Convolution Kinetics with Generation and Decay for Reversible Excited-State Processes

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Transient diffusion-mediated reversible association accompanied by generation and decay is studied using the method of convolution kinetics for the general scheme of intermolecular two-state excited-state processes. This scheme describes several important photochemical and photophysical processes including excimer formation, acid−base equilibria in the excited state, and association−dissociation of ions with their fluorescent indicators. The convolution-type integral kinetic equations are derived. The relation of the present approach to the extended Smoluchowski method is discussed.

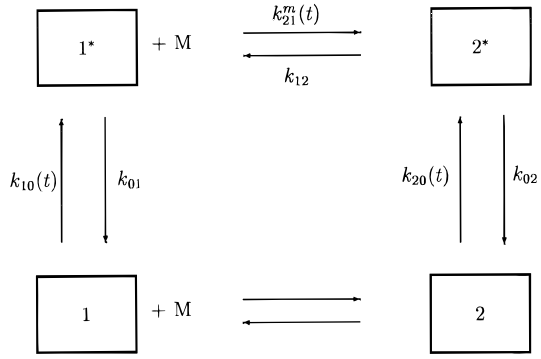
I. Introduction

Recent developments in picosecond fluorometry combined with the global treatment of experimental fluorescence decays allow detailed kinetic studies of complex photophysical processes.[1−3] The standard global analysis recovers the phenomenological rate *constants*,[4] which mix forward and reverse microscopic diffusional and reactive fluxes and, therefore, do not allow a direct determination of the relevant molecular quantities: the intrinsic rates, encounter distances, and diffusion coefficients. In order to utilize the information contained in transient kinetics, one needs to develop a description of diffusional nonequilibrium effects for complex kinetic schemes. In the present paper we pursue this issue and develop a theory of transient diffusion-mediated kinetics of the reversible two-state excited-state processes as depicted in Scheme 1.

The stars on 1* and 2* indicate the excited state of species 1 and 2. The first subscript on a rate constant or coefficient refers to the product molecule, 1* or 2*, and the second to the reactant molecule. The ground-state species are denoted by a 0. The notation [1*] , [2*], and [Q] means the concentration of the corresponding species. We will assume that the excitation is weak so that the ground-state equilibrium is not disturbed, [1] = const. and [2] = const., and that the concentration of M is such that the association 1* + M → 2* is pseudo-first-order. The molecular rate coefficient $k_{21}^{m}(t)$ is defined as the proportionality coefficient between the *molecular* rate of the process (=the number of elementary reactive events per unit volume and time) and the density of reactive pairs.[4−6] The rate coefficient $k_{21}^{m}(t)$ reflects the time evolution of the spatial distribution of 1*M pairs. For slow association, 1* + M → 2*, this distribution is an equilibrium one and the molecular coefficient $k_{21}^{m}(t)$ is equal to the intrinsic rate constant k_{21}^{0}. For rapid association, spatial disequilibrium develops and $k_{21}^{m}(t)$ deviates from k_{21}^{0}. Scheme 1 describes several important photochemical and photophysical processes including excimer formation, acid−base base equilibria in the excited state, and association−dissociation of ions with fluorescent ion indicators.

Transient effects on bimolecular reactions have recently been a subject of considerable interest from both theoretical and experimental viewpoints.[4−17] The various approaches to transient kinetics can be roughly classified as related to the method

SCHEME 1: Reversible Excited-State Association with Generation and Decay



of convolution kinetics[10−12] or as an extended Smoluchowski-type method.[4,8,17] Both methods are based on Smoluchowski's idea that fast reaction in combination with slow diffusion leads to spatial disequilibrium and that this disequilibrium can be understood in terms of a diffusion equation which is modified (e.g. via boundary conditions) to allow for the effect of reaction. The convolution and extended Smoluchowski approaches are equivalent[8] for the basic *irreversible* reaction 1* + M → 2*. The difference shows up, however, in the way concurrent processes (excitation, back reaction) are treated.

The approach that we adopt here is the convolution kinetics, which has proved useful in describing complex schemes relevant to photochemical kinetics.[7−12] Specifically, Agmon and Szabo[7−9] focused on reversible association, and on its combination with decay,[8] and Berberan-Santos and Marthino[10−12] dealt with the excimer formation Scheme 2. In this work, we extend the convolution formalism to include generation and decay in the excited-state kinetics of Scheme 1. Our motivation is, in part, to develop a formalism that can be incorporated into the global analysis of experimental data.

This paper is organized as follows. In the next section we present the main result of this work and compare the kinetic treatment of Scheme 1 in terms of the rate equations and convolution kinetics. The integral convolution kinetic equations are derived in section III. In section IV, limiting cases of the formalism are considered. Finally, in section V we make some comments and summarize the paper.

