Influence of diffusion on the kinetics of excited-state association–dissociation reactions: Comparison of theory and simulation

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Several recent theories of the kinetics of diffusion influenced excited-state association–dissociation reactions are tested against accurate Brownian dynamics simulation results for a wide range of parameters. The theories include the relaxation time approximation (RTA), multiparticle kernel decoupling approximations and the so-called kinetic theory. In the irreversible limit, none of these theories reduce to the Smoluchowski result. For the pseudo-first-order target problem, we show how the RTA can be modified so that the resulting formalism does reduce correctly in the irreversible limit. We call this the unified Smoluchowski approximation, because it unites modern theories of reversible reactions with Smoluchowski's theory of irreversible reactions. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1649935]

I. INTRODUCTION

In this paper we consider the kinetics of pseudo-first-order (large B-concentration), excited-state diffusion influenced reactions, where both excited A and C can decay to their ground states with rate constants k_A and k_C,

$$A+B \underset{\kappa_r}{\overset{\kappa_f}{\rightleftharpoons}} C \qquad (1.1)$$
$$\downarrow k_A \qquad \downarrow k_C$$

The classic example for this reaction is excited-state proton transfer to solvent.[1] In this context, Weller has solved the rate equations of chemical kinetics nearly 50 years ago.[2] His solution is valid only in the reaction-controlled limit, when diffusion of the reactants is fast compared with the intrinsic reactivities (i.e., the forward and reverse rates κ_f and κ_r, respectively). More general theories are desirable because recent experiments[3,4] on excited-state proton transfer reactions show that the role of diffusion cannot be overlooked.

In the geminate limit (an isolated $A-B$ pair or C molecule) the diffusion problem can be solved exactly for arbitrary lifetimes.[5,6] For the bimolecular case, a number of approximate theories of increasing sophistication have been developed for this reaction.[7–11] Special attention has been paid to the pseudo-first-order limit when the concentrations of A's and C's are low compared to that of B's so that correlation between different A and C molecules can be neglected. When both A and C are static (the so-called "target problem"), accurate kinetic traces obtained from Brownian dynamics (BD) simulations have been reported[12,13] and compared with selected theories for a rather limited range of

parameters. In the present work, these simulations are extended to cover a larger range of parameters, both farther from and closer to the irreversible limit.

Recently a general theory, the relaxation time approximation (RTA), that is applicable to arbitrary reaction schemes, initial concentrations and diffusivities, has been formulated.[14] This theory can be implemented using either the steady-state rate constants (SSRTA) or self-consistently, when it is termed SCRTA. Thus far, this new theory has been compared[14] with simulated ground-state kinetics for the $A+B \rightleftharpoons C$ reaction,[15] and more recently for the $A+B \rightleftharpoons C+D$ reaction.[16,17] It is thus of interest to determine how well it works in the special case of the excited-state reaction in Eq. (1.1).

In this paper we compare the predictions of SCRTA and two multiparticle kernel theories[8–11] (MPK2/KT and MPK3) with BD simulations of the above excited state reaction, Eq. (1.1), in the "target" limit. We find that SCRTA works well except near the irreversible limit when $k_C > k_A$. As in the case of equal lifetimes,[14,16,17] this is because in this limit the SCRTA does not reduce to Smoluchowski's result[18] which exactly describes the simulations in this limit. To remedy this situation, we modify the SCRTA equations so that they reduce correctly also in the irreversible limit. We call the resulting formalism the unified Smoluchowski approximation (USA), because it unites modern theories of reversible reactions with Smoluchowski's theory of irreversible reactions. For equal lifetimes, it reduces to the MPK1 theory of Sung and Lee,[19] which in this case shows the best agreement with simulations for all tested parameters.[15]

The outline of this paper is as follows: Section II describes a variety of theoretical approaches to excited-state reversible reactions. We start with conventional chemical kinetics. Then we present SCRTA and compare it to MPK2 and

MPK3 for this reaction. We then modify SSRTA to obtain our USA. Section III compares the various approximate theories with simulations. Finally, in Sec. IV we present some concluding remarks.

