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Role of excitation lifetime in electron transfer reactions

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Abstract

Within the framework of the unified theory of electron transfer reactions in solutions the influence of lifetime of excitations on kinetics and quantum yields of ionization and recombination was studied. The effect of the lifetime on the shape of the initial ion distribution was analyzed and found to be very important when ionization is diffusionally controlled. The Stern–Volmer constant was also calculated and compared with one obtained within the contact approximation. © 1997 Elsevier Science S.A.

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1. Introduction

Photo-induced intra- and intermolecular electron transfer has been the subject of very extensive experimental and theoretical study in recent decades because of its dominant role in many important photochemical processes including conversion and storage of Solar energy. After light-induced excitation of an electron donor (D), an electron can be transferred to acceptor (A)

$$D^* + A \rightarrow [D^+ \cdots A^-] \qquad (1)$$

This bimolecular reaction is widely studied as an efficient mechanism of energy quenching in solution [1,2].

The ion pair produced by the photoionization may either recombine to the ground state or separate according to the kinetic scheme

$$[D \cdots A] \leftarrow [D^+ \cdots A^-] \rightarrow D^+ + A^- \qquad (2)$$

The unified theory of bimolecular ionization followed by geminate charge recombination and separation is now well developed [3–6]. The quantitative approach to kinetics of such consecutive reactions is based on the position dependent rates of electron transfer between the reactants separated by distance r. Both forward and backward transfers are activated processes

$$W_{\mathrm{I,R}}(r) = w_{\mathrm{I,R}}(r)\mathrm{e}^{-U/kT} \qquad (3)$$

where the subscripts I and R stand for ionization and recombination processes correspondingly. Activation energies in Eq. (3) are given by the Marcus' formula

$$U = \frac{(\Delta G + \lambda)^2}{4\lambda}$$

where ΔG is the free energy of the reaction and λ is the reorganization energy of the surroundings. In the region considered as "normal", $\Delta G > -\lambda$, the more exothermic reaction is the faster it proceeds. With further increase of $|\Delta G|$ into the region referred to as "inverted", $\Delta G < -\lambda$, the reaction rate decreases owing to the Arrhenius factor in Eq. (3). The rate is maximal between these regions (at $\Delta G = -\lambda$), where the reaction is activationless.

When the diffusion is fast and the bottleneck of the ionization is the transfer rate, Eq. (3), the reaction is kinetically controlled, and it may be expected that the stationary rate constant $k_{\mathrm{I}}(\infty) = k_{\mathrm{i}} \approx W_{\mathrm{I}}(\sigma)v$ reproduces general properties of the ionization rate W_{I} at the closest approach distance, σ (v is the volume of the contact reaction zone). Alternatively, at values of $\Delta G_{\mathrm{i}} = \Delta G_{\mathrm{I}}(\sigma)$ in some region around $-\lambda(\sigma)$ the transfer rate is large enough, and the reaction rate can be determined by the rate of bringing about the reactants, so that the reaction becomes diffusionally controlled. The measured rate is given then by diffusional rate constant $k_{\mathrm{D}} = 4\pi R_{\mathrm{Q}} D$, where D is the diffusion constant and R_{Q} is the effective ionization radius which depends on ΔG_{i} rather weakly [7].

The total quantum yield of free ions ϕ is determined by the ionization yield and the relative recombination and separation efficiencies. The last two quantities are affected by both the initial ion distribution and the diffusion rate. One has to note, however, that, while in course of the bimolecular ionization diffusion supports the reaction bringing about the reactants, in geminate recombination it also constitutes a

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competitive channel, the separation of ions shown by the right arrow in the kinetic scheme of Eq. (2).

In this work we study the effect of the lifetime of excitations on the reaction kinetics and quantum yield. Our consideration is based on numerical solution of the encounter theory equations which take account of remote electron transfer and provide a proper binary (low concentration of reactants) description of photo-induced ionization accompanied by recombination. We show that the effect at hand is two-fold. Decrease of the lifetime makes the excitation decay channel more effective compared with ionization, which obviously results in a decrease of ionization and consequently of total quantum yields. Within this context we also study the Stern–Volmer constant which characterizes the efficiency of excitation quenching. On the other hand, we show that, when the lifetime becomes shorter, the initial ion distributions shrink towards the contact, which can result in a decrease of the separation quantum yield. The latter effect is pronounced when a significant part of the distribution is outside the recombination layer. The decrease of lifetime shifts the distribution closer or even inside the recombination layer and the separation quantum yield can be suppressed by orders of magnitude.

