9688 *J. Phys. Chem. A* **2003,** *107,* 9688−9694

Theories of Reversible Dissociation: A Comparative Study

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Received: June 11, 2003; In Final Form: August 5, 2003

Reversible dissociation after instantaneous excitation and the fluorescence quantum yields of excited molecules and the products of their dissociation are considered in the framework of integral kinetic equations. A number of different theories are brought to the same integral form, and the kernels of corresponding integral equations are specified. All of the theories are compared using as criteria the concentration dependence of either their kernels or the corresponding Stern−Volmer constants.

I. Introduction

In the last few decades, the attention of many theorists has been focused on the reversible association/dissociation reaction of excited particles in liquid solutions. Such a reaction is usually represented by the following formal scheme:

$$\begin{array}{ccc} \mathrm{A}^* + B & \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\rightleftarrows}} & \mathrm{C}^* \\ \downarrow\ u_\mathrm{A} & & \downarrow\ u_\mathrm{C} \end{array} \tag{1.1}$$

where $u_\mathrm{A} = 1/\tau_\mathrm{A}$ and $u_\mathrm{C} = 1/\tau_\mathrm{C}$ are the decay rates of excitations that may be either equal or different. The best-studied example is the reversible proton transfer from an excited photoacid to the solvent:[1−6]

$$\begin{array}{ccc} \mathrm{R^*OH} & \underset{k_\mathrm{a}}{\overset{k_\mathrm{d}}{\rightleftharpoons}} & \mathrm{R^*O^-} + \mathrm{H^+} \\ \downarrow\ u_\mathrm{C} & & \downarrow\ u_\mathrm{A} \end{array} \tag{1.2}$$

The reaction may develop in opposite directions depending on what was initially created by a light pulse, A* or C*.

The vast majority of competing theories were aimed at specifying the kinetics of a system's approach to equilibrium at $u_\mathrm{A} = u_\mathrm{C} = 0$, assuming that B's are present in great excess, so that $c = [\mathrm{B}]$ remains constant. In the case of reaction 1.2, the desirable concentration of $\mathrm{H^+}$ in solution is provided by the addition of an inert acid (e.g., $\mathrm{HClO_4}$). The added protons compete with a geminate proton for the restoration of C*. The kinetics of approaching the equilibrium is universally described by the relaxation function $R(t)$, which is defined as follows:

$$\frac{P_\mathrm{C}(t) - \mathscr{P}_\mathrm{C}}{P_\mathrm{C}(0) - \mathscr{P}_\mathrm{C}} = R(t) = \frac{\mathscr{P}_\mathrm{A} - P_\mathrm{A}(t)}{\mathscr{P}_\mathrm{A} - P_\mathrm{A}(0)} \tag{1.3}$$

Here, $P_\mathrm{C}(t) = N_\mathrm{C}(t)/[N_\mathrm{C}(0) + N_\mathrm{A}(0)]$ and $P_\mathrm{A}(t) = N_A(t)/[N_\mathrm{C}(0) + N_A(0)]$ are the fractions of C and A molecules whose equilibrium values are

$$\mathscr{P}_\mathrm{C} = \frac{cK_\mathrm{eq}}{1 + cK_\mathrm{eq}} = 1 - \mathscr{P}_\mathrm{A} \tag{1.4}$$

where $K_\mathrm{eq} = k_\mathrm{a}/k_\mathrm{d}$ is the equilibrium constant. It is now firmly established that $R(t)$ follows the asymptotic power law:[7−11]

$$R(t) \propto t^{-3/2} \tag{1.5}$$

The power law dependence was unambiguously confirmed experimentally,[12,13] though in the case of nonzero u_A and u_C it is combined with the exponential drop in the survival probabilities.[14−16]

The asymptotic expression (eq 1.5) represents the very end of the kinetics when, for instance, $P_\mathrm{C}(t)$ starting from $P_\mathrm{C}(0) = 1$ is already 3 or 4 orders of magnitude smaller. This tail is hardly available for detection even with contemporary single-photon counting. Besides, the question arises, What is the difference in the precursor time evolution of $P_\mathrm{C}(t)$ or $P_\mathrm{A}(t)$ predicted using a number of different theoretical methods?

Here we are going to switch our attention from the asymptote to the total time evolution of $P_\mathrm{C}(t)$ or $P_\mathrm{A}(t)$, both of which entirely contribute to the relative quantum yields of the fluorescence:

$$\eta_\mathrm{A} = u_\mathrm{A}\int_0^\infty P_\mathrm{A}(t)\,\mathrm{d}t \qquad \eta_\mathrm{C} = u_\mathrm{C}\int_0^\infty P_\mathrm{C}(t)\,\mathrm{d}t \tag{1.6}$$

Both of them can be universally expressed through the Stern−Volmer constant κ. Using the latter as a standard for comparison between the theories of irreversible quenching, we have already demonstrated how the $\kappa(c)$ dependence for each particular theory deviates from that represented by differential encounter theory (DET).[17] The latter was commonly recognized as being exact for at least a target problem.[18,19] But even for a mobile A, DET remains a good approximation.[20]

In the case of a reversible reaction of the type shown in eq 1.1, the problem becomes more difficult. After the dissociation,

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10.1021/jp030733g CCC: $25.00

other B molecules can be involved in the reaction with A. This many-particle competition for the partner couples the motion of the molecules, making the problem unsolvable analytically. Thus, only approximate solutions were obtained using rather different methods and assumptions whose validity very often remains unclear.

