Diffusion-influenced reversible geminate recombination in one dimension. III. Field effect on the excited-state reaction

Hyojoon Kim[a)] and Kook Joe Shin[b)]
School of Chemistry, Seoul National University, Seoul 151-747, Korea

(Received 13 January 2004; accepted 20 February 2004)

We obtain exact analytic solutions of the diffusion-influenced excited-state reversible geminate recombination reaction, $A^*+B\leftrightarrow(AB)^*$, with two different lifetimes and quenching under the influence of a constant external field in one dimension. These fundamental solutions generalize two previous results [Kim *et al.*, J. Chem. Phys. **111**, 3791 (1999); **114**, 3905 (2001)] and provide us with the insight necessary to analyze their specific relations and asymptotic kinetic transition behaviors. We find that the number of kinetic transitions can be changed due to interplay between the field strength and lifetimes. Unlike the previous works, the number of lifetime dependent transitions is found to be one or zero. On the other hand, the number of the field dependent transitions becomes two, one, or zero. We find a new pattern of kinetic transition $e^t \to t^{-1/2} \to e^t$ when there is only one field dependent transition. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1704632]

I. INTRODUCTION

Recently Gopich and Agmon[1,2] found that an interesting kinetic transition behavior can be observed at long times for a diffusion-influenced excited-state reversible germinate recombination when the lifetimes of reactant and product are different. Agmon[3] extended the results to the case with a competing quenching process. At nearly the same time, Kim and Shin[4] found a way to obtain the exact Green functions or the fundamental solutions for geminate reversible reaction in three dimensions (3D). This result led Gopich and Agmon[5] to find the exact solutions including two different lifetimes and quenching in 3D. This theoretical prediction of the kinetic transition was confirmed experimentally with the kinetics of excited-state proton transfer from a photoacid to solvent.[6]

On the other hand, Kim *et al.*[7] (Part I) were successful to obtain the exact results of the excited-state geminate recombination in one dimension (1D) and found that the different lifetime effect can cause the similar kinetic transition behavior in 1D as well as in 3D. The exact results in 1D are important not only because they can be applied to a class of effectively 1D systems such as polymers or DNA chains[8–10] but also because they are practically useful to obtain the numerical results for the nongeminate case by the efficient Brownian dynamics simulations.[11–16] Later on, Kim *et al.*[17] (Part II) proved that the external field could also cause kinetic transitions by obtaining the exact solutions considering both the reversibility and the external field effect in the ground-state geminate system. They noted an interesting mathematical isomorphism between solutions of Part I and Part II.

Then, it is a natural question what effect the external field can give to the dynamics in the excited-state geminate reversible recombination. The main purpose of the present paper is to obtain the general exact solutions by combining the previous works of Part I with Part II. The general solutions can give us the straight answer for the external field effect on the excited-state geminate system as well as the theoretical insight about the interplay between the field and lifetime effects. Indeed, we find that the field effect can destroy the lifetime-dependent kinetic transition of Part I and the lifetime effect can play a destructive role in the field-dependent kinetic transitions of Part II. Thus, we will show that the number of asymptotic kinetic transitions can be changed as the values of lifetime or the field strength are varied.

This paper is organized as follows: We obtain the exact solutions in Sec. II and three special cases are investigated in Sec. III. Long-time asymptotic behaviors are obtained in Sec. IV and the numerical results are discussed in Sec. V followed by concluding remarks in Sec. VI.

II. EXACT SOLUTIONS

Consider a pair of point particles, an electronically excited A^* particle and a ground state B particle diffusing on a line under the influence of a constant external field. When two particles collide, they can associate with the intrinsic rate constant k_a into the excited-state bound pair $(AB)^*$, which can dissociate reversibly with the rate k_d. The competing contact quenching reaction with the rate k_q can also occur. The excited-states A^* and $(AB)^*$ can decay to their ground state with the rate k_0' and k_0, respectively. The present mechanism can be depicted as follows:

$$A^*+B \underset{k_d}{\overset{k_a}{\rightleftarrows}} (AB)^*, \tag{2.1}$$

a)Present address: Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas.
b)Author to whom correspondence should be addressed. Electronic mail: statchem@plaza.snu.ac.kr

$$A^* + B \xrightarrow{k_q} A + B, \tag{2.2}$$

$$(AB)^* \xrightarrow{k_0} AB, \tag{2.3}$$

$$A^* \xrightarrow{k_0'} A. \tag{2.4}$$

Let $p(x,t)$ be the probability density for observing the particles separated by a distance x at time t. The following diffusion equation can describe the present system:

$$\frac{\partial p(x,t)}{\partial t} = D\left(\frac{\partial^2}{\partial x^2} + 2a\frac{\partial}{\partial x}\right)p(x,t) - k_0' p(x,t), \tag{2.5}$$

where D is the relative diffusion constant and a determines the magnitude of the external field. A positive value of a makes the pair prefer getting close to each other. The boundary conditions are given by

$$D\left[\frac{\partial p(x,t)}{\partial x} + 2ap(x,t)\right]_{x=0} = (k_a + k_q)p(0,t) - k_d p(*,t), \tag{2.6}$$

$$p(\infty,t) = 0. \tag{2.7}$$

Let $p(*,t)$ denote the binding probability which obeys the following time evolution equation

$$\frac{\partial}{\partial t}p(*,t) = k_a p(0,t) - (k_d + k_0)p(*,t). \tag{2.8}$$

Initial conditions of the pair in the bound and unbound state at $x = x_0$ are given, respectively, by

$$p(x,0|*) = 0, \quad p(*,0|*) = 1. \tag{2.9}$$

$$p(x,0|x_0) = \delta(x - x_0), \quad p(*,0|x_0) = 0. \tag{2.10}$$

As Smoluchowski noted,[17,18] the above equations can be more tractable utilizing the following transformations,

$$q(x,t|x_0) = \exp[a(x - x_0 + aDt)]p(x,t|x_0), \tag{2.11}$$

$$q(*,t|x_0) = \exp[a(-x_0 + aDt)]p(*,t|x_0), \tag{2.12}$$

$$q(x,t|*) = \exp[a(x + aDt)]p(x,t|*), \tag{2.13}$$

$$q(*,t|*) = \exp[a^2 Dt]p(*,t|*). \tag{2.14}$$

Thus, Eqs. (2.5), (2.6), and (2.8) can be transformed to

$$\frac{\partial q(x,t)}{\partial t} = D\frac{\partial^2 q(x,t)}{\partial x^2} - k_0' q(x,t), \tag{2.15}$$

$$D\frac{\partial}{\partial x}q(x,t)\bigg|_{x=0} = (k_a + k_q - aD)q(0,t) - k_d q(*,t), \tag{2.16}$$

$$\frac{\partial}{\partial t}q(*,t) = k_a q(0,t) - (k_d + k_0 - a^2 D)q(*,t). \tag{2.17}$$

