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Excited-state reversible geminate reaction. II. Contact geminate quenching

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Results of Part I are extended to include the effect of contact quenching by the geminate partner. The long-time and asymptotic solutions derived herein are compared with numerical and experimental data for excited-state proton transfer to solvent, involving both quenching and two different lifetimes. © 1999 American Institute of Physics. [S0021-9606(99)51104-5]

I. INTRODUCTION

A realistic description of the kinetics of excited-state proton transfer to solvent (PTTS) involves several simultaneous processes. Perhaps most well-studied is the reversibility of this diffusion-influenced reaction, leading to the $t^{-3/2}$ asymptotic decay of the initially bound state.¹⁻⁶ This shows that the solvated geminate proton may recombine with the base adiabatically, in the excited electronic state. At the same time, the acid and base forms decay to their ground electronic state. To simplify the problem, it has mostly been assumed that their excited-state lifetimes are equal. In reality, the base has a longer lifetime, particularly in nonprotic solvents. The effect of the different lifetimes has been treated in Part I of this work⁷, revealing an interesting transition in the long-time asymptotic behavior.⁸

In addition to reversible binding, there appears to be a strong proton-induced excited-state quenching under certain conditions. Already the steady-state work of Harris and Selinger⁹ showed strong quenching of 1-naphthol by homogeneous protons. The quenching effect has been attributed to a nonadiabatic proton attack on a ring site.¹⁰ However, low pH medium is not a prerequisite for promoting this reaction. Pines and Fleming^{11,12} demonstrated that the geminate proton itself may quench the 1-naphthol. The excited acid then decays according to the $t^{-3/2}$ law, whereas the excited base approaches its limiting behavior with the $t^{-1/2}$ law characteristic of irreversible binding reactions.¹³

The assumption of Pines and Fleming,¹¹ that at asymptotically long times the two reaction channels available to the geminate proton are independent, has never been rigorously proven. This is shown by Eq. (3.18) below, which provides the long-time asymptotics for the acid and base forms in the presence of *both* quenching and different lifetimes. In addition, an extended long-time solution is obtained which is seen to be a useful approximation over a wide time range. This is demonstrated in comparison with experimental data, involving both the quenching and the two-lifetime effects. Thus a realistic description of geminate PTTS reactions in the excited state is finally achieved.

Mathematically, the present work bears heavily on the exposition of Part I.⁷ The addition of quenching is a seemingly minor modification to the partial differential Smoluchowski-type equation. Nevertheless, it leads unavoid-

ably to more tedious algebraic manipulations. Since it represents a more specialized phenomenon, we did not find it useful to include quenching in our treatment of the two-lifetime effect.⁷ In comparison with the detailed derivation of Part I, the present exposition represents a brief overview, highlighting the role of quenching in the more fundamental expressions. While a reader interested in the details of the derivation may consult Part I, the presentation below is self-contained, providing a useful summary of the most general results in the field.

II. THEORY

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*, through an interaction potential, *V(r)* (in units of the thermal energy $k_B T$). The particles diffuse, with a fixed (relative) diffusion coefficient $D = D_A + D_B$. The unbound pair undergoes two parallel reactions: The *B*-particle may either bind to *A* or quench its excitation, with rate functions $W_a(r)$ and $W_q(r)$, respectively. The latter possibility leads nonadiabatically to the ground electronic state. The bound *AB* pair may dissociate with a rate function $W_d(r)$, producing the excited *A + B* pair at a distance $r \geq a$. In addition, the bound (*AB*) and unbound (*A + B*) excited molecules decay to their ground electronic states with rate constants k_0 and k'_0 , respectively.

Denote by $p(*, t)$ the probability of finding the (geminate) pair in the bound excited state at time *t*, and by $p(r, t)$ its probability density to be unbound at a separation *r*. These quantities obey the spherically symmetric Debye-Smoluchowski equation in three dimensions with the appropriate "sink terms,"

$$\frac{\partial}{\partial t} p(r, t) = \mathcal{L} p(r, t) - [W_a(r) + W_q(r) + k'_0] p(r, t) + W_d(r) p(*, t), \quad (2.1a)$$

$$\frac{\partial}{\partial t} p(*, t) = 4\pi \int_a^\infty W_a(r) p(r, t) r^2 dr - (k_d + k_0) p(*, t). \quad (2.1b)$$