The repeating binding−unbinding processes change the spatial distribution of B's around A. But the movement of A also affects the concentration profile of the B particles. Therefore, the motion of both A and B should have an influence on the reaction. We have to restrict our consideration by only two opposite limits: the "target problem", when A and C are static ($D_A = D_C = 0$) while the pointlike B molecules move independently ($D_B \neq 0$), and the "trap problem", in which a single particle A accomplishing diffusion with $D_A \neq 0$ between immovable B particles can be trapped by one of them and form an immovable C ($D_B = D_C = 0$). Besides, we will assume that the reaction takes place only at the contact distance, which is definitely the case for the proton transfer (eq 1.2). Owing to the mentioned complexity of the problem, the vast majority of existing theories also deal only with contact reactions, although a few of them can be extended to the distant (electron or energy) transfer as well.

The comparative analysis of the $\kappa(c)$ dependencies undertaken here allowed us to discriminate between different theories judging by the result. Moreover, it points the way to how they may be inspected experimentally. By comparison with easily available data for $\kappa(c)$, one can make the right choice of the best theory.

This paper is constructed as follows. In section II, we outline the central points of the kinetics of reversible reactions. In section III, DET is briefly discussed. Section IV describes several of the foremost approaches to reversible reactions. In the Results section, we compare the concentration dependencies of the kernels and Stern−Volmer constants for all of the theories under investigation, and we summarize all of the findings in the Conclusions.

II. Kinetics of Reversible Dissociation

To describe the kinetics of dissociation in the pseudo-unimolecular limit, when excited A molecules are surrounded by the B particles present in great excess, we propose the following set of integro-differential equations that are linear in c:

$$\frac{\mathrm{d}P_A}{\mathrm{d}t} = -u_A P_A - c\int_0^t F_a(t-\tau)\, P_A(\tau)\, \mathrm{d}t + \int_0^t F_d(t-\tau)\, P_C(\tau)\, \mathrm{d}\tau \quad (2.1a)$$

$$\frac{\mathrm{d}P_C}{\mathrm{d}t} = -u_C P_C + c\int_0^t F_a(t-\tau)\, P_A(\tau)\, \mathrm{d}\tau - \int_0^t F_d(t-\tau)\, P_C(\tau)\, \mathrm{d}\tau \quad (2.1b)$$

They may be obtained by means of the matrix integral encounter theory (IET) reviewed in ref 21, together with the particular definitions of kernels that are concentration-independent in IET. However, from a more general point of view, eqs 2.1 are an implementation of memory function formalism in chemical kinetics. The form of these equations shows the essentially non-Markovian character of reversible reactions in solution: the convolution integrals entail the prehistoric evolution of the process. They constitute the formal basis for the treatment of the transfer phenomenon that is qualitatively different from the conventional rate equations. We have already proven that all of the theories of irreversible transfer are reducible to the proper integral equation and differ only by the definitions given to its kernel.[17] The theories of reversible geminate dissociation proposed by Berg,[22] Burshtein,[23] Agmon,[24] and Szabo[25] can also be represented by eq 2.1b at $c = 0$.[26] Now we extend this conclusion to $c \neq 0$. In many sophisticated theories that we will compare, the results are presented differently. However, all of them after some manipulation can be shown to obey eqs 2.1, although the kernels are specific to each of them. Omitting these manipulations, we will concentrate on the results: the difference between concentration dependencies of the kernels obtained from different theories.

Assuming a spherical symmetry of the reactions, one has to represent them by the distance-dependent rates of association, $W_a(r)$, and dissociation, $W_d(r)$. In the contact approximation, they are replaced by the kinetic rate constants, k_a and k_d, of the corresponding reactions that occur only at the closest approach distance, σ:

$$k_a = \int_\sigma^\infty W_a(r)\, 4\pi r^2\, \mathrm{d}r \qquad k_d = \int_\sigma^\infty W_d(r)\, 4\pi r^2\, \mathrm{d}r \quad (2.2)$$

Kernels F_a and F_d take the following form

$$F_a(t) = k_a \Sigma(t) \qquad F_d(t) = k_d \Sigma(t) \quad (2.3)$$

where $\Sigma(t)$ remains a single parameter that is specific to each theory. This kernel holds the memory effect. In the framework of ordinary chemical kinetics, $\Sigma(t) = \delta(t)$, and therefore the system (eq 2.1) acquires the pure differential form. In fact, this is possible only in the limit when the reaction is entirely under kinetic control.

In their contact form, eqs 2.1 are perfect if the exact $\Sigma(t)$ is known.[27] They can be formally solved in the Laplace domain. The quantities

$$\tilde{P}_{A,C}(s) = \int_0^\infty P_{A,C}(t)\, \exp(-st)\, \mathrm{d}t$$

which are the Laplace images of $P_A(t)$ and $P_C(t)$, can be expressed through the Laplace transformation $\tilde{\Sigma}(s)$ of kernel $\Sigma(t)$ in the following way:

$$\tilde{P}_A(s) = \frac{(s + u_C)P_A(0) + k_d\tilde{\Sigma}(s)}{Q(s)} \quad (2.4a)$$

$$\tilde{P}_C(s) = \frac{(s + u_A)P_C(0) + ck_a\tilde{\Sigma}(s)}{Q(s)} \quad (2.4b)$$

where the denominator

$$Q(s) = (s + u_C)(s + u_A) + (ck_a(s + u_C) + k_d(s + u_A))\tilde{\Sigma}(s) \quad (2.5)$$

and the sum of the initial probabilities $P_A(0) + P_C(0) = 1$.