If Eqs. (2.15)–(2.17) are compared with Eqs. (2.9) and (2.10) in Part II, a mathematical isomorphism can be invoked again. Thus we can get the Laplace transformed Green function $\tilde{p}(x,s|x_0) = \int_0^\infty p(x,t|x_0)\exp(-st)dt$ using relation (2.11) and replacing k_q and k_0 in Eq. (2.13) of Part I with $k_q - aD$ and $k_0 - a^2 D$, respectively,

$$\begin{aligned}\tilde{q}(x,s-k_0'|x_0) &= e^{a[x-x_0]}\tilde{p}(x,s-k_0'-a^2D|x_0) = \tilde{f}(x,s|x_0) \\ &\quad - \frac{(\alpha_1+\alpha_2+\alpha_3)\sqrt{D}s + \alpha_1\alpha_2\alpha_3 D\sqrt{D}}{(\sqrt{s}+\alpha_1\sqrt{D})(\sqrt{s}+\alpha_2\sqrt{D})(\sqrt{s}+\alpha_3\sqrt{D})} \\ &\quad \times \frac{e^{-(x+x_0)\sqrt{s/D}}}{\sqrt{Ds}},\end{aligned} \tag{2.18}$$

$$\tilde{f}(x,s|x_0) = \frac{1}{2\sqrt{Ds}}[e^{-|x-x_0|\sqrt{s/D}} + e^{-(x+x_0)\sqrt{s/D}}], \tag{2.19}$$

where $\tilde{f}(x,s|x_0)$ is the Laplace transformed Green function for the reflecting boundary (all rate constants and a are 0) and α_1, α_2, and α_3 are roots satisfying the following relations:

$$b_1 \equiv \alpha_1 + \alpha_2 + \alpha_3 = (k_a + k_q)/D - a, \tag{2.20}$$

$$b_2 \equiv \alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1 = (k_0 - k_0' + k_d)/D - a^2, \tag{2.21}$$

$$\begin{aligned}b_3 \equiv \alpha_1\alpha_2\alpha_3 = [&(k_0 - k_0' - a^2 D)(k_a + k_q - aD) \\ &+ k_d(k_q - aD)]/D^2.\end{aligned} \tag{2.22}$$

We can get the roots by solving the cubic equation[19]

$$\alpha_1 = A_1 + A_2 + \frac{b_1}{3}, \tag{2.23}$$

$$\alpha_2 = -\frac{1}{2}(A_1 + A_2) + \frac{b_1}{3} + \frac{i\sqrt{3}}{2}(A_1 - A_2), \tag{2.24}$$

$$\alpha_3 = -\frac{1}{2}(A_1 + A_2) + \frac{b_1}{3} - \frac{i\sqrt{3}}{2}(A_1 - A_2), \tag{2.25}$$

where $A_1 = \sqrt[3]{B_2 + \sqrt{B_1^3 + B_2^2}}$, $A_2 = \sqrt[3]{B_2 - \sqrt{B_1^3 + B_2^2}}$, $B_1 = (3b_2 - b_1^2)/9$, and $B_2 = (27b_3 - 9b_1b_2 + 2b_1^3)/54$.

We find that the following amusing relations hold:

$$b_3 = b_1 b_2 - k_a k_d/D^2, \tag{2.26}$$

$$(\alpha_1 + \alpha_2)(\alpha_2 + \alpha_3)(\alpha_3 + \alpha_1) = k_a k_d/D^2, \tag{2.27}$$

$$(\alpha_2 + \alpha_3)(\alpha_1^2 b_1 + b_3) = \alpha_1 k_a k_d/D^2, \tag{2.28}$$

$$(\alpha_1 + a)(\alpha_2 + a)(\alpha_3 + a)D^2 = (k_0 - k_0')(k_a + k_q) + k_d k_q, \tag{2.29}$$

$$\begin{aligned}&(\alpha_1 - a)(\alpha_2 - a)(\alpha_3 - a)D^2 \\ &\quad = (k_0 - k_0')(k_a + k_q) + k_d k_q - 2aD(k_0 - k_0' + k_d).\end{aligned} \tag{2.30}$$

In the time domain the Green function in the present system becomes

$$q'(x,t|x_0) = e^{a(x-x_0+aDt)}e^{k_0't}p(x,t|x_0) = f(x,t|x_0)+\sum_{i=1}^{3}\alpha_i(\alpha_k+\alpha_i)(\alpha_i+\alpha_j)\Phi_{ijk}(x+x_0), \tag{2.31}$$

where

$$\Phi_{ijk}(x)=\frac{1}{(\alpha_k-\alpha_i)(\alpha_i-\alpha_j)}W\left(\frac{x}{\sqrt{4Dt}},\alpha_i\sqrt{Dt}\right), \tag{2.32}$$

$$W(x,y)=\exp(2xy+y^2)\operatorname{erfc}(x+y) \tag{2.33}$$

and $i\neq j\neq k=1,2,3$. Here we define $q'\equiv e^{k_0't}q$ and erfc(x) is the complementary error function. We call $q'(x,t)$ by the *effective* Green function. One can note that $W(0,\alpha_i\sqrt{Dt}) = \exp(\alpha_i^2 Dt)\operatorname{erfc}(\alpha_i\sqrt{Dt})$.

The binding probabilities can be calculated in the same way as above. The expressions of the binding probability of initially unbound state in the Laplace domain and the time domain are given by

$$\tilde{q}(*,s-k_0'|x_0)=\frac{k_a}{(\sqrt{s}+\alpha_1\sqrt{D})(\sqrt{s}+\alpha_2\sqrt{D})(\sqrt{s}+\alpha_3\sqrt{D})}\times\frac{e^{-x_0\sqrt{s/D}}}{\sqrt{D}}, \tag{2.34}$$

$$q'(*,t|x_0)=\frac{k_a}{D}\sum_{i=1}^{3}\alpha_i\Phi_{ijk}(x_0). \tag{2.35}$$

For the binding probability of initially bound state, we get

$$\tilde{q}(*,s-k_0'|*)=\frac{\sqrt{s}+b_1\sqrt{D}}{(\sqrt{s}+\alpha_1\sqrt{D})(\sqrt{s}+\alpha_2\sqrt{D})(\sqrt{s}+\alpha_3\sqrt{D})}, \tag{2.36}$$

$$q'(*,t|*)=\sum_{i=1}^{3}\alpha_i(\alpha_j+\alpha_k)\Phi_{ijk}(0). \tag{2.37}$$

The probability function $p(x,t|*)$ can be obtained by the detailed balance condition

$$p(x,t|*)=k_d e^{-2ax_0}p(*,t|x)/k_a, \tag{2.38}$$

which can be simplified for the effective probability functions as

$$k_a q'(x,t|*)=k_d q'(*,t|x). \tag{2.39}$$

Let us define the survival probability of the unbound or bound state by

$$S(t|x_0 \text{ or } *)=\int_0^\infty p(x,t|x_0 \text{ or } *)dx. \tag{2.40}$$

The present survival probabilities have different structures from those in the previous works because the latter correspond formally to the integration procedure of $p(x,t)e^{ax}$ over x [see Eq. (2.18)]. Their expressions in the Laplace and time domains are given by