II. THEORETICAL FORMALISMS

A. Chemical kinetics

We begin with the chemical kinetic approach where one solves two coupled ordinary differential equations for the time dependence of the concentrations of A and C, $[A]$ and $[C]$, respectively.[2] In the pseudo-first-order limit when $[B]_0$ is constant, these equations are

$$\frac{d[A]}{dt} = -\kappa_f[B]_0[A] + \kappa_r[C] - k_A[A],$$

$$\frac{d[C]}{dt} = \kappa_f[B]_0[A] - \kappa_r[C] - k_C[C]. \tag{2.1}$$

The Laplace transform $[\hat{f}(s) = \int_0^\infty f(t)\exp(-st)dt]$ of the time-dependent concentration of A, denoted by $[\hat{A}]$, is

$$[\hat{A}] = \frac{(s + k_C + \kappa_r)[A]_0 + \kappa_r[C]_0}{(s + k_A)(s + k_C) + (s + k_A)\kappa_r + (s + k_C)\kappa_f[B]_0}, \tag{2.2}$$

where $[A]_0$ and $[C]_0$ are the initial concentrations. Taking the inverse Laplace transform, we get

$$[A] = (\{[A]_0(\Delta k - \lambda_- + \kappa_r) + [C]_0\kappa_r\}e^{-\lambda_- t - k_A t}$$
$$- \{[A]_0(\Delta k - \lambda_+ + \kappa_r) + [C]_0\kappa_r\}e^{-\lambda_+ t - k_A t})$$
$$\times ((\kappa_0 - \Delta k)^2 + 4\kappa_r\Delta k)^{1/2}, \tag{2.3}$$

where we have defined

$$\kappa_0 \equiv \kappa_f[B]_0 + \kappa_r, \tag{2.4a}$$

$$\Delta k \equiv k_C - k_A, \tag{2.4b}$$

and $\lambda_\pm + k_A$ are the roots of the denominator in Eq. (2.2),

$$2\lambda_\pm = \kappa_0 + \Delta k \pm \sqrt{(\kappa_0 - \Delta k)^2 + 4\kappa_r\Delta k}. \tag{2.5}$$

The decay of C may subsequently be found using the following, generally valid, "conservation law,"

$$(s + k_A)[\hat{A}] + (s + k_C)[\hat{C}] = [A]_0 + [C]_0. \tag{2.6}$$

We will show that the approximate theories considered below have the same structure as Eq. (2.2), namely,

$$[\hat{A}] = \frac{(s + k_C + \mathcal{K}_r(s))[A]_0 + \mathcal{K}_r(s)[C]_0}{(s + k_A)(s + k_C) + (s + k_A)\mathcal{K}_r(s) + (s + k_C)\mathcal{K}_f(s)[B]_0}, \tag{2.7}$$

with the key difference that the rate constants are replaced by the s-dependent functions $\mathcal{K}_f(s)$ and $\mathcal{K}_r(s)$,

$$\mathcal{K}_f(s) \equiv \kappa_f/F(s), \quad \mathcal{K}_r(s) \equiv \kappa_r/F(s), \tag{2.8}$$

where $F(s)$ is the diffusion factor function.[15,19] This function factors out the diffusion effects in the sense that it contains all the dependence on the diffusion coefficient. Below we present explicit expressions for $F(s)$ for various theories.

B. The relaxation time approximation (RTA)

The relaxation time approximation (RTA) is a general formalism applicable to chemical reactions with arbitrary kinetic schemes, concentrations and diffusivities.[14] The procedure for modifying the rate equations of ordinary chemical kinetics to incorporate the influence of diffusion is described in Sec. VII of Ref. 14. Using these results one can readily obtain the equations that describe the reaction we consider in this paper for arbitrary concentrations. Here we shall consider only the pseudo-first-order case when the concentration of B is sufficiently large so as to be time independent.

Our starting point is the formally exact rate equations for the concentrations in the framework of a microscopic model in which a reaction occurs at a contact distance a,

$$\frac{d[A]}{dt} = -\kappa_f[B]_0[A] - \kappa_f p_{AB}(a,t) + \kappa_r[C] - k_A[A],$$

$$\frac{d[C]}{dt} = \kappa_f[B]_0[A] + \kappa_f p_{AB}(a,t) - \kappa_r[C] - k_C[C]. \tag{2.9}$$

Here $p_{AB}(r,t)$ is the deviation of the pair distribution function from the ordinary chemical kinetics value, $[A][B]_0$. In the case of fast diffusion, $p_{AB}(r,t) = 0$ and the concentrations of A and C obey the rate equations of conventional chemical kinetics, Eq. (2.1).

