the nonadiabatic sink term model with distance-dependent reaction rate under a random initial quencher distribution failed to explain the experimental data, which showed a rapid decay of fluorescence on a picoseconds time scale followed by a slower decay on a longer time scale. A radial distribution function estimated by a Lennard-Jones potential between fluorescer and quencher was introduced as an initial distribution of quencher to reproduce the experimental decay profiles. The theoretical prediction at high concentrations of quencher was improved significantly by using the diffusion coefficient obtained at low quencher concentrations. © 1997 Elsevier Science S.A.

Keywords: Transient effects; Radial distribution function; Fluorescence quenching; Electron transfer

1. Introduction

A great deal of effort has been put into the investigation of bimolecular chemical reactions in the solution phase over many years, and many studies, both experimental and theoretical, can be found in the literature [1–6]. Analyses of the transient effects in the fluorescence quenching by intermolecular electron transfer for a variety of donor–acceptor pairs were previously performed to obtain the "real" reaction rate constant of the encounter pair [6–8]. However, the time resolution of these studies was limited by the instrumental response function (30 ps or lower) which made the evaluation of the simple models used (Smoluchowski (SK) [9], Collins and Kimball (CK) [10]) rather difficult. With the development of experimental techniques and the availability of femtosecond time resolution the study of a diffusion controlled bimolecular reaction has advanced to a new stage.

It should be stressed here that both the SK and CK models have obvious physical limitations. In particular, the SK model assumes that the reaction occurs with infinite rate at fixed reaction distance. The CK model takes into account the finiteness of the reaction rate, although the reaction occurs only at a fixed distance between fluorescer and quencher molecules. According to the Marcus theory of electron transfer [11], the idea of a distance-independent rate is inadequate. Another questionable point of the SK and CK models is that they do not include any possible contribution of a short-range order of quencher molecules around a fluorescer molecule. The latter could play a significant role in the earlier times of reactions under high concentrations of quencher.

Several attempts were made to include the distance dependence of the reaction rate. Willemski and Fixman [12] introduced a position-dependent rate coefficient $k(r)$, which decreases exponentially with increasing distance, r, between the reactants. Szabo's model [13] incorporates a position-dependent intrinsic reaction rate additional to a diffusion rate. Eads et al. [14] analyzed their subpicosecond time-resolved fluorescence data for the rhodamine B-ferrocyanide system. They found a better agreement with the Szabo's model compared with the CK model or the model in which the rate constant decreases exponentially with increasing distance. Nevertheless, no sufficient agreement between the full complement of experimental data and the model used was found.

Shannon and Eads [15] investigated the fluorescence quenching of 7-aminocoumarin (coumarin 1) by aniline and *N,N*-dimethylaniline in methanol by subpicosecond time-resolved and steady state fluorescence measurements. They examined the models of SK, CK, Willemski and Fixman, the static quenching Collins and Kimball (SQCK) and the model incorporating a nonadiabatic electron transfer sink function

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[12] in the diffusion equation. They stressed the importance of taking into account the correlated motion of reactants and the possible breakdown of bulk hydrodynamics in the systems with higher quencher concentrations.

Another fundamental point to mention is that a liquid displays a definite structure in the radial distribution of molecules surrounding a given molecule. This structure occurs over several molecular diameters, the region of space determining the fast initial dynamics. The higher the quencher concentration is, the greater their contribution will be to this structure. This physical aspect, however, remained somewhat overlooked in the models discussed and in attempts to explain the quenching dynamics on the ultrashort time scale for higher quencher concentrations. Molski [16] has developed a modified Smoluchowski theory that involves two-particle potentials. However, the modified equation could not be solved analytically. Numerical methods must be applied to carry out quantitative analysis. We used the random walk method to solve the diffusion equation with the nonadiabatic sink term. This numerical treatment also allows us to introduce the radial distribution function and two-particle potentials in the equation developed; these are, from our point of view, of crucial importance for explanation of the experimental data at earlier times and higher quencher concentrations.

In this paper, we present the results of the time-resolved fluorescence quenching reaction via intermolecular electron transfer for the coumarin 151 (C151)–*N,N*-dimethylaniline (DMA) system in anisole over a broad range of quencher concentrations. The SK, CK, and nonadiabatic electron transfer sink term models were used to fit the data. The random walk method has been used to solve the diffusion equation under the initial conditions derived from the intermolecular potential between fluorescer and quencher. The importance is noted of the "radial distribution function" instead of "random particle distribution" of the quencher molecules for explanation of the quenching dynamics at earlier times and higher quencher concentrations.