For stable particles ($u_A = u_C = 0$), one can easily deduce from the last equation the Laplace transformation of the relaxation function:

$$\tilde{R}(s) = \frac{\tilde{P}_C(s) - \mathscr{P}_C/s}{1 - \mathscr{P}_C} = \frac{1}{s + (k_d + k_a c)\tilde{\Sigma}(s)} \quad (2.6)$$

The concentration-independent kernel of IET denoted later as $\tilde{\Sigma}_0(s)$ can be borrowed from the integral encounter theory of purely geminate dissociation:[26]

$$\tilde{\Sigma}_0(s) = \frac{1}{1 + k_a g(s)} \tag{2.7}$$

where $g(s) \equiv \tilde{G}_0(\sigma, \sigma, s)$ is the Laplace transformation of the Green function of the free diffusion around a hard sphere with the reflecting boundary condition at the contact:[23]

$$g(s) = \frac{1}{k_D(1 + \sqrt{s\tau_d})} \tag{2.8}$$

Here $k_D = 4\pi\sigma D$ is the diffusional rate constant; $\tau_d = \sigma^2/D$ is the encounter time; and $D = D_A + D_B$ is the relative diffusion coefficient of particles A and B.

Gopich and Doktorov also obtained a result similar to eq 2.6 except that instead of $\tilde{G}_0(\sigma, \sigma, s)$ they used the Green function of penetrable spheres.[28] Even earlier, the same result was derived in the framework of statistical nonequilibrium thermodynamics, but using instead of contact $\tilde{G}_0(\sigma, \sigma, s)$ the free-space Green function[29] $\tilde{G}_0(\sigma, 0, s) = \exp(-\sqrt{s\sigma^2/D})/k_D$. At small $s \ll D/\sigma^2$, the difference between the Green functions disappears because all of them are approximated as $g(s) \approx [1 - \sqrt{s\sigma^2/D}]/k_D$. Using this approximation in eq 2.7 and then taking the inverse Laplace transformation of eq 2.6, one obtains the asymptotic relaxation to the equilibrium:[29]

$$R(t) = \frac{K_{eq}}{(1 + cK_{eq})\,(4\pi Dt)^{3/2}} \qquad \text{at } t \to \infty \tag{2.9}$$

It obeys the same power law as in eq 1.5, but the multiplier $(1 + cK_{eq})$ is peculiar to IET, whose kernel is concentration-independent unlike those in most other theories compared below. When more adequate methods were used to study the target[7-10,30] and trap problems,[8,28,30] it was proven that

$$R(t) = \begin{cases} \dfrac{K_{eq}}{(1 + cK_{eq})^2 (4\pi Dt)^{3/2}} & \text{target problem} \\[2ex] \dfrac{K_{eq}}{\sqrt{1 + cK_{eq}}(4\pi Dt)^{3/2}} & \text{trap problem} \end{cases} \tag{2.10}$$

The most general theory valid for the arbitrary diffusion coefficients, D_A, D_B, and D_C, also corrects only the denominator of eq 2.9, in full accordance with both the target and trap limits.[11]

If $c = 0$, then only the dissociation of C makes any sense. In the contact approximation, this geminate case was repeatedly discussed in the literature.[22,26] When $u_{A,C} \neq 0$, the dissociation starting from $P_C(0) = 1$ proceeds as follows:

$$\tilde{P}_C(s) = \frac{1}{s + u_C + k_d \tilde{\Sigma}_0(s + u_A)} \tag{2.11}$$

At infinitely large D (kinetic control limit), $\tilde{\Sigma}_0(s) = 1$, and we return to the exponential decay, $P_C(t) = \exp(-(u_C + k_d)t)$, which is imposed by conventional chemical kinetic laws.

At $c \neq 0$, there is an alternative: either A ($P_A(0) = 1$, $P_C(0) = 0$) or C ($P_A(0) = 0$, $P_C(0) = 1$) can be initially excited. The former case is typical of impurity quenching (by B's) whose relative quantum yield η_{AA} can be obtained from eqs 1.6 and 2.4a by setting $P_A(0) = 1$:

$$\frac{1}{\eta_{AA}} = 1 + c\kappa \tag{2.12}$$

This is the conventional Stern−Volmer law but with the constant defined as follows:

$$\kappa = \frac{k_a \tilde{\Sigma}(0)/u_A}{1 + k_d \tilde{\Sigma}(0)/u_C} \tag{2.13}$$

If the fluorescence of C is registered at the same initial conditions, then its quantum yield η_{CA} can be found from eqs 1.6 and 2.4b:

$$\eta_{CA} = \eta_C|_{P_A(0)=1} = 1 - \eta_{AA} \tag{2.14}$$

This conservation law for excitations holds because there is no recombination to the ground state accompanying the transfer in either direction.

