Irina V. Gopich
Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, Novosibirsk 630090, Russia

Kyril M. Solntsev and Noam Agmon
The Fritz Haber Research Center, Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel

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We obtain an accurate long-time solution for the diffusive kinetics of an excited geminate pair dissociating reversibly in solution, where the excited-state lifetimes of the bound and unbound states may be nonequal. We analyze the long-time asymptotic behavior, finding a transition between two types of behaviors. In region A, the excited bound pair decays as \( t^{-\frac{3}{2}} \exp(-t/\tau_0^*) \), where \( \tau_0^* \) is the lifetime of the unbound state. In region AB, the decay is a pure exponential. At the critical value of the parameters where the transition occurs, we find a \( t^{-\frac{3}{2}} \exp(-t/\tau_0^*) \) decay. These predictions are tested against an exact numerical solution of the corresponding coupled partial differential equations. For region A, we supply an experimental example involving time-resolved excited-state proton transfer from 5-cyano-2-naphthol to dimethyl sulfoxide. © 1999 American Institute of Physics. [S0021-9606(99)51004-0]

I. INTRODUCTION

Solution-phase chemistry provides several important examples of reversible diffusion-influenced reactions in the excited electronic state. One example involves excimer-monomer kinetics, where a monomeric dye molecule, such as pyrene, is excited and undergoes a reversible reaction of exciplex formation upon collision with ground-state monomers.\(^1\)–\(^5\) Another well-studied problem is excited-state proton transfer to solvent (PTTS) from excited hydroxyarenes.\(^6\)–\(^13\) Both reactions are schematically depicted by the scheme

\[
AB \rightarrow A + B, \quad k_0 \quad \rightarrow \quad k_0',
\]

(1.1)

where \( k_0 \) and \( k_0' \) are the reciprocal excited-state lifetimes of the bound and unbound states, respectively.

The initial state differs, however, between the two reactions. In the excimer-monomer case, an unbound \( B \) molecule is excited, with an initial equilibrium distribution of \( B \) molecules around it. In the excited-state PTTS reaction, one excites the \( B \) state. At neutral pH values, the concentration of protons (\( B^+ \)) is so low that only geminate recombination within the (originally dissociated) anion-proton pair occurs during the excited-state lifetime. Changing the pH allows one to span a range of \( B \) particle concentrations, bridging between the geminate and homogeneous recombination limits.

For a ground-state reaction, one may set \( k_0 = k_0' = 0 \). Even for this simple case, it is possible to solve the diffusion equation for the \( A-B \) pair only in the absence of a potential of interaction.\(^14\)–\(^15\) With a potential of interaction, only the long-time asymptotic behavior has been obtained in a closed form. The probability for observing the initially prepared bound state, \( p(\ast, t \ast) \), is not exponential as predicted by conventional chemical kinetics. In three dimensions, it obeys the asymptotic power law\(^9\)–\(^16\)

\[
p(\ast, t \ast) = \frac{K_{eq}}{(4 \pi D t)^{3/2}}.
\]

(1.2a)

where \( K_{eq} \) is the association equilibrium constant and \( D \) the relative (translational) diffusion coefficient of \( A \) and \( B \). This power-law behavior, which comes from the probability of a random walker to return to the origin of its walk, indicates that diffusion effects on reversible reactions in solution are persistent.

For an excited-state reaction in the special case that \( k_0 = k_0' \neq 0 \), the asymptotic behavior becomes

\[
p(\ast, t \ast) = \frac{K_{eq}}{(4 \pi D t)^{3/2}} \exp(-k_0 t).
\]

(1.2b)

It has been observed experimentally for fast excited-state PTTS.\(^8\)–\(^9\),\(^12\)

The more complicated pseudounimolecular case involving competition over binding between geminate and homogeneous protons at low pH values has been studied experimentally,\(^11\) simulated in one dimension\(^17\)–\(^20\) and approximated by various theoretical approaches.\(^16\),\(^21\)–\(^27\) From the latter studies, a consensus arises (however, see Ref. 27) that the asymptotic approach to equilibrium for a uniform concentration, \( c \), of \( B \) particles, becomes

\[
p(\ast, t \ast) \sim \frac{c K_{eq}}{1 + c K_{eq}} \left( 1 + \frac{K_{eq}}{(1 + c K_{eq})^3 (4 \pi D t)^{3/2}} \right) \exp(-k_0 t).
\]

(1.2c)

\(^a\)Also at the Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel.
\(^b\)Also at the School of Chemistry, Tel-Aviv University, Tel-Aviv 69978, Israel.
Thus the power-law and exponential factors persist, but the prefactor now depends on \( \gamma \). Extension of these many-body approaches to nonequal lifetimes may be truly demanding. Therefore we limit the present discussion to the geminate case.

For PTTS from hydroxypropene-trisulfonate to water,\(^{5,11}\) \( k_0 = k'_0 \) happens to be a reasonable approximation. However, this is not generally true. For example, the ‘super’ photoacid 5-cyano-2-naphthol (5CN2OH)\(^{28} \) can transfer its proton to a variety of organic solvents.\(^{29} \) A recent time-resolved study of this reaction\(^{30} \) revealed that the lifetime of the anion is appreciably longer than that of the acid form \(( k_0 > k'_0 \)\), particularly in nonprotic solvents such as dimethyl-sulfoxide (DMSO). Unfortunately, this case has received little, if any, theoretical attention.

The present work generalizes the theory of reversible geminate recombination to the case of two different lifetimes for the excited bound and unbound pair. It extends the preliminary report of Agmon and Gopich.\(^{31} \) We demonstrate that the long-time asymptotics undergoes an interesting transition, from the power-law behavior discussed above, to pure exponential decay which dominates when the lifetime of the (unbound) base becomes very short. In addition, we obtain an excellent analytic approximation unifying the behavior in both regimes for all times.\(^{31} \) It is compared with the numerical solution of the corresponding Smoluchowski equation and with experimental data for excited-state proton transfer from 5CN2OH to DMSO.

II. THEORY

A. The model

Consider a reversible geminate recombination reaction in the excited (electronic) state. In our model, a spherical molecule \( A \) of radius \( a \), which is electronically excited, interacts with a point particle, \( B \). This interaction is composed of two parts. Its physical part is a distance \(( r \) \) dependent interaction potential, \( V(r) \), which is given in units of the thermal energy \( k_B T \). The chemical part of the interaction is described by rate coefficients. The unbound pair may associate (or bind) from distance \( r \) with a rate function \( W_A(r) \). The bound \( AB \) pair may dissociate, with a rate function \( W_d(r) \), to form a geminate pair separated to a distance \( r \approx a \). As the reaction occurs in solution, the particles diffuse (diffusion coefficients \( D_A \) and \( D_B \), and their relative diffusion coefficient is \( D = D_A + D_B \)).