2. Experimental section

A time-correlated single photon counting (SPC) system with a time resolution of about 30 ps and a fluorescence up-conversion system with a time resolution of about 270 fs were employed. Both are based on an Ar-ion laser pumped Ti^{3+}:Al_2O_3 laser operated at the repetition rate of 82 MHz. (Spectra Physics, Tsunami; 80 fs FWHM, 450 mW at 795 nm).

The second harmonic (397.5 nm) of the laser pulse was generated in 0.8 mm BBO crystal and was focused onto the sample cell with a 1 mm optical pass length. The fluorescence of the sample and a fundamental laser pulse (795 nm) were focused into a 0.8 mm BBO type I crystal to generate a signal at the sum frequency. After passing through an appropriate optical filter and a grating monochromator, the signal was detected with a photon counting system (Hamamatsu C1230; photomultiplier, R464-02). Fluorescence decay curves were obtained by varying the optical path length of the fundamental pulse. Measuring a cross-correlation signal between fundamental and second harmonics, we estimated the instrumental response function. In up-conversion measurements, in order to avoid contributions of solvation effects to the fluorescence decay, the fluorescence was monitored at 460 nm which was slightly longer than the maximum of steady state fluorescence of C151. For the analysis of SPC data the SALS program of Osaka University computation center was used.

The concentration of C151 was fixed at about 10^{-5} M for SPC, and 10^{-3} M for up-conversion measurements, while the concentration of DMA was varied over a broad range from 0.005 M to 1 M. Anisole was selected as a solvent to minimize the effects on the physical properties of solution by the addition of the quencher over a wide range of concentrations. The sample solutions were degassed by several freeze–pump–thaw cycles. We used a magnetic stirrer to avoid a degradation of the sample in the excitation volume. All measurements were performed at ambient temperature (ca. 295 K).

3. Results and discussion

On the basis of the SK model, the time dependence of the fluorescence intensity is

$$I(t) = I_0 \exp(-at - b\sqrt{t}) \qquad (1)$$

where

$$a = \frac{1}{\tau_0} + 4\pi\left(\frac{k_E}{k_D + k_E} R\right) D N' Q$$

$$b = 8\left(\frac{k_E}{k_D + k_E} R\right)^2 \sqrt{\pi D} N' Q$$

and

$$k_D = 4\pi R D$$

R is the reaction distance, Q the concentration of the quencher, D the mutual diffusion coefficient, k_E the quenching rate constant at the encounter, k_D the diffusion rate constant, and τ_0 the fluorescence lifetime without quencher.

The prediction of the fluorescence decay by CK model can be written as;

$$I(t) = I_0 \exp\left(\frac{Q k_E^2}{2c^2 (k_D + k_E)}\right) \times \exp\left[-at - b\sqrt{t} - \frac{\sqrt{\pi} b}{2c} \exp(c^2 t)\, \mathrm{erf}(c\sqrt{t})\right] \qquad (2)$$

with

$$c = \frac{\sqrt{D}}{R}\left(1 + \frac{k_E}{k_D}\right)$$

Table 1
The fitting parameters a and b obtained from SPC data for different quencher concentrations Q using the SK model

Q/M	$a/10^8\ \mathrm{s}^{-1}$	$b/\mathrm{s}^{-1/2}$	χ^2
0	2.10	–	1.19
0.005	2.58	2.13	1.19
0.025	3.90	1.87×10^3	1.06
0.05	5.44	4.13×10^3	1.03
0.1	8.65	8.75×10^3	1.21

All other parameters here are the same as in the SK model.

The fluorescence decay curves for different quencher concentrations measured by SPC were fitted to the SK and CK models. The fitting parameters a, b and c are listed in Tables 1 and 2 for each model, respectively. Judging from χ^2, quality of the fitting to both models was satisfactorily. Typical decay curve and the corresponding residuals are shown in Fig. 1. The mutual diffusion coefficient, D, should be almost constant even if concentration of solute increases up to 5 mol.% according to Reid et al. [17]. Therefore, D can be derived from a and b in the SK model using the Van der Waals radii as molecular radii. We found a good agreement between the D obtained from our fluorescence decay at quencher concentrations lower than the order of 10^{-2} M and that obtained from the Wilke–Chang empirical equation [18],

$$D=7.8\times10^{-8}\frac{(\phi M_{\mathrm{A}})^{1/2}T}{\eta_{\mathrm{A}}}\left(\frac{1}{V_{\mathrm{C151}}^{0.6}}+\frac{1}{V_{\mathrm{DMA}}^{0.6}}\right) \qquad (3)$$