2. Description of ionization and recombination processes

2.1. *Electron transfer rates*

Within the framework of conventional non-adiabatic perturbation theory of electron transfer with a single assisting mode [8] the pre-exponents in Eq. (3) are given by

$$w_{\mathrm{I,R}}(r) = \frac{\sqrt{\pi} V_{\mathrm{i,r}}^2}{\sqrt{\lambda T}} e^{-2(r-\sigma)/L} \tag{4}$$

where $V_{\mathrm{i,r}}$ are off-diagonal matrix elements of exchange interactions at the closest approach distances for ionization and recombination. For simplicity, in Eq. (4) we neglect the difference between the closest approach distances and spatial decrements, as well as matrix elements of the interactions, assuming the same σ, L and V for both forward and backward electron transfer. For the numerical calculation we assume throughout this paper $\sigma = 5$ Å, $L = 1$ Å and $W_{\mathrm{i,r}}(\sigma) = 10^3\ \mathrm{ns}^{-1}$.

The r-dependence of the rates in Eqs. (3) and (4) is rather complicated since both ΔG and λ depend on spatial coordinates. Indeed, for ionization we have

$$\Delta G_{\mathrm{I}}(r) = \Delta G_{\mathrm{I}}(\infty) - T\frac{r_{\mathrm{c}}}{r} = \Delta G_{\mathrm{i}} + T\frac{r_{\mathrm{c}}}{\sigma}\left(1 - \frac{\sigma}{r}\right) \tag{5}$$

where $r_{\mathrm{c}} = e^2/\epsilon kT$ is the Onsager radius for Coulomb attraction between ions, ϵ is the static dielectric constant, and ΔG_{i} is the ionization free energy at the contact distance. We assume the values characteristic for water, $\epsilon = 81$, $r_{\mathrm{c}} = 7$ Å.

The free energy of the recombination process is determined by conservation law

$$-\Delta G_{\mathrm{R}} - \Delta G_{\mathrm{I}} = \mathscr{E}_0 \tag{6}$$

where $\mathscr{E}_0$ is the excitation energy of the donor.

The reorganization energy of the solvent is expressed as

$$\lambda(r) = \lambda_{\mathrm{c}}\left(2 - \frac{\sigma}{r}\right) \qquad \lambda_{\mathrm{c}} = kT\frac{r_0 - r_{\mathrm{c}}}{\sigma} \tag{7}$$

where $\lambda_{\mathrm{c}} = \lambda(\sigma)$ is the contact reorganization energy ($55kT$ with the parameters chosen), $r_0 = e^2/\epsilon_0 kT$ is determined by the optical dielectric constant $\epsilon_0 \simeq 2$. In the following we restrict our consideration to outer-sphere reactions in polar solvents where Eq. (7) provides the main contribution to the total reorganization energy so that the reorganization energy of inner-sphere modes can be neglected.

A very important feature of the rates in Eqs. (3) and (4) is that only in normal region $\Delta G_{\mathrm{i,r}} > -\lambda_{\mathrm{c}}$ they show up the quasi-exponential behavior. In the inverted region, $\Delta G_{\mathrm{i,r}} < -\lambda_{\mathrm{c}}$, transfer rate (3) is not a monotonous function of coordinate and its maximum is shifted away from the contact [8].

2.2. *Unified theory*

The ionization of Eq. (1) which provides the initial conditions for subsequent competitive recombination and separation is described by the differential non-Markovian encounter theory (ET) [10]. This theory accounts for stochastic wandering of the reactants, occasionally entering the reaction zone. The total number of excited donors within ET obeys binary kinetic equation

$$\frac{\partial}{\partial t}N(t) = -k_{\mathrm{I}}(t)cN(t) - \frac{N}{\tau_{\mathrm{D}}} \tag{8}$$

where τ_{D} is the lifetime of excitation, c is the concentration of acceptors, $k_{\mathrm{I}}(t)$ is non-stationary ionization rate. Since ionization occurs with the rate of Eq. (3) at any distance, the time-dependent rate constant is defined as

$$k_{\mathrm{I}} = 4\pi \int W_{\mathrm{I}}(r) n(r,t) r^2\, \mathrm{d}r \tag{9}$$

where $n(r,t)$ is a pair distribution function of reactants. The encounter diffusion of neutral reactants with the diffusion coefficient D is described by equation

$$\frac{\partial}{\partial t}n(r,t) = -W_{\mathrm{I}}(r)n(r,t) + \frac{D}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}n(r,t) \tag{10}$$

with the constant initial and the reflecting boundary conditions

$$n(r,0) = 1 \qquad \left.\frac{\partial n(r,t)}{\partial r}\right|_{\sigma} = 0 \tag{11}$$

If created ions are immobile and do not recombine, the kinetic equation for the distribution function of ion pairs, $m(r,t)$, is simply