$$e^{-ax_0}\tilde{S}(s-k_0'-a^2D|x_0)=\frac{e^{-ax_0}}{s-a^2D}-\frac{a\sqrt{D}}{\sqrt{s}(s-a^2D)}e^{-x_0\sqrt{s/D}} - \frac{b_1\sqrt{D}s+b_3D\sqrt{D}}{(\sqrt{s}+\alpha_1\sqrt{D})(\sqrt{s}+\alpha_2\sqrt{D})(\sqrt{s}+\alpha_3\sqrt{D})(\sqrt{s}+a\sqrt{D})\sqrt{s}}e^{-x_0\sqrt{s/D}}, \tag{2.41}$$

$$\begin{aligned} S'(t|x_0) &\equiv e^{k_0't}e^{-ax_0+a^2Dt}S(t|x_0) \\ &= e^{-ax_0+a^2Dt}-\frac{1}{2}W\left(\frac{x_0}{\sqrt{4Dt}},-a\sqrt{Dt}\right) \\ &\quad -\frac{(\alpha_1+a)(\alpha_2+a)(\alpha_3+a)}{2(\alpha_1-a)(\alpha_2-a)(\alpha_3-a)}W\left(\frac{x_0}{\sqrt{4Dt}},a\sqrt{Dt}\right) \\ &\quad -\sum_{i=1}^{3}\frac{\alpha_i(\alpha_k+\alpha_i)(\alpha_i+\alpha_j)}{(\alpha_i-a)}\Phi_{ijk}(x_0), \end{aligned} \tag{2.42}$$

$$\tilde{S}(s-k_0'-a^2D|*) = \frac{k_d}{(\sqrt{s}+\alpha_1\sqrt{D})(\sqrt{s}+\alpha_2\sqrt{D})(\sqrt{s}+\alpha_3\sqrt{D})(\sqrt{s}+a\sqrt{D})}, \tag{2.43}$$

$$\begin{aligned} S'(t|*)\frac{D}{k_d} &\equiv e^{k_0't+a^2Dt}S(t|*)\frac{D}{k_d} \\ &= \frac{-a}{(\alpha_1-a)(\alpha_2-a)(\alpha_3-a)}W(0,a\sqrt{Dt}) \\ &\quad -\sum_{i=1}^{3}\frac{\alpha_i}{(\alpha_i-a)}\Phi_{ijk}(0). \end{aligned} \tag{2.44}$$

Here we similarly define the effective survival probability, $S'(t|x_0 \text{ or } *)$.

The generalized normalization condition does not depend on the field strength and, therefore, is the same as in Part I,

$$(s+k_0')\tilde{S}(s)+(s+k_0)\tilde{p}(*,s)+k_q\tilde{p}(0,s)=1. \tag{2.45}$$

In the time domain, this condition can be rewritten as

$$[S(t)+p(*,t)]e^{k_0' t}=1-(k_0-k_0')\int_0^t p(*,t)e^{k_0' t}dt -k_q\int_0^t p(0,t)e^{k_0' t}dt. \tag{2.46}$$

III. SPECIAL CASES

The general exact results in the previous section contain complicated expressions of the roots. In some special cases, the roots and, thus, the results can be simplified. Here we consider the following three important cases.

A. The transition region

One can see from Eq. (2.22) that at least one of the roots vanishes when

$$(k_0-k_0'+k_d-a^2D)(k_a+k_q-aD)=k_a k_d. \tag{3.1}$$

As in Parts I and II, the transition behavior can appear in this case. Suppose that the vanishing root is α_3, then

$$\alpha_1+\alpha_2=(k_a+k_q)/D-a, \tag{3.2}$$

$$\alpha_1\alpha_2=(k_0-k_0'+k_d)/D-a^2. \tag{3.3}$$

If we define $\Delta_1^2 \equiv (k_a+k_q-aD)^2-4[(k_0-k_0'+k_d)-a^2D]$, the two roots can be rewritten as

$$2D\alpha_1=k_a+k_q-aD+\Delta_1, \tag{3.4}$$

$$2D\alpha_2=k_a+k_q-aD-\Delta_1. \tag{3.5}$$

The binding and survival probabilities for this case can be easily obtained by substituting these roots,

$$q'(x,t|x_0)=f(x,t|x_0)+\frac{\alpha_1+\alpha_2}{\alpha_1-\alpha_2}\left[\alpha_2 W\left(\frac{x+x_0}{\sqrt{4Dt}},\alpha_2\sqrt{Dt}\right) -\alpha_1 W\left(\frac{x+x_0}{\sqrt{4Dt}},\alpha_1\sqrt{Dt}\right)\right], \tag{3.6}$$

$$q'(*,t|x_0)=\frac{k_a}{D(\alpha_1-\alpha_2)}\left[W\left(\frac{x_0}{\sqrt{4Dt}},\alpha_2\sqrt{Dt}\right) -W\left(\frac{x_0}{\sqrt{4Dt}},\alpha_1\sqrt{Dt}\right)\right], \tag{3.7}$$

$$q'(*,t|*)=\frac{1}{\alpha_1-\alpha_2}[\alpha_1 W(0,\alpha_2\sqrt{Dt})-\alpha_2 W(0,\alpha_1\sqrt{Dt})], \tag{3.8}$$

$$S'(t|x_0)=e^{-ax_0+a^2Dt}-\frac{1}{2}W\left(\frac{x_0}{\sqrt{4Dt}},-a\sqrt{Dt}\right) +\frac{(\alpha_1+a)(\alpha_2+a)}{2(\alpha_1-a)(\alpha_2-a)}W\left(\frac{x_0}{\sqrt{4Dt}},a\sqrt{Dt}\right) -\frac{\alpha_1+\alpha_2}{\alpha_1-\alpha_2}\left[\frac{\alpha_2}{\alpha_2-a}W\left(\frac{x_0}{\sqrt{4Dt}},\alpha_2\sqrt{Dt}\right) -\frac{\alpha_1}{\alpha_1-a}W\left(\frac{x_0}{\sqrt{4Dt}},\alpha_1\sqrt{Dt}\right)\right], \tag{3.9}$$

$$S'(t|*)\frac{D}{k_d}=\frac{1}{(\alpha_1-a)(\alpha_2-a)}W(0,a\sqrt{Dt}) -\frac{1}{\alpha_1-\alpha_2}\left[\frac{1}{\alpha_2-a}W(0,\alpha_2\sqrt{Dt}) -\frac{1}{\alpha_1-a}W(0,\alpha_1\sqrt{Dt})\right]. \tag{3.10}$$

Note that $\alpha_1-\alpha_2=\Delta_1/D$.