where D [$\mathrm{cm}^2\ \mathrm{s}^{-1}$] is the mutual diffusion coefficient of solutes (C151 and DMA) in solvent A (here anisole), T the absolute temperature, η_{A} [cP] the viscosity of the solvent A, M_{A} the molecular weight of solvent A, V_{C151} and V_{DMA} the molar volumes of solutes at their normal boiling temperature, and ϕ (dimensionless) the association factor of solvent A (for anisole it is equal to 1). Using the Van der Waals radii of acceptor and donor as 4.3 Å for R_{C151} and 3.88 Å for R_{DMA} estimated from Van der Waals radii of atoms, one obtains a mutual diffusion coefficient D of $1.62\times10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ from Eq. (3). If the reaction distance is set to be the sum of the Van der Waals radii of fluorescer and quencher, the electron transfer rate is estimated to be $1.4\times10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, which seems to be large enough to satisfy the boundary conditions required for the SK model.

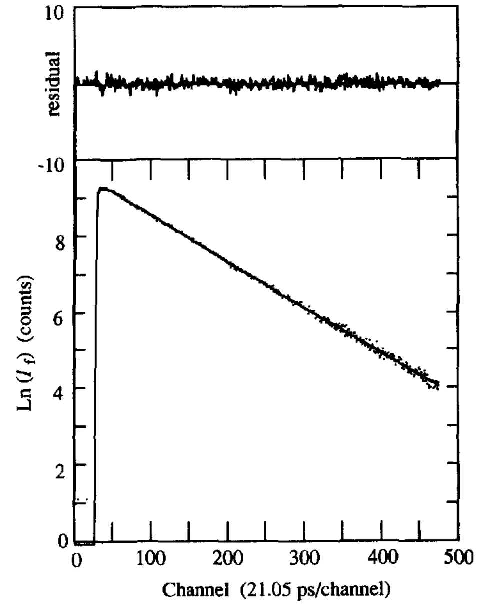

Fig. 1. An example of the fluorescence decay curve of C151 in anisole with 0.05 M quencher (DMA) concentration measured by SPC apparatus and fitting result by CK model. The corresponding residuals of the fit are shown in the top of the figure. $\chi^2=1.02$, $DW=1.74$.

The fitting results by CK model are given in Table 2(a). The parameters a and b derived from the fitting of the experimental decays by CK model are rather similar to those derived from the SK model. The physical relevant quantities such as k_{D}, k_{E} in the CK model depend on the parameter c. The diffusion coefficient and rate constants obtained from a, b, and c are presented in Table 2(b). The values are in good agreement with those estimated from the SK model except in the case of 0.1 M. Thus we can conclude that the SK and CK models are applicable for low quencher concentrations.

Fig. 2 displays the fluorescence decay curve obtained by the up-conversion method at the quencher concentrations of

Table 2
(a) The fitting parameters a, b and c obtained from SPC data for different quencher concentrations Q by using CK model

Q/M	$a/10^8\ \mathrm{s}^{-1}$	$b/\mathrm{s}^{-1/2}$	$c/\mathrm{s}^{-1/2}$	χ^2
0.005	2.58	2.13	–	1.19
0.025	3.87	2.28×10^3	6.52×10^4	1.09
0.05	5.25	6.59×10^3	4.49×10^4	1.02
0.1	8.65	8.73×10^3	3.85×10^7	1.19

(b) Reaction radius, diffusion coefficient, diffusion rate constant, and reaction rate constant of electron transfer obtained from the parameters of a, b and c

Q/M	$R/10^{-10}$ m	$D/10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$	$k_{\mathrm{D}}/10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$k_{\mathrm{E}}/10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$
0.025	11.4	1.6	1.4	1.2
0.05	14.3	1.2	1.3	1.1
0.1	5.0	1.7	0.64	300

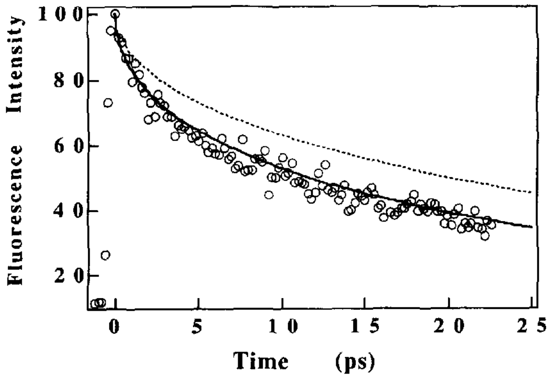

Fig. 2. Fluorescence decay curve of C151 in anisole measured by the up-conversion technique at the quencher concentration of 1.0 M. The predicted decays from the SK model for the diffusion coefficient $D = 1.62 \times 10^{-5}$ cm^2 s^{-1} (dotted line) and $D = 1.0 \times 10^{-5}$ cm^2 s^{-1} which gives the best fit (solid line).