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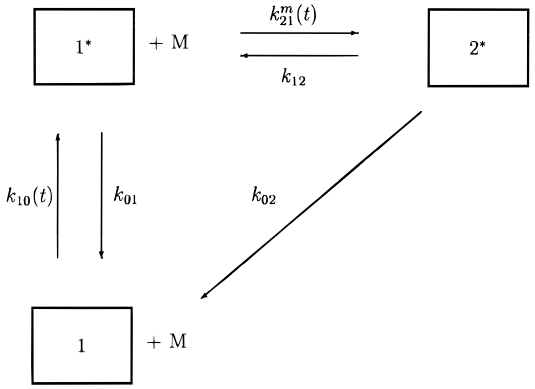
SCHEME 2: Excimer Formation



II. Differential Rate Equations vs Integral Convolution Kinetics

The kinetics associated with Scheme 1 can be represented in terms of the differential rate equations

$$\frac{d}{dt}[1^*(t)] = -k_{21}^{m}(t)[M][1^*(t)] + k_{12}[2^*(t)] - k_{01}[1^*(t)] + k_{10}(t)[1] \quad (1)$$

$$\frac{d}{dt}[2^*(t)] = -k_{21}^{m}(t)[M][1^*(t)] + k_{12}[2^*(t)] - k_{02}[2^*(t)] + k_{20}(t)[2] \quad (2)$$

where the association $1^* + M \rightarrow 2^*$ is described by the molecular rate coefficient $k_{21}^{m}(t)$. The rate equation 1 and 2 are formally exact, but the rate coefficient $k_{21}^{m}(t)$ needs to be determined separately.[4−6]

First, let us consider the limiting situation when the association is slow, or when the pseudo-steady state develops, so that the time-dependent coefficient, $k_{21}^{m}(t)$, can be replaced by a rate constant k_{21}. A delta function pulse produces the initial concentrations [1*(0)] and [2*(0)]. The concentrations [1*(*t*)] and [2*(*t*)] are given by:

$$[1^*(t)] = \alpha_{11}\exp(\gamma_1 t) + \alpha_{12}\exp(\gamma_2 t) \quad (3)$$

$$[2^*(t)] = \alpha_{21}\exp(\gamma_1 t) + \alpha_{22}\exp(\gamma_2 t) \quad (4)$$

where

$$\gamma_{1,2} = -\frac{1}{2}\{X_1 + X_2 ((X_1 - X_2)^2 + 4k_{12}k_{21}[M])^{1/2}\} \quad (5)$$

$$X_1 = k_{01} + k_{21}[M], \qquad X_2 = k_{02} + k_{12} \quad (6)$$

and

$$\alpha_{11} = \frac{1}{\gamma_2 - \gamma_1}\{+[1^*(0)](X_1 + \gamma_2) - [2^*(0)]k_{12}\} \quad (7)$$

$$\alpha_{12} = \frac{1}{\gamma_2 - \gamma_1}\{-[1^*(0)](X_1 + \gamma_1) + [2^*(0)]k_{12}\} \quad (8)$$

$$\alpha_{21} = \frac{1}{\gamma_2 - \gamma_1}\{-[1^*(0)]k_{21}[M] + [2^*(0)](X_2 + \gamma_2)\} \quad (9)$$

$$\alpha_{22} = \frac{1}{\gamma_2 - \gamma_1}\{-[1^*(0)]k_{21}[M] + [2^*(0)](X_2 + \gamma_1)\} \quad (10)$$

At the steady state produced by constant excitation rates, $I_1^{ss} = k_{10}^{ss}$ and $I_2^{ss} = k_{20}^{ss}[2]$, the concentrations are

$$[1^*(\infty)] = \frac{I_1^{ss}(k_{12} + k_{02}) + I_2^{ss}k_{12}}{k_{21}[M]k_{02} + k_{01}(k_{12} + k_{02})} \quad (11)$$

$$[2^*(\infty)] = \frac{I_1^{ss}k_{21}[M] + I_2^{ss}(k_{21}[M] + k_{01})}{k_{21}[M]k_{02} + k_{01}(k_{12} + k_{02})} \quad (12)$$

Equations 3, 4 and 11, 12 are valid only when the time-independent rate constant k_{21} provides an adequate description of the kinetics. Here we are interested in the effects of transient kinetics which produce deviation from the classical results in eqs 3, 4 and 11,12.

A different approach, which is favored in photochemistry, is the convolution method.[10−12] This approach assumes that fluorophores are independent, and therefore, one can focus on the fate of a single fluorophore molecule. The quantity of primary interest is the survival probability $S(t)$ of a fluorophore excited at time $t = 0$ and initially surrounded by a given distribution of reactive partners. The macroscopic effect of excitation then is obtained through the summation (convolution) of the effects due to individual "isolated" molecules. Because of the characteristic convolution integrals appearing in the ensuing formulae, we call this approach the convolution kinetics method.