B. Irreversible case

For the irreversible case $k_d=0$ or $k_a=0$. Thus $k_a k_d=0$ and $b_3=b_1 b_2$ as can be seen from Eq. (2.26). One can also see from Eq. (2.27) that one of the summations of two roots vanishes. Suppose that $\alpha_1+\alpha_2=0$, then the roots are given by

$$\alpha_1=-\alpha_2=\sqrt{a^2-(k_0-k_0'+k_d)/D}, \tag{3.11}$$

$$\alpha_3=(k_a+k_q)/D-a, \tag{3.12}$$

in which either k_d or k_a must be set to zero. The probabilities can also be obtained by the substitution of these roots,

$$q'(x,t|x_0)=f(x,t|x_0)-\alpha_3 W\left(\frac{x+x_0}{\sqrt{4Dt}},\alpha_3\sqrt{Dt}\right), \tag{3.13}$$

$$p(*,t|*)=\exp[-(k_0+k_d)t], \tag{3.14}$$

$$S'(t|x_0)=e^{-ax_0+a^2Dt}-\frac{1}{2}W\left(\frac{x_0}{\sqrt{4Dt}},-a\sqrt{Dt}\right) -\frac{\alpha_3+a}{2(\alpha_3-a)}W\left(\frac{x_0}{\sqrt{4Dt}},a\sqrt{Dt}\right) +\frac{\alpha_3}{\alpha_3-a}W\left(\frac{x_0}{\sqrt{4Dt}},\alpha_3\sqrt{Dt}\right). \tag{3.15}$$

Here, the expressions of $q'(*,t|x_0)$ and $S'(t|*)$ for the irreversible case are not much simplified and thus omitted here.

For the case that Eq. (3.1) also holds, namely, for the transition region in the irreversible case, $aD=k_a+k_q$ and/or $a^2D=k_0-k_0'+k_d$. For the latter relation, two roots (α_1 and α_2) vanish and we can get further simplified probability expressions as follows:

$$q'(*,t|x_0)=\frac{k_a}{D\alpha_3}\left[\operatorname{erfc}\left(\frac{x_0}{\sqrt{4Dt}}\right)-W\left(\frac{x_0}{\sqrt{4Dt}},\alpha_3\sqrt{Dt}\right)\right], \tag{3.16}$$

$$S'(t|*)\frac{D}{k_d} =\frac{1}{\alpha_3 a}+\frac{1}{\alpha_3-a}\left[\frac{1}{\alpha_3}W(0,\alpha_3\sqrt{Dt})-\frac{1}{a}W(0,a\sqrt{Dt})\right]. \tag{3.17}$$

C. One root is $-a$

One can see from Eq. (2.29) that one root, say, α_3 becomes $-a$ when the following condition is satisfied:

$$(k_0-k_0'+k_d)(k_a+k_q)=k_ak_d. \tag{3.18}$$

Interestingly, this relation corresponds to the transition region in Part I and it always holds in Part II. This case can be regarded as a generalized case of Part II in that one root (α_3) is $-a$. We can calculate the other roots as

$$2D\alpha_1=k_a+k_q+\Delta_2, \tag{3.19}$$

$$2D\alpha_2=k_a+k_q-\Delta_2, \tag{3.20}$$

where $\Delta_2^2=(k_a+k_q)^2+4D[a^2D-a(k_a+k_q)-(k_0-k_0'+k_d)]$. The survival probability functions can be simplified to

$$S'(t|x_0)=e^{-ax_0+a^2Dt}-(\alpha_1+\alpha_2)\sum_{i=1}^{3}\alpha_i\Phi_{ijk}(x_0), \tag{3.21}$$

$$S'(t|*)=\frac{k_d}{(\alpha_1-a)(\alpha_2-a)D}\times\left[e^{a^2Dt}-\sum_{i=1}^{3}\alpha_i(\alpha_j+\alpha_k)\Phi_{ijk}(0)\right], \tag{3.22}$$

where $(\alpha_1-a)(\alpha_2-a)D=k_0-k_0'+k_d$ as one can see from Eqs. (2.29) and (2.30).

The generalized normalization conditions can be reduced to the following relations:

$$S'(t|x_0)+q'(*,t|x_0)=e^{-ax_0+a^2Dt}-\frac{k_q}{D}\sum_{i=1}^{3}\alpha_i\Phi_{ijk}(x_0), \tag{3.23}$$

$$S'(t|*)+q'(*,t|*)=\frac{1}{k_0-k_0'+k_d}\left[k_de^{a^2Dt}+(k_0-k_0')\times\sum_{i=1}^{3}\alpha_i(\alpha_j+\alpha_k)\Phi_{ijk}(0)\right]. \tag{3.24}$$

If there is no quenching reaction, Eq. (3.23) is further reduced to $S(t|x_0)+q(*,t|x_0)=\exp(-k_0't)$. For the equal lifetimes case, Eq. (3.24) is simplified to $S(t|*)+q(*,t|*)=\exp(-k_0't)$.

IV. ASYMPTOTIC SOLUTIONS

The unimolecular reactions make all the excited molecules decay to their ground states at very long times. To effectively cancel out the unimolecular decay effect, we multiply the probabilities by $\exp(k_0't)$. The effective excited-state probabilities are of interest because they show kinetic transition behaviors at long times.

From a physical point of view, the kinetic transition behavior from the power-law decrease to the exponential increase results from the fact that the diffusion effect becomes less dominant as the field effect and/or the lifetime effect become(s) stronger, recalling that the power-law behavior is a characteristic of the diffusion-influenced reactions. From a mathematical point of view, the kinetic transition behavior arises from the following feature of the error function or the W-function for large t,

$$W\left(\frac{x}{\sqrt{4Dt}},\alpha\sqrt{Dt}\right)=\begin{cases}\dfrac{1}{\alpha\sqrt{\pi Dt}}-\dfrac{1}{2Dt\sqrt{\pi Dt}}\left(\dfrac{x^2}{2\alpha}+\dfrac{x}{\alpha^2}+\dfrac{1}{\alpha^3}\right), & \text{when } |\arg\alpha|<3\pi/4,\\ 2e^{\alpha^2Dt+\alpha x}-W\left(\dfrac{-x}{\sqrt{4Dt}},-\alpha\sqrt{Dt}\right), & \text{when } |\arg\alpha|>3\pi/4,\end{cases} \tag{4.1}$$

which is Eq. (4.1) of Part II. Therefore, the asymptotic long time behavior critically depends on the sign of the root α. Since the sign of $b_3(=\alpha_1\alpha_2\alpha_3)$ directly depends on each sign of the roots, it plays an important role in determination of the long time behavior. This is the reason why the transition region appears when $b_3=0$ in the previous works.

A. Power-law decrease region

In order to have the long time power-law behavior, the exponential term should not appear in the W-function or all roots should be positive. We can prove that all roots are positive if $b_1(=\alpha_1+\alpha_2+\alpha_3)$ and b_3 are both positive. This can be realized when (1) all roots are positive or (2) one root is positive with two negative roots. According to Eq. (2.28), when both b_1 and b_3 are positive, the signs of α_1 and $\alpha_2+\alpha_3$ should be the same. Therefore, the case (2) is not allowed. Consequently, both b_1 and b_3 should be positive to give the power-law behavior at long times.