Previous work has shown that this seemingly simple model describes remarkably well reversible geminate recombination in the equal lifetime limit.\(^{7,9} \) Molecular aspects, and complicating effects such as vibrational relaxation, heat conduction and rotational diffusion of the base, occur on faster time scales. By the time geminate recombination takes place, the \( A-B \) excursions are so extensive that translational motion appears diffusive and the \( A-B \) interaction—spherically symmetric. In the present work, we extend the model by having the bound (\( AB \)) and unbound (\( A+B \)) states decay to their ground electronic state with (possibly) different rate constants, \( k_0 \) and \( k'_0 \), respectively.

B. Basic equations

Let us denote by \( p(*, t) \) the probability of finding the (geminate) pair in the bound excited state at time \( t \), whereas \( p(r, t) \) denotes the probability density to find the pair in the unbound excited state and with a separation \( r \). It obeys the spherically symmetric Debye-Smoluchowski equation in three dimensions with the appropriate ‘sink terms,’ \( W_A(r) \) and \( W_d(r) \). It is complemented by a kinetic equation for the binding probability, \( p(*, t) \). Hence we have

\[
\frac{\partial}{\partial t} p(r, t) = \mathcal{L} p(r, t) - [W_d(r) + k'_0] p(r, t) + W_d(r) p(*, t),
\]

(2.1a)

\[
\frac{\partial}{\partial t} p(*, t) = 4\pi \int_a^\infty W_d(r)p(r, t) r^2dr - (k_0 + k'_0)p(*, t),
\]

(2.1b)

with \( a \leq r < \infty \) and a dissociation rate constant defined by

\[
k_d = 4\pi \int_a^\infty W_d(r)r^2dr.
\]

(2.2)

Here \( \mathcal{L} \) is the spherically symmetric Smoluchowski operator in three dimensions, given by

\[
\mathcal{L} = r^{-2} \frac{\partial}{\partial r} D(r) r^2e^{-V(r)} \frac{\partial}{\partial r} e^{V(r)}.
\]

(2.3)

We assume that \( D \) is independent of the interparticle separation, \( r \). A reflective boundary condition is imposed at contact, \( \partial p(r, t)\exp(V(r))/\partial r = 0 \), at \( r = a \).

The experimentally accessible quantities are the binding probability, \( p(*, t) \), and the “survival probability” of the unbound pair

\[
S(t) = 4\pi \int_a^\infty p(r, t) r^2dr.
\]

(2.4)

When \( k_0 = k'_0 \), the total probability of finding the geminate pair in either of its two states normalizes as

\[
p(*, t) + S(t) = \exp(-k_d t).
\]

(2.5)

It then suffices to calculate only one of the two quantities. In the general case of unequal lifetimes, such a simple relationship does not hold, so that both attributes have to be evaluated.

C. Laplace transform

We begin by transforming to Laplace space. The Laplace transform of a function \( f(t) \), denoted \( \tilde{f}(s) \), is defined by

\[
\tilde{f}(s) = \int_0^\infty f(t)e^{-st}dt.
\]

(2.6)

For brevity, we introduce the notation

\[
q(r) \equiv \tilde{p}(r, s), \quad q(*) \equiv \tilde{p}(*, s).
\]

(2.7)

Upon Laplace transforming Eq. (2.1), we get

\[
(s + k_0)q(r) - p(r, 0) = \mathcal{L}q(r) - W_d(r)q(r) + W_d(r)q(*),
\]

(2.8a)
\( (s + k_d + k_0)q(*) - p(*,0) = 4\pi \int_{-\infty}^{\infty} W_a(r)q(r)r^2dr. \)

(2.8b)

Substituting the expression for \( q(*) \), Eq. (2.8b), into Eq. (2.8a), we get

\[
(s + k_d^*)q(r) - p(r,0) = \frac{k_d}{s + k_d + k_0} p(*)
\]

\[
= \mathcal{L}q(r) - W_a(r)q(r) + \frac{4\pi W_a(r)}{s + k_d + k_0} \int_{-\infty}^{\infty} W_a(r'q(r')r^2dr'.
\]

(2.9)

This is the basic equation that needs be solved.

Before attempting a solution, let us further simplify the equation by assuming contact reactivity

\[
W_a(r) = \frac{k_a \delta(r-a)}{4\pi a^2}, \quad W_a(r) = \frac{k_d \delta(r-a)}{4\pi a^2}.
\]

(2.10)

\( k_a \) and \( k_d \) are the association and dissociation rate constants, respectively. Upon substitution, this gives

\[
(s + k_d^*)q(r) - p(r,0) = \frac{k_d}{s + k_d + k_0} \frac{\delta(r-a)}{4\pi a^2} p(*,0)
\]

\[
= \mathcal{L}q(r) - (s + k_d)k_d \frac{\delta(r-a)}{4\pi a^2} q(a).
\]

(2.11a)

\[ q(*) = \frac{1}{s + k_d + k_0}[p(*,0) + k_a q(a)].
\]

(2.11b)

We are now ready to substitute the initial conditions of interest: The particles are initially either bound, \((\cdot|\cdot)\), or separated to a distance \( r_0 \), \((\cdot|r_0)\). In the second event, we have

\[
p(r,0|r_0) = \frac{\delta(r-r_0)}{4\pi r_0^2}, \quad p(*,0|r_0) = 0.
\]

(2.12)

Substituting into Eq. (2.11) gives

\[
(s + k_d^*)q(r|r_0) = \frac{k_d}{s + k_d + k_0} \frac{\delta(r-a)}{4\pi a^2} q(a|r_0).
\]

(2.13a)

\[ q(*|r_0) = \frac{k_a}{s + k_d + k_0} q(a|r_0).
\]

(2.13b)

When starting from the (excited) bound state, one has

\[
p(r,0|*) = 0, \quad p(*,0|*) = 1.
\]

(2.14)

Substituting into Eq. (2.11a) gives

\[
(s + k_d^*)q(r|*) = \frac{k_d}{s + k_d + k_0} \frac{\delta(r-a)}{4\pi a^2} q(a|*).
\]

(2.15)

Upon comparison with \( q(r|*) \), Eq. (2.13a), it is clear that

\[ q(r|*) = \frac{k_d}{s + k_d + k_0} q(r|a).
\]

(2.16a)

This result follows also from detailed balancing.32 In the time domain it becomes

\[
p(r,t|*) = k_d \int_0^t e^{-(k_d + k_0)t'} p(r,t - t'|a)dt',
\]

(2.16b)

which generalizes a previously derived convolution relation.55 Upon substitution of \( q(a|*) \) and Eq. (2.14) into Eq. (2.11b), we find that

\[ q(*|r) = \frac{1 + k_d q(*|a)}{s + k_d + k_0}, \]

(2.16c)

where \( q(*|a) \) is given by Eq. (2.13b). Thus the solution for both initial conditions is determined by \( q(r|0) \).

