

Integral encounter theories of the multistage reactions.

III. Reversible intramolecular energy transfer

K. L. Ivanov

International Tomography Center, Novosibirsk 630090, Russia and Novosibirsk State University, Novosibirsk 630090, Russia

N. N. Lukzen

International Tomography Center, Novosibirsk 630090, Russia

A. B. Doktorov

Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia

A. I. Burshtein^{a)}

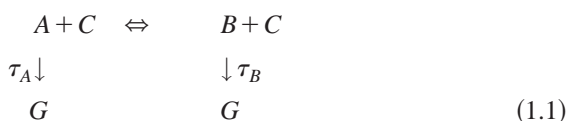
Weizmann Institute of Science, Rehovot 76100, Israel

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The matrix Integral Encounter Theory (IET) and its modified version (MET) developed earlier are used to study the kinetics of the reversible transitions between two metastable (as singlet and triplet) states of the fluorescent particle. Induced by binary encounters with inert catalysts, these transitions result in either (a) energy quenching or (b) energy conservation, depending on what lifetime of these two states is longer. Integral encounter theory describes adequately the kinetics of energy conservation followed by delayed fluorescence while differential or Markovian versions of the same theory fail. Another advantage of the IET is the natural accounting for arbitrary strong light pumping which makes the Stern–Volmer constant dependent on light intensity, differently for cases (a) and (b). © 2001 American Institute of Physics. [DOI: 10.1063/1.1353546]

I. INTRODUCTION

The general matrix formalism of integral and modified encounter theories (IET and MET) developed in part I of this work¹ was applied in part II to a quasiresonant intermolecular energy transfer.² Here we consider an important application of the same formalism to the intramolecular energy transfer between metastable states A to B , induced by encounters with inert particles C . This reaction can be represented by a following formal scheme:



which describes, for instance, the singlet–triplet conversion in excited dyes stimulated by encounters with particles containing heavy atoms like iodine or bromine.³ The study of the fluorescence quenching of dyes in liquid solutions has a long story starting from experimental evidence of diffusional quenching obtained in Refs. 4,5 and reviewed in Ref. 6. Since the C particles do not change when induced by the interconversion $A \rightleftharpoons B$, their concentration $c = [C]$ remains constant in principle. In contrast, both excitations disappear with time; they decay to the ground state G with the rates $1/\tau_A$ and $1/\tau_B$, respectively. Besides, one can account for the light induced transition from the ground to fluorescent (singlet) state A running with a rate I_0 ;



After excitation, the energy transfers from A to B and backward during diffusional encounters with C . Usually the encounter diffusion coefficient is assumed to be independent on the level of excitation, $D = D_A + D_C = D_B + D_C$. This coefficient determines the encounter time $\tau_d = \sigma^2/D$, where σ is the closest approach distance.

Recently, it was shown that the reversible reaction of such kind is beyond the reach of either superposition approximation (SA) or differential encounter theory (DET).⁷ Not a rate concept, but an integrodifferential formalism, employed by IET and MET, is the only one able to cope with such a problem. Hence, the analysis of this reaction within this formalism is the main goal of this paper as well as a tight comparison with the approach of Yang, Lee, and Shin (YLS) (Ref. 8) reduced to the differential version of the theory. The approximate reduction of integral equations to differential (rate) equations is incorrect when decay times of excited states are different. It was demonstrated a few times by the example of reversible intermolecular energy transfer^{9–11} that such a reduction makes the fluorescence quantum yield calculation impossible. The same is true for the reversible intramolecular transfer. If B (presumably triplet) has longer lifetime than A , not only the quantum yield but the kinetics of fluorescence is qualitatively distorted as well.^{9–11} We will show that non-Markovian kinetics of long-lived state consists of a short geminate stage and a long bimolecular energy quenching accompanied by delayed fluorescence. Neither of these effects are properly described within the rate concept.

^{a)} Author to whom correspondence should be addressed. Electronic mail: anatoly.burshtein@weizmann.ac.il

We will also confirm the Stern–Volmer Law and specify the light intensity dependence of its constant for reversible energy transfer like it was done for a similar irreversible reaction in Refs. 12 and 13.