If the C particle surrounded by B's (given in concentration c) is initially excited, then the quantum yields of fluorescence through both channels, η_{CC} and η_{AC}, can be found from the same equations but with opposite initial conditions: $P_A(0) = 0$, $P_C(0) = 1$. The conservation law applied to this case as well:

$$\eta_{CC} = \eta_C|_{P_C(0)=1} = 1 - \eta_A|_{P_C(0)=1} = 1 - \eta_{AC} \tag{2.15}$$

However, instead of the Stern−Volmer law, we have another one:

$$\frac{1}{1 - \eta_{CC}} = \frac{u_C K_{eq}}{u_A \kappa}[1 + c\kappa] = \frac{1}{\eta_{AC}} \tag{2.16}$$

From this linear relationship, two essential parameters of the problem can be obtained by fitting the experimental data: $(u_C/u_A)K_{eq}$ and κ. The latter is an invariant of the problem that is easily available experimentally in a few ways.

The quantity $\kappa_0 = \lim_{c \to 0} \kappa(c)$ may be considered to be an "ideal" Stern−Volmer constant, conforming to the original, truly linear Stern−Volmer dependence. In the contact approximation, this value of κ can be derived from eq 2.13 with $\tilde{\Sigma}(0) = \tilde{\Sigma}_0(u_A)$:

$$\kappa_0 = \frac{k_a/u_A}{1 + k_a g(u_A) + k_d/u_C} = \frac{k'_a/u_A}{1 + k'_a g(u_A)} \tag{2.17}$$

where $k'_a = k_a/(1 + k_d/u_C)$ is the overall association rate constant that is renormalized due to the reverse reaction. This is the relationship that also follows from the equations of ordinary chemical kinetics applied to reaction 1.1.

If the association is irreversible ($k_d = 0$), then κ from eq 2.13 is proportional to $\tilde{\Sigma}(0)$. The concentration dependence of this κ has been investigated in ref 17 in the framework of several theories, contact and noncontact, and compared with the exact solution given by DET for the target problem.

For reversible reactions, κ is constructed from two parts that are responsible for the forward ($k_a\tilde{\Sigma}(0)/u_A$) and backward ($k_d\tilde{\Sigma}(0)/u_C$) processes. Both of them are proportional to $\tilde{\Sigma}(0)$, which in turn is an even better standard for the comparison of different theoretical approaches. The majority of them provide $\tilde{\Sigma}(s)$ when two lifetimes are equal, $u_A = u_C$. In this case, the formal solution is the same as for the reversible reaction between the ground-state particles, but it is multiplied by $\exp(-u_\mathrm{A}t)$. In the Laplace space, it leads to a shift in the Laplace variable, $s \to s + u_\mathrm{A}$.

III. Irreversible Reactions

For irreversible reactions, DET allows for the spatial dependence of the sink terms. The survival probability $P_\mathrm{A}(t)$ in the framework of this theory is[23]

$$e^{u_\mathrm{A}t}P_\mathrm{A}(t) = S_\mathrm{irr}(t;c) \equiv \exp\left(-c\int_0^t k_\mathrm{irr}(t')\,\mathrm{d}t'\right) \qquad (3.1)$$

The ultimate fate of A in the irreversible case is to turn into product C, provided it did not dissipate earlier. Therefore, $P_\mathrm{A}(t)$ goes to zero with a rate of $u_\mathrm{A} + ck_\mathrm{irr}(t)$. The time-dependent rate constant

$$k_\mathrm{irr}(t) = \int W_a(r)\, n(r,t)\, \mathrm{d}^3r$$

but in the contact approximation and in absence of electrostatic interactions, it is defined as follows:[31]

$$k_\mathrm{irr}(t) = k_\mathrm{a} n(\sigma, t) = 4\pi\sigma^2 D \left.\frac{\partial n}{\partial r}\right|_{r=\sigma} \qquad (3.2)$$

This is actually the boundary condition to the equation for the pair correlation function $n(r, t)$, which in highly polar solvents takes the simplest form:[32]

$$\frac{\partial}{\partial t} n(r,t) = D\Delta n(r,t) \qquad n(r,0) = 1 \qquad (3.3)$$

The well-known solution of this equation allows one to specify the rate constant[31,33]

$$k_\mathrm{irr}(t) = \frac{k_\mathrm{a}k_\mathrm{D}}{k_\mathrm{a} + k_\mathrm{D}} \times \left[1 + \frac{k_\mathrm{a}}{k_\mathrm{D}} \exp\left(\left(1 + \frac{k_\mathrm{a}}{k_\mathrm{D}}\right)^2 \frac{t}{\tau_\mathrm{d}}\right) \mathrm{erfc}\left(\left(1 + \frac{k_\mathrm{a}}{k_\mathrm{D}}\right)\sqrt{\frac{t}{\tau_\mathrm{d}}}\right)\right] \qquad (3.4)$$

as well as its Laplace transformation

$$\tilde{k}_\mathrm{irr}(s) = \frac{k_\mathrm{a}/s}{1 + k_\mathrm{a} g(s)} \qquad (3.5)$$