The pair function $p_{AB}(r,t)$ changes due to diffusion, the bimolecular reaction, and the decay of the excited states. An A particle from the $A-B$ pair can react with some other B to generate a $C-B$ pair. The latter may disappear due to dissociation of C, producing an $A-B$ pair. Let us assume that this can be described using rate equations with effective rate constants k_f and k_r that give the correct equilibrium constant, $K_{eq} = k_f/k_r = \kappa_f/\kappa_r$. Note that we are using Latin letters for the effective rate constants (k_f and k_r) and Greek ones for the intrinsic ones (κ_f and κ_r). Thus $p_{AB}(r,t)$ is coupled to $p_{CB}(r,t)$. The two functions are assumed to satisfy the following reaction-diffusion equations,

$$\partial p_{AB}(r,t)/\partial t = D_{AB}\nabla^2 p_{AB} - k_f[B]_0 p_{AB} + k_r p_{CB}$$
$$- k_A p_{AB},$$

$$\partial p_{CB}(r,t)/\partial t = D_{CB}\nabla^2 p_{CB} + k_f[B]_0 p_{AB} - k_r p_{CB}$$
$$- k_C p_{CB}, \tag{2.10}$$

where $D_{AB} = D_A + D_B$ and $D_{CB} = D_C + D_B$ are the relative diffusion constants of the $A-B$ and $C-B$ pairs, respectively. The boundary condition for $p_{AB}(r,t)$ is found from the condition that flux of $p_{AB}(r,t)$ at contact must be equal to the total rate of the bimolecular reaction,

$$4\pi a^2 D_{AB}\frac{\partial}{\partial r}p_{AB}(r,t)\Big|_{r=a}$$
$$= \kappa_f([A][B]_0 + p_{AB}(a,t)) - \kappa_r[C]. \tag{2.11}$$

In contrast, $p_{CB}(r,t)$ describes the unreactive pair and therefore obeys a reflecting boundary condition at $r=a$. For uniform (equilibrium) initial conditions, both $p_{AB}(r,0)$ and $p_{CB}(r,0)$ are equal to zero. Thus the structure of this formal-

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ism is very simple. It is based on two formally exact relations, Eqs. (2.9) and (2.11), and a physically transparent approximation, Eq. (2.10).

Using the technique described in Ref. 14, these equations can be solved analytically. The Laplace transform of the concentration of A is given by Eqs. (2.7) and (2.8) with

$$F_{\text{RTA}}(s) = \kappa_f \sum_{i=1}^{2} \frac{T_{1i}(\mathbf{T}^{-1})_{i1}}{\sigma_i \hat{k}_{\text{irr}}(\sigma_i)}, \tag{2.12}$$

where $\hat{k}_{\text{irr}}(s)$ is the Laplace transform of the Smoluchowki–Collins–Kimball irreversible rate coefficient,

$$\frac{1}{s\hat{k}_{\text{irr}}(s)} = \frac{1}{\kappa_f} + \frac{1}{k_D(1+\sqrt{s\tau_D})}. \tag{2.13}$$

Here $k_D = 4\pi D_{AB} a$ is the diffusion-controlled rate constant and $\tau_D = a^2/D_{AB}$ is the diffusion time. The matrix $\mathbf{T}$ and the diagonal matrix $\boldsymbol{\sigma}$ (with elements σ_1 and σ_2) in Eq. (2.12) are defined by the eigenvalue problem,

$$D_{AB}\mathbf{D}^{-1}(s\mathbf{I}+\mathbf{K})\mathbf{T} = \mathbf{T}\boldsymbol{\sigma}, \tag{2.14}$$

where $\mathbf{D}$ is the diagonal matrix of relative diffusion constants (D_{AB}, D_{CB}) and $\mathbf{K}$ is

$$\mathbf{K} = \begin{pmatrix} k_f[B]_0 + k_A & -k_r \\ -k_f[B]_0 & k_r + k_C \end{pmatrix}. \tag{2.15}$$

We give here explicit expressions for the case $D_{AB} = D_{CB} = D$. In this case $\sigma_{1,2} = s + k_A + \lambda_\pm$ and the diffusion factor function is

$$\kappa_f^{-1} F_{\text{RTA}}(s) = \frac{\mu}{(s+k_A+\lambda_-)\hat{k}_{\text{irr}}(s+k_A+\lambda_-)}$$
$$+ \frac{1-\mu}{(s+k_A+\lambda_+)\hat{k}_{\text{irr}}(s+k_A+\lambda_+)}, \tag{2.16}$$

where

$$\mu = \frac{\lambda_+ - k_f[B]_0}{\lambda_+ - \lambda_-}. \tag{2.17}$$

The $\lambda_\pm$ are the same as those in chemical kinetics [see Eq. (2.5)],

$$2\lambda_\pm = k_0 + \Delta k \pm \sqrt{(k_0 - \Delta k)^2 + 4k_r\Delta k}, \tag{2.18a}$$

$$k_0 \equiv k_f[B]_0 + k_r, \tag{2.18b}$$

but with the effective rate constants, k_f and k_r, replacing κ_f and κ_r, respectively.