In Part I, only the sign of b_3 needs to be considered to analyze the long time asymptotic behavior since b_1 is always positive there. In Part II and the present system, however, b_1 can be negative when $aD>k_a$ and $aD>k_a+k_q$, respectively, and so we have to check the sign of b_1 as well as that of b_3. There are three roots $a=0$, $a=a_\pm$, where $a_\pm \equiv (k_a \pm \sqrt{k_a^2+4k_dD})/2D$, satisfying the condition $b_3=0$ in Part II. But b_1 is negative for $a=a_+$ which makes the effective binding probabilities increase exponentially at long times. Since we considered the effective deviation function of the binding probability from the equilibrium value in Part II which shows $t^{-1/2}$ transition behavior. This was the reason that $a=a_+$ was regarded as a transition point in Part II.

We can see from Eqs. (2.20) and (2.26), b_1 and b_3 can be positive, respectively, when the parameters satisfy the following relations:

$$aD \leqslant k_a+k_q \quad \text{and} \quad b_1b_2D^2 > k_ak_d. \tag{4.2}$$

Thus the effective binding probabilities show the $t^{-3/2}$ power behavior at long times as follows:

$$q'(*,\infty|x_0) \sim \frac{k_a}{D}\frac{1}{2Dt\sqrt{\pi Dt}}\frac{1}{b_3}\left(x_0+\frac{b_2}{b_3}\right), \tag{4.3}$$

$$q'(*,\infty|*) \sim \frac{1}{2Dt\sqrt{\pi Dt}}\frac{1}{b_3}\left(\frac{b_1b_2}{b_3}-1\right). \tag{4.4}$$

The following generalized relation holds analogous to Eq. (4.6a) in Part I:

$$k_dp(*,\infty|0)=(k_0-k_0'+k_d-a^2D)p(*,\infty|*). \tag{4.5}$$

One can easily check, with the help of Eq. (2.26), that Eqs. (4.3) and (4.4) reduce to those in Part I when $a=0$. On the other hand, these reduce to those in Part II ($k_0=k_0'=k_q=0$) only when $a<0$. When $a>0$, one root becomes negative in Part II and the asymptotic behavior becomes an exponential increase.

The effective survival probabilities show different asymptotic behaviors from earlier works. They show $t^{-1/2}$ behavior in Part I [see Eq. (4.3) in Part I] and exponentially increasing behavior in Part II. Notice that the latter behavior can be seen from Eqs. (3.21) and (3.22) with $k_0=k_0'=0$ and $k_q=0$. In the present case the asymptotic expressions of the effective survival probabilities become

$$S'(\infty|x_0) \sim \left[1-\frac{(\alpha_1+a)(\alpha_2+a)(\alpha_3+a)}{(\alpha_1-a)(\alpha_2-a)(\alpha_3-a)}e^{2ax_0}\right] \times H(-a)e^{-ax_0+a^2Dt}+\text{const}\cdot\frac{1}{t\sqrt{t}}, \tag{4.6}$$

$$S'(\infty|*) \sim \frac{-2ak_dH(-a)}{D(\alpha_1-a)(\alpha_2-a)(\alpha_3-a)} \times e^{a^2Dt}+\text{const}\cdot\frac{1}{t\sqrt{t}}, \tag{4.7}$$

where $H(a)$ is the Heaviside function. These survival probabilities show the $t^{-3/2}$ behavior when $a \geqslant 0$ while increase exponentially when $a<0$. This different asymptotic behavior from the previous works arises from the different interplays of terms containing $a\sqrt{Dt}$ and $-a\sqrt{Dt}$ in Eqs. (2.42) and (2.44).

Notice that asymptotic expressions of Parts I and II cannot be obtained from Eqs. (4.6) and (4.7) either by taking limits of $a\to 0$ or $k_0, k_0' \to 0$. This kind of situation also arises when we take the irreversible limits as shown in Parts I and II.

B. Exponential increase region

There is at least one negative root when either b_1 or b_3 is negative and the long time asymptotic behavior shows exponentially increasing behavior. This can occur when the following relations are satisfied:

$$aD > k_a+k_q \quad \text{or} \quad b_1b_2D^2 < k_ak_d. \tag{4.8}$$

The asymptotes in this region are controlled by the terms containing the negative root. One has to apply the second relation in Eq. (4.1) to the corresponding probabilities in order to obtain asymptotic solutions. When only one root is negative (say, $\alpha_1<0$), we get the following asymptotic expression for the binding probability of the initially bound state:

$$q'(*,\infty|*) \sim \frac{2\alpha_1(\alpha_2+\alpha_3)}{(\alpha_3-\alpha_1)(\alpha_1-\alpha_2)}\exp(\alpha_1^2Dt). \tag{4.9}$$

Asymptotic expressions of other probabilities can be easily obtained similarly.

C. Transition region

The transition behavior can be obtained when $b_3=0$ [Eq. (3.1)] and $b_1>0$. In this case one root vanishes. From Eq. (2.28), we can prove that two roots are either positive or complex conjugate with positive real parts. As mentioned in Sec. IV A, we should also check the sign of b_1 in the transition region unlike Part I where it is always positive. From the corresponding equations in Sec. III A, we obtain the asymptotic expressions of the binding probabilities as follows:

$$q'(*,\infty|x_0) \sim \frac{k_a}{D}\frac{1}{\alpha_1\alpha_2}\frac{1}{\sqrt{\pi Dt}}, \tag{4.10}$$

$$q'(*,\infty|*) \sim \frac{\alpha_1+\alpha_2}{\alpha_1\alpha_2}\frac{1}{\sqrt{\pi Dt}}. \tag{4.11}$$

The asymptotic expressions of the binding probabilities, Eqs. (4.10) and (4.11), again reduce to those in Part I when $a=0$ but reduce to those in Part II only when $a<0$. When $a>0$, the asymptotic behavior belongs to the exponentially increasing region as explained in Sec. IV A.

The effective survival probabilities show different asymptotic behaviors from earlier works. They converge toward constant values with $t^{-1/2}$ decreasing behavior in Part I [see Eq. (4.9) of Part I] and exponentially increasing behavior in Part II. The latter behavior can be also seen from Eqs. (3.21) and (3.22) with $k_0=k_0'=0$ and $k_q=0$. In the present case, we obtain the asymptotic effective survival probabilities as follows:

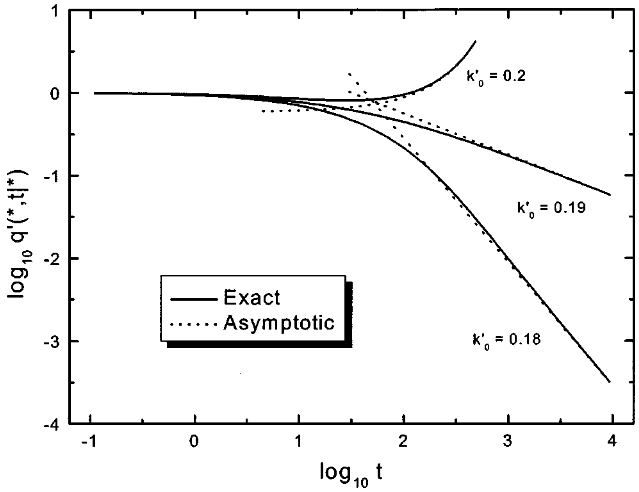

FIG. 1. The lifetime-dependent kinetic transition of $q'(*,t|*)$ for several values of k_0': $t^{-3/2}$ decrease for $k_0'=0.18$, $t^{-1/2}$ decrease for $k_0'=0.19$ (transition region) and exponential increase for $k_0'=0.20$. The solid lines are evaluated from the exact expression and the dotted lines from the asymptotic expressions. The values of parameters are $k_0=0.2$, $k_a=1.0$, $k_d=0.1$, $k_q=0.1$, $D=1.0$, and $a=0.1$.