**D. Connection with nonreactive diffusion**

We can rewrite Eq. (2.13a) in terms of the solution for nonreactive diffusion, \( f(r,t) \), in the sense that the association/dissociation terms in Eq. (2.1a) are set to zero. Thus \( f(r,t) \) obeys

\[
\frac{\partial f(r,t)}{\partial t} = (\mathcal{L} - k_0)f(r,t),
\]

(2.17)

with a reflecting boundary condition at \( r=a \). In Laplace space, \( g(r|r_0) = f(r,s|r_0) \) obeys

\[
(s + k_d^*)g(r|r_0) = \frac{\delta(r-r_0)}{4\pi r_0^2} = \mathcal{L}g(r|r_0),
\]

(2.18)

with \( \delta[g(r|r_0)\exp(V(r))]S\tau = 0 \) at \( r=a \).

With these notations, it is easy to check that Eq. (2.13a) becomes

\[
q(r|0) = g(r|0) - g(r|a) \frac{(s + k_d)k_a}{s + k_d + k_0 + (s + k_0)k_a} g(a|a) g(a|r_0).
\]

(2.19)

This extends a known result for irreversible association reactions,33,34

\[
q(r|0) = g(r|0) - \frac{k_a g(r|a) g(a|0)}{1 + k_a g(a|a)},
\]

(2.20)

which follows by setting \( k_d = 0 \) in Eq. (2.19). In the time domain, this relation between the Green functions for diffusion with radiation and reflective boundary conditions becomes a so-called Dyson integral equation.33

We are particularly interested in the solution for the initially bound state, given in Eq. (2.16). By substituting \( q(r|a) \) from Eq. (2.19), we find that

\[
q(r|*) = \frac{k_d g(r|a)}{s + k_d + k_0 + (s + k_0)k_a g(a|a)},
\]

(2.21a)

\[
q(*|r) = \frac{1 + k_a g(a|a)}{s + k_d + k_0 + (s + k_0)k_a g(a|a)}.
\]

(2.21b)
The Laplace-transformed survival probability of the unbound, $A + B$, pair
\[ \bar{S}(s) = 4\pi \int_{a}^{\infty} q(r) r^2 dr, \]  
(2.22)
is then given by
\[ (s + k_0') \bar{S}(s) = \frac{k_d}{s + k_d + k_0 + (s + k_0) g(a|a)}, \]  
(2.23)
where we have used the fact that $4\pi f_a^\infty g(r) r^2 dr = (s + k_0')^{-1}$, see Eq. (2.18).

The present section is devoted to the derivation of approximate solutions for (excited-state) reversible binding with two different lifetimes, starting from a bound, $AB$, state. We begin with the easier problem of determining the long-time (but not asymptotic) behavior of slow (dissociation) reactions. We will see how the familiar kinetic expressions are regained in this limit, and introduce definitions for the steady-state rate coefficients. We extend the derivation to obtain an excellent approximate solution valid over a wide time range, including the $t \to \infty$ limit. We show that in this limit the asymptotic behavior exhibits a transition, depending on the values of the rate parameters. We obtain the analogous results for the alternative initial condition of a contact pair finding that, when the lifetimes are unequal, the asymptotic behavior depends on the initial condition. Finally, the derivation is also utilized to obtain the absolute fluorescence quantum yields.

### III. APPROXIMATE SOLUTIONS

The present section is devoted to the derivation of approximate solutions for the reversible geminate recombination problem.

#### A. Kinetic approximation

We begin by considering the reduction of the diffusion problem to the more elementary chemical rate equations. These are obtained by neglecting $a_{\text{eff}}$ in comparison with unity in Eq. (2.26b) namely,
\[ g(a|a) = k^{-1}_D. \]  
(3.1)
Our basic equations, (2.21) and (2.23), then simplify to
\[ \bar{q}(s|s) = (s + k_0 + k_{\text{off}})^{-1}, \]  
(3.2a)
\[ (s + k_0') \bar{S}(s) = k_{\text{off}}/(s + k_0 + k_{\text{off}}), \]  
(3.2b)
where we have introduced the steady-state dissociation rate coefficient $k_{\text{off}}$.

\[ k_{\text{off}} = \frac{k_d k_D}{k_{\text{off}} + k_{\text{off}}}. \]  
(3.3)
After factorization, Eq. (3.2b) becomes
\[ \bar{S}(s) = Z \left( \frac{1}{s + k_0' - s + k_0 + k_{\text{off}}} \right), \]  
(3.4)
with the factor $Z$ defined by
\[ Z = \frac{k_{\text{off}}}{k_{\text{off}} + k_0 - k_0'}. \]  
(3.5)
Evidently, $Z$ reduces to unity in the limit of equal lifetimes. Now both Laplace transforms are easily inverted,
\[ p(*,t) = e^{-(k_0 + k_{\text{off}})t}, \]  
(3.6a)
\[ S(t|*) = Z[e^{k_0't} - e^{-(k_0 + k_{\text{off}})t}]. \]  
(3.6b)
This solution is readily recognized as that of the rate equations
\[
\frac{d[AB]}{dt} = -(k_{\text{off}} + k_0) [AB], \tag{3.7a}
\]
\[
\frac{d[A + B]}{dt} = k_{\text{eff}} [AB] - k_0' [A + B], \tag{3.7b}
\]
where we identify \( p(\ast, t|\ast) = [AB] \) and \( S(t|\ast) = [A + B] \). It represents the reaction scheme in Eq. (1.1), where dissociation is irreversible and with a rate constant \( k_{\text{off}} \).