The effective rate constants, k_f and k_r, should be chosen so as to give the best approximation for the interconversion of the AB and CB pair functions [see Eq. (2.10)] in the framework of simple chemical kinetics. The simplest choice would be the steady state (SS) rate constants for the bimolecular reaction $A+B \rightleftarrows C$ without unimolecular decay,

$$k_f^{\text{ss}} = \frac{\kappa_f k_D}{\kappa_f + k_D}, \quad k_r^{\text{ss}} = \frac{\kappa_r k_D}{\kappa_f + k_D}, \tag{2.19}$$

resulting in the SS relaxation time approximation (SSRTA). A better choice is to define the self-consistent (SC) rate constants from the same condition used for $\Delta k = 0$ in Ref. 14,

$$k_f^{\text{sc}} = \kappa_f/F_{\text{SCRTA}}(0), \quad k_r^{\text{sc}} = \kappa_r/F_{\text{SCRTA}}(0). \tag{2.20}$$

Combining Eq. (2.20) and Eq. (2.16) when $\Delta k = 0$ gives

$$\frac{\kappa_0}{k_0^{\text{sc}}} = 1 + \frac{\kappa_f}{k_D} \frac{1 + \kappa_r\sqrt{k_0^{\text{sc}}\tau_D}/\kappa_0}{1+\sqrt{k_0^{\text{sc}}\tau_D}}. \tag{2.21}$$

From this equation one gets k_0^{sc} and, therefore, $k_f^{\text{sc}} = k_0^{\text{sc}}K_{\text{eq}}/(1+K_{\text{eq}}[B]_0)$ and $k_r^{\text{sc}} = k_0^{\text{sc}}/(1+K_{\text{eq}}[B]_0)$. This defines the self-consistent relaxation time approximation (SCRTA). SCRTA reduces to ordinary chemical kinetics in the reaction controlled limit, when $D \to \infty$. In the small concentration limit, it reduces correctly to the geminate limit.[5]

C. Multiparticle kernel theories (MPK2/KT and MPK3)

Multiparticle kernel theories, MPK2 and MPK3, were derived by decoupling the hierarchy of equations for the reduced distribution functions in various ways.[9,10] The results of MPK2 are the same as those of kinetic theory (KT),[8,11] which is based on a perturbation expansion.

Although the structure of these formalisms appears to be more complex than the RTA, for the reaction considered in this paper there is a close formal similarity among the final results. The diffusion factor function $F(s)$ of MPK3 can be obtained from Eqs. (2.16)–(2.18) by setting

$$k_f \to (s+k_A)\hat{k}_{\text{irr}}(s+k_A), \quad k_r \to \frac{\kappa_r}{\kappa_f}(s+k_A)\hat{k}_{\text{irr}}(s+k_A). \tag{2.22}$$

The diffusion factor function of MPK2/KT can be obtained from Eqs. (2.16) and (2.18) by setting

$$k_f \to \kappa_f/F(s), \quad k_r \to \kappa_r/F(s) \tag{2.23}$$

and solving the resulting equations for $F(s)$ for each value of s. This more elaborate self-consistent procedure has the disadvantage that, unlike the SCRTA, MPK2/KT does not give the correct asymptotics when the lifetimes are equal. Because of these similarities, it is expected that their predictions are similar except at long times.

D. The unified Smoluchowski approximation (USA)

While SCRTA reduces correctly in the reaction-controlled and geminate limits, it does not reduce in the irreversible limit to Smoluchowski's result,[18] which is exact for the target problem considered here. The same is true for the MPK2/KT and MPK3. Hence one should expect significant deviations of the SCRTA kinetics from the simulation results near the irreversible limit. We now modify the RTA equations so that they reduce correctly in this limit. We call the resulting formalism the unified Smoluchowski approximation (USA).