At $k_\mathrm{d} = 0$, the Stern−Volmer constant (eq 2.13) returns to its irreversible analog

$$\kappa_\mathrm{irr} = \frac{k_\mathrm{a}\tilde{\Sigma}_\mathrm{irr}(0;c)}{u_\mathrm{A}} \qquad (3.6)$$

where

$$\tilde{\Sigma}_\mathrm{irr}(s;c) = \frac{1}{ck_\mathrm{a}}[\tilde{S}_\mathrm{irr}^{-1}(s + u_\mathrm{A}; c) - (s + u_\mathrm{A})] \qquad (3.7)$$

IV. Reversible Reactions

All of the theories compared below reproduce the ideal Stern−Volmer constant (eq 2.17) that coincides with IET at $c = 0$. The only exceptions are the theory of Vogelsang et al.[34,35] and the so-called phenomenological rate equations proposed by Lee and Karplus[36] and used in a number of other works.[29,37,38]

TABLE 1: $\tilde{\Sigma}(s)$ for the Target Problem

theory	$\tilde{\Sigma}(s)^{-1}$
CA	$\tilde{\Sigma}_\mathrm{irr}^{-1}(s; c)$
MRE, $u_\mathrm{A} = u_\mathrm{C}$	$\tilde{\Sigma}_\mathrm{irr}^{-1}(s; c + K_\mathrm{eq}^{-1})$
LSA = IET	$\tilde{\Sigma}_0^{-1}(s + u_\mathrm{A})$
LESA, $u_\mathrm{A} = u_\mathrm{C}$	$P_\mathrm{A}\tilde{\Sigma}_0^{-1}(s + u_\mathrm{A}) + P_\mathrm{C}\tilde{S}_0^{-1}(s + u_\mathrm{A} + ck_\mathrm{a} + k_\mathrm{d})$
MPK1, $u_\mathrm{A} = u_\mathrm{C}$	$P_\mathrm{A}\tilde{\Sigma}_0^{-1}(s + u_\mathrm{A}) + P_\mathrm{C}\tilde{\Sigma}_\mathrm{irr}^{-1}(s; c + K_\mathrm{eq}^{-1})$
MPK2	$(1 - \nu(s))\tilde{\Sigma}_0^{-1}(s + \alpha_-(s)) + \nu(s)\tilde{\Sigma}_0^{-1}(s + \alpha_+(s))$
at $u_\mathrm{A} = u_\mathrm{C}$	$P_\mathrm{A}\tilde{\Sigma}_0^{-1}(s + u_\mathrm{A}) + P_\mathrm{C}\tilde{\Sigma}_0^{-1}(s + u_\mathrm{A} + (ck_\mathrm{a} + k_\mathrm{d})\tilde{\Sigma}(s))$
MPK3 = MET	$(1 - \mu(s))\tilde{\Sigma}_0^{-1}(s + \beta_-(s)) + \mu(s)\tilde{\Sigma}_0^{-1}(s + \beta_+(s))$
(at $u_\mathrm{A} = u_\mathrm{C}$)	$P_\mathrm{A}\tilde{\Sigma}_0^{-1}(s + u_\mathrm{A}) + P_\mathrm{C}\tilde{\Sigma}_0^{-1}(s + u_\mathrm{A} +$ $(ck_\mathrm{a} + k_\mathrm{d})\tilde{\Sigma}_0(s + u_\mathrm{A}))$
SCRTA, $u_\mathrm{A} = u_\mathrm{C}$	$P_\mathrm{A}\tilde{\Sigma}_0^{-1}(s + u_\mathrm{A}) + P_\mathrm{C}\tilde{\Sigma}_0^{-1}\,(s + u_\mathrm{A} + \lambda)$ $\lambda = (ck_\mathrm{a} + k_\mathrm{d})/(1 + k_\mathrm{a}g(\lambda)/[k_\mathrm{D}g(P^2{}_\mathrm{A}\lambda)])$
	auxiliary functions
	$\alpha_\pm(s) = {}^1/_2(Y(s) \pm \sqrt{Y(s)^2 - 4Z(s)})$
	$Y(s) = u_\mathrm{A} + u_\mathrm{C} + (ck_\mathrm{a} + k_\mathrm{d})\tilde{\Sigma}(s)$
	$Z(s) = u_\mathrm{A}u_\mathrm{C} + (ck_\mathrm{a}u_\mathrm{C} + k_\mathrm{d}u_\mathrm{A})\tilde{\Sigma}(s)$
	$\nu(s) = (\alpha_+(s) - u_\mathrm{C} - k_\mathrm{d}\tilde{\Sigma}(s))/(\alpha_+(s) - \alpha_-(s))$
	$\beta_\pm(s) = {}^1/_2(y(s) \pm \sqrt{y(s)^2 - 4z(s)})$
	$y(s) = u_\mathrm{A} + u_\mathrm{C} + (ck_\mathrm{a} + k_\mathrm{d})\tilde{\Sigma}_0(s + u_\mathrm{A})$
	$z(s) = u_\mathrm{A}u_\mathrm{C} + (ck_\mathrm{a}u_\mathrm{C} + k_\mathrm{d}u_\mathrm{A})\tilde{\Sigma}_0(s + u_\mathrm{A})$
	$\mu(s) = (\beta_+(s) - u_\mathrm{C} - k_\mathrm{d}\tilde{\Sigma}_0(s+u_\mathrm{A}))/(\beta_+(s) - \beta_-(s))$