The method of convolution kinetics for Scheme 1 considers two states of a fluorophore molecule: unbound (=1*) and bound (=2*). The macroscopic kinetics is viewed as the average of sequences of elementary generation events, each separated by a sequence of dissociation−association events and followed by a decay event. The kinetics of association events is characterized by the survival probability of the unbound state, 1*, with respect to association, $1^* + M \rightarrow 2^*$. In this paper we deal with association at the distance of closest approach R, i.e. with the Smoluchowski−Collins−Kimball reactivity model. This allows one to express approximately the complicated kinetics in terms of the well-known time-dependent rate coefficient of irreversible association, $k_{21}(t)$.[7−9] It is important to stress that, in general, the molecular rate coefficient $k_{21}^{m}(t)$ in the rate equations 1 and 2 depends on the rates of all the processes in Scheme 1 and is different from $k_{21}(t)$. In the next section we derive the following integral convolution equations representing the kinetics of Scheme 1 (see also Appendix)

$$[1^*(t)] = I_1(t) \otimes [S(t|\mathrm{eq})e^{-k_{01}t}] + k_{12}[2^*(t)] \otimes [(k_{21}(t)/k_{21}^{0})S(t|\mathrm{eq})e^{-k_{01}t}] \quad (13)$$

and

$$[1^*(t)] + [2^*(t)] = [I_1(t) + I_2(t)] \otimes e^{-k_{02}t} + (k_{02} - k_{01})[1^*(t)] \otimes e^{-k_{02}t}$$

$$= [I_1(t) + I_2(t)] \otimes e^{-k_{01}t} + (k_{01} - k_{02})[2^*(t)] \otimes e^{-k_{01}t} \quad (14)$$

where $\otimes$ denotes a convolution. The excitation rates are $I_1(t) = k_{10}(t)$ [1] and $I_2(t) = k_{20}(t)$[2], and the survival probability is given by

$$S(t|\mathrm{eq}) = \exp(-[\mathrm{M}]\int_0^t k_{21}(t')\,\mathrm{d}t') \tag{15}$$

Equations 13 and 14 describe the kinetics of Scheme 1, where allowance is made for decay and generation of *both* species 1 and 2. Equations 13 and 14 are the main results of this paper and can be solved numerically to determine the individual concentrations [1*] and [2*]. In the general case, when the rate coefficient $k_{21}(t)$ is time dependent and M > 0, the convolution kinetics 13 and 14 offer an approximate representation of the underlying many-particle problem. When the rate coefficient k_{21} becomes a constant and [M] > 0, the convolution kinetics 13 and 14 become exact and reduce, as expected, to the classical case of eqs 3 and 4. In the limiting situation where [M] → 0, the convolution formulae 3 and 4 also become exact and represent the kinetics of a mixture of independent fluorophores 1* and 2* (see section IV.C).

It is instructive to compare the differential rate equations 1 and 2, which are usually associated with extended Smoluchowski approaches, to the integral equations 13 and 14 of convolution kinetics. They provide different, approximate representations of the kinetics. Similarly to the case of monomer−excimer kinetics,[10−12] the convolution kinetics 13 and 14 can be cast in the form of differential equations 1 and 2, to give approximate expressions for the molecular rate coefficient $k_{21}^{\mathrm{m}}(t)$. To see this let us first note that upon adding eqs 1 and 2 one recovers the rate equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\{[1^*(t)] + [2^*(t)]\} = -k_{01}[1^*(t)] - k_{02}[2^*(t)] + k_{10}(t)[1] + k_{20}(t)[2] \tag{16}$$

whose formal solution is given by eq 14. Thus, it is enough to show that eq 13 can be converted into eq 1. Following Berberan-Santos and Marthino,[11] one can use the relation

$$\frac{\mathrm{d}}{\mathrm{d}t}[x(t) \otimes y(t)] = x(t) \otimes \frac{\mathrm{d}y(t)}{\mathrm{d}t} + x(t)\,y(0+) \tag{17}$$

and differentiate eq 13 to recover eq 1 with the molecular rate coefficient determined by

$$k_{21}^{\mathrm{m}}(t)[\mathrm{M}][1^*(t)] = k_{01}[1] \otimes [k_{21}(t)S(t|\mathrm{eq})\mathrm{e}^{-k_{01}t}][\mathrm{M}] + k_{12}[2^*(t)] \otimes \{(k_{21}(t)/k_{21}^0)S(t|\mathrm{eq})\mathrm{e}^{-k_{01}t}(k_{21}(t)[\mathrm{M}] - \mathrm{d}[\ln k_{21}(t)]/\mathrm{d}t)\} \tag{18}$$

The concentrations [1*(*t*)] and [2*(*t*)] in eq 18 are obtained by solving the convolution kinetics equations 13 and 14. This can be accomplished formally by Laplace transforming eqs 13 and 14, solving the resulting systems of linear equations for the Laplace transforms of [1*(*t*)] and [2*(*t*)], and then back Laplace transforming. Since the Laplace transforms cannot be done analytically, the resulting formulae are unwieldy and are not given here. The formal result (eq 18) shows that the rate coefficient $k_{21}^{\mathrm{m}}(t)$ corresponding to the convolution kinetics 13 and 14 is a function of time and concentration.