Here $a \leq r < \infty$, $k_d \equiv 4\pi \int W_d(r) r^2 dr$, \mathcal{L} is the spherically symmetric Smoluchowski operator in three dimensions,

$$\mathcal{L} \equiv r^{-2} \frac{\partial}{\partial r} D(r) r^2 e^{-V(r)} \frac{\partial}{\partial r} e^{V(r)}, \quad (2.2)$$

and $\partial[p(r,t)\exp(V(r))]/\partial r = 0$, at $r=a$. We will assume that D is independent of the interparticle separation r . The problem becomes tractable when contact reactivity is assumed for all three sink terms,

$$W_d(r) = \frac{k_d \delta(r-a)}{4\pi a^2}, \quad W_a(r) = \frac{k_a \delta(r-a)}{4\pi a^2}, \quad (2.3)$$

$$W_q(r) = \frac{k_q \delta(r-a)}{4\pi a^2}.$$

Here k_d, k_a and k_q denote the dissociation, association and quenching rate constants, respectively. In our previous notations,^{2,4} $k_d \equiv \kappa_d, k_a \equiv 4\pi a^2 \kappa_r$ and $k_q \equiv 4\pi a^2 \kappa_q$.

Following the derivation of Part I, let us take the Laplace transforms $q(r) \equiv \tilde{p}(r,s) \equiv \int_0^\infty p(r,t) \exp(-st) dt$ and $q(*) \equiv \tilde{p}(*,s)$. Let us consider these transforms for the following two different initial conditions. When the particles are initially separated to a distance r_0 , one sets $p(r,0|r_0) = \delta(r-r_0)/(4\pi r_0^2)$ and $p(*,0|r_0) = 0$, obtaining

$$\begin{aligned} (s+k'_0) q(r|r_0) - \frac{\delta(r-r_0)}{4\pi r_0^2} \\ = \mathcal{L} q(r|r_0) - \left[k_q + \frac{(s+k_0)k_a}{s+k_d+k_0} \right] \frac{\delta(r-a)}{4\pi a^2} q(a|r_0), \end{aligned} \quad (2.4a)$$

$$q(*|r_0) = \frac{k_a}{s+k_d+k_0} q(a|r_0). \quad (2.4b)$$

Note that for irreversible association, $k_d=0$, the two rate constants, k_a and k_q , play an identical role in Eq. (2.4a). When the excited molecule is initially bound, $p(r,0|*) = 0$ and $p(*,0|*) = 1$, one finds

$$q(r|*) = k_d q(r|a)/(s+k_d+k_0), \quad (2.5a)$$

$$q(*|*) = [1 + k_d q(*|a)]/(s+k_d+k_0), \quad (2.5b)$$

where $q(r|a)$ and $q(*|a)$ are given by Eq. (2.4). The solution for both initial conditions is thus determined by $q(r|r_0)$.

The equations are next written in terms of the solution for nonreactive diffusion, $f(r,t)$, which obeys

$$\partial f(r,t)/\partial t = (\mathcal{L} - k'_0) f(r,t). \quad (2.6)$$

In Laplace space, $g(r|r_0) \equiv \tilde{f}(r,s|r_0)$ obeys

$$(s+k'_0) g(r|r_0) - \frac{\delta(r-r_0)}{4\pi r_0^2} = \mathcal{L} g(r|r_0), \quad (2.7)$$

with $\partial[g(r|r_0)\exp(V(r))]/\partial r = 0$ at $r=a$. Subsequently, Eq. (2.4a) becomes

$$q(r|r_0) = g(r|r_0)$$

$$-g(r|a) \frac{(s+k_0)k_a + (s+k_0+k_d)k_q}{Q(s)} g(a|r_0), \quad (2.8)$$

where the denominator, $Q(s)$, is the function

$$\begin{aligned} Q(s) = s + k_d + k_0 + (s+k_0)k_a g(a|a) \\ + (s+k_0+k_d)k_q g(a|a). \end{aligned} \quad (2.9)$$