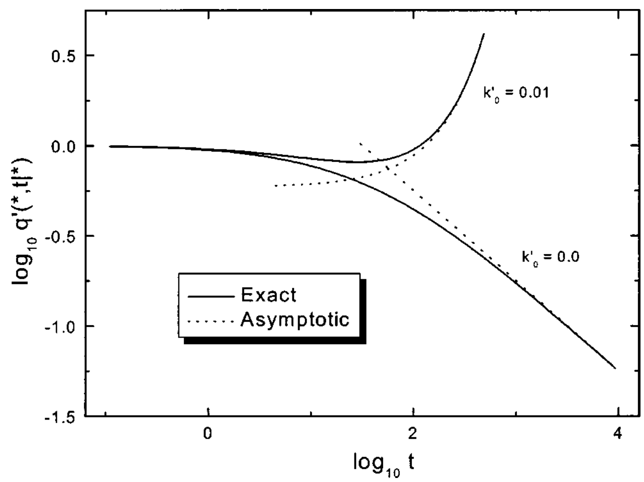

FIG. 2. The evolution of $q'(*,t|*)$ for two values of k_0'; exponential increase for $k_0'=0.01$ and $t^{-1/2}$ decrease for $k_0'=0.0$ below which there is no $t^{-3/2}$ decrease region. The values of parameters are the same as in Fig. 1 except $k_0=0.01$, which is the critical value for satisfying the condition for transition given by Eq. (5.2).

$$S'(\infty|x_0)\sim\left[1+\frac{(\alpha_1+a)(\alpha_2+a)}{(\alpha_1-a)(\alpha_2-a)}e^{2ax_0}\right]\times H(-a)e^{-ax_0+a^2Dt}+\frac{1}{a\sqrt{\pi Dt}}, \tag{4.12}$$

$$S'(\infty|*)\sim\frac{2k_dH(-a)}{D(\alpha_1-a)(\alpha_2-a)}e^{a^2Dt}+\frac{k_d}{Da\alpha_1\alpha_2}\cdot\frac{1}{\sqrt{\pi Dt}}. \tag{4.13}$$

These survival probabilities show the $t^{-1/2}$ behavior when $a\geqslant 0$ while increase exponentially when $a<0$.

For the irreversible case, the long time expressions of Eqs. (3.16) and (3.17) are given by

$$q'(*,\infty|x_0)\sim\frac{k_a}{D\alpha_3}\left[1-\left(x_0+\frac{1}{\alpha_3}\right)\frac{1}{\sqrt{\pi Dt}}\right], \tag{4.14}$$

$$S'(\infty|*)\frac{D}{k_d}\sim\frac{1}{\alpha_3 a}-\frac{a+\alpha_3}{a^2\alpha_3^2}\frac{1}{\sqrt{\pi Dt}}. \tag{4.15}$$

Note that the dependence on x_0 appears in Eq. (4.14) unlike Eq. (4.10).

V. NUMERICAL RESULTS

We investigate numerically the kinetic transition behaviors with respect to k_0' (the lifetime effect) and a (the field effect) since both effects take parts in the long time behavior in the present system.

A. The lifetime effect

In order to investigate the lifetime effect (with two different lifetimes), we display the time-dependence of $q'(*,t|*)$ for several values of k_0' in Fig. 1. We use the same parameters as those in Part I except $a=0.1$, namely, $k_a=1.0$, $k_d=0.1$, $k_q=0.1$, $k_0=0.2$, and $D=1.0$. We can observe the usual transition pattern from Fig. 1: $t^{-3/2}$ decrease for $k_0'=0.18$, $t^{-1/2}$ decrease for $k_0'=0.19$ (transition region) and exponential increase for $k_0'=0.20$. Rearranging Eq. (3.1), we obtain

$$k_0'=k_0-a^2D+k_d(k_q-aD)/(k_a+k_q-aD), \tag{5.1}$$

from which one transition point is calculated. In the present parameter set, the transition occurs at $k_0'=0.19$. The solid lines are the exact results from Eq. (2.37). The dotted lines are from appropriate asymptotic expressions: Equation (4.4) for the power-law decrease region, Eq. (4.9) for the exponential region, and Eq. (4.11) for the transition region.

Although Eq. (5.1) is a generalized version of Eq. (3.1) in Part I, there is an interesting difference. Since k_0' cannot be negative and $b_1>0$ in order to have the transition behavior, there is no transition if following relations hold:

$$k_0<a^2D-k_d(k_q-aD)/(k_a+k_q-aD) \tag{5.2}$$

or

$$aD\geqslant k_a+k_q, \tag{5.3}$$

In other words, only exponentially increasing asymptotic behavior exists for all values of k_0'. To demonstrate this fact, we plot the evolution of $q'(*,t|*)$ for two values of k_0'; exponential increase for $k_0'=0.01$ and $t^{-1/2}$ decrease for $k_0'=0.0$ below which there is no $t^{-3/2}$ decrease region. The values of parameters are the same as in Fig. 1 except $k_0=0.01$, which is the critical value for satisfying the condition for transition given by Eq. (5.2). When $k_0<0.01$, there is no lifetime-dependent transition and $q'(*,t|*)$ always increases exponentially regardless of values of k_0' (Fig. 2).

Another demonstration of nontransition behavior is related to Eq. (5.3). We plot the evolution of $q'(*,t|*)$ for two values of k_0' in Fig. 3 showing no lifetime-dependent kinetic transition. The values of parameters are the same as in Fig. 1 except $a=1.1$, which is the critical value given by Eq. (5.3).