III. Microscopic Model and Transient Kinetics

The model we study here is an idealization of the situation in a typical single-photon timing experiment. We assume that the concentration of the fluorophores is small compared to that of M, that the excitation intensity is low, and that the duration of the excitation pulse is short. All this combined allows us to focus on an ensemble of isolated 1* molecules, each surrounded by an excess of M molecules. We will consider two survival probabilities of 1*s, that differ from each other by a different initial distribution of M's surrounding a 1*. The survival probability $S(t|\mathrm{eq})$ is the probability that a 1* created at $t = 0$, and surrounded initially by an equilibrium distribution of M's, has not undergone an association reaction, 1* + M → 2*, until the moment *t*. Thus, $S(t|\mathrm{eq})$ is the survival probability with respect to association with M, when an 1* is generated by external excitation. The survival probability $S(t|R)$ is the survival probability of an 1* generated by an elementary dissociation event 2* → 1* + M. Now the initial distribution of M's is a nonequilibrium one, since the geminate M is added to the sea of equilibrated M's. The notation |eq) serves as a reminder of an initial equilibrium distribution of M's, whereas |*R*) means that an additional M is present at the contact distance *R*. The two survival probabilities can be related as[7]

$$S(t|R) = S_2(t|R)\,S(t|\mathrm{eq}) \tag{19}$$

where $S_2(t|R)$ is the survival probability of an isolated 1*M *pair*, initially separated by *R*. Equation 19 is exact for an immobile 1* and noninteracting point M's. In general, however, eq 19 is only an approximation equivalent to the assumption that a geminate pair is independent of other M's in the system.

Further development depends on the assumed model of the association. Here, we consider the Smoluchowski−Collins−Kimball (SCK) reactivity model, i.e. association upon *contact* at the distance of closest approach *R*. The intrinsic rate constant is k_{21}^0. For the sake of simplicity we ignore the interparticle forces. For the SCK model we have[7]

$$S_2(t|R) = \frac{k_{21}(t)}{k_{21}^0} \tag{20}$$

The survival probability

$$S(t|\mathrm{eq}) = \exp(-[\mathrm{M}]\int_0^t k_{21}(t')\,\mathrm{d}t') \tag{21}$$

now involves the well-known SCK time-dependent rate coefficient[18]

$$k_{21}(t) = \frac{k_{21}^0}{1+\kappa_{21}^0}[1 + \kappa_{21}^0 \exp(x^2)\,\mathrm{erfc}(x)] \tag{22}$$

where

$$x(t) = (1+\kappa_{21}^0)t^{1/2}/\tau_D^{1/2} \quad \kappa_{21}^0 = k_{21}^0/k_D, \quad k_D = 4\pi RD, \quad \tau_D = R^2/D \tag{23}$$

The time integral of the SCK rate coefficient is also known[18]

$$\int_0^t k_{21}(t')\,\mathrm{d}t' = \frac{k_{21}^0}{1+\kappa_{21}^0}t + \frac{\kappa_{21}^0\tau_D k_{21}^0}{(1+\kappa_{21}^0)^3}[\exp(x^2)\,\mathrm{erfc}(x) - 1 + 2x/\pi^{1/2}] \tag{24}$$

Thus, for the SCK model adopted here, the survival probabilities, $S(t|\mathrm{eq})$ and $S(t|R)$, are known explicitly.

Now we introduce the kinetic formalism for Scheme 1 extending the approach developed by Agmon and Szabo.[7,8] First, let us consider reversible association, 1* + M ⇌ 2*, with no generation and decay. In this case, the sum of the concentrations [1*] + [2*] of species 1* and 2* is a constant equal to its initial value [1*(0)] + [2*(0)] , but the individual concentrations, [1*]- and [2*] , change in time. For the concentration of species 1*, one can write

$$[1^*(t)] = [1^*(0)]S(t|\mathrm{eq}) + k_{12}\int_0^t [2^*(t')]S(t-t'|R)\,\mathrm{d}t' \quad (25)$$

Equation 25 expresses the fact that there are two contributions to [1*] , one coming from the 1*s present at $t = 0$ and the other from those generated by dissociation of 2*s at different instances t'. We assume that each 1* present at $t = 0$ is surrounded by an equilibrium distribution of M's. Thus the decay of the initial population of 1*s is described by the survival probability $S(t|\mathrm{eq})$. At each time interval $\mathrm{d}t'$, the number density of the 1*s generated by dissociation is $k_{12}[2^*(t')]\,\mathrm{d}t'$, and the number density of those that have survived till time t is $k_{12}[2^*(t')]S(t-t'|R)\,\mathrm{d}t$. The integral on the right of eq 25 is the sum of additive contributions since the initial moment $t = 0$. Using relations 19 and 20, eq 25 can be cast into the form

$$[1^*(t)] = [1^*(0)]S(t|\mathrm{eq}) + K_\mathrm{d}^*[2^*(t)] \otimes [k_{21}(t)S(t|\mathrm{eq})] \quad (26)$$

where $K_\mathrm{d}^* = k_{12}/k_{21}^0$. In the second step, we include the decays, $1^* \rightarrow 1$ and $2^* \rightarrow 2$, but still leave out the excitation. Now, the sum of the concentrations changes in time according to

$$\frac{\mathrm{d}}{\mathrm{d}t}\{[1^*(t)] + [2^*(t)]\} = -k_{01}[1^*(t)] - k_{02}[2^*(t)] \quad (27)$$

and the time evolution of [1*] in eq 26 is modified by the decay $1^* \rightarrow 1$ as

$$[1^*(t)] = [1^*(0)]S(t|\mathrm{eq})\mathrm{e}^{-k_{01}t} + K_\mathrm{d}^*[2^*(t)] \otimes [k_{21}(t)S(t|\mathrm{eq})\mathrm{e}^{-k_{01}t}] \quad (28)$$

Equation 28 differs from eq 26 by the factor $\exp(-k_{01}t)$, so that the product $S(t|\mathrm{eq})\mathrm{e}^{-k_{01}t}$ is the survival probability with respect to association and decay.