**B. Extended long-time solution**

To obtain an approximate solution under more general conditions, let us extend the derivation from the previous section. Since Eq. (2.26b) is valid for
\[
0 < \sigma a_{\text{eff}} < 1
\]
we utilize this inequality to replace \((1 + \sigma a_{\text{eff}})^{-1}\) by \(1 - \sigma a_{\text{eff}}\). Following the steps which have led to Eq. (3.2) now gives
\[
q(\ast|\ast) = [D\sigma^2 + k_0 - k_0' + k_{\text{off}} (1 + \sigma a_{\text{eff}}')]^{-1}, \tag{3.9a}
\]
\[
D\sigma^2 S(\sigma|\ast) = \frac{k_{\text{off}} (1 + \sigma a_{\text{eff}}')}{D\sigma^2 + k_0 - k_0' + k_{\text{off}} (1 + \sigma a_{\text{eff}}')} \tag{3.9b}
\]
Thus the denominator of Eq. (2.21), a cubic polynomial in \( \sigma \), has been reduced to a quadratic polynomial. It assumes this simple form when we define a “modified effective radius,” \( a'_{\text{eff}} \), by
\[
a'_{\text{eff}} = \frac{k_a a_{\text{eff}}}{k_{\text{eff}} K_{\text{eq}}} = \frac{k_{\text{off}} K_{\text{eq}}}{4\pi D}. \tag{3.10}
\]
Here \( K_{\text{eq}} \) is the equilibrium coefficient for association,
\[
K_{\text{eq}} = k_a e^{-v(a)/k_d}. \tag{3.11}
\]
Equation (3.9) can now be inverted analytically, as follows. First, we evaluate the two roots of the denominator
\[
\sigma_{\pm} = \frac{\sigma_{\text{eff}} a'_{\text{eff}}}{2D} (-1 \pm \sqrt{1 + \beta}), \tag{3.12}
\]
where \( \beta \) is the dimensionless parameter
\[
\beta = \frac{(k_0' - k_0 - k_{\text{off}}) 4D}{(k_{\text{off}} a_{\text{eff}}')^2}. \tag{3.13}
\]
For equal lifetimes, \( \beta = -4D/(k_{\text{off}} a_{\text{eff}}')^2 \). Equation (3.9) is subsequently rewritten as
\[
D q(\ast|\ast) = [(\sigma - \sigma_+) - (\sigma - \sigma_-)]/(\sigma_+ - \sigma_-), \tag{3.14a}
\]
\[
D S(\sigma|\ast) = k_{\text{eff}} (1 + \sigma a_{\text{eff}}') q(\ast|\ast) / \sigma^2. \tag{3.14b}
\]
Taking Laplace inverses, we finally get
\[
p(\ast, t|\ast) = \frac{e^{-k_0' t}}{2} \left( \phi_+ (t) + \phi_- (t) - \frac{\phi_+ (t) - \phi_- (t)}{\sqrt{1 + \beta}} \right), \tag{3.15a}
\]
\[
S(t|\ast) = \frac{e^{-k_0' t} (1 + \sigma a_{\text{eff}}') \phi_+ (t) - 1}{\sqrt{1 + \beta} \sigma a_{\text{eff}}'} - \frac{(1 + \sigma a_{\text{eff}}') \phi_- (t) - 1}{\sigma a_{\text{eff}}'}. \tag{3.15b}
\]
Note that the exponential factor involves only the lifetime, \(1/k_0'\), of the separated pair. The functions \( \phi_{\pm} (t) \) are defined by
\[
\phi_{\pm} (t) = e^{\sigma^2 D t} \text{erfc}(-\sigma \pm \sqrt{D t}). \tag{3.16}
\]
\( \text{erfc} \) is the complementary error function for a possibly complex argument, \( z \), and \( \text{erfc}(-z) = 2 - \text{erfc}(z) \).

Note that in deriving Eq. (3.15), we have not modified the highest order term in \( \sigma \). Hence it goes correctly to the limit \( p(\ast, 0|\ast) = 1 \) at \( t = 0 \). However, it does not possess the correct short time behavior near \( t = 0 \), as it is valid for sufficiently long times that \( \text{erfc} \) obeys \( t \gg \sigma a_{\text{eff}} / D \). However, if by that time \( p(\ast, t|\ast) \) has not decayed much as compared with unity, we might expect our approximation to hold for all times. Now, at short times \( p(\ast, t|\ast) \) decays as \( \exp[-(k_0 + k_0') t] \), slowing down to \( \text{erfc}[-(k_0 + k_0')] \). Therefore, the approximation should hold over the whole decay range if the characteristic decay time, \( (k_{\text{off}} + k_0)^{-1} \), is long as compared with \( a_{\text{eff}} / D \). This occurs for sufficiently slow reactions obeying \( k_{\text{off}} + k_0 \ll D / a_{\text{eff}}^2 \). Under such conditions, one might also expect that the kinetic approximation, Eq. (3.6), holds for a rather wide time window, up to (but not including) the asymptotic regime.

**C. Asymptotic behavior**

While the above results are of general validity, they conceal an interesting property of the asymptotic behavior, which undergoes a transition as a function of \( \beta \). To see this, one can utilize the asymptotic behavior of the error function in Eqs. (3.15) and (3.16), or begin with the Laplace transforms in Eq. (3.9). The \( t \to \infty \) behavior is determined from that of the Laplace transform near its rightmost irregular point, i.e., either near the branching point \( \sigma = 0 \) or near the pole defined by the root \( \sigma_+ \), when it becomes positive. It is thus evident that a transition occurs when \( \sigma_+ = 0 \), namely \( \beta = 0 \) or
\[
k_0' = k_0 + k_{\text{off}}. \tag{3.17}
\]
If \( \beta < 0 \) (“A-regime”), both roots have a negative real part and the asymptotic behavior is determined by that of the Laplace transform near \( \sigma = 0 \). When \( \beta > 0 \) (“AB-regime”), the asymptotic behavior is determined by that of the Laplace transform near \( \sigma_+ \). At the transition, the average overall lifetimes of the bound state \((k_0' + k_{\text{off}})\) and the infinitely separated pair \((k_0')\) become equal. We shall now derive explicit expressions for the long-time asymptotic behavior in both regimes. Note, however, that since Eq. (2.26b) becomes exact near \( \sigma = 0 \) (and not near \( \sigma_+ \)), our approximation is asymptotically exact only in the A-regime.

**1. The A-regime**

The A-regime (\( \beta < 0 \)) extends the equal-lifetime case considered in earlier work. In this regime the A molecule is
relatively long lived, and the asymptotic decay is controlled by the diffusing unbound pair, leading to power-law asymptotics. Since $\sigma$ is the small parameter, one may neglect the $\sigma^2$ term in the denominator of Eq. (3.9), leading to

$$q(\ast \ast) \sim \frac{1 - Z\sigma a'_{\text{eff}}}{k_0 - k'_0 + k_{\text{off}}},$$  \hspace{1cm} (3.18a)

$$D \sigma^2 \tilde{S}(\ast \ast) \sim Z[1 + (1 - Z)\sigma a'_{\text{eff}}],$$  \hspace{1cm} (3.18b)

where $Z$ and $a'_{\text{eff}}$ are defined in Eqs. (3.5) and (3.10), respectively. When the above equations are inverted, we get the following asymptotic behavior:

$$p(\ast \ast, t \ast) \sim Z^2 \frac{K_{\text{eq}}}{(4\pi D t)^{3/2}} e^{-k'_0 t'},$$  \hspace{1cm} (3.19a)

$$S(t \ast) \sim Z \left[ 1 + \frac{K_{\text{eq}}(k_0 - k'_0)}{4\pi D} \left( \frac{1}{\sqrt{\pi D t}} \right) \right] e^{-k'_0 t'}.$$  \hspace{1cm} (3.19b)

This result is rigorous because it is based on taking the $\sigma \rightarrow 0$ limit, for which the approximation inherent in Eq. (2.26b) becomes exact. Thus in the $A$-regime, the bound state decays with the lifetime of the unbound state. Only the preexponential depends on $k_0$. Consider the asymptotic behavior of $p(\ast \ast, t \ast) \exp(k_0 t')$ as compared with that of $S(t \ast) \exp(k_0 t')$. The first approaches zero with the $t^{-3/2}$ law, whereas the second approaches a plateau ($Z$) from above, with the asymptotic $t^{-1/2}$ behavior characteristic of irreversible recombination. This latter aspect is similar to the behavior of reversible binding with quenching. Extension of the theory to contact geminate quenching will be given in Part II of this series.