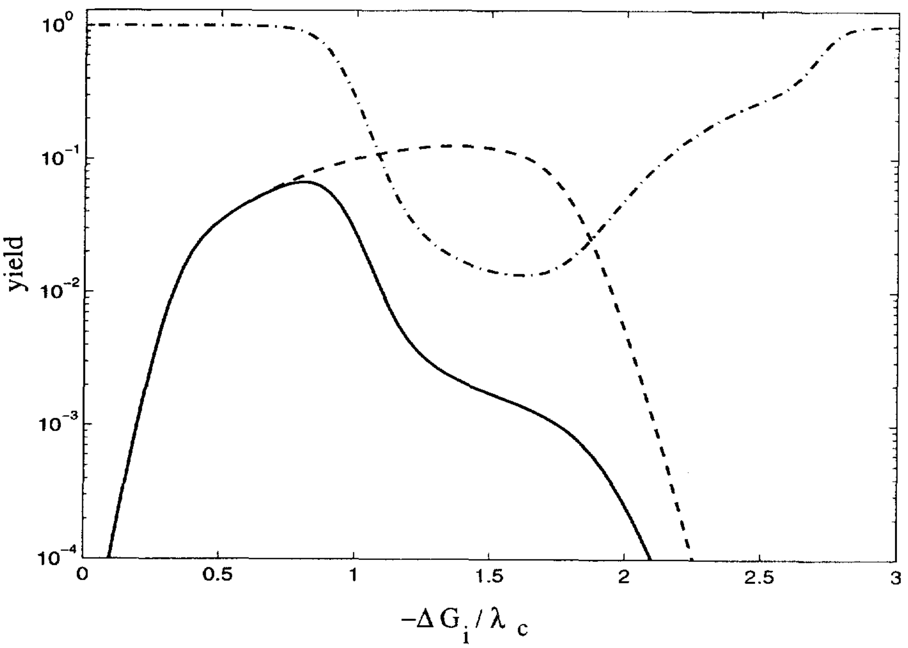

Fig. 1. Ionization yield ψ (dashed line), charge separation yield $\bar{\varphi}$ (dot-dashed line) and free ion yield $\phi = \psi \cdot \bar{\varphi}$ (solid line); $\mathscr{E}_0 = 3\lambda_c$, $\tau_D = 1$ ns, $D = 10^{-7}$ cm^2 s^{-1}, $W_i(\sigma) = 10^3$ ns^{-1}.

$$\frac{\partial}{\partial t} m(r,t) = W_I(r) n(r,t) N(t) \tag{12}$$

Under these conditions the stationary distribution of ions is

$$m_0(r) = m(r,\infty) = W_I(r) \int_0^{\infty} n(r,t) N(t)\, \mathrm{d}t \tag{13}$$

and the quantum yield of ionization is given by

$$\psi = 4\pi c \int_{\sigma}^{\infty} m_0(r) r^2\, \mathrm{d}r \tag{14}$$

It has been shown [5] that in the general case of competing ionization and recombination processes the total quantum yield of free charges (see example Fig. 1) is

$$\phi = \psi \bar{\varphi} \tag{15}$$

where ψ is the quantum yield of ionization process defined in Eq. (14), and the separation quantum yield is given by

$$\bar{\varphi} = 4\pi \int_{\sigma}^{\infty} \varphi(r) f_0(r) r^2\, \mathrm{d}r \tag{16}$$

Here, the normalized initial distribution of ions is

$$f_0(r) = m_0(r) \Big/ \int_{\sigma}^{\infty} m_0(r)\, \mathrm{d}^3 r \tag{17}$$

and position-dependent yield $\varphi(r)$ which characterizes separation of a geminate pair created at distance r, obeys the equation [9]

$$W_R(r)\varphi(r) = \frac{D}{r^2} \exp\left(\frac{-r_c}{r}\right) \frac{\partial}{\partial r} r^2 \exp\left(\frac{-r_c}{r}\right) \frac{\partial}{\partial r} \varphi(r)$$

$$\frac{\partial}{\partial r} \varphi(r) \,|_{r=0} = 0$$

$$\varphi(\infty) = 1 \tag{18}$$

Such a straightforward calculation of $\bar{\varphi}$ and hence the total yield ϕ is equivalent to more general scheme, involving solution of coupled system of equations for both $n(r,t)$, $N(t)$ and the distribution function of ions

$$\frac{\partial}{\partial t} m(r,t) = W_I(r) n(r,t) N(t) - W_R(r) m(r,t)$$

$$+ \frac{D}{r^2} \frac{\partial}{\partial r} r^2 \exp\left(\frac{r_c}{r}\right) \frac{\partial}{\partial r} \exp\left(\frac{-r_c}{r}\right) m(r,t) \tag{19}$$

with zero initial and reflecting boundary conditions

$$m(r,0) = 0 \quad \left. \frac{\partial}{\partial r} \exp\left(\frac{-r_c}{r}\right) m(r,t) \right|_{r=\sigma} = 0 \tag{20}$$

With the help of this solution one can determine the total amount of ion pairs

$$P(t) = 4\pi c \int_{\sigma}^{\infty} m(r,t) r^2\, \mathrm{d}r \tag{21}$$

and the total separation quantum yield is given then by $\bar{\varphi} = P(\infty)$. It is the latter scheme of calculation of $\bar{\varphi}$ that the numerical package at our disposal utilizes.