Finally, we introduce the effect of production of 1* and 2* with the rates $I_1(t) = k_{01}[1]$ and $I_2(t) = k_{02}[2]$, respectively. The rate equation 27 becomes eq 16, and the concentration of 1* evolves according to

$$[1^*(t)] = I_1(t) \otimes [S(t|\mathrm{eq})\mathrm{e}^{-k_{01}t}] + K_\mathrm{d}^*[2^*(t)] \otimes [k_{21}(t)S(t|\mathrm{eq})\mathrm{e}^{-k_{01}t}] \quad (29)$$

Note that the production rate $I_1(t) = k_{10}[1]$ enters only the first term on the right of eq 29. This is because this term describes the 1*s created by excitation and surrounded initially by an equilibrium distribution of M's. The second term is only indirectly dependent on the generation rate via the concentration $[2^*(t)]$ and the rate equation 27. Equations 16 and 29 can be easily transformed to the form in eqs 13 and 14 that is more suitable for numerical calculations. An alternative derivation of the convolution kinetics is outlined in the Appendix. We also note that similar convolution relations were suggested by Berg.[19]

Scheme 1, unlike in the excimer formation Scheme 2, allows for direct excitation of species 2. This opens up a possibility of using convolution kinetics to determine whether species 2 is present in equilibrium with 1, given that 2 is directly excitable. A closely related question is whether transient kinetics can be distinguished from classical kinetics and used to access the molecular parameters. To illustrate those issues, we focus on the δ-function pulse generation mode producing a nonzero initial concentration $[2^*(0)] > 0$. It is convenient to introduce the characteristic diffusional lifetime $\tau_D = R^2/D$ and the characteristic rate $k_D = 4\pi RD$ and use the following scaled, dimensionless quantities

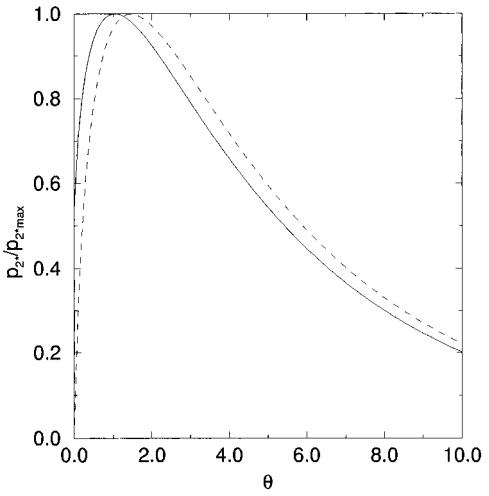


Figure 1. Dimensionless concentration p_{2^*} normalized to $p_{2^*\mathrm{max}} = 1$ as a function of dimensionless time θ for $\phi = 0.5/3$, $\kappa_{21}^0 = 5$, $\kappa_{12} = 2$, and $\kappa_{01} = \kappa_{02} = 0.2$. The initial concentration is $p_{2^*}(0) = 0.2$, solid line; 0, broken line.

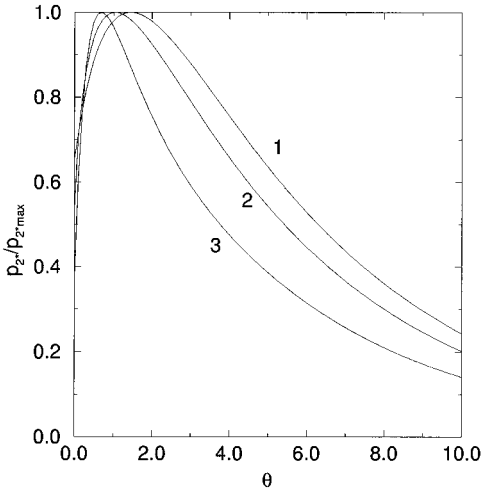


Figure 2. Same as Figure 1 with $p_{2^*}(0) = 0.2$. Line 2 is calculated using the convolution kinetics. Line 1 is calculated using the "long time" rate constants $\kappa_{21}(\infty)$ replacing $\kappa_{21}(\theta)$. Line 3 is calculated with the rate coefficient replaced by its initial value $\kappa_{21}(\theta) \rightarrow \kappa_{21}^0$.

$$\theta = t/\tau_D, \quad \kappa_{21}(t) = k_{21}(t)/k_D, \quad \kappa_{21}^0 = k_{21}^0/k_D, \quad \kappa_{12} = k_{12}\tau_D, \quad \kappa_{01} = k_{10}\tau_D, \quad \kappa_{02} = k_{20}\tau_D, \quad \phi = {}^4/_3\pi R^3[\mathrm{M}] \quad (30)$$

and the scaled concentrations

$$p_{1^*}(\theta) = \frac{[1^*(\theta)]}{[1^*(0)] + [2^*(0)]}, \quad p_{2^*}(\theta) = \frac{[2^*(\theta)]}{[1^*(0)] + [2^*(0)]} \quad (31)$$

Equations 13 and 14 can be nondimensionalized and solved recursively by discretizing the dimensionless time, $\theta = n\Delta\theta$, using the trapezoidal rule. Given $p_{1^*}(0)$ and $p_{2^*}(0)$, the values $p_{1^*}(\Delta\theta)$ and $p_{2^*}(\Delta\theta)$ are first obtained, then $p_{1^*}(2\Delta\theta)$ and $p_{2^*}(2\Delta\theta)$ follow, and so on.