TABLE 2: $\tilde{\Sigma}(s)$ for the Trap Problem

theory	$\tilde{\Sigma}(s)^{-1}$
MPK3 = MET (at $u_\mathrm{A} = u_\mathrm{C}$)	$\tilde{\Sigma}_0^{-1}\left(s + u_\mathrm{A} + ck_\mathrm{a}/\left[\frac{k_\mathrm{d}}{s + u_\mathrm{C}} + \tilde{\Sigma}_0^{-1}(s + u_\mathrm{A})\right]\right)$
SCRTA, $u_\mathrm{A} = u_\mathrm{C}$	$\tilde{\Sigma}_0^{-1}\left(s + u_\mathrm{A} + ck_\mathrm{a}/\left[\frac{k_\mathrm{d}}{s + u_\mathrm{A}} + \tilde{\Sigma}_0^{-1}(0)\right]\right)$

In Vogelsang's approach, the ideal Stern−Volmer constant takes the form

$$\kappa_0 = \frac{k'_\mathrm{a}/u_\mathrm{A}}{1 + k_\mathrm{a}g(u_\mathrm{A})}$$

which is different from the exact form, eq 2.17. The main point of this theory is that at the moment just after dissociation all B particles (including the released one) form the equilibrium distribution around A. It is clear that only the fast diffusion or fast relaxation of C can validate the theory, but it is irrelevant in the majority of other cases. Moreover, Vogelsang's theory gives an incorrect result for the equilibrium probabilities (eq 1.4), thus violating the mass action law.[25] For all of these reasons, we exclude this theory from further consideration.

The modified or phenomenological rate equations have already been heavily criticized in ref 26, but they will nevertheless be included in the following comparison with the rest of the theories. The kernels related to all of them are collected in Table 1 (for the target problem) and Table 2 (for the trap problem). These are kernels obtained from the original theories in the framework of the contact approximation.

A. Convolution Approaches. Berg's work[22] was chronologically the first theory of a diffusion-influenced reversible reaction that was later well grounded and analyzed by Agmon and Szabo.[24] Berg made the assumption that at any moment of dissociation a newborn A−B pair is surrounded by the equilibrium distribution of B particles. As a result, this theory works better near the irreversible limit, where the dissociation events are rare and the trap is mostly bound. Also, it correctly reduces

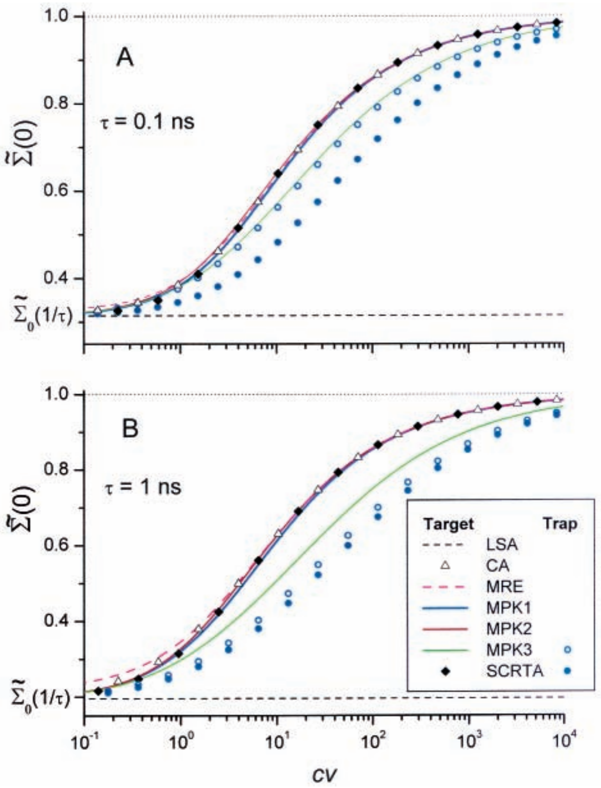

Figure 1. Laplace transformation of the kernel of integral equations, $\tilde{\Sigma}(0)$, plotted as a function of dimensionless concentration cv ($v = 4\pi\sigma^3/3$ is an inaccessible volume). Different theories are compared at $u_A = u_C = {}^1/_\tau$ for (A) short and (B) long τ. The rest of the data are the following: $\sigma = 7$ Å, $k_a/v = 43$ ns^{-1}, $k_d = 5$ ns^{-1}, $D = 100$ Å^2/ns $= 10^{-5}$ cm^2/s.

to the geminate limit, eq 2.11, when an isolated A−B pair is formed due to the decay of C. There are also other authors who started later from the same assumption and obtained the same result.[24,25,39] In ref 24, it was called the convolution approximation (CA).