1 M. The dotted line is the analytical solutions of Eq. (1) for diffusion coefficients of 1.62×10^{-5} cm^2 s^{-1}. The reaction distance was assumed to be 8.2 Å, which is the sum of the Van der Waals radii. Although the measured decay curve could not be reproduced by the SK and/or CK model if we used D evaluated from the measurements at low concentrations, it could be better reproduced if D was chosen as 1×10^{-5} cm^2 s^{-1} for the concentrations of quencher of 1.0 M, (solid curve). In other words, in the SK and CK models D should decrease almost 2 times when the quencher concentration at 1 M, which indicates that the SK or CK model fails to reproduce the experimental data.

In the nonadiabatic sink term model a distance-dependent reaction rate $k(r)$ is introduced. The diffusion equation for the survival probability, $U(r,t)$, of the fluorescer–quencher pair has the following form [19]:

$$\frac{\partial U(r,t)}{\partial t} = D\left(\frac{\partial^2}{\partial r^2} + \frac{2\partial}{r\,\partial r}\right)U(r,t) - k(r)\,U(r,t) \tag{4}$$

The last term takes into account that the fluorescer–quencher pair is removed from the system by the quenching. Since the quenching occurs via electron transfer, it is more natural to use the Marcus equation for $k(r)$ [11]. We used a simplified form of the distance-dependent reaction rate

$$k(r) = k_E \exp[-\beta(r-R)] \tag{5}$$

with

$$k_E = \frac{2\pi}{\hbar} J_0^2 \frac{1}{\sqrt{4\pi\lambda kT}} \exp\left[-\frac{(\Delta G + \lambda)^2}{4\lambda kT}\right]$$

where β is the attenuation coefficient, J_0 the magnitude of the electronic coupling energy between the reactant and product states, ΔG the free energy difference of the reaction and λ the solvent reorganization energy.

The initial and boundary conditions are

$$U(r,0) = 1, \quad \left(\frac{\partial U(r,t)}{\partial r}\right)_{r=R} = 0, \quad U(\infty,1) = 1 \tag{6}$$

The fluorescence decay in the presence of the quencher can be expressed with the following expression:

$$I(t) = \exp\left(-\frac{t}{\tau_0} - 4\pi Q \int_R^{\infty} [1 - U(r,t)]\, r^2\, dr\right) \tag{7}$$

We note that the initial distribution of the $U(r,t)$ at the present stage of the model is assumed to be completely random. However, this simplification can lead in some cases to false results if, for instance, some special interactions exist in the ground state fluorescer–quencher pair. Similarly, this assumption will be doubtful if the distributions of uncomplexed fluorescer and quencher molecules are not random. Hence, if this effect could be neglected at longer time scales and for lower quencher concentrations, the question should naturally arise in the cases of higher quencher concentrations whether the initial distribution is random or not. As we shall see below, the possible nonrandom (in the simplest case, radial) initial distribution can significantly influence on the temporal evolution of the quenching reaction in earlier times within first 10 ps.

Eq. (4) under the conditions of Eq. (6) was solved numerically. In Fig. 3 the comparison between experimental decays and those calculated (labelled A, B, C, D and E) using the nonadiabatic sink term model for different quencher concen-