Figures 1 and 2 present the dimensionless concentration p_{2^*} as a function of dimensionless time θ for $\phi = 0.5/3$, $\kappa_{21}^0 = 5$, and $\kappa_{12} = 2$, and $\kappa_{01} = \kappa_{02} = 0.2$. The solid lines correspond to the initial concentration $p_{2^*}(0) = 0.2$, i.e. one out of five molecules excitated by the initial pulse is a 2* molecule. The curves are normalized so that the maximum value $p_{2^*\mathrm{max}} = 1$. Figure 1 compares the normalized decays calculated for the initial value $p_{2^*}(0) = 0.2$ (solid line) and for the case where

species 2 is not directly excited, $p_{2^*}(0) = 0$ (broken line). Figure 1 shows that the proper timing of the initial pulse can be critical for the kinetic identification of the process $2 \rightarrow 2^*$.

Figure 2 compares the convolution kinetics (line 2) with the classical predictions of eqs 3 and 4 (lines 1 and 3). The line indicated as "1" was calculated using the "long time" rate constants $\kappa_{21}(\infty)$ replacing $\kappa_{21}(\theta)$. This is equivalent to the classical result 3 and 4 with the forward rate constant $k_{21} = k_{21}^0 k_D/(k_{21}^0 + k_D)$ and the renormalized backward rate constant $k_{12} \rightarrow k_{12}k_D/(k_{12}^0 + k_D)$. The "3" line was calculated with the rate coefficient $\kappa_{21}(\theta)$ replaced by its initial value $\kappa_{21}(\theta) \rightarrow \kappa_{21}^0$. This corresponds to the choice $k_{21} = \kappa_{21}^0$ in the classical formulae 3 and 4. The convolution kinetics 2 clearly deviate from the classical ones 1 and 3. We note that curve 2 is sandwiched between the classical kinetics predictions 1 and 3. This suggests that with an appropriate choice of the parameters, the classical kinetics can be used to fit the transient kinetics, but the recovered parameters will have no simple relation to the microscopic quantities.

IV. Limiting Situations

In this section we examine three limiting situations of the general formalism. First, we show that for the reversible association, $1^* + M \rightleftharpoons 2^*$, with no generation or decay the convolution kinetics produces the correct equilibrium concentrations. Second, we consider steady states and show how the present approach can be formulated in terms of the molecular rate coefficients. Third, we consider the low M density limit where the convolution kinetics become exact.

A. Reversible Association with No Decay and Generation. As a check on the convolution kinetics, let us consider reversible association $1^* + M \rightleftharpoons 2^*$, when decay is turned off, eq 26. In this case the system should reach equilibrium, where the concentrations $[1^*(\infty)]$ and $[2^*(\infty)]$ are determined by $K_d^* = k_{12}/k_{21}^0$

$$K_d^* = \frac{[1^*(\infty)][M]}{[2^*(\infty)]} \tag{32}$$

irrespective of the initial values $[1^*(0)]$ and $[2^*(0)]$. Agmon and Szabo[7,8] considered the case where all the excited fluorophores are initially bound, $[2^*(0)] > 0$ and $[1^*(0)] = 0$, as well as the case of initially unbound fluorophores, $[2^*(0)] = 0$ and $[1^*(0)] > 0$, and showed that the equilibrium limit of the convolution kinetics are independent of the initial condition, as it should be. A similar approach can be used to show that the convolution kinetics (eq 26) give the correct equilibrium limit in the general case $[1^*(0)] > 0$ and $[2^*(0)] > 0$. Laplace transforming eq 25 and using the relation[7]

$$\int_0^\infty e^{-st} k_{21}(t)\, S(t|eq)\, dt = [M]^{-1}\,[1 - s\hat{S}(s|eq)] \tag{33}$$

that follows from the definition 21, we get

$$[\hat{1}^*(s)] = [1^*(0)]\hat{S}(s|eq) + \frac{K_d^*}{[M]}\left(\frac{[1^*(0)] + [2^*(0)]}{s} - [\hat{1}^*(s)]\right)(1 - s\hat{S}(s|eq)) \tag{34}$$

Multiplying by the Laplace variable s and taking the long time limit $s \rightarrow 0$, we finally get

$$\frac{[1^*(\infty)]}{[1^*(0)] + [2^*(0)]} = \frac{K_d^*}{[M] + K_d^*}, \qquad \frac{[2^*(\infty)]}{[1^*(0)] + [2^*(0)]} = \frac{[M]}{[M] + K_d^*} \tag{35}$$

Note that relations 35 are independent of the initial ratio $[1^*(0)]/[2^*(0)]$, and of a particular form of $k_{21}(t)$, and are consistent with the equilibrium constant expression 32.