By substituting $q(r|a)$ from Eq. (2.8) into Eq. (2.5), the latter is converted to

$$q(r|*) = k_d g(r|a)/Q(s), \quad (2.10a)$$

$$q(*|*) = [1 + (k_a + k_q) g(a|a)]/Q(s). \quad (2.10b)$$

By integrating our equations over space, using $4\pi \int_a^\infty g(r|a) r^2 dr = (s+k'_0)^{-1}$, one obtains the “survival probability” of the unbound, $A+B$, pair

$$S(t|*) \equiv 4\pi \int_a^\infty p(r,t|*) r^2 dr, \quad (2.11a)$$

$$(s+k'_0) \tilde{S}(s|*) = k_d/Q(s), \quad (2.11b)$$

where $\tilde{S}(s|*)$ is, evidently, the Laplace transform of $S(t|*)$. The problem has thus been reduced to finding the solution of Eq. (2.7).

III. APPROXIMATE SOLUTIONS

The approximate long-time solution derived in this sequel is based on the asymptotic solution of free diffusion, Eq. (2.7). Since the main goal is to determine the experimentally relevant kinetic functions, $p(*,t)$ and $S(t)$, the free diffusion Green function $f(a,t|a)$ is all that is required. Its Laplace transform admits the following asymptotic solution for small σ ,

$$g(a|a)^{-1} \sim k_{-D} (1 + a_{\text{eff}} \sigma), \quad (3.1)$$

where σ is the positive constant

$$\sigma \equiv \sqrt{(s+k'_0)/D}. \quad (3.2)$$

In the above expressions, k_{-D} denotes the diffusion controlled separation rate constant

$$k_{-D} \equiv k_D e^{V(a)}, \quad k_D \equiv 4\pi D a_{\text{eff}}, \quad (3.3)$$

and the effective contact radius, a_{eff} , is defined by

$$a_{\text{eff}} = \left(\int_a^\infty e^{V(r)} r^{-2} dr \right)^{-1}. \quad (3.4)$$

Note that in the absence of an interaction potential, when $V(r)=0$, $a_{\text{eff}}=a$ and Eq. (3.1) is exact for all σ . Equation (2.10) can then be inverted analytically, in terms of the three roots of the cubic polynomial $Q(s)$.^{4,14} This field-free solution will be discussed in Part III of this series.

Let us begin with the easier problem of reducing the diffusion problem to familiar kinetic expressions. By neglecting σa_{eff} in comparison with unity in Eq. (3.1) and substituting $g(a|a) \sim k_{-D}^{-1}$ in Eqs. (2.10b) and (2.11b), one gets

$$q(*|*) \approx (s + k_0 + k_{\text{off}}^q)^{-1}, \quad (3.5a)$$

$$\tilde{S}(s|*) \approx k_{\text{off}} q(*|*)/(s + k'_0). \quad (3.5b)$$

Here two different steady-state “off” rate coefficients were introduced,

$$k_{\text{off}} = \frac{k_d k_{-D}}{k_a + k_{-D} + k_q}, \quad k_{\text{off}}^q = \frac{k_d (k_{-D} + k_q)}{k_a + k_{-D} + k_q}. \quad (3.6)$$

k_{off} is a steady-state rate constant for the diffusional separation of A and B , in the presence of the quenching reaction, whereas k_{off}^q represents the elimination of AB by both diffusion and quenching.

The Laplace transforms are now easily inverted,

$$p(*, t|*) \approx e^{-(k_0 + k_{\text{off}}^q)t}, \quad (3.7a)$$

$$S(t|*) \approx Z[e^{-k'_0 t} - e^{-(k_0 + k_{\text{off}}^q)t}], \quad (3.7b)$$

with the factor Z defined by

$$Z \equiv \frac{k_{\text{off}}}{k_{\text{off}}^q + k_0 - k'_0}. \quad (3.8)$$

The solution in Eq. (3.7) is readily identified as that of the rate equations

$$\frac{d[AB]}{dt} = -(k_{\text{off}}^q + k_0)[AB], \quad (3.9a)$$

$$\frac{d[A+B]}{dt} = k_{\text{off}}[AB] - k'_0[A+B], \quad (3.9b)$$

after setting $p(*, t|*) \equiv [AB]$ and $S(t|*) \equiv [A+B]$. In this simplistic description, the bound pair disappears due to both diffusion and quenching (k_{off}^q), whereas the separated pair is created only by diffusion (k_{off}).