The procedure we use is based on a generalization of the transformation suggested in Ref. 14 for several special cases of $A+B \rightleftarrows C$ and $A+B \rightleftarrows C+D$ with equal lifetimes. For $A+B \rightleftarrows C$ with equal lifetimes in the target limit, this transformation gave Sung and Lee's MPK1 result,[19] which is an excellent agreement with simulation over the whole time and parameter range investigated in Ref. 15.
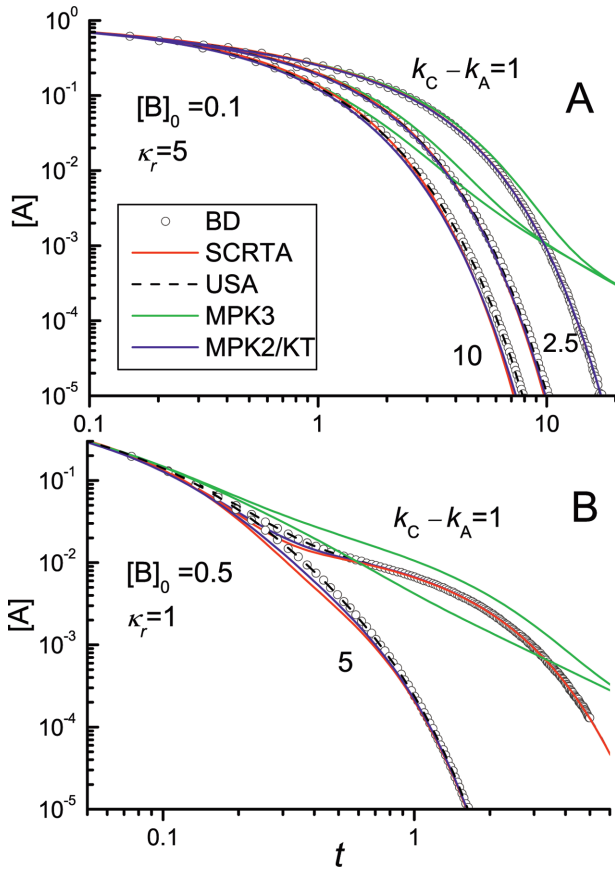
FIG. 1. (Color) The kinetics of the excited-state association-dissociation reaction (1.1) for static A and C. Brownian dynamics simulations (gray circles) were conducted using the algorithm of Ref. 13, and compared with the four approximate theories (color lines, see key). In all of the simulations, $D_B=1$ and $\kappa_f=125$. Here $k_A=0$, whereas the other rate parameters vary as indicated (see also Table I). The $\Delta k=1$ case in panel A is from Fig. 3 of Ref. 13, whereas the remaining data are new. Note the log–log scale.

FIG. 2. (Color) Same as Fig. 1 for other parameters (here $k_C=0$ and k_A varies). k_{eff} for the curves from top to bottom is 0.23, 0.46, 0.72, 1.054 (panel A) and 0.015, 0.065 (panel B), respectively. Data in panel A are from Figs. 4 and 8 of Ref. 13, whereas the data in panel B are new.

Consider the relaxation function of the Smoluchowski form,

$$
\mathcal{R}_\pm(t)=\exp\left(-\frac{\lambda_\pm^{\text{ss}}}{k_f^{\text{ss}}}\int_0^t k_{\text{irr}}(t')dt'\right)
$$

$$
=\exp\left(-\lambda_\pm^{\text{ss}}t-\frac{\lambda_\pm^{\text{ss}}}{k_f^{\text{ss}}}\int_0^t \Delta k_{\text{irr}}(t')dt'\right),\qquad(2.24)
$$

with the effective concentrations $\lambda_\pm^{\text{ss}}/k_f^{\text{ss}}$, and defining $\Delta k_{\text{irr}}(t)=k_{\text{irr}}(t)-k_{\text{irr}}(\infty)=k_{\text{irr}}(t)-k_f^{\text{ss}}$. The superscript "ss" means that the steady state values are used for the forward and reverse effective rate constants in Eqs. (2.18). Taking the Laplace transform, expanding it to linear order in Δk_{irr}, and assuming that the first two terms form a geometric series, we find

$$
\hat{\mathcal{R}}_\pm(s)\approx\left(s+\frac{\lambda_\pm^{\text{ss}}}{k_f^{\text{ss}}}(s+\lambda_\pm^{\text{ss}})\hat{k}_{\text{irr}}(s+\lambda_\pm^{\text{ss}})\right)^{-1}.\qquad(2.25)
$$