3. The role of the excitation lifetime

In the previous theoretical studies, the excitation lifetime τ_D in Eq. (8) was usually assumed to be infinite. However,

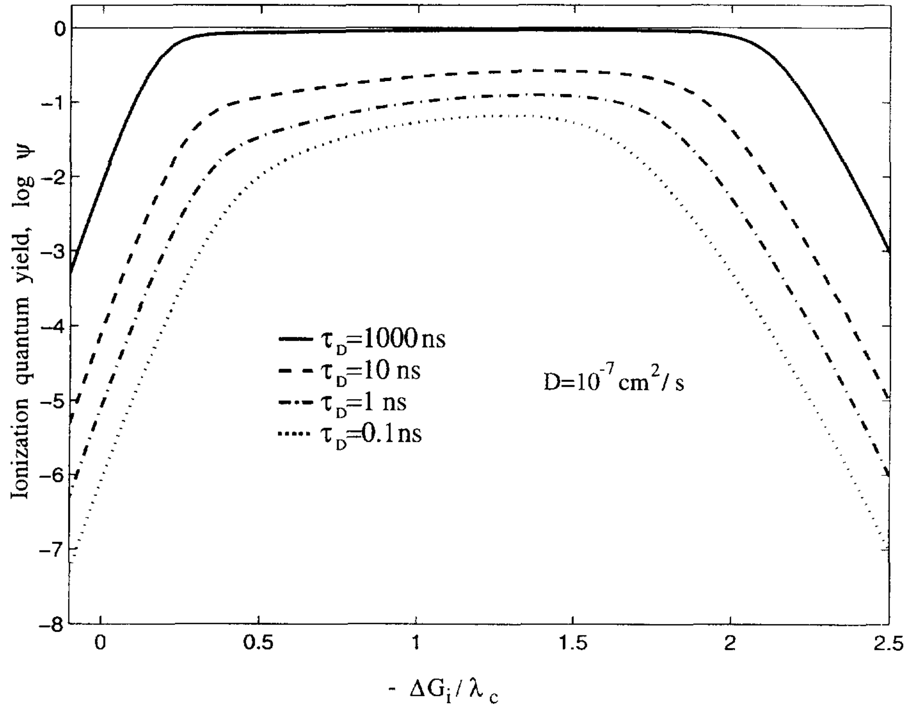

Fig. 2. Free energy dependence of ionization yield ψ at different τ_D.

in reality it strongly affects kinetics and quantum yields of ionization and recombination. At $\tau_D=\infty$ the quantum yield of ionization $\psi\equiv 1$, since ionization, regardless of its rate, is the only possible reaction channel. At finite τ_D the existence of the competitive quenching channel results not only in decrease of ψ, but also in changes of a shape of initial ion distribution $m_0(r)$; the latter in turn strongly affects the charge separation yield.

The evolution of ionization yield ψ with decrease of τ_D is presented in Fig. 2. The higher the activation energy is, the more suppression of ionization is pronounced, since the reaction rate of Eq. (3) is exponentially small for large U and the luminescence channel becomes relatively more efficient. It is useful to consider the complementary quantity, the quantum yield of luminescence,

$$\eta = 1-\psi = \frac{1}{\tau_D}\int_0^\infty N(t)\,\mathrm{d}t \tag{22}$$

In the limit of low concentration of acceptors the Stern–Volmer law

$$\eta = \frac{1}{1+ck_q\tau_D} \tag{23}$$

is approximately valid, where k_q is the quenching constant (concentration independent). Using the relation between η and ψ, the quenching constant can be calculated as

$$k_q = \frac{1}{c\tau_D}\left(\frac{1}{\eta}-1\right) = \frac{1}{c\tau_D\left(\frac{1}{\psi}-1\right)} \tag{24}$$

On the other hand, if the electron transfer reaction is assumed to proceed at the closest approach distance (contact approximation) then analytical expression for the quenching constant can be obtained [11]

$$k_q = \frac{k_0k_D}{k_D+\dfrac{k_0}{1+\sqrt{\tau_d/\tau_D}}} = \frac{k_0}{1+\dfrac{\tilde{\tau}_d}{1+\sqrt{\tilde{\tau}_d/\tilde{\tau}_D}}} \tag{25}$$

where $k_0 = 4\pi\int W_I(r)r^2\,\mathrm{d}r = k_I(0)$ is the kinetic rate constant, $k_D = 4\pi\sigma D$ is the diffusional rate constant within contact approximation, and encounter time is $\tau_d = \sigma^2/D$ (i.e. the latter is proportional to a solvent viscosity). Dimensionless times $\tilde{\tau}_d$, $\tilde{\tau}_D$ are in units of $\tau_0 = 4\pi\sigma^3/k_0$. The quenching constant of Eq. (25) is plotted versus $\tilde{\tau}_d \sim 1/D$ in Fig. 3 for several values of τ_D. At $\tau_D=\infty$, k_q coincides with the stationary rate constant of contact approximation $k_i = k_I(\infty) = k_0/(1+\tilde{\tau}_d)$. As soon as $\tau_D \ll \tau_d$ the viscosity dependence of k_q is more smooth, $k_q \simeq k_0/(1+\sqrt{\tilde{\tau}_d\tilde{\tau}_D})$.