2. The AB-regime

In the $AB$-regime ($\beta > 0$), the behavior is controlled by the bound $AB$ pair. The diffusion motion of the separated pair is of too short duration to influence the asymptotic behavior, which becomes exponential. Here $\sigma - \sigma_+$ is the small parameter, so that one may neglect $(\sigma - \sigma_-)^{-1}$ in Eq. (3.14a), which reduces to

$$D \cdot q(\ast \ast) \sim 1[1(\sigma - \sigma_+)(\sigma_+ - \sigma_-)].$$  \hspace{1cm} (3.20)

In Eq. (3.15), one may neglect the $\phi_-(t)$ terms and substitute $\phi_+(t) \sim 2\exp(\sigma_+ t D t)$. This gives

$$p(\ast \ast, t \ast) \sim \left( 1 - \frac{1}{\sqrt{1 + \beta}} \right) \exp[-(k_0 + k_{\text{off}} (1 + \sigma_+ a'_{\text{eff}})) t],$$  \hspace{1cm} (3.21a)

$$S(t \ast) \sim \frac{2}{\sqrt{1 + \beta}} \frac{1 + \sigma_+ a'_{\text{eff}}}{\sigma_+ a'_{\text{eff}}} \times \exp[-(k_0 + k_{\text{off}} (1 + \sigma_+ a'_{\text{eff}})) t].$$  \hspace{1cm} (3.21b)

In particular, when $\beta \gg 1$, the binding probability reduces to

$$p(\ast \ast, t \ast) \sim \exp[-(k_0 + k_{\text{off}})] + k_{\text{off}} a'_{\text{eff}} \sqrt{(k'_0 - k_0 - k_{\text{off}}) / D} t.$$

In the $AB$-regime, the asymptotic decay becomes pure exponential, although the exponent in Eq. (3.21) is only approximate. Note that while in the $A$-regime both species decay with the characteristic lifetime of the unbound molecule, in the $AB$-regime they both decay with the overall lifetime of the bound pair. Thus the species always decays with the overall lifetime of the long-lived molecule.

3. The transition region

The transition regime, $\beta = 0$, should be handled separately. Returning to the Laplace transform, Eq. (3.14), setting $\sigma_+ = 0$ and neglecting the terms $(\sigma - \sigma_-)^{-1}$ and $\sigma a'_{\text{eff}}$, gives

$$q(\ast \ast) \sim \frac{1}{D \sigma \sigma_-},$$  \hspace{1cm} (3.23a)

$$\tilde{S}(\ast \ast) \sim -\frac{k_{\text{off}}}{D^2 \sigma^3}.$$

Setting $\sigma_- = -k_{\text{off}} a'_{\text{eff}} / D$, it is a simple matter to invert these expressions to yield

$$p(\ast \ast, t \ast) \sim \frac{1}{k_{\text{off}}} \sqrt{\frac{D}{\pi a'_{\text{eff}}^2}} e^{-k_0 t'},$$  \hspace{1cm} (3.24a)

$$S(t \ast) \sim \sqrt{\frac{4Dt}{\pi a'_{\text{eff}}^2}} e^{-k_0 t'}.$$  \hspace{1cm} (3.24b)

Thus at the critical value of the parameters, $\beta = 0$, the exponent is the same as in the $A$-regime, but the power law in the prefactor has changed.

D. Initial contact pair

We can use the above results to obtain analogous expressions for a pair initially at the contact distance, $r = a$. By differentiating the convolution relation (2.16b) with respect to $t$, we obtain the following connection between the two initial conditions:

$$p(r, t | a) = \frac{e^{-k_d + k_0 t}}{k_d} \frac{d}{dt} \left( e^{(k_d + k_0 t)} p(r, t | \ast \ast) \right).$$  \hspace{1cm} (3.25)

A relation of this type holds also in the pseudounimolecular case of many $B's$. Using it, we find that the approximation (3.15) becomes

$$p(\ast \ast, t | a) = \xi p(\ast \ast, t | \ast \ast) + \left[ \frac{D^2 (\sigma_+^3 \phi_- (t) - \sigma_-^3 \phi_+ (t))}{k_{\text{off}} a'_{\text{eff}}^2 \sqrt{1 + \beta}} - \frac{k_{\text{off}} a'_{\text{eff}}}{\sqrt{\pi D t}} \right] e^{-k_0 t'}.$$

(3.26a)
\[ S(t|a) = \xi S(t|\ast) + \frac{D e^{-k_d t}}{\sqrt{1 + \beta}} \left( (a'_{\text{eff}} - 1 + \sigma_+) \sigma_+ \phi_+(t) - (a'_{\text{eff}} + 1 + \sigma_-) \sigma_- \phi_-(t) \right) \]  

(3.26b)

where \( \xi = (k_d + k_0 - k'_d)/k_d \) is the “decay misbalance factor.” Unlike Eq. (3.15) which, for an initially bound pair, goes to the correct limit at \( t = 0 \), Eq. (3.26) diverges as \( t \to 0 \) and may therefore be used only as a long-time approximation.

The asymptotic behavior is subsequently modified in the following manner. In the transition and \( A \)-regimes (\( \beta \leq 0 \)), Eqs. (3.19) and (3.24) become

\[ p(\ast,t|a) = \xi p(\ast,t|\ast), \]  

(3.27a)

and similarly for \( S(t|a) \). In the \( AB \)-regime (\( \beta > 0 \)), Eq. (3.21) is modified so that

\[ p(\ast,t|a) = \frac{k_d - k_{\text{off}}(1 + \sigma_+ a'_{\text{eff}})}{k_d} p(\ast,t|\ast), \]  

(3.27b)

and similarly for \( S(t|a) \). Note that for equal lifetimes, the reaction is in the \( A \)-regime and Eq. (3.27a) reduces to

\[ p(\ast,t|a) = p(\ast,t|\ast). \]  

Thus while for \( k'_d = k_0 \) the long-time asymptotic behavior is independent of the initial condition, for different lifetimes it is not.