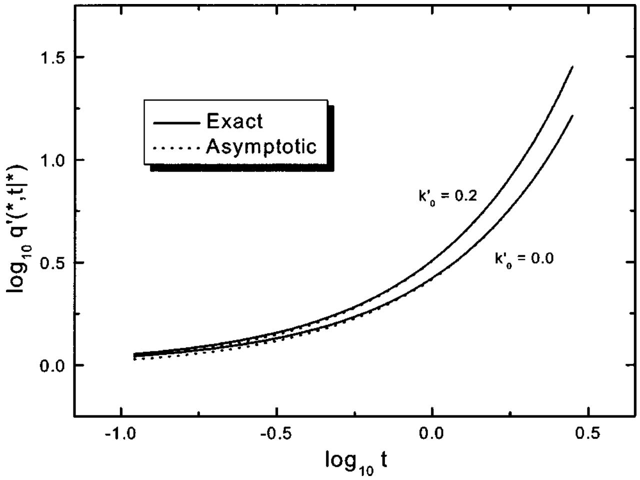

FIG. 3. The evolution of $q'(*,t|*)$ for two values of k_0' showing no lifetime-dependent kinetic transition. The values of parameters are the same as in Fig. 1 except $a=1.1$, which is the critical value given by Eq. (5.3).

Notice that Part I is a special case where the condition of Eq. (5.3) cannot be met unless $k_a=k_q=0$. This is why there is always one transition point in Part I.

B. The field effect

In order to investigate the field effect, we rearrange Eq. (3.1) in terms of a to get the following cubic equation:

$$a^3-\frac{k_a+k_q}{D}a^2-\frac{k_0-k_0'+k_d}{D}a+\frac{(k_a+k_q)(k_0-k_0'+k_d)-k_ak_d}{D^2}=0. \tag{5.4}$$

The transition region is obtained when Eq. (5.4) and the condition $aD<k_a+k_q$ (or $b_1>0$) are satisfied. However, one root of Eq. (5.4) is always bigger than $(k_a+k_q)/D$ as proved in the Appendix and it does not satisfy the condition of $b_1>0$. Therefore, the transition region can occur at most at two values of a. Actually, the number of the transition points is determined by the number of real roots of Eq. (5.4) smaller than $(k_a+k_q)/D$. It depends on the sign of the discriminant of Eq. (5.4).[19] Two transitions exist for the negative discriminant, one transition for zero value of discriminant, and no transition for positive discriminant.

In Fig. 4, we plot the evolution of $q'(*,t|*)$ for several values of a showing two field-dependent kinetic transitions. The values of parameters are the same as in Fig. 1 except $k_0'=0.0$. For the present parameter set, the discriminant is negative and, therefore, two transition regions exist. The roots of Eq. (5.4) are $a_1=-0.486806$, $a_2=0.397144$, and $a_3=1.189662$. Since a_3 is bigger than 1.1 $[=(k_a+k_q)/D]$, there are two transition regions at a_1 and a_2. The first transition behaviors around a_1 are plotted in dotted lines; exponential increase for $a=-0.49$, $t^{-1/2}$ decrease for $a=a_1$ (first transition region), $t^{-3/2}$ decrease for $a=-0.48$. The second transition behaviors around a_2 are shown in solid lines; $t^{-3/2}$ decrease for $a=0.39$, $t^{-1/2}$ decrease for $a=a_2$ (second transition region) and exponential increase for $a=0.40$ and $a=a_3$. An additional curve is plotted to show that the exponentially increasing behavior appears at $a=a_3$. Altogether, the transition behaviors follow $e^t(a<a_1)\rightarrow t^{-1/2}(a=a_1)\rightarrow t^{-3/2}(a_1<a<a_2)\rightarrow t^{-1/2}(a=a_2)\rightarrow e^t(a>a_2)$ pattern. In other words, e^t behavior appears in the outer region ($a<a_1$ or $a>a_2$) and $t^{-3/2}$ behavior in the inner region ($a_1<a<a_2$). This pattern is similar to that in Part II.

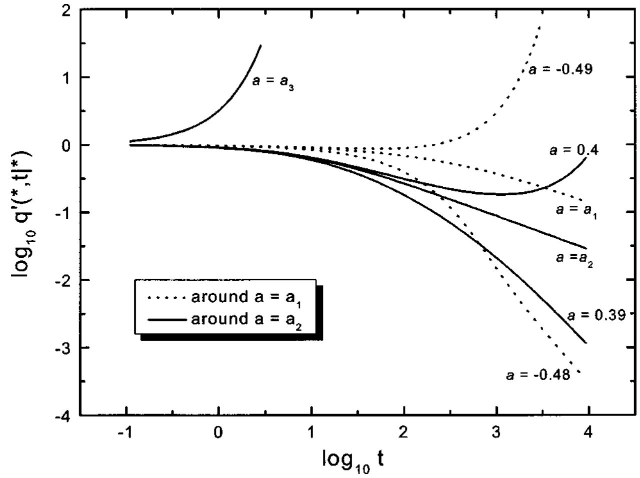

FIG. 4. The evolution of $q'(*,t|*)$ for several values of a showing two field-dependent kinetic transitions; exponential increase for $a=-0.49$, $t^{-1/2}$ decrease for $a=a_1=-0.486806$ (first transition region), $t^{-3/2}$ decrease for $a=-0.48$ and $a=0.39$, $t^{-1/2}$ decrease for $a=a_2=0.397144$ (second transition region) and exponential increase for $a=0.40$ and $a=a_3=1.189662$. The values of parameters are the same as in Fig. 1 except $k_0'=0.0$.

For $k_0'=0.3$ and the same other parameters, the discriminant is positive and the roots of Eq. (5.4) are $a_1=-0.036357+0.289742i$, $a_2=-0.036357-0.289742i$ and $a_3=1.172714$. Notice that a_1 and a_2 are complex conjugates and $a_3>1.1$. Therefore, there is no transition for these parameters as shown in Fig. 5.

One peculiar transition occurs for the zero discriminant when $k_0'=0.210683$ with other parameters same as in Fig. 1. The two roots of Eq. (5.4) coalesce to $a_1=a_2=-0.03857$ and the other root is $a_3=1.177140$ (>1.1) which does not

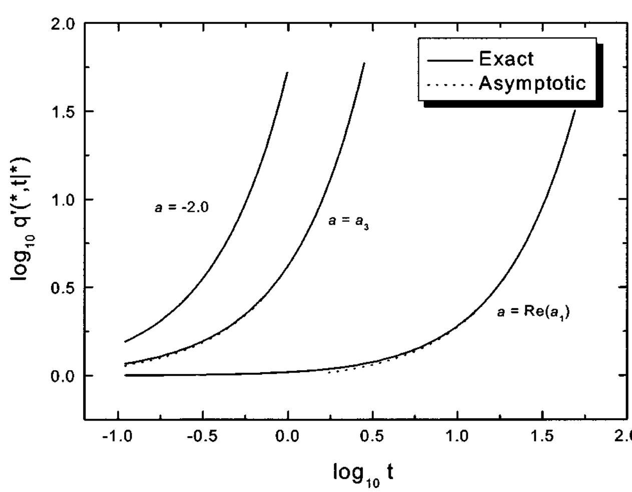

FIG. 5. The evolution of $q'(*,t|*)$ for several values of a showing no field-dependent kinetic transition. Only exponentially increasing behaviors appear at $a=a_3=1.172714$, $a=\mathrm{Re}(a_1)=-0.036357$, and $a=-2.0$. The values of parameters are the same as in Fig. 1 except $k_0'=0.3$.