In Fig. 4 we compare the analytical curves for contact quenching with the results of our calculations for remote electron transfer at two values of $\tau_D = 0.1$, 100 ns (at $-\Delta G_i = 0.55\lambda_c$, $\tau_0 = 0.23$ ns). It is clear that in the static limit ($\tau_d \to \infty$) Eq. (25) is inapplicable, since k_q tends to zero, while in the case of remote electron transfer the quenching constant is finite in this limit. However, one can see from the Fig. 4 that at small τ_D the contact approximation fails to predict the value of quenching constant even when diffusion is rather fast, $\tilde{\tau}_d \sim 1$. The reason is that at small τ_D the quenching constant is completely determined by initial, non-stationary stage of ionization which is more sensible to whether the quenching is contact or remote.

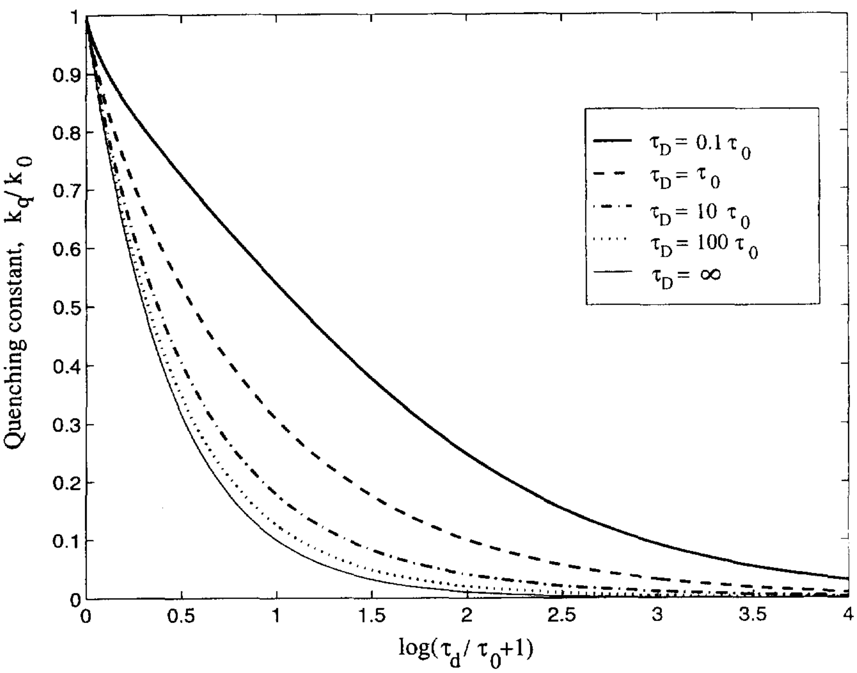

Fig. 3. Viscosity dependence of quenching constant k_q within contact approximation at different excitation lifetimes ($\tau_d/\tau_0 = k_0/k_D \sim \eta$).