E. Quantum yields

Another quantity of interest that can be calculated from the Laplace transform is the absolute fluorescence quantum yield (AQY), which measures the ratio between emitted and absorbed photons. It is calculated as the product of the radiative (fluorescence) rate constant with the average lifetime of the excited state. When the latter involves two chemical species, such as the bound and unbound states (from which it is possible to collect radiation at different wavelengths), two corresponding AQYs can be defined,

\[ \varphi = k_f \int_0^\infty p(\ast,t) \, dt, \]  

(3.28a)

\[ \varphi' = k'_f \int_0^\infty S(t) \, dt. \]  

(3.28b)

\( k_f \) and \( k'_f \) are the radiative (fluorescence) rate constants for the bound and unbound states, respectively. The two integrals represent their respective lifetimes. Due to the possible presence of additional nonradiative processes, \( k_f = k_{\text{off}} = k'_f = k'_{\text{off}} \). The accurate procedure for determining the radiative rate constants then involves two measurements: A steady-state measurement from which AQYs are extracted, and a time-resolved measurement which gives the integrated lifetimes.

Limiting our interest to the initially bound state, we can relate the AQYs to the Laplace transforms calculated in Sec. II D above,

\[ \varphi(\ast)/k_f = \bar{p}(\ast,0|\ast) = \frac{1 + k_d \bar{f}(a,0|a)}{k_d + k_0[1 + k_d \bar{f}(a,0|a)]}, \]  

(3.29a)

\[ \varphi'(\ast)/k'_f = \bar{S}(0|\ast) = \frac{k_d/k'_0}{k_d + k_0[1 + k_d \bar{f}(a,0|a)]}. \]  

(3.29b)

In the absence of nonradiative processes, \( k_0 = k_f \) and \( k'_0 = k'_f \), and the AQYs normalize to unity, \( \varphi + \varphi' = 1 \), as they should. In order to calculate the AQYs in the presence of interactions, we use the \( s \to 0 \) limit in Eq. (2.26b), to write

\[ \bar{f}(a,0|a) = \frac{1 - k_d}{1 + a_{\text{eff}} k_d}, \]  

(3.30)

When \( V(r) = 0 \), \( a_{\text{eff}} = a_{\text{eff}} \) and Eq. (3.30) is exact. For \( V(r) \neq 0 \), it is a good approximation when \( k_{\text{off}} a_{\text{eff}} \ll D \). By setting \( s = 0 \) in Eq. (3.9), we can rewrite Eq. (3.29) as

\[ k_f \varphi(\ast) = k_0 + k_{\text{off}}(1 + a_{\text{eff}} k_d/k_d), \]  

(3.31a)

\[ k'_f/\varphi'(\ast) = k'_0[1 + k_0(1 - a_{\text{eff}} k'/k_d)/k_{\text{off}}]. \]  

(3.31b)

This produces a new, useful approximation for the AQYs.

IV. TECHNICAL DETAIL

We set out to test the approximate and asymptotic solutions for reversible geminate dissociation against the exact numerical solution of the partial differential equations (2.1), and compare them with experiments on excited-state PTTS. The numerical solution was obtained using the user-friendly Windows application for solving the spherical symmetric diffusion problem (SSDP 2.53), which is described in Ref. 39. The experimental data are from a recent study\(^\text{30}\) of the photochemistry of 5-cyano-2-naphthol (5CN2OH). We have chosen dimethyl-sulfoxide (DMSO) as a solvent because, in contrast with some protic solvents, 5CN2OH in DMSO does not seem to be strongly quenched by protons. Below we give a brief description of the experimental and data fitting procedures.

A. Experimental data collection and manipulation

DMSO (Merck, max 0.03% H\(_2\)O) was found to be free of fluorescent impurities and was used as supplied. 5CN2OH was synthesized by Tolbert and co-workers as previously described.\(^\text{28}\) Fluorescence spectra of 5CN2OH in dilute (non-deoxygenated) DMSO solutions were recorded on a SLM-AMINCO-Bowman 2 luminescence spectrometer, and corrected for instrumental factors using files supplied by the manufacturer.

Fluorescence quantum yields were determined using dilute solutions of anthracene in aerated ethanol (EtOH) as a standard reference. Quantum yields were subsequently calculated from the expression\(^\text{40}\)

\[ \varphi = \frac{F A_{\text{ref}}}{F_{\text{ref}} A} \left( \frac{n_D(DMSO)}{n_D(EtOH)} \right)^2 \varphi_{\text{ref}}, \]  

(4.1)

where \( \varphi_{\text{ref}} = 0.28 \) is the fluorescence quantum yield of anthracene in ethanol,\(^\text{41}\) \( n_D(EtOH) = 1.3594 \) and \( n_D(DMSO) = 1.4773 \) are the refractivity indices of EtOH and DMSO, respectively.\(^\text{42}\) \( F \) and \( F_{\text{ref}} \) are the areas under the fluorescence spectra of 5CN2OH (in DMSO) and anthracene (in ethanol),
measured under the same conditions. \( A \) and \( A_{\text{ref}} \) are the corresponding absorbance of the two molecules, recorded on a Perkin-Elmer 551S UV-Vis spectrophotometer at the excitation wavelength (342 nm).

The steady-state fluorescence spectra are presented elsewhere.\(^{28,29} \) They do not depend on the excitation wavelength.\(^{29} \) The emission exhibits two peaks, one around 398 and another at 543 nm. These peaks are attributed to fluorescence from the acid (R^*OH) and anion (R^*O^-) forms, respectively.\(^{28} \)

To observe PTTS in the time-domain, the sample was excited by a ps laser at about 295 nm (the doubled frequency of Rhodamine 6G dye laser, driven by a Nd:YAG laser), which corresponds to the \( S_0 \rightarrow S_2 \) electronic transition. It appears that ultrafast relaxation to the vibrationally equilibrated \( S_1 \) state occurs, since PTTS rates do not depend on the excitation wavelength.\(^{30} \)

Transient fluorescence data were collected at 370 nm (R^*OH) and 570 nm (R^*O^-) using the time-correlated single-photon-counting system in Huppert’s lab.\(^{30} \) The temperature was \( T = 293 \pm 1 \) K. The instrument response function (IRF) has a full width at half maximum (FWHM) of about 40 ps. The full scale was 50 ns, corresponding to 48.8 ps/channel. Measurement at the R^*OH wavelength was immediately followed by a second measurement at the R^*O^- wavelength, so that the two time axes coincide. The maximal number of counts reached about 35 000 and 3000 counts for the acid and anion forms, respectively. The smaller count levels for R^*O^- are due to its much slower decay.