B. Phenomenological Rate-Equation Approach. The modified rate-equation approximation (MRE)[25] was also built to describe the non-Markovian character of diffusion-controlled reversible reactions. The forward reaction rate $k_{irr}(t)$ was left as it appeared in the conventional contact theory, eq 3.4. As for the backward reaction rate, it was modified to be proportional to $k_{irr}(t)$:

$$\frac{d}{dt}P_A = -ck_{irr}(t)P_A + \frac{k_d}{k_a}k_{irr}(t)P_C - u_AP_A \tag{4.1a}$$

$$\frac{d}{dt}P_C = ck_{irr}(t)P_A - \frac{k_d}{k_a}k_{irr}(t)P_C - u_CP_C \tag{4.1b}$$

This was done to “predict the correct equilibrium solution at long times” if $u_A = u_C = 0$. In the case of equal lifetimes, when $u_A = u_C \neq 0$, the solution of eqs 4.1 is expressed through the function $S_{irr}(t;\, c)$. With kernel $\tilde{\Sigma}(s)$ presented in Table 1, one can find κ_0 from eq 2.13:

$$\kappa_0 = K_{eq}(1 - u_A\tilde{S}_{irr}(u_A;\, K_{eq}^{-1}))$$

This result does not coincide with that of IET, eq 2.17; that is, MRE does not hold the geminate limit (Figure 1). In ref 40, eqs 4.1, which are also called “phenomenological rate equations,”[29,37,38] were extended to the noncontact case of distant transfer reactions. However, either of such equations can be justified in the kinetic control limit only. Moreover, at $u_A \neq u_C$, MRE loses the phenomenon of delayed fluorescence through the particle with a shorter lifetime.[26]

C. Encounter Theories. The contact IET provides the following Laplace transformation of the kernels (eq 2.3):[41]

$$\tilde{F}_a(s) = (s + u_A)\tilde{k}_{irr}(s + u_A) \qquad \tilde{F}_d(s) = \frac{k_d}{k_a}\tilde{F}_a(s) \tag{4.2}$$

With $\tilde{k}_{irr}(s)$ from eq 3.5 substituted into this equation, one can see that the corresponding $\tilde{\Sigma}(s)$ is exactly equal to $\tilde{\Sigma}_0(s + u_A)$. This is not surprising because IET represents just the small concentration limit, that is, the ideal Stern−Volmer constant, κ_0.

The unified theory (UT) developed recently in refs 23 and 26 allows one to add the bimolecular generation of exciplexes (i.e., C particles) or their light-induced generation to the process of their subsequent reversible dissociation. Under the condition of instantaneous exciplex formation, this theory reduces to IET (eqs 6 and 54 of ref 26).

The most elaborated modified encounter theory (MET)[42,43] is one that gives different forms for $\tilde{\Sigma}(s)$ in the trap (Table 1) and target (Table 2) limits. In the case of a contact reaction with $u_A = u_C$, MET was shown to be identical to MPK3.[44]

D. Superposition Approach. The superposition approximation (SA) was suggested in refs 25 and 45. It is essentially a nonlinear theory that cannot be represented in the form of eqs 2.1. The same is true for the extended version of SA.[46] Because of this, we focus on two derivatives of these theories linearized near the equilibrium. These are the linearized superposition approximation (LSA) and the linearized extended superposition approximation (LESA). It was found that LSA developed in a number of works[25,36,40,46] is in fact identical to IET (Table 1). They both have the same concentration-independent kernel $\tilde{\Sigma}(s)$. As for LESA, it was strictly created for the reactions in the ground state[7,8] but can be easily extended to the case of equal lifetimes, $u_A = u_C$.

E. Multiparticle Kernel Approximation. In refs 27, 44, 47, and 48, a set of approximate solutions for the contact reactions were suggested. These solutions are based on a hierarchical system of diffusion equations for n-particle probabilities. The truncation of this system at second order has led to the so-called multiparticle kernel 3 (MPK3) approximation[44] and third order has given MPK2 theory,[27,47] but the most accurate approximation, MPK1, has been obtained in ref 48 by truncating this system at fourth order. The latter theory is a remarkable one because it correctly reduces to all of the limits available for a strict investigation: to the irreversible case, $k_d = 0$, where it coincides with DET and to the geminate case, $c = 0$, where it reproduces IET.

A comparison with the Brownian dynamics simulations of reaction 1.1 in the target limit for infinite lifetimes[49] showed excellent agreement even at the unusually large value of c. MPK1 was probably not generalized for the case of different lifetimes because of the complexity of the derivation.

Whereas MPK1 and MPK2 describe only the target problem, MPK3 is able to treat the trap problem as well (Table 2). At equal lifetimes, it exactly reproduces MET in both these limits.[42,44]

F. SCRTA. A. Szabo and I. Gopich suggested the self-consistent relaxation time approximation[30] (SCRTA). This approach considers two pair correlation functions, $p_{AB}(r,\, t)$ and $p_{CB}(r,\, t)$, that describe the density of B’s around the unbound and bound traps, respectively. These functions are bounded by the set of equations taking into account that a given couple, A and B, disappear not only because of their own association in C but also because of a similar alliance of A with some other B (a "bachelor" coming from the bulk). These functions become equal on reaching equilibrium.

SCRTA deals with equal lifetimes but can account for the arbitrary diffusion coefficients of the reactants. It can also afford the use of the distance-dependent reaction rates but breaks down near the irreversible limit.[30]

V. Results

Because only some of the theories deal with the case in which $u_A \neq u_C$, we examine here only the case of equal lifetimes, $u_A = u_C$. As a standard for comparison, we chose the Laplace transformation of the kernel, $\tilde{\Sigma}(0)$, which determines the Stern−Volmer constant and all related quantum yields. The kernels specified in all of the theories are listed in the Tables and are represented in Figure 1 for the entire concentration range up to the kinetic limit where all $\tilde{\Sigma}(0)$ approach 1. The Figure allows us to distinguish between the target and trap limits. In the latter case, particle A during its motion can hit only one of the B molecules (the others do not move). This is why the efficiency of the reaction does not increase with c as rapidly as it does in the opposite case, when A is stable and the B's are moving. However, at a short lifetime (0.1 ns), this difference in MPK3 is not as pronounced as in SCRTA, and at longer lifetimes (1 ns), both theories predict a larger difference and almost coincide for the trap problem.