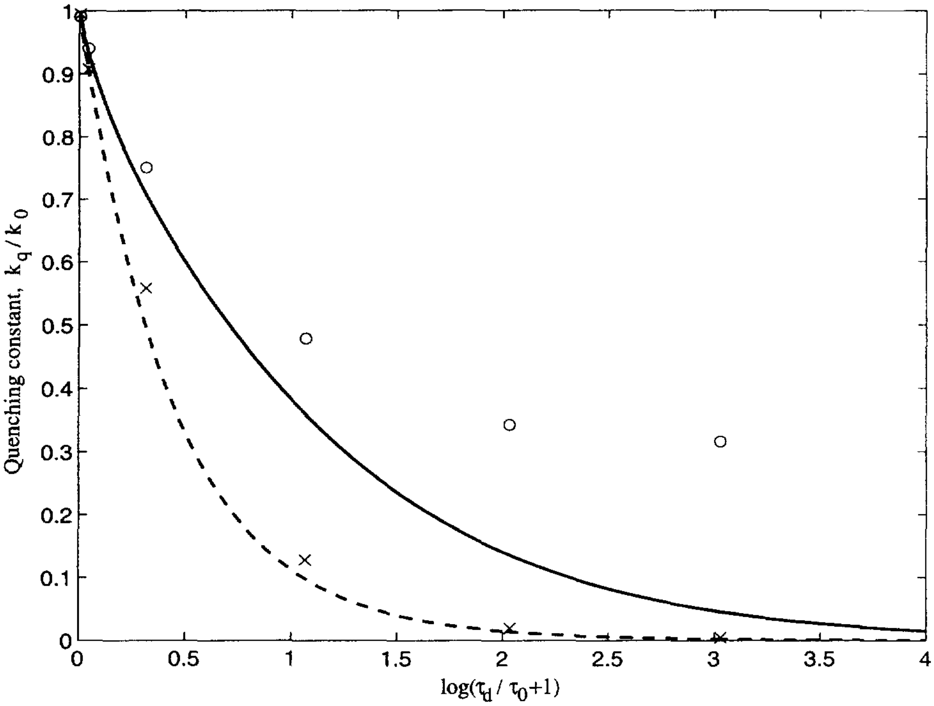

Fig. 4. The quenching constant at $\tau_D = 0.1$ ns within contact approximation (solid line) and within encounter theory (open circles). The same for $\tau_D = 100$ ns (dashed line, contact approximation; crosses, encounter theory). $\tau_0 = 0.23$ ns.

Let us now consider the τ_D dependence of ion distribution $m_0(r)$ (Fig. 5), which serves as the initial condition for geminate recombination. If ionization is kinetically controlled, then the pair distribution function $n(r,t)$ remains uniform at any time and $m_0(r)$ from Eq. (13) reproduces the shape of the position-dependent ionization rate $W_I(r)$. The situation is completely different if the ionization is diffusionally controlled. At large τ_D the contribution of initial non-stationary stage of the reaction is negligible. In the course of the reaction the population of excitations in the vicinity of an acceptor decreases fast, approaching stationary distribution $n_s(r)$ which is almost zero in the reaction sphere of radius R_Q. The ions are created in a thin layer adjusted to R_Q, where the maximum of $m_0(r)$ is hence pinned. With decrease of the excitation lifetime, the contribution of the initial stage becomes more important, because a larger share of excitations decay before the stationary reaction regime is established. At short enough τ_D the distribution $n(r,t)$ has no time to deviate