B. Nonequilibrium Steady States. In this section we consider nonequilibrium steady states produced by the constant generation rates $k_{21}^0 I_1^{ss} = k_{10}[1]$ and $I_2^{ss} = k_{20}[2]$. The steady-state form of eq 16 is

$$k_{01}[1^*(\infty)] + k_{02}[2^*(\infty)] = I_1^{ss} + I_2^{ss} \tag{36}$$

From definition 21 follows the following relation

$$\int_0^\infty e^{-st} k_{21}(t)\, S(t|eq) e^{-k_{01}t}\, dt = [M]^{-1}[1 - (s + k_{01})\,\hat{S}(s + k_{01}|eq)] \tag{37}$$

that can be used to write the Laplace transform of eq 29 as

$$[1^*(\infty)] - [2^*(\infty)]K_d^*[M]^{-1}[1 - k_{01}\,\hat{S}(k_{01}|eq)] = I_1^{ss}\,\hat{S}(k_{01}|eq) \tag{38}$$

Upon solving eqs 36 and 38 for the steady-state concentrations, we get

$$[1^*(\infty)] = \frac{(I_1^{ss} + I_2^{ss})K_d^*[M]^{-1}[1 - k_{01}\hat{S}(k_{01}|eq)] + I_1^{ss}k_{02}\hat{S}(k_{01}|eq)}{k_{02} + k_{01}K_d^*[M]^{-1}[1 - k_{01}\hat{S}(k_{01}|eq)]} \tag{39}$$

and

$$[2^*(\infty)] = \frac{I_1^{ss}[1 - k_{01}\hat{S}(k_{01}|eq)] + I_2^{ss}}{k_{02} + k_{01}K_d^*[M]^{-1}[1 - k_{01}\hat{S}(k_{01}|eq)]} \tag{40}$$

Equations 39 and 40 can be used to calculate the Stern−Volmer plots. When the rate coefficient k_{21} is a constant, $\hat{S}(k_{01}|eq) = (k_{01} + k_{21}[M])^{-1}$ and eqs 39 and 40 reduce to the classical result 11 and 12. In this connection we note that the magnitude of the transient effects is determined by the quantity $\hat{S}(k_{01}|eq)$. This fact can be used to construct a measure of transient effects for Scheme 1.

It is important to distinguish between the irreversible rate coefficient $k_{21}(t)$, determining the survival probability $S(t|eq)$, and the molecular rate coefficient of association, k_{21}^m, defined via the number of elementary association events per unit volume and time. To illustrate the difference between those two quantities, we formulate the steady-state problem in terms of the steady-state molecular rate coefficient, k_{12}^{ss}. At steady state, the rate equations 1 and 2 become

$$0 = -k_{21}^{ss}[M][1^*(\infty)] + k_{12}[2^*(\infty)] - k_{01}[1^*(\infty)] + I_1^{ss} \tag{41}$$

$$0 = +k_{21}^{ss}[M][1^*(\infty)] - k_{12}[2^*(\infty)] - k_{02}[2^*(\infty)] + I_2^{ss} \tag{42}$$

Equations 41 and 42 are an exact representation of the steady-state problem, but the coefficient k_{21}^{ss} is still undetermined. Equations 41 and 42 can be solved to give

$$[1^*(\infty)] = \frac{I_1^{ss}(k_{12} + k_{02}) + I_2^{ss}k_{12}}{k_{21}^{ss}[M]k_{02} + k_{01}k_{12} + k_{01}k_{02}} \quad (43)$$

$$[2^*(\infty)] = \frac{I_1^{ss}k_{21}^{ss}[M] + I_2^{ss}(k_{21}^{ss}[M] + k_{01})}{k_{21}^{ss}[M]k_{02} + k_{01}k_{12} + k_{01}k_{02}} \quad (44)$$

Equations 39, 40 and 43, 44 allow one to approximate the steady-state molecular rate coefficient k_{21}^{ss} using convolution kinetics. For instance, one can identify the right hand sides of eqs 39 and 43 and solve for k_{21}^{ss}. Here suffice it to say that the formulation in terms of the rate equations involving the molecular rate coefficient involves the molecular rate coefficient, k_{21}^{ss}, which is concentration dependent, and is a function of the rates of all concurrent processes in the system.

C. Low-Density Limit. Convolution kinetics are not exact when the rate coefficient $k_{21}(t)$ is time dependent and the concentration of M is finite, [M] > 0. This is because the formalism assumes that each 2* is surrounded by an equilibrium distribution of M's, irrespective of whether an 2* has just been generated by light absorption or has undergone a series of previous association and dissociation events. In the latter case the distribution of M's is a nonequilibrium one, so that a dissociation event produces a geminate pair in a sea of nonequilibrated M's. In general, the ensuing association kinetics can only approximately be described by the survival probability $S(t|R)$ given by eq 19. However, for slow association or when [M] → 0, the above formalism becomes exact. In the first case, the association rate coefficient becomes a constant k_{21}, and the convolution kinetics reduce to the classical kinetics 3 and 4.