This result is actually an identity to linear order in $\int_0^t \Delta k_{\text{irr}}(t')dt'$. This suggests that one can obtain a formal-
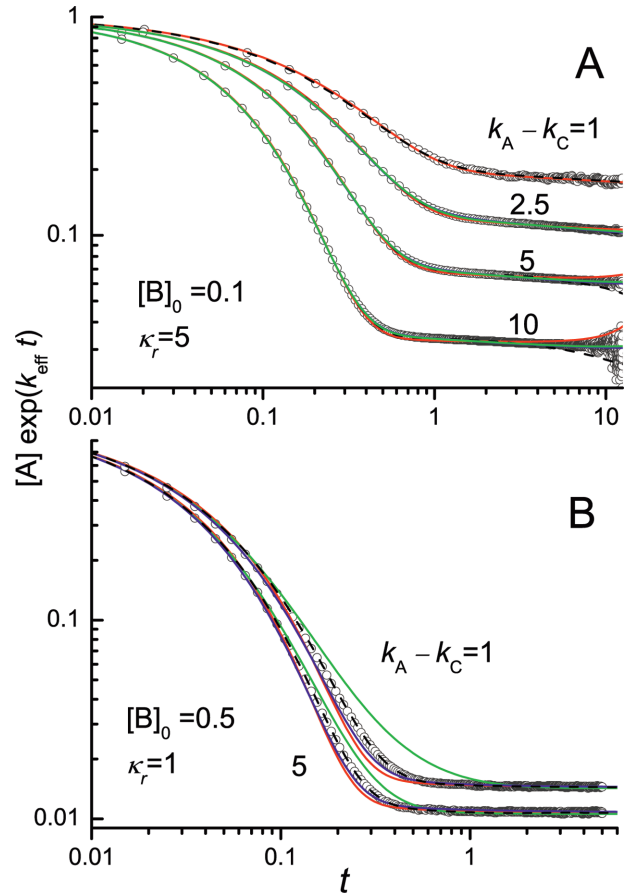
ism that correctly reduces in the irreversible limit, by eliminating $\hat{k}_{\text{irr}}(s+\lambda_\pm^{\text{ss}})$ in favor of $\hat{\mathcal{R}}_\pm(s)$ in $F_{\text{SSRTA}}(s)$ using the transformation,

$$
(s+\lambda_\pm^{\text{ss}})\hat{k}_{\text{irr}}(s+\lambda_\pm^{\text{ss}})\Leftrightarrow(\hat{R}_\pm^{-1}(s)-s)k_f^{\text{ss}}/\lambda_\pm^{\text{ss}}.\qquad(2.26)
$$

In this way we find that

$$
\frac{F_{\text{USA}}(s)}{\kappa_f[B]_0}=\frac{\nu}{\hat{\mathcal{R}}_-(s+k_A)^{-1}-(s+k_A)}
$$

$$
+\frac{1-\nu}{\hat{\mathcal{R}}_+(s+k_A)^{-1}-(s+k_A)}\qquad(2.27)
$$

and

$$
\nu=\frac{\lambda_+^{\text{ss}}-k_0^{\text{ss}}}{\lambda_+^{\text{ss}}-\lambda_-^{\text{ss}}}.\qquad(2.28)
$$

This approximation describes the kinetics of the pseudo-first order reaction with $D_{AB}=D_{CB}$. It reduces correctly in the reaction controlled, irreversible and geminate limits. Moreover, it reduces to MPK1 (Ref. 19) in the equal lifetime limit.
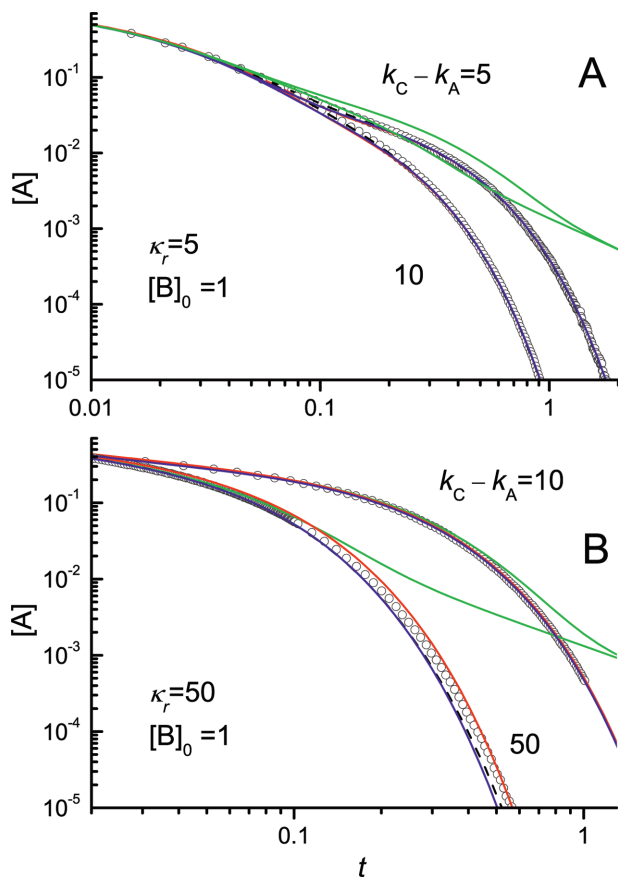
FIG. 3. (Color) Same as Fig. 1 for other parameters. The $\Delta k = 5$ case in panel A is from Fig. 5 of Ref. 13, whereas the remaining data are new.