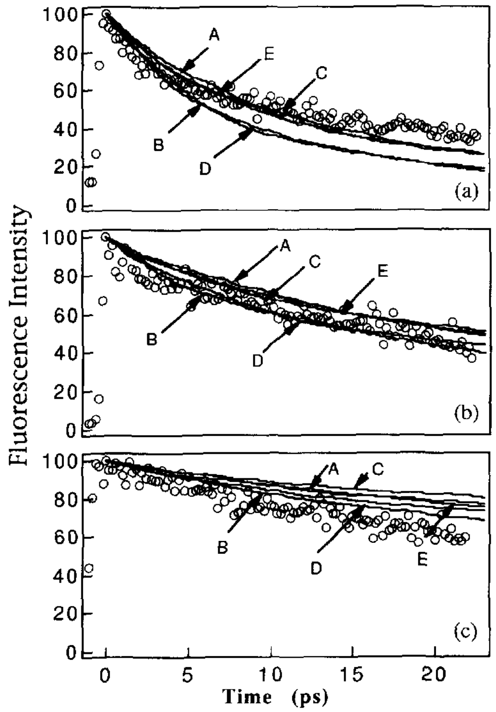

Fig. 3. The calculated decay curves by non-adiabatic sink term model: (i) 1.0 M DMA; (ii) 0.5 M DMA; (iii) 0.2 M DMA. In all calculations the critical distance $R = 8.2$ Å and the diffusion coefficient $D = 0.82 \times 10^{-5}$ cm^2 s^{-1} are fixed. The parameters β and k_E, corresponding to curves marked A, B, C, D and E, are listed in Table 2. Circles are shown the experimental results obtained by a the up-conversion technique.

trations are shown and the corresponding parameter sets, k_E and β, are given in Table 3. It is shown that the experimental decays for different quencher concentrations cannot be reproduced with unified parameters whatever values of β and k_E are chosen. Especially the initial rapid decrease of fluorescence intensity cannot be reproduced well. We should stress that these calculations were carried out under the assumption that the initial quencher distribution is random and independent of distance. However, from our point of view, this simplification is the main reason for the inadequacy of the model. The importance of the initial quencher distribution is evident from Fig. 4, where the results of the experimental decay curve at 1.0 M DMA concentration and the numerical calculations using the nonadiabatic sink term model with distance-dependent reaction rate for two different diffusion coefficients are plotted. In the simulations the parameter β was assumed to be 0.8 $Å^{-1}$ and the parameter k_E was 1.0×10^{11} s^{-1} (curves A) and 1.5×10^{11} s^{-1} (curves B). We found that the time dependence of the fluorescence at times shorter than 20 ps was essentially determined by β and k_E but not by D. Moreover, it can be concluded that within the first 10–20 ps the fluorescence quenching reaction is kinetically limited rather than diffusion controlled. This situation occurs when a fraction of the quencher is located sufficiently close to the fluorescer at the time of the excitation and should be extremely dependent on the quencher concentration and initial distribution.

The initial distribution of the $U(r,t)$ at the present stage of the model is assumed to be completely random. However, this simplification may be doubtful even if the ground state complex between fluorescer and quencher was not formed. It is well known that the radial distribution function (RDF) of liquids is much larger at the contact compared with that of the bulk. Under the high quencher concentration conditions, the deviation of $U(r,0)$ at short r from the uniform distribution of quencher should be significant. As we demonstrated, the possible nonrandom initial distribution can affect on the temporal evolution of the quenching reaction in shorter than 10 ps.

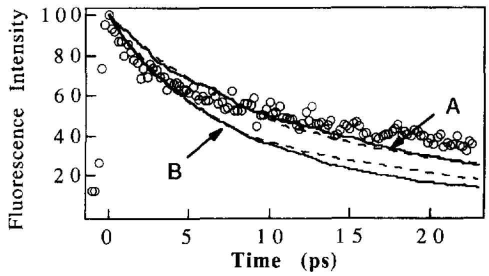

Fig. 4. The calculated decay curves by non-adiabatic sink term model with distance dependent reaction rate for the following sets of the parameters. (A) $D = 8.2 \times 10^{-5}$ cm^2 s^{-1}, $\beta = 0.8$ $Å^{-1}$, $k_E = 1.0 \times 10^{11}$ s^{-1} (solid line), $D = 1.6 \times 10^{-5}$ cm^2 s^{-1}, $\beta = 0.8$ $Å^{-1}$, $k_E = 1.0 \times 10^{11}$ $s-^{1}$ (dotted line). (B) $D = 8.2 \times 10^{-5}$ cm^2 s^{-1}, $\beta = 0.8$ $Å^{-1}$, $k_E = 1.5 \times 10^{11}$ s^{-1} (solid line), $D = 1.6 \times 10^{-5}$ cm^2 s^{-1}, $\beta = 0.8$ $Å^{-1}$, $k_E = 1.5 \times 10^{11}$ s^{-1} (dotted line). Circles are shown the experimental results for 1.0 M quencher concentration.