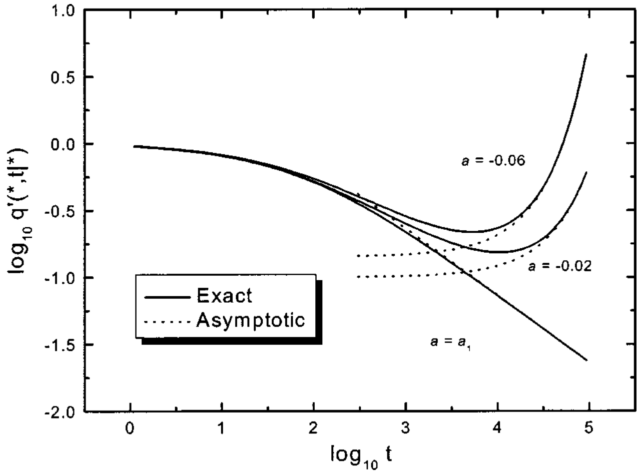

FIG. 6. The evolution of $q'(*,t|*)$ for several values of a showing one field-dependent kinetic transition; exponential increase for $a=-0.06$, $t^{-1/2}$ decrease for $a=a_1=a_2=-0.03857$ (transition region), and exponential increase for $a=-0.02$. The values of parameters are the same as in Fig. 1 except $k_0'=0.210683$. Notice that we can observe new type of kinetic transition: $e^t \rightarrow t^{-1/2} \rightarrow e^t$ as the field strength a is increased.

show the transition. So we can expect only one transition behavior in this case. In Fig. 6, we plot the evolution of $q'(*,t|*)$ for several values of a showing one field-dependent kinetic transition; exponential increase for $a=-0.06$, $t^{-1/2}$ decrease for $a=-0.03857$ (transition region), and exponential increase for $a=-0.02$. It is surprising that, unlike the transitions in other cases, there is no $t^{-3/2}$ region and a peculiar transition behavior of $e^t \rightarrow t^{-1/2} \rightarrow e^t$ pattern appears as a is increased. This can be understood by the fact that the inner region ($a_1 < a < a_2$) is collapsed due to the coalescence of two roots causing the disappearance of the $t^{-3/2}$ region.

VI. CONCLUDING REMARKS

We have obtained the exact Green function and binding and survival probabilities for the diffusion-influenced excited-state geminate reversible reaction with two different lifetimes and quenching under the influence of a constant external field in one dimension. The binding probabilities have the same structures as those in the previous works even though the detailed expressions of roots are different. This is the reason why we can use the mathematical isomorphism. However, the survival probabilities have more complicated and different structures than those of previous works.

By investigating the long time asymptotic expressions of the effective probability functions, we found that the number of asymptotic kinetic transitions can be changed depending on certain conditions. In our previous works, the number of transitions is always fixed. As the difference of lifetimes is changed, the number of lifetime dependent transitions is found to be one ($t^{-3/2} \rightarrow t^{-1/2} \rightarrow e^t$) or zero. The latter case is due to the destructive interplay of the field strength with lifetimes.

On the other hand, as the field strength is changed, the number of the field dependent transitions becomes two, one, or zero. It depends on the sign of the discriminant of a cubic equation for a at transition [Eq. (5.4)]. When the discriminant is negative, two transition regions appear and the asymptotic behaviors follow $e^t \rightarrow t^{-1/2} \rightarrow t^{-3/2} \rightarrow t^{-1/2} \rightarrow e^t$ pattern. When the discriminant is positive, there is no transition behavior and only the exponentially increasing behavior is shown. When the discriminant becomes zero, only one peculiar kinetic transition behavior ($e^t \rightarrow t^{-1/2} \rightarrow e^t$) appears as a is increased. This can be understood by the fact that the $t^{-3/2}$ region is collapsed due to the coalescence of two roots.

ACKNOWLEDGMENTS

This work was supported by Korea Research Foundation Grant (KRF-2001-041-D00108).

APPENDIX: A ROOT OF EQ. (5.4)

In this Appendix, we will prove that only one root of Eq. (5.4) is bigger than $(k_a+k_q)/D$. If we denote the roots of Eq. (5.4) by a_1, a_2, and a_3, then the following relations hold:

$$a_1+a_2+a_3=(k_a+k_q)/D, \tag{A1}$$

$$(a_1+a_2)(a_2+a_3)(a_3+a_1)=-k_a k_d/D^2. \tag{A2}$$

Notice that the latter relation is similar to Eq. (2.27). Since the product of sum of two roots is negative, three sums should be $+$, $+$, $-$ or $-$, $-$, $-$. By Eq. (A1), the latter is not possible and only one sum is negative. To satisfy Eq. (A1), the root which is not included in the negative sum should be bigger than $(k_a+k_q)/D$. As a result only one root is bigger than $(k_a+k_q)/D$.

[1] N. Agmon and I. V. Gopich, Chem. Phys. Lett. **302**, 399 (1999).
[2] I. V. Gopich, K. M. Solntsev, and N. Agmon, J. Chem. Phys. **110**, 2164 (1999).
[3] N. Agmon, J. Chem. Phys. **110**, 2175 (1999).
[4] H. Kim and K. J. Shin, Phys. Rev. Lett. **82**, 1578 (1999).
[5] I. V. Gopich and N. Agmon, J. Chem. Phys. **110**, 10433 (1999).
[6] K. M. Solntsev, D. Huppert, and N. Agmon, Phys. Rev. Lett. **86**, 3427 (2001).
[7] H. Kim, K. J. Shin, and N. Agmon, J. Chem. Phys. **111**, 3791 (1999) (referred to as Part I).
[8] I. G. Hunt, D. Bloor, and B. Movaghar, J. Phys. C **18**, 3497 (1985).
[9] Y. Okahata, T. Kobayashi, K. Tanaka, and M. Shimomura, J. Am. Chem. Soc. **120**, 6165 (1998).
[10] M. Bixon and J. Jortner, J. Phys. Chem. B **104**, 3906 (2000).
[11] A. L. Edelstein and N. Agmon, J. Chem. Phys. **99**, 5396 (1993).
[12] H. Kim, M. Yang, and K. J. Shin, J. Chem. Phys. **110**, 3946 (1999).
[13] H. Kim, M. Yang, and K. J. Shin, J. Chem. Phys. **111**, 1068 (1999).
[14] A. V. Popov and N. Agmon, J. Chem. Phys. **115**, 8921 (2001).
[15] C. Oh, H. Kim, and K. J. Shin, J. Chem. Phys. **117**, 3269 (2002).
[16] A. V. Popov and N. Agmon, J. Chem. Phys. **117**, 4376 (2002).
[17] H. Kim, K. J. Shin, and N. Agmon, J. Chem. Phys. **114**, 3905 (2001) (referred to as Part II).
[18] M. Smoluchowski, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **92**, 129 (1917).
[19] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, New York, 1982).