FIG. 4. (Color) Same as Fig. 1 for other parameters (here $k_C = 0$ and k_A varies). $k_{\rm eff}$ for the curves from top to bottom is 0.18, 0.38 (panel A) and 2.45, 9.60 (panel B), respectively. The $\Delta k = 10$ case in panel A is from Fig. 6 of Ref. 13, whereas the remaining data are new.

III. COMPARISON WITH SIMULATIONS

In Figs. 1–4 we compare the predictions of SCRTA (red), MPK2/KT (blue), MPK3 (green), and USA (black) with BD simulations (gray circles, using the algorithm of Ref. 13) in the pseudo-first-order case, when both A and C are static ($D_A = D_C = 0$). Specifically, we examine the time dependence of $[A]$ for the initial condition $[A]_0 = 1$ and $[C]_0 = 0$. We have performed this comparison for over 20 parameters sets and present results only for the most edifying ones.

The parameters were selected as follows. Two of them were fixed, $D_B = 1$ and $\kappa_f = 125$ (these values determine our dimensionless units). The remaining parameters were varied as outlined in Table I: Figs. 1 and 2 consider the case of small B-concentration, whereas in Figs. 3 and 4 $[B]_0$ is larger. The odd-numbered figures have $\Delta k > 0$, whereas in the even ones $\Delta k < 0$. κ_r is varied between the two panels (A and B) as indicated. Thus in Figs. 1 and 2 panels B are closer to the irreversible limit, whereas in Figs. 3 and 4 panels B are more remote from it.

For $\Delta k < 0$ (Figs. 2 and 4) we noticed that at long times $[A]$ decays exponentially over a significant time interval.[13] To highlight the preasymptotic behavior, we plot $[A]\exp(-k_{\rm eff}t)$ vs time, where $-k_{\rm eff}$ is the largest root of the real part of the denominator in Eq. (2.7) with the SCRTA rate parameters for $\mathcal{K}_f(s)$ and $\mathcal{K}_r(s)$. In Figs. 1 and 3 the A-concentration is not sc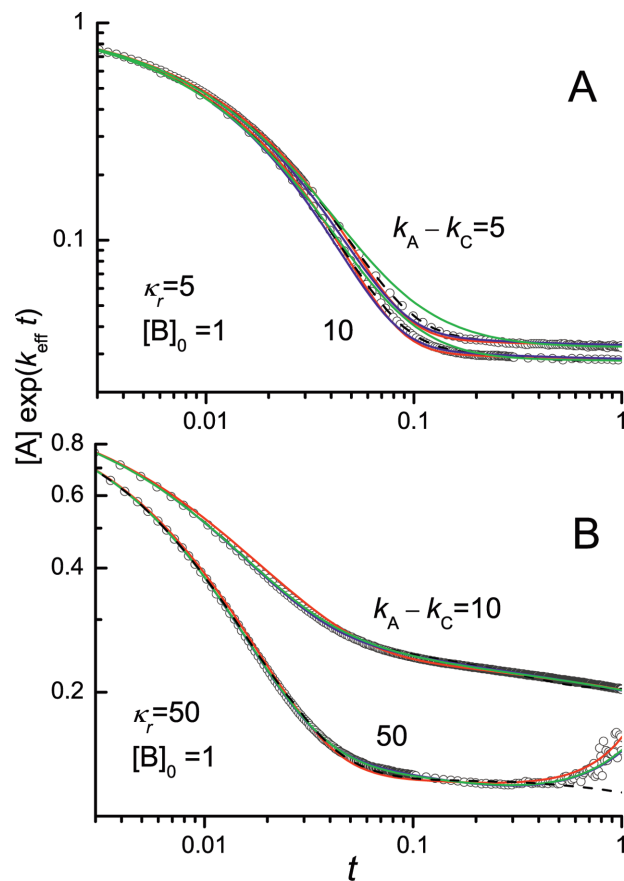aled, but we limit the presentation to the first five decades. We also use a double-logarithmic scale in order to cover more evenly the many orders of magnitude probed by our simulations.