Others theories are applicable to only the target problem, but the dispersion of the results is not much less. Judging from our previous investigation, we are inclined to believe that the results for MPK1 are the most reliable because in the case of irreversible transfer they were exact.[17] However, the genuine discrimination between the theories can be made either by numerical simulations or by a comparison of theoretical $\kappa(c)$ dependencies (Figure 2) with those obtained experimentally. According to eq 2.13, κ differs from $\tilde{\Sigma}(0)$, especially at large c where it approaches the upper limit,

$$\kappa_m = \frac{k_a \tau}{(1 + k_d \tau)} \rightarrow K_{eq} \qquad \text{at } \tau \rightarrow \infty$$

In Figure 2, only those theories are compared that give the same minimal and maximal values of κ at $c = 0$ and ∞, correspondingly. However, they are very different in between. Two of them, LESA and MPK3, essentially deviate from all the rest of the theories describing the target problem (Figure 2A). This is not a surprise because we have already detected the same by studying the irreversible quenching.[17] Some discrimination between others can be made judging by the right asymptotic behavior at long times, eq 2.10. There are only two between them that are capable of reproducing it: MPK1 and SCRTA. The difference between them is noticeable but greatly diminishes with increasing τ. Nevertheless, MPK1 has the advantage of excellent correspondence with the Brownian dynamic simulations of the whole time behavior of $R(t)$ obtained in ref 49. The experimental investigation of the same dependencies is possible only in a limited range of concentrations where the results should be compared with those presented in Figure 2B. We hope that the result obtained here will stimulate progress in both experimental and numerical studies of reversible dissociation at moderate and high concentrations, correspondingly.

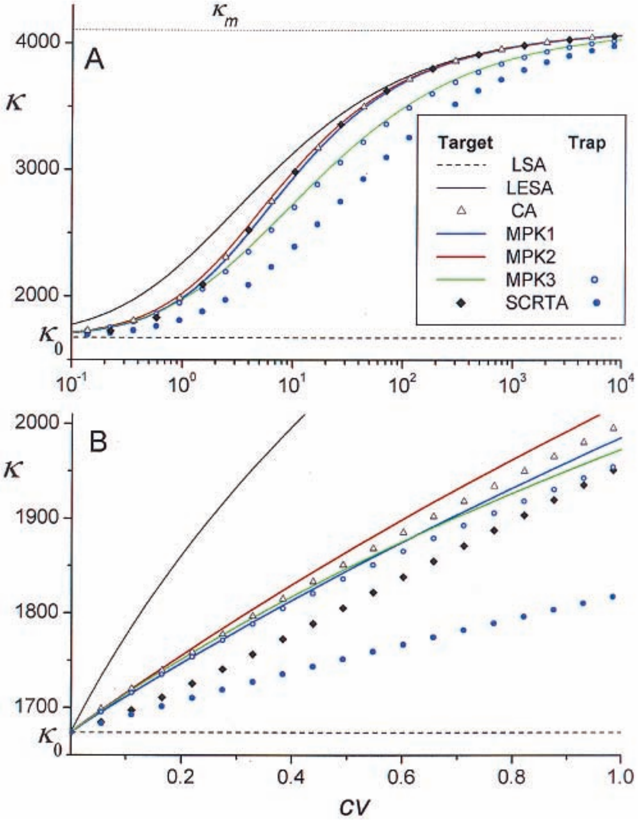

Figure 2. Stern−Volmer constant, κ, from eq 2.13 at $u_A = u_C = {}^1/_\tau$ as a function of the dimensionless concentration of B's in the same theories as in Figure 1 including LESA but without MRE because it is alone, which is not brought to a point κ_0 at $c \rightarrow 0$. Over a wide range of concentration (A) all curves increase from this ideal value up to the maximal one, κ_m. At low concentrations (B) the difference between them is more pronounced. All parameters are the same as in Figure 1A.

VI. Conclusions

The non-Markovian nature of diffusion reactions in solution so far has attracted the attention of only those who investigate the power asymptote of approaching the equilibrium. Here we emphasize that the entire kinetics is of no less interest, especially the integral of it that determines the quantum yields of fluorescence from either an initially excited particle or reaction product. We showed that both of the quantum yields that are easily available experimentally are determined by one and the same Stern−Volmer constant. The latter, in turn, is expressed through a single invariant of the theory: the kernel of integral equations that governs the kinetics of transfer reactions. These equations are really universal. We were able to deduce them from almost all of the available theories and specify the kernel for each of them.

Having in hand the collections of these kernels, we proved once again that as [B] → 0 all of them coincide with that of IET except for only two methods, which were recognized as incorrect. At higher concentration, all of the kernels monotonically increase when approaching the common upper limit but differ essentially in between. Some difference may be attributed to the objective difference in the diffusion coefficients of the partners if one of them moves while another does not or vice versa. However, there is a difference between the theories in each of these cases, and this is the price for the inaccuracy in the basic assumptions. From now on, it is possible to discriminate between them by using for comparison real experimental data or computer simulations.

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