To facilitate visualization of the long-time behavior, we have smoothed the experimental data using a simple routine which averages (iteratively) adjacent data points. This eliminates the highest frequency noise, but does not otherwise influence the center of gravity of the experimental data. Two counts were then subtracted as a constant background. Time zero (for both R^*OH and R^*O^-) was set to one channel before the peak of the R^*OH signal. The intensities of both decay signals, which are recorded in arbitrary count numbers, were normalized to the corresponding theoretical curves.

### B. Theoretical fitting procedures

The experimental data were fitted to the numerical solution of the transient Smoluchowski equation (2.1) using SSDP version 2.53.\(^{39} \) The parameters used are collected in Table I. Most of the parameters (except two) were estimated from literature values as follows.

The contact radius, \( a = 5.5 \) Å, is a typical literature value.\(^{7} \) The Debye radius, \( R_D \), was calculated from

\[
R_D = \frac{|z_1 z_2| e^2}{\kappa k_B T},
\]

where \( z_1 = 1, z_2 = -1 \) are the charges of the proton and anion, respectively. \( e \) is the electronic charge, \( e = 46.7 \) is the (static) dielectric constant of room temperature DMSO.\(^{42} \)

The diffusion constant of the proton in DMSO, \( D_{H^+} \), has been estimated from mobility data\(^{43} \) and extrapolated to infinite dilution. The diffusion constant for the anion, \( D_{RO^-} \), in water was assumed to be about \( 0.75 \times 10^{-5} \) cm^2/s. This value is within the range of \( 0.55–0.95 \) cm^2/s observed for various aromatic compounds.\(^{44} \) It was scaled to DMSO by the viscosity ratio of the two solvents, \( \eta_{H_2O}/\eta_{DMSO} = 0.9/2.0 \). The relative diffusion coefficient, \( D = D_{H^+} + D_{RO^-} \), was subsequently used in the program.

The excited-state lifetime of the anion, \( \tau_0 = 1/k_0 \), was determined directly from the long-time exponential decay of the R^*O^- fluorescence signal (see below). Determination of the R^*OH lifetime, \( \tau_0 \), is more problematic, because of PTTS. Measurements under acidic conditions could lead to quenching by protons. We have therefore used the major decay component of 5-cyano-2-methoxynaphthalene (from which no PTTS is possible). Our experience with solvents to which 5CN2OH does not transfer its proton is that the difference in R^*OH lifetimes between 5CN2OH and its methoxy derivative does not exceed 10%.

The SSDP program was propagated for the above parameters, on a spatial grid extending from \( a = 5.5 \) to 1000 Å (which, for the present parameters is essentially infinity) using 500 grid points (0.5 Å/point), and a logarithmic time scale (from 5 ps to 100 ns). The two contact rate parameters were adjusted manually. In our previous notations,\(^{7} \) these parameters are \( \kappa_d = k_d \) and \( \kappa_r = k_r / (4 \pi a^2) \). We usually started with \( k_d = 0 \), adjusting \( k_d \) to the initial decay. Then \( k_d \) was gradually increased until the nonexponential tail was adequately fitted. Both acid and anion signals were fitted with the same parameter set.

For the present parameters \( \beta = -467 \), so that a complex error-function routine is required for evaluating the long-time solution in Eq. (3.15). This routine is based on Eq. (7.1.29) of Ref. 45 and calls, in turn, a real double-precision error-function routine from the IMSL library.

In the present work we have not convoluted the calculated curves with the IRF, because we focus on the long-time behavior, which is unaffected by convolution. This way the theoretical curves retain their identity, unmodified by convolution.

### Table I. Parameters used in fitting the time-resolved fluorescence decay of 5CN2OH in DMSO to the solution of Eq. (2.1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ), Å</td>
<td>5.5</td>
</tr>
<tr>
<td>( R_D ), Å</td>
<td>12.1</td>
</tr>
<tr>
<td>( D_{H^+} ), cm^2/s</td>
<td>0.65 \times 10^{-3}</td>
</tr>
<tr>
<td>( D_{RO^-} ), cm^2/s</td>
<td>0.35 \times 10^{-3}</td>
</tr>
<tr>
<td>( 1/k_0 ), ns</td>
<td>5.7</td>
</tr>
<tr>
<td>( 1/k_0' ), ns</td>
<td>22.5</td>
</tr>
<tr>
<td>( 1/k_d ), ns</td>
<td>4.0</td>
</tr>
<tr>
<td>( k_a ), Å^3/10^6 s</td>
<td>456</td>
</tr>
</tbody>
</table>
V. RESULTS

We shall now compare the exact numerical solution for excited-state reversible geminate dissociation with the approximate and asymptotic analytic solutions and with transient experimental data for PTTS from a “super” photoacid to DMSO. We will also utilize the measured AQYs to estimate the radiative lifetimes of the acid and anion.

A. Comparison with theory

The main theoretical results of this work include the analytic approximation, Eq. (3.15), and its asymptotic behavior. These are compared in Fig. 1 with the exact numerical solution of Eq. (2.1) for the binding probability, \( p(\ast, t\mid \ast) \). The bold lines represent this numerical solution for the parameters of Table I, but with different values of \( \tau'_0 \) indicated (in ns). Dashed curves are the analytical approximation of Eq. (3.15a). Dash-dotted lines are its asymptotic behavior discussed in the sequel.

FIG. 1. Decay of the initial bound state in reversible diffusion-influenced dissociation with two different lifetimes. Lines are the numerical solution of Eq. (2.1) for the parameters of Table I and the values of \( \tau'_0 \) indicated (in ns). Dashed curves are the analytical approximation of Eq. (3.15a). Dash-dotted lines are its asymptotic behavior discussed in the sequel.

decay of Eq. (3.21a) appears to hold over a wide time range. However, as seen from the figure, the value of the exponent is only approximate.

B. Comparison with experiment

Figure 2 compares experimental fluorescence data from excited SCN2OH in DMSO (points) with the numerical solution of Eq. (2.1) (full lines). The decaying curve is the \( R^\ast OH \) signal \([I(t) = p(\ast, t\mid \ast)]\), whereas the rising curve is the \( R^\ast O^- \) signal \([I(t) = S(t\mid \ast)]\). These signals were multiplied by \( \exp(\mu/\tau'_0) \), where \( \tau'_0 = 22.5 \) ns is the lifetime of the excited anion. Other parameters used in our fitting routine are summarized in Table I (see discussion in Sec. IV B). The theoretical curves were not convoluted with the IRF, hence the discrepancy at short times (which can be eliminated by proper convolution). With \( \beta = -467 \), these data are well within the A-regime.