To proceed beyond the kinetic approximation, one retains σa_{eff} in Eq. (3.1). Keeping in mind that $0 \leq \sigma a_{\text{eff}} \leq 1$, one may exchange $(1 + \sigma a_{\text{eff}})^{-1}$ by $1 - \sigma a_{\text{eff}}$. After some algebra, Eqs. (2.10) become

$$q(*|*) = (D\sigma^2 + k_0 - k'_0 + k_{\text{off}}^q + k_{\text{off}} a'_{\text{eff}} \sigma)^{-1}, \quad (3.10a)$$

$$\tilde{S}(\sigma|*) = [k_{\text{off}}(1 + a_{\text{eff}}^q \sigma)] q(*|*)/(D\sigma^2). \quad (3.10b)$$

Whereas the denominators of the exact Laplace transforms involve a cubic polynomial in σ , the present approximation has reduced it to a quadratic polynomial. The simpler kinetic approximation discussed above involved the additional neglect of the linear term in this polynomial. In the above equations, it proved useful to define two different modified effective radii,

$$a'_{\text{eff}} \equiv \frac{k_a a_{\text{eff}}}{k_a + k_{-D} + k_q}, \quad a_{\text{eff}}^q \equiv \frac{(k_a + k_q) a_{\text{eff}}}{k_a + k_{-D} + k_q}. \quad (3.11)$$

Note how these definitions parallel those of k_{off} and k_{off}^q in Eq. (3.6).

Equation (3.10) can now be inverted analytically, as follows. First, one evaluates the two roots of the denominator

$$\sigma_{\pm} = \frac{k_{\text{off}} a'_{\text{eff}}}{2D} (-1 \pm \sqrt{1 + \beta}), \quad (3.12)$$

where β is the dimensionless parameter

$$\beta \equiv \frac{(k'_0 - k_0 - k_{\text{off}}^q) 4D}{(k_{\text{off}} a'_{\text{eff}})^2}. \quad (3.13)$$

In terms of these roots, Eq. (3.10a) becomes

$$D q(*|*) = [(\sigma - \sigma_+)^{-1} - (\sigma - \sigma_-)^{-1}]/(\sigma_+ - \sigma_-). \quad (3.14)$$

Taking Laplace inverses,¹⁵ one finally gets

$$p(*, t|*) = \frac{e^{-k'_0 t}}{2} \left(\phi_+(t) + \phi_-(t) - \frac{\phi_+(t) - \phi_-(t)}{\sqrt{1 + \beta}} \right), \quad (3.15a)$$

$$S(t|*) = \frac{e^{-k'_0 t}}{\sqrt{1 + \beta}} \left(\frac{(1 + \sigma_+ a_{\text{eff}}^q) \phi_+(t) - 1}{\sigma_+ a'_{\text{eff}}} - \frac{(1 + \sigma_- a_{\text{eff}}^q) \phi_-(t) - 1}{\sigma_- a'_{\text{eff}}} \right), \quad (3.15b)$$

where the function $\phi_{\pm}(t)$ is defined by

$$\phi_{\pm}(t) \equiv e^{\sigma_{\pm}^2 D t} \text{erfc}(-\sigma_{\pm} \sqrt{D t}). \quad (3.16)$$

$\text{Erfc}(z)$ is the complementary error function for a possibly complex argument, z .

The above results display an interesting transition in their asymptotic behavior as a function of β . This transition occurs when $\beta = 0$, or

$$k'_0 = k_0 + k_{\text{off}}^q. \quad (3.17)$$

In the A regime, $\beta < 0$ (which includes, in particular, the equal-lifetime case), one gets the following asymptotic behavior:

$$p(*, t|*) \sim Z^2 \frac{K_{\text{eq}}}{(4\pi D t)^{3/2}} e^{-k'_0 t}, \quad (3.18a)$$

$$S(t|*) \sim Z \left\{ 1 + \frac{[K_{\text{eq}}^q (k_0 - k'_0) + k_q e^{-V(a)}] Z}{4\pi D \sqrt{\pi D t}} \right\} e^{-k'_0 t}, \quad (3.18b)$$

where two equilibrium coefficients are defined,

$$K_{\text{eq}} \equiv k_a e^{-V(a)}/k_d, \quad K_{\text{eq}}^q \equiv (k_a + k_q) e^{-V(a)}/k_d. \quad (3.19)$$