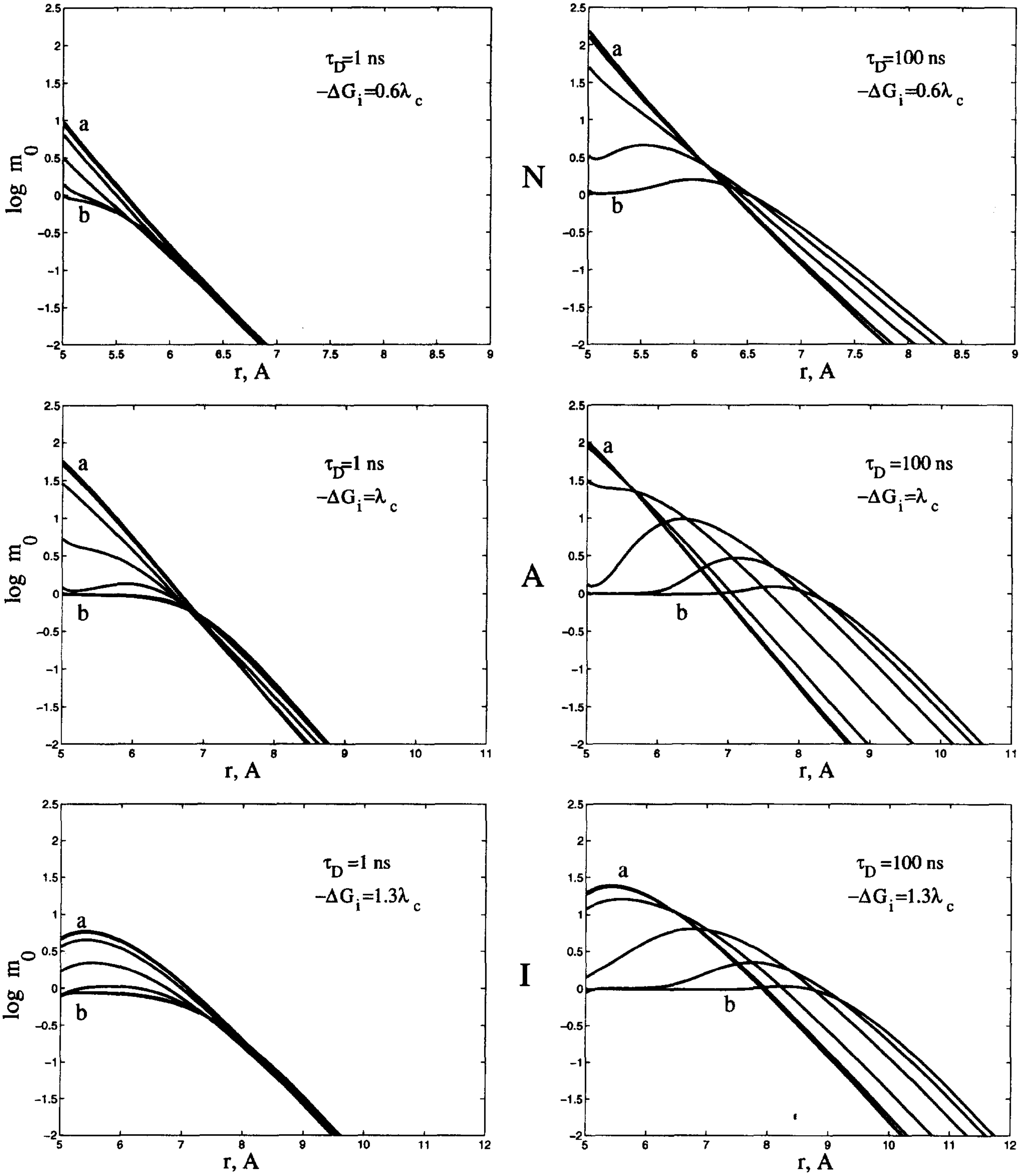

Fig. 5. Initial ion distribution $m_0(t)$ at $\tau_D = 100$ ns and $\tau_D = 1$ ns and different diffusion coefficients $D = 10^{-3}$ (labelled 'a'), 10^{-4}, ..., 10^{-9} (labelled 'b') cm^2 s^{-1} (from top to bottom at contact distance in each subplot) for normal (N), activationless (A) and inverted (I) ionization.

essentially from the uniform one and then the distribution of products $m(r,t)$ reproduces the shape of $W_I(r)$. As the result the maximum of $m_0(r)$ either disappears (in normal region, $\Delta G_i > -\lambda_c$) or coincides with that of $W_I(r)$ (in inverted region, $\Delta G_i < -\lambda_c$).

The effect of decrease of excitation lifetime on the separation quantum yield φ is illustrated in Fig. 6 for excitation energies $\mathscr{E}_0 = \lambda_c$, $2\lambda_c$, and $3\lambda_c$. Each plot is accompanied by one illustrating ΔG_i dependence of

$$X = 1/\phi - 1 \qquad (26)$$

Within the oversimplified "exponential model" this quantity follows the parabolic dependence of $\ln W_r(\sigma)$ on ΔG_r, but in reality this is true only for kinetically controlled recombi-