The analytic approximation of Eq. (3.15a) is depicted by the dashed curves. For the present parameters, this approximation is surprisingly good, as it is almost indistinguishable from the exact results for all values of \( k'_0 \). Its asymptotic behavior is shown by the dash-dotted lines in Fig. 1. In regime A, the decay is a power law, Eq. (3.19a). It is depicted by straight lines in a log-log scale. At the critical value of \( \tau'_0 = 2.654 \) ns, the transition from the \( t^{-3/2} \) to a \( t^{-1/2} \) asymptotic decay, Eq. (3.24a), is clearly evident. In contrast to the A-regime, where the limiting behavior sets in only asymptotically, in the AB-regime the asymptotic exponential

FIG. 2. Excited-state proton transfer from 5-cyano-2-naphthol to DMSO. Points are the transient fluorescence data (Ref. 30) for the excited acid (decaying signal) and anion (rising signal). Lines are the numerical solution of Eq. (2.1) with the parameters of Table I. The dashed curve is our analytic approximation for the anion signal, see Eq. (3.15b). It nearly coincides with the full line. Dash-dotted lines represent its long-time asymptotic limits. See text for additional detail.
of Eq. (3.19a), which is shown by the dash-dot line. It gives the correct short-to-intermediate time behavior, but does not describe correctly even the approach to the asymptotic behavior.

The binding probability for a pair initially at the contact distance is shown in Fig. 4. \( p(\ast, t | a) \) starts from zero and increases to a maximum due to binding. This region is not well reproduced by the analytic approximation in Eq. (3.26a), which is nevertheless a useful long-time solution (dashed curve). The asymptotic behavior of Eq. (3.27a) is shown by the dash-dot line. Its amplitude is larger than that of \( p(\ast, t | \ast) \) by the factor \( \xi \): This contrasts with the equal-lifetime case, where both initial states decay with the identical asymptotic law of Eq. (3.19a). Note that the experimental data in Fig. 3 do not show the initial increase predicted for \( p(\ast, t | a) \). Thus under our experimental conditions, the

![FIG. 3. Decay of 5CN2OH acid fluorescence signal by proton transfer to DMSO. Fig. 2, displayed on a log-log scale. The line is the exact numerical solution, using parameters from Table I. The dashed line is the kinetic approximation, Eq. (3.6a). The dash-dotted line is the analytic asymptotic behavior, Eq. (3.19a).](image1)

![FIG. 4. Same as Fig. 3, for a contact initial condition. Dashed line is the analytic long time solution of Eq. (3.26a). Dash-dotted line is the asymptotic behavior, Eq. (3.27a). Our PTTS data do not correspond to this initial condition.](image2)

TABLE II. Absolute quantum yields and fluorescence lifetimes for 5CN2OH in DMSO.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \varphi )</th>
<th>( \tau_f )</th>
<th>( \varphi )</th>
<th>( \tau_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{R}^+ \text{OH} )</td>
<td>2.58</td>
<td>0.14</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>( \text{R}^+ \text{O}^- )</td>
<td>12.3</td>
<td>0.33</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>

The present work has extended the theory of reversible diffusion-influenced reactions of geminate pairs\(^{16}\) to the case of two different excited-state lifetimes.\(^{31}\) Since different lifetimes represent the typical situation in photochemical reactivity, this generalization is an essential step toward a realistic description of the transient behavior. Mathematically, we have first obtained the complete Laplace transformed solution in the case of a vanishing interaction potential, and an approximate solution in the presence of interactions. Both transforms may be inverted analytically. The exact field-free solution will be discussed and analyzed in Part III of this series. For the case of an interaction potential, which is important experimentally, we have obtained a surprisingly accurate approximation for the time dependence of the binding and survival probabilities of an initially bound pair. This analytical solution, overlooked by previous treatments of reversible geminate recombination, could serve to fit experimental data in future work. So far, this was achieved by a manual adjustment of the parameters in the partial differential equation (2.1).

We have subsequently analyzed the asymptotic long-time behavior of \( p(\ast, t | \ast) \exp(t/\tau^0_0) \), finding that it exhibits a transition between exponential (region \( AB \)) and \( t^{-3/2} \) (region \( A \)) behaviors. At the transition, a third type of asymptotic behavior takes place. These findings were verified in comparison with an exact numerical solution of the corresponding Smoluchowski equation (2.1). For nonequal lifetimes we find that the asymptotic behavior does depend on the initial condition. It is interesting to note that a transition in the long

C. Quantum yields

The absolute fluorescence quantum yields (AQYs) are related to the area under the decay curves by Eqs. (3.28). These areas can be calculated from our time-resolved data, either numerically or from Eq. (3.31). To three-digit accuracy, both routes lead to the same results (\( \varphi , \tau_f \) in Table II). Thus Eq. (3.31) provides a useful approximation to the area under the decay curves. The experimentally determined AQYs (see Sec. IV A for detail) are also given in the table. The two data together provide the most reliable estimate for the radiative fluorescence lifetimes of the acid and anion, see Table II. Upon comparison with the observed excited-state lifetimes, \( \tau_0 \) and \( \tau^0_0 \) (Table I), it becomes evident that non-radiative processes in DMSO are more pronounced for the acid than for the anion.

VI. CONCLUSION

The absolute fluorescence quantum yields (AQYs) are related to the area under the decay curves by Eqs. (3.28). These areas can be calculated from our time-resolved data, either numerically or from Eq. (3.31). To three-digit accuracy, both routes lead to the same results (\( \varphi , \tau_f \) in Table II). Thus Eq. (3.31) provides a useful approximation to the area under the decay curves. The experimentally determined AQYs (see Sec. IV A for detail) are also given in the table. The two data together provide the most reliable estimate for the radiative fluorescence lifetimes of the acid and anion, see Table II. Upon comparison with the observed excited-state lifetimes, \( \tau_0 \) and \( \tau^0_0 \) (Table I), it becomes evident that non-radiative processes in DMSO are more pronounced for the acid than for the anion.
time behavior as a function of the relative excited-state lifetimes was previously suggested for the excitation transfer reaction $A^* + B \rightarrow A + B^*$.46

The above achievements are not merely a theoretical curiosity; we have produced a clear experimental indication for the applicability of the theory in the A-regime. Although more accurate measurements to longer times could be useful, the example of excited-state proton transfer to solvent (DMSO) from an excited hydroxyaryl compound (5CN2OH) fits the predicted behavior very nicely. Diffusion thus exerts more profound effects on fast chemical reactions than previously anticipated. Its clear manifestation is only a matter of accurate experimentation. The challenge remains, for the experimentalist, to find a system which exhibits the transition between the different regimes analyzed in this work.

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