The ultimate “escape probability,” Z , is given in Eq. (3.8). For equal lifetimes, $Z = k_{\text{off}}/k_{\text{off}}^q = k_{-D}/(k_{-D} + k_q)$ is the branching ratio between escape and quenching. $p(*, t|*) \exp(k'_0 t)$ then decays according to the modified $t^{-3/2}$ law, whereas $S(t|*) \exp(k'_0 t)$ goes through a maximum, and decays to its ultimate value, Z , with the $t^{-1/2}$ law suggested by Pines and Fleming.¹¹ Indeed, for equal lifetimes, the asymptotic behavior in Eq. (3.18b) has the same form as that found by Hong and Noolandi¹³ for irreversible recombination with a rate constant $k_q e^{-V(a)}$, proving the hypothesis in Ref. 11, that at asymptotically long times the reversible binding and quenching reactions are independent. In the case of different lifetimes, an additional contribution comes from the difference in the excited state rate constants.⁷

In the AB -regime, $\beta > 0$, the asymptotic behavior becomes

TABLE I. Parameters used for calculating the binding probability in the figures.

| Fig. | System | Ref. | a , Å | R_D , Å | D , cm ² /s | $1/k_0$, ns | $1/k'_0$, ns | k_d , ns ⁻¹ | k_a , Å ³ /ns | k_q , Å ³ /ns |
|------|----------------------|------|---------|-----------|--------------------------|--------------|---------------|--------------------------|----------------------------|----------------------------|
| 1 | 5CN2OH/MeOH | 16 | 5.5 | 17.2 | $3.65 \cdot 10^{-5}$ | 5.7 | 10.2 | 0.22 | 6 080 | 870 |
| 2 | 1OH/D ₂ O | 12 | 5.5 | 7.1 | $7.4 \cdot 10^{-5}$ | 4.5 | 23.2 | 8.55 | 13 305 | 14 635 |

$$p(*, t|*) \sim \left(1 - \frac{1}{\sqrt{1+\beta}}\right) \exp[-(k_0 + k_{\text{off}}^q + k_{\text{off}} a'_{\text{eff}} \sigma_+) t], \quad (3.20a)$$

$$S(t|*) \sim \frac{2}{\sqrt{1+\beta}} \frac{1 + \sigma_+ a'_{\text{eff}}}{\sigma_+ a'_{\text{eff}}} \times \exp[-(k_0 + k_{\text{off}}^q + k_{\text{off}} a'_{\text{eff}} \sigma_+) t]. \quad (3.20b)$$

In contrast to Eq. (3.18), which gives the *exact* long-time asymptotic behavior, Eq. (3.20) is only approximate, because it is based on taking the limit $\sigma \rightarrow \sigma_+$, for which Eq. (3.1) is only approximate. Finally, at the transition, $\beta = 0$, one gets

$$p(*, t|*) \sim \frac{1}{k_{\text{off}}} \sqrt{\frac{D}{\pi a'^2_{\text{eff}} t}} e^{-k'_0 t}, \quad (3.21a)$$

$$S(t|*) \sim \sqrt{\frac{4Dt}{\pi a'^2_{\text{eff}}}} e^{-k'_0 t}. \quad (3.21b)$$

The transition is manifested in the time dependence of the asymptotic ratio of the bound to unbound populations

$$\frac{S(t|*)}{p(*, t|*)} \sim \begin{cases} \frac{(4\pi Dt)^{3/2}}{Z K_{\text{eq}}}, & \beta < 0, \\ 2k_{\text{off}} t, & \beta = 0, \\ \frac{k_{\text{off}} (1 + \sigma_+ a'_{\text{eff}})}{D \sigma_+^2}, & \beta > 0. \end{cases} \quad (3.22)$$

This ratio grows asymptotically as $t^{3/2}$ in the A-regime, it is linear in t at the transition, and independent of time in the AB-regime.