The second case when the convolution approach becomes exact is the limit of low M concentration, with arbitrary $k_{21}(t)$. In the limit [M] → 0, the dynamics of the present model reduce to those of a (somewhat artificial) system of independently generated 1*s and 2*s, where a 2* can dissociate to produce a geminate M and is allowed to recombine only with that M. In this limit, the survival probability $S(t|\text{eq}) = 1$ so that expression 13 becomes

$$[1^*(t)] = I_1(t) \otimes e^{-k_{01}t} + k_{12}[2^*(t)] \otimes [(k_{21}(t)/k_{21}^0)e^{-k_{01}t}] \quad (45)$$

whereas equation 14 stays unchanged. Equations 14 and 15 are exact and generalize to arbitrary excitation shapes the result of Agmon and Szabo[7,8] who considered a δ function excitation producing initially [2*(0)] > 0 and [1*(0)] = 0. For this particular case, eq 45 becomes

$$[1^*(t)] = k_{12}[2^*(t)] \otimes [(k_{21}(t)/k_{21}^0)e^{-k_{01}t}] \quad (46)$$

which is equivalent to the result found previously.[7,8]

V. Comments and Summary

In this paper we have presented a convolution kinetic description of Scheme 1. The main result was stated in section 2. In section 3 we derived the convolution kinetics from a microscopic model. The resulting evolution equations 13 and 14 involve the time-dependent rate coefficient, $k_{21}(t)$, of irreversible association, 1* + M → 2*. The convolution kinetics reduce to the classical rate equations when k_{21} is a rate constant.

We stress that naively replacing the rate constant k_{21} in a classical rate equation by its irreversible time-dependent counterpart, $k_{21}(t)$, may lead to unsatisfactory results. For instance, the rate equation corresponding the irreversible reaction 1* + M → 2*

$$\frac{d}{dt}[1^*(t)] = -k_{21}(t)[M][1^*(t)] \quad (47)$$

can be formally obtained by the substitution $k_{21} \rightarrow k_{21}(t)$ in the classical rate equation. However, when an input, 1 → 1*, with the rate $I_1(t)$ is also present, the rate equation

$$\frac{d}{dt}[1^*(t)] = -k_{21}(t)[M][1^*(t)] + I_1(t) \quad (48)$$

can only be considered as an ad hoc approximation, unless $k_{21}(t)$ is identified to be the *molecular* rate coefficient $k_{21}^m(t)$, $k_{21}^m(t) \neq k_{21}(t)$. The use of the molecular rate coefficients is crucial in the extended Smoluchowski approach.[4,17] Here, we followed a route more familiar in photochemistry, and used the convolution kinetics approach, so-called because of the characteristic convolution integrals it involves. Accordingly, in place of eq 48, we write the convolution relation

$$[1^*] = \int_0^t I_1(t')\, S(t-t')\, dt, \quad S(t) = \exp(-[M]\int_0^t k_{21}(t')\, dt') \quad (49)$$

In section IV.B we found that the transient effects are determined by the quantity $\hat{S}(k_{01}|\text{eq})$. This is the Laplace transform of the survival probability $\hat{S}(s|\text{eq})$, where the Laplace variable is substituted by the rate constant k_{01}. This suggest that the coefficient

$$r = \{k_{01} + k_{21}(\infty)[M]\}\, \hat{S}(k_{01}|\text{eq}) \quad (50)$$

could be used as a measure of the transient effects in complex kinetic schemes. As illustrated in section IV.B on the example of the steady-state molecular rate coefficient, the overall contribution of the transient effects depends on the rates of all concurrent processes. Nevertheless, a deviation from unity of the coefficient r is a necessary condition for the transients to be visible.

In short, we have applied the method of convolution kinetics to describe the transient, diffusion-mediated evolution of the photochemical square, Scheme 1, for the Smoluchowski−Collins−Kimball reactivity model. The main result of this work is the two coupled evolution equations 13 and 14 determining the concentrations of the excited-state species [1*] and [2*]. The present approach has been developed with a view to interpreting single-photon timing experiments. Work along this line is in progress.

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Appendix

Here we present another derivation of the evolution equations following the formal recipe developed by Berberan-Santos et al.[12] The concentration of 1* is composed of the contribution from the primary production rate $I_1(t) = k_{10}(t)$ [1] , i.e. from external excitation, and the secondary production rate, I_1^{sec}, i.e. by dissociation. Accordingly, we have

$$[1^*(t)] = I_1(t) \otimes [S(t|\text{eq})e^{-k_{01}t}] + I_1^{sec}(t) \otimes [S(t|R)e^{-k_{01}t}],$$
$$I_1^{sec}(t) = k_{12}[2^*(t)] \quad (51)$$

and similarly

$$[2^*(t)] = I_2(t) \otimes \mathrm{e}^{-(k_{01}+k_{12})t} + I_2^{\mathrm{sec}}(t) \otimes \mathrm{e}^{-(k_{01}+k_{12})t},$$
$$I_2(t) = k_{20}(t)[2] \tag{52}$$

where, according to Berberan-Santos et al.,[12] one has

$$I_2^{\mathrm{sec}}(t) = I_1(t) \otimes [S'(t|\mathrm{eq})\mathrm{e}^{-k_{01}t}] + k_{12}[2^*(t)] \otimes [S'(t|R)\mathrm{e}^{-k_{01}t}] \tag{53}$$

The primes on $S'(t|\mathrm{eq})$ and $S'(t|R)$ in eq 53 denote differentiation with respect to time. Using relation 17 one can recover the evolution equations 27 and 29.

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