It can be seen from Figs. 1 and 3 that MPK3 performs poorly when $\Delta k > 0$. The other three theories are typically much closer to the BD data. However, as the irreversible limit is approached, SCRTA and MPK2 deteriorate in comparison with the USA as can be seen from Fig. 1(A), where Δk increases. When the irreversible limit is approached by decreasing κ_r (panel B), the discrepancy occurs at intermediate times. Further away from the irreversible limit (smaller Δk or/and larger κ_r) the various theories become almost indistinguishable [e.g., Figs. 2(A) and 4(B)].

TABLE I. Overview of parameters used in the four figures in their panels A/B.

Figure	$[B]_0$	$k_C - k_A$	κ_r
1	0.1/0.5	>0	5/1
2	0.1/0.5	<0	5/1
3	1	>0	5/50
4	1	<0	5/50

IV. CONCLUDING REMARKS

In this paper, we have compared the predictions of several modern theories for the kinetics of the excited-state diffusion-influenced association-dissociation reaction in Eq. (1.1) with simulations. While none of the theories agrees perfectly with the simulations for all times and all parameters, it appears that overall the USA is the most satisfactory. The reason is that it is only the USA that reduces in the irreversible limit to the Smoluchowski result, which is exact in this limit for the microscopic model that was simulated (i.e., the ''target'' problem).

To get the USA, we modify the RTA results so as to reduce to Smoluchowski's kinetics in the irreversible limit. This procedure is a generalization of a simpler transformation suggested previously,[14] for certain special cases of both the $A + B \rightleftharpoons C$ and the $A + B \rightleftharpoons C + D$ reactions for equal lifetimes. The present procedure is applicable to any reaction scheme for which the RTA eigenvalues in Laplace space are of the form $s + \text{const}$. For example, this includes excited state $A + B \rightleftharpoons C + D$ in the pseudo-first-order target limit. When this is not the case (e.g., when all the reactants diffuse), the Smoluchowski result is no longer exact in the irreversible limit, though it may still provide a good approximation.[20] Under such conditions, it is not clear how or even whether one should modify the RTA formalism.

[1] L. M. Tolbert and K. M. Solntsev, Acc. Chem. Res. **35**, 19 (2002).
[2] A. Weller, Z. Phys. Chem., Neue Folge **15**, 438 (1958).
[3] K. M. Solntsev, D. Huppert, and N. Agmon, J. Phys. Chem. A **105**, 5868 (2001).
[4] D. Pines and E. Pines, J. Chem. Phys. **115**, 951 (2001).
[5] I. V. Gopich, K. M. Solntsev, and N. Agmon, J. Chem. Phys. **110**, 2164 (1999).
[6] I. V. Gopich and N. Agmon, J. Chem. Phys. **110**, 10433 (1999).
[7] A. Szabo, J. Chem. Phys. **95**, 2481 (1991).
[8] M. Yang, S. Lee, and K. J. Shin, J. Chem. Phys. **108**, 9069 (1998).
[9] J. Sung and S. Lee, J. Chem. Phys. **111**, 10159 (1999).
[10] J. Sung and S. Lee, J. Chem. Phys. **112**, 2128 (2000).
[11] K. Kwac, M. Yang, and K. J. Shin, J. Chem. Phys. **114**, 3883 (2001).
[12] C. Oh, H. Kim, and K. J. Shin, J. Chem. Phys. **117**, 3269 (2002).
[13] A. V. Popov and N. Agmon, J. Chem. Phys. **117**, 4376 (2002).
[14] I. V. Gopich and A. Szabo, J. Chem. Phys. **117**, 507 (2002).
[15] A. V. Popov and N. Agmon, J. Chem. Phys. **115**, 8921 (2001).
[16] A. V. Popov and N. Agmon, J. Chem. Phys. **118**, 11057 (2003).
[17] N. Agmon and A. V. Popov, J. Chem. Phys. **119**, 6680 (2003).
[18] M. von Smoluchowski, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **92**, 129 (1917).
[19] J. Sung and S. Lee, J. Chem. Phys. **111**, 796 (1999).
[20] A. Szabo, R. Zwanzig, and N. Agmon, Phys. Rev. Lett. **61**, 2496 (1988).