To obtain useful expressions for the absolute fluorescence quantum yield (AQY), which is important in steady-state measurements, one begins with its definition

$$\varphi \equiv k_f \int_0^\infty p(*, t) dt = k_f \tilde{p}(*, 0), \quad (3.23a)$$

$$\varphi' \equiv k'_f \int_0^\infty S(t) dt = k'_f \tilde{S}(0). \quad (3.23b)$$

Here k_f and k'_f are the radiative (fluorescence) rate constants for the bound and unbound states, respectively. Due to the possible presence of additional nonradiative processes, $k_f \leq k_0$ and $k'_f \leq k'_0$. By setting $s = 0$ in Eq. (3.10), one finds for the initially bound state that

$$\frac{k_f}{\varphi(*)} = k_{\text{off}}^q + k_0 + k_{\text{off}} \sqrt{a'^2_{\text{eff}} k'_0 / D}, \quad (3.24a)$$

$$\frac{k'_f}{\varphi'(*)} = \frac{k'_0}{k_{\text{off}}} \left[k_{\text{off}}^q + k_0 - \left(k_0 + \frac{k_d k_q}{k_a + k_q} \right) \sqrt{a'^2_{\text{eff}} k'_0 / D} \right]. \quad (3.24b)$$

This produces a new, useful approximation for the AQYs.

IV. RESULTS

This section compares the long-time approximation, Eq. (3.15), with the exact numerical solution on the one hand and the asymptotic solutions on the other. The parameters chosen in Table I correspond to two experimental examples involving geminate quenching. The first is PTTS from the novel “super” photoacid, 5-cyano-2-naphthol (5CN2OH), to methanol.¹⁶ The second is the ultrafast PTTS from 1-naphthol (1OH) to D₂O.^{11,12} Both reactions are in the “A-regime.” Experimental data collection methods are summarized in Part I.⁷ Numerical computations were performed using SSDP version 2.54.¹⁷ As compared with the calculations without quenching, reported in Part I, the addition of quenching is found to make the numerical solution of the partial differential equations much more demanding. It was not possible to obtain an accurate long-time solution without the incorporation of a strongly spatially nonuniform grid, which is very dense near the boundary at $r = a$ (SSDP “space step ratio” parameter of < 0.1).

Figures 1 and 2 show the solutions for both binding and survival probabilities under the two sets of experimental conditions. The long-time solution, Eq. (3.15), shown by the dashed line, is almost indistinguishable from the exact numerical solution (bold curve) for the binding probability. For the survival probability, $S(t|*)$, it exhibits larger deviations at short times. The approximation (3.15b) is expected to hold for

$$t \geq a'^2_{\text{eff}} / D, \quad (4.1)$$

which is 0.9 and 0.13 ns for 5CN2OH and 1OH, respectively. This convergence criterion is obeyed very nicely, since deviations are indeed observed only at shorter times. Presently, these deviations are of little experimental significance, as they occur within the instrument-response-function of the time-correlated single-photon-counting method (see Part I).

The asymptotic behavior of Eq. (3.18) is exhibited by the dash-dot line. Whereas $p(*, t|*)$ converges to this line only in its asymptotic tail (panel a), $S(t|*)$ approaches the asymptotic behavior immediately after the peak. It is followed by a $t^{-1/2}$ decay to the asymptotic limit, Z (dash-dot line in panel b). This results predominantly from the quenching effect, as discussed by Pines and Fleming.¹¹ Although, according to Eq. (3.18b), the difference in excited-