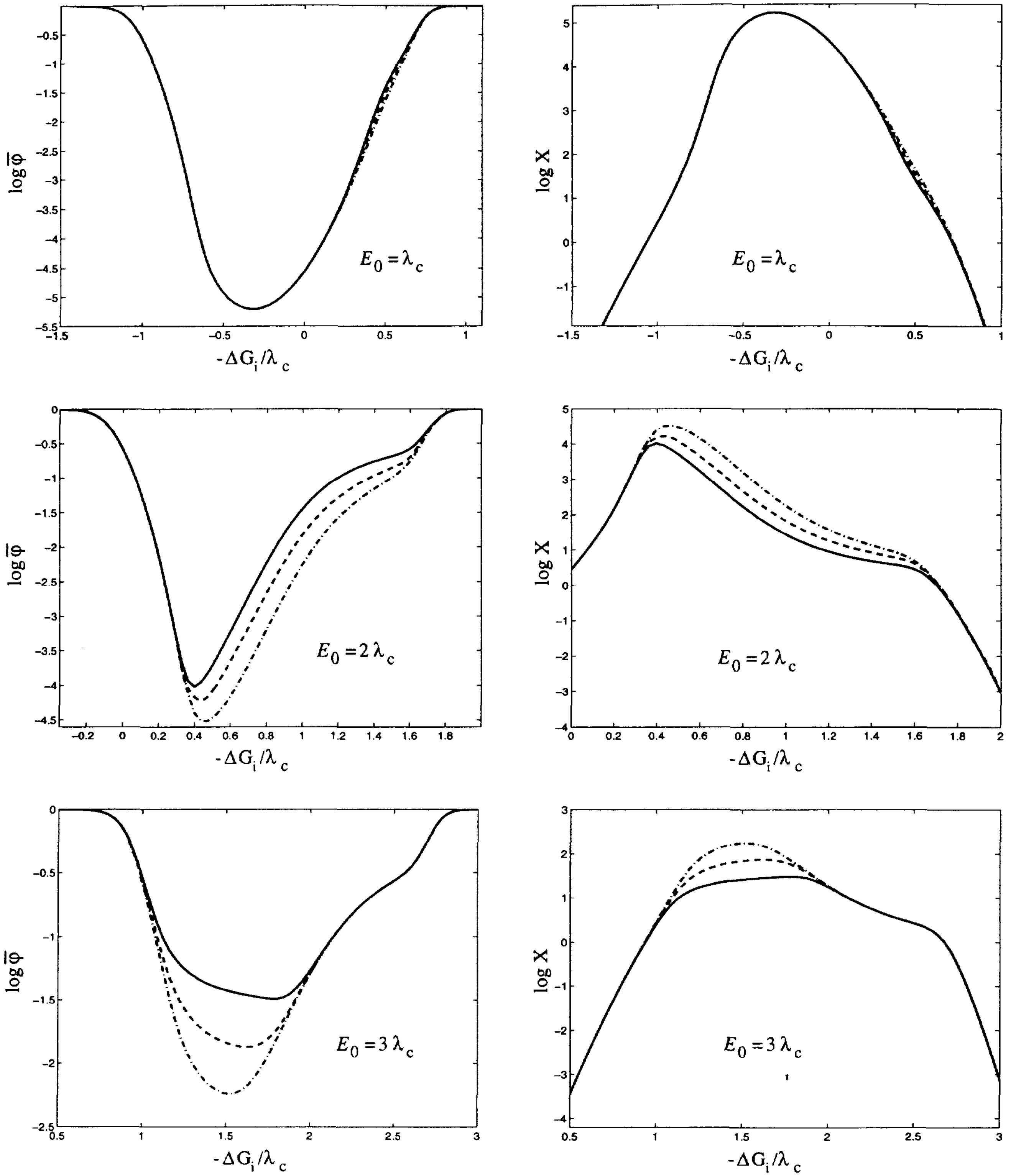

Fig. 6. Charge separation yield $\bar{\varphi}$ and $X = 1/\bar{\varphi} - 1$ versus ionization free energy for $\mathscr{E}_0 = \lambda_c$, $\mathscr{E}_0 = 2\lambda_c$ and $\mathscr{E}_0 = 3\lambda_c$ at $\tau_D = 100$ ns (solid line), $\tau_D = 1$ ns (dashed line) and $\tau_D = 0.1$ (dot-dashed line). Diffusion coefficient $D = 10^{-7}$ cm^2 s^{-1}.

nation [5]. The effect of finite lifetime should be expected only in some range of $-\Delta G_i$ near λ_c, in which ionization is diffusionally controlled and hence the location of ion creation layer is τ_D dependent. If ions are created inside the recombination layer, then the shape of $m_0(r)$ does not affect the charge separation yield [12]. The deformation of $m_0(r)$ due to fast excitation decay is essential only in case when ions are generated outside the recombination layer and their delivery to the latter is diffusionally controlled. Ionization and recombination are the fastest at $\Delta G_i = -\lambda_c$ and $\Delta G_r = -\lambda_c$ (i.e. $\Delta G_i = \lambda_c - \mathscr{E}_0$) correspondingly. Hence the effect of short excitation decay time should be looked for in a vicinity of $-\Delta G_i = -\Delta G_r = \mathscr{E}_0/2$, when the electron transfer is expected to be diffusionally controlled. This conclusion is fully confirmed by the results presented in Fig. 6: the most significant deviations are always near the point $-\Delta G_i = \mathscr{E}_0/2$.

One can see that with the parameters chosen, the effect is weak at $\mathscr{E}_0 = \lambda_c$. The reason is that ionization becomes diffusionally controlled when $-\Delta G_i$ exceeds $0.4\lambda_c$, but the recombination in this range of ΔG_i switches to kinetic control. Alternatively, at $\mathscr{E}_0 = 2\lambda$ ionization and recombination are simultaneously diffusionally controlled in the same range of ΔG_i and the separation yield is strongly suppressed by shortening the excitation lifetime. At $\mathscr{E}_0 = 3\lambda$ the recombination becomes noticeable when ionization is already under diffusional control, at $-\Delta G_i > \lambda_c$. The effect develops fast with further increase of $|\Delta G_i|$, because the recombination becomes faster and switches to diffusional control. When $-\Delta G_i$ exceeds $2\lambda_c$ the ionization becomes kinetically controlled and the effect disappears, in spite of rather fast recombination.

4. Summary

Within the framework of encounter theory we analyzed the effect of finite lifetime of excitations on the kinetics and quantum yields of bimolecular ionization followed by geminate recombination. We found that the effect is two-fold. In addition to obvious suppression of ionization quantum yield with decrease of τ_D, we observed considerable changes in initial distributions of ions, which in turn can strongly affect the separation quantum yield. If ionization is kinetically controlled, then the effect is absent since $m_0(r)$ is pinned on $W_I(r)$ regardless of the value of τ_D. However, if ionization is diffusionally controlled then with decrease of τ_D the initial ion distribution shifts towards the $W_I(r)$ contour, strongly affecting the charge separation yield, provided the recombination is also diffusionally controlled. The suppression can amount to orders of magnitude if diffusional control is well pronounced for both ionization and recombination.

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