In order to introduce the nonrandom initial distribution of quencher, a radial distribution function of quencher molecules around the fluorescer molecule must be used. The RDF may be obtained from the molecular dynamics calculations [20], but we chose the easiest way where the RDF is approximated by the Boltzmann distribution following a Lennard-Jones (LJ) potential between fluorescer and quencher. Although it cannot reproduce the typical oscillating behavior of the RDF in liquids [21,22], the use of an LJ potential can be justified because the translational motion of the molecules, i.e. the distance they travel within the first 10–20 ps, remains almost under the peak area of the LJ potential. So, the first peak of the RDF can be approximated using the Boltzmann distribution obtained from the LJ potential. The LJ potential is expressed by the following equation:

$$\Phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{8}$$

where ε is a potential energy constant and σ is a potential length constant. The constant ε was estimated from a critical temperature, T_c [17]. Using the T_c of 687 K and 869.3 K for DMA and C151, respectively, we can obtain ε for pure liquids and then estimate ε between DMA and C151 as $\varepsilon = (\varepsilon_{DMA}\varepsilon_{C151})^{1/2}$. Since the ε thus obtained is known to give a lower limit, 420 cm^{-1} was used for our calculations. The potential length constant σ of the LJ potential was evaluated from the relation $\sigma = 0.89R$, where R is the critical distance between fluorescer and quencher.

The results of the calculations using the nonadiabatic sink term model are shown in Fig. 5. Curves A and B correspond to the random initial distribution and the initial distribution derived from the LJ potential, respectively. Solvent viscosity, molecular radii, and diffusion coefficient are common for each simulation. Because the LJ potential was used only for the initial distribution of quencher, the diffusion of the quencher molecules is not controlled by the LJ potential. In spite of such simplification, the simulation results for B reproduce the experimental data much better than do those for A. It is quite important that we can reproduce the experimental results over a wide range quencher concentration up to 1.0 M without changing solvent viscosity, molecular radii, and dif-

Table 3
Parameters k_E and β used in the calculation curves in Fig. 3

	Curve A	Curve B	Curve C	Curve D	Curve E
k_E/s^{-1}	1.0×10^{11}	1.5×10^{11}	1.5×10^{11}	2.0×10^{11}	2.0×10^{11}
β/m^{-1}	8.0×10^{9}	8.0×10^{9}	10.0×10^{9}	10.0×10^{9}	12.0×10^{9}

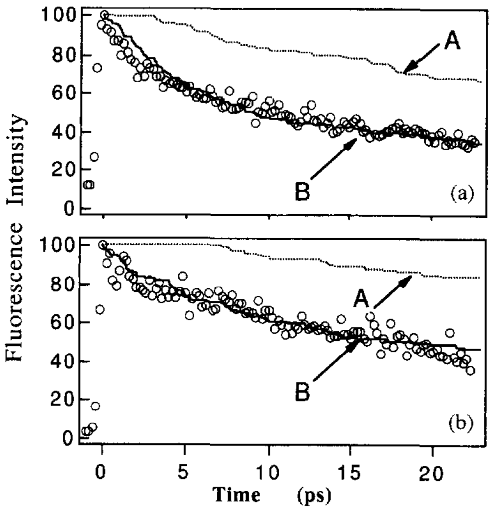

Fig. 5. The calculated decay curves for different quencher concentrations by non-adiabatic sink term model: (i) 1.0 M DMA; (ii) 0.5 M DMA. A (dotted lines): the initial quencher distribution is random. B (solid lines): the initial quencher distribution is Boltzmann distribution obtained from LJ potential. Circles are shown the experimental results.

fusion coefficient. The electron transfer rate of $3\times10^{10}\ \mathrm{s}^{-1}$ and $\beta = 1.0\ \text{Å}^{-1}$ estimated from the nonrandom initial distribution seems to lie in a reasonable range [23].

4. Conclusion

Neither the classical SK nor CK model can reproduce the quenching dynamics of C151/DMA system under the higher quencher concentrations with unified parameters at picosecond time scale. The nonadiabatic sink term model with distance-dependent reaction rate and random initial quencher distribution also failed to explain the data. If we introduce the short range order of liquid for the initial distribution of quencher, the agreement between the experimental data and the theoretical prediction was improved significantly. The rapid decay of fluorescence observed in the short time scale was reproduced even if we used D obtained at low concentrations of quencher. Indeed, the simple analyses used do not include the molecular structures and site chain orientational effects in the quenching reactions. Nevertheless, this treatment indicates generally the importance of including the RDF in the analyses of the quenching reactions in the subpicosecond to picoseconds time scale and for higher quencher concentrations, and opens a new stage for deeper understanding of transient effects in intermolecular fluorescence quenching reactions.

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