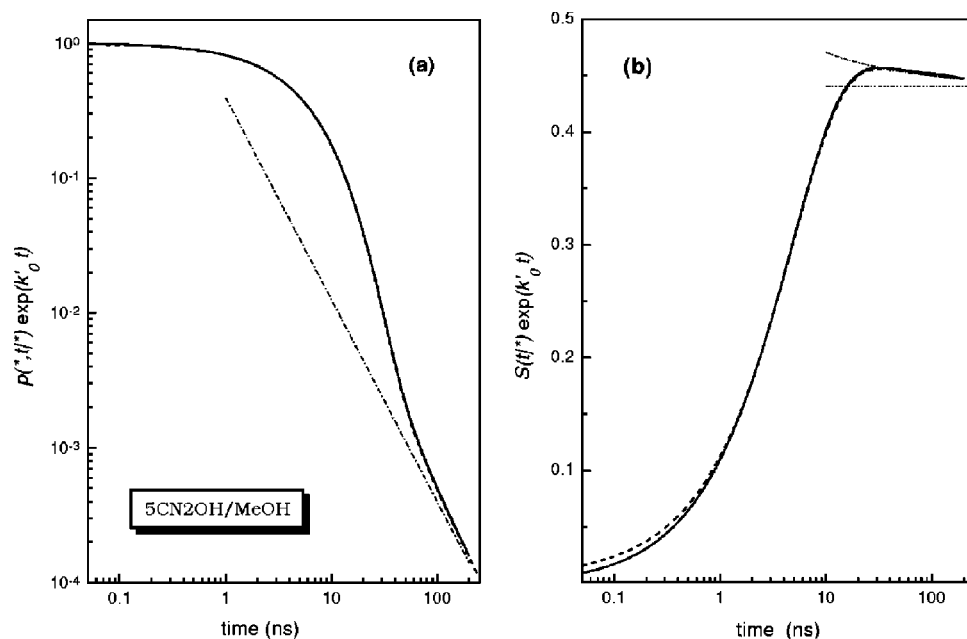


FIG. 1. Excited-state proton transfer from 5CN2OH to methanol (Ref. 16). (a) Acid signal; (b) anion signal. Full line is exact numerical solution of Eq. (2.1), with the parameters from Table I. Dashed curves are the long-time solution from Eq. (3.15), and the dash-dotted curves are its asymptotic solutions, as detailed in the sequel. Note the logarithmic scales.

state decay rates also contributes to the peak, for the parameters of 1OH in D₂O, $(k_a + k_d)(k_0 - k'_0)/k_d = 5000 \text{ \AA}^3/\text{ns}$, which is only about a third of k_q .

Figures 3 and 4 demonstrate the transition between the different asymptotic behaviors in the case of significant quenching, by varying the (hypothetical) lifetime of the 1OH anion while keeping the other parameters at their best-fit values, see Table I. The transition occurs here for $\tau'_0 = 1/(k_0 + k_{\text{off}}^q) = 150 \text{ ps}$, a very small value as compared with the experimental lifetime of 23.2 ns. For longer lifetimes, the reaction is in the *A*-regime. It exhibits the power-law asymptotics of Eq. (3.18), which reflects the relative diffusion of the *A*–*B* pair. For shorter lifetimes, the unbound pair has insufficient time to diffuse and the decay becomes exponential, see Eq. (3.20). Exactly at the transition, one gets the

asymptotics of Eq. (3.21). These different asymptotic laws are depicted by the dashed lines in Figs. 3 and 4. The full lines there are from our approximate long-time solution, Eq. (3.15), not from the numerical calculation. In the *A*-regime, this solution becomes exact as $t \rightarrow \infty$.

V. CONCLUSION

Many excited-state PPTS reactions exhibit contact quenching by the diffusing geminate proton. It was therefore important to extend the results from Part I, involving two different lifetimes (for the excited acid and anion), to incorporate the quenching effect. Long-time asymptotic solutions were derived for both binding and survival probabilities in

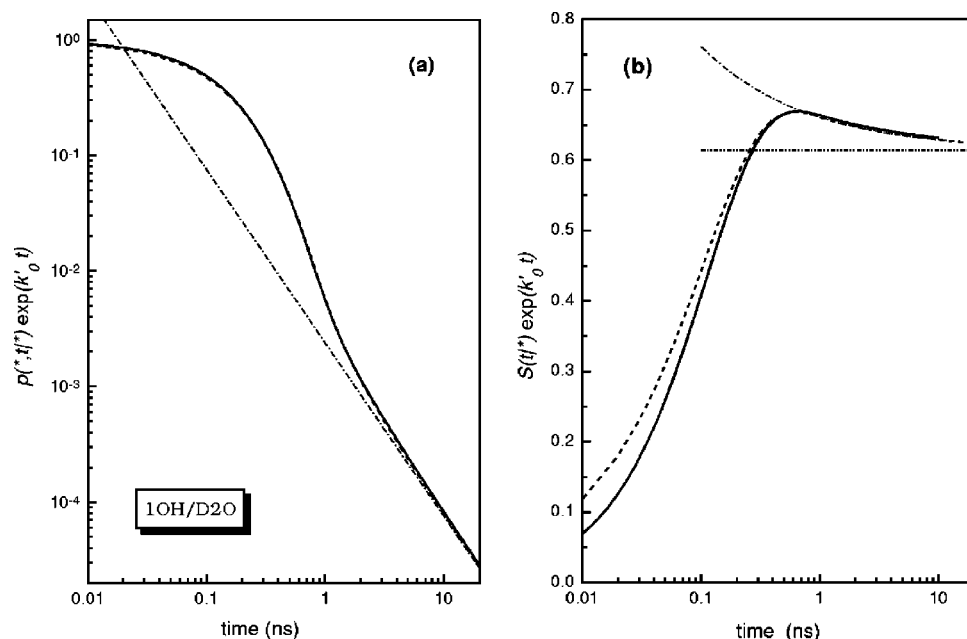


FIG. 2. Same as Fig. 1, using the fitting parameters for 1-naphthol in D₂O (Ref. 12).

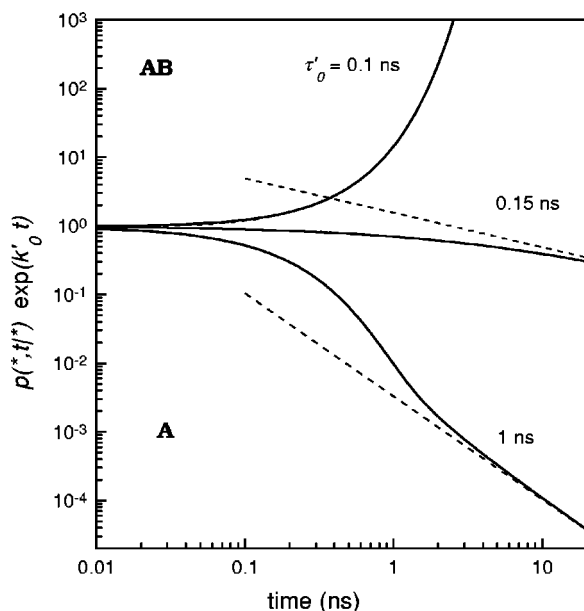


FIG. 3. The transition expected in the acid signal from excited 1-naphthol if the anion lifetime could be shortened as indicated. Full lines are the approximate long-time solution, Eq. (3.15), and the dashed curves are its corresponding asymptotic solutions. Note the log-log scale.

the presence of geminate quenching. In addition, an approximate solution was obtained which is valid over a much wider time window than the asymptotic laws. Its accuracy seems to be sufficiently high for extracting the intrinsic rate parameters by experimental data fitting. The corresponding least-squares procedure should be simpler to use than the manual adjustment of the partial differential equation solver. In the absence of an interaction potential, an exact solution may be found for all components of the Green function, in the presence of *both* quenching and different lifetimes. This solution will be discussed in Part III of this series.

The theoretical analysis verified that quenching may indeed be manifested in a peak in the signal from the base form.¹¹ However, the difference in lifetimes also contributes to this peak, see Eq. (3.18). Likewise, the quenching process contributes to the transition between the two kinetic regimes (the *A* and *AB* regimes), although a difference in lifetimes is a prerequisite for its occurrence. The experimental examples provided in this work all fall in the *A*-regime. One wonders whether a photoacid with sufficiently short anion lifetime can be found to exemplify the behavior in the *AB*-regime.

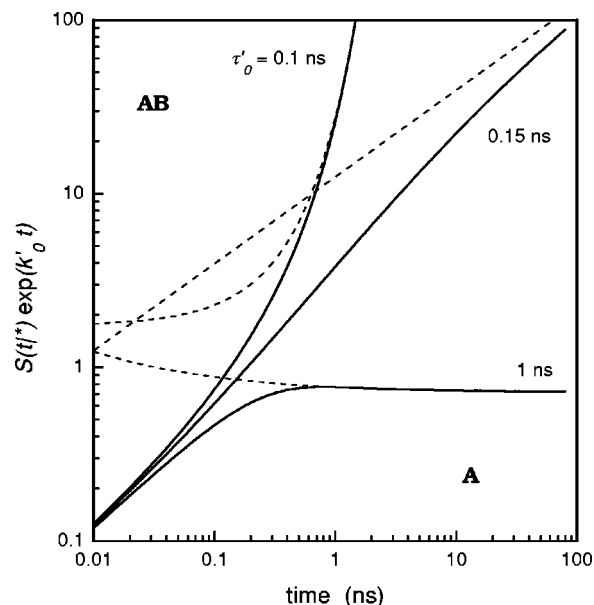


FIG. 4. Same as Fig. 3, for the anion signal of excited 1-naphthol.

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