II. IET AND MET KINETIC EQUATIONS

From the general formalism of part I (Ref. 1) it is easy to get the integrodifferential equations for intermolecular transfer which are simpler than for intramolecular transfer (see part II, Ref. 2) because of C particles conservation. The IET equation takes the following form:

$$\frac{\partial \sigma(t)}{\partial t} = \hat{Q} \sigma(t) - c \int_0^t \hat{R}(t-\tau) \sigma(\tau) d\tau, \quad (2.1)$$

where the vector

$$\sigma = \begin{pmatrix} N_A \\ N_B \\ N_G \end{pmatrix} \quad (2.2)$$

is composed from the populations of excited and ground states of an active particle, $N_A(t) = [A]$, $N_B(t) = [B]$, $N_G(t) = [G]$. Because the structureless C s conserve in the course of Eq. (2.1) are linear in time variable densities which are components of σ .

The intramolecular relaxation is given by an operator,

$$\hat{Q} = \begin{pmatrix} -1/\tau_A & 0 & I_0 \\ 0 & -1/\tau_B & 0 \\ 1/\tau_A & 1/\tau_B & -I_0 \end{pmatrix}, \quad (2.3)$$

which includes the natural decay of the excited states with the lifetimes τ_A and τ_B and light pumping with a rate I_0 . Another important operator is the kernel (memory function) of the IET, $\hat{R}(t)$, which is represented via the Green function of the reactant pair \hat{G} and reactivity matrix \hat{W} (the Liouvillian of the bimolecular reactions)¹

$$\hat{R}(t) = - \int d\mathbf{r} \hat{W}(\mathbf{r}) \left[\delta(t) + \int d\mathbf{r}_0 \hat{G}(\mathbf{r}|\mathbf{r}_0, t) \hat{W}(\mathbf{r}_0) \right]. \quad (2.4)$$

Restricting ourselves to contact approximation employed in preceding article² we obtain the reactivity matrix,

$$\hat{W} = \begin{pmatrix} -w_f(r) & w_r(r) & 0 \\ w_f(r) & -w_r(r) & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{\delta(r-\sigma)}{4\pi\sigma^2} \begin{pmatrix} -k_f & k_r & 0 \\ k_f & -k_r & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (2.5)$$

which is expressed through kinetic rate constants of forward and reverse transfer between excited states, $k_f = \int w_f(r) d^3r$ and $k_r = \int w_r(r) d^3r$. The equation for the Green function is as follows:¹

$$(\partial_t - \hat{L}_r - \hat{W}(\mathbf{r}) - \hat{Q}) \hat{G}(\mathbf{r}|\mathbf{r}_0, t-t_0) = \delta(t-t_0) \delta(\mathbf{r}-\mathbf{r}_0) \hat{I}, \quad (2.6)$$

where \hat{L}_r is the operator of the encounter diffusion of the reactants, and \hat{I} is the unity operator.

The matrix-form equations of MET are also of the integrodifferential type,

$$\frac{d\sigma(t)}{dt} = \hat{Q} \sigma(t) - c \int_0^t \hat{\Sigma}(t-\tau) \sigma(\tau) d\tau, \quad (2.7)$$

but with concentration-corrected kernel $\hat{\Sigma}$,¹

$$\hat{\Sigma}(t) = \int d\mathbf{r} \hat{W}(\mathbf{r}) \left[\delta(t) + \int d\mathbf{r}_0 \hat{G}_{\text{eff}}(\mathbf{r}|\mathbf{r}_0, t) \hat{W}(\mathbf{r}_0) \right]. \quad (2.8)$$

It is expressed through the auxiliary Green function \hat{G}_{eff} which obeys the matrix equation,¹

$$[\partial_t - \hat{L}_r + \hat{R} - \hat{Q} - \hat{W}(\mathbf{r})] \hat{G}_{\text{eff}}(\mathbf{r}|\mathbf{r}_0, t-t_0) = \delta(t-t_0) \delta(\mathbf{r}-\mathbf{r}_0) \hat{I}, \quad (2.9)$$

with the concentration-dependent modifying operator \hat{R} , which tends to zero at infinite dilution. This operator acts on the Green function \hat{G}_{eff} as follows:¹

$$\hat{R} \hat{G}_{\text{eff}}(\mathbf{r}|\mathbf{r}_0, t-t_0) = c \int_0^t \hat{R}(t-t') \hat{G}_{\text{eff}}(\mathbf{r}|\mathbf{r}_0, t'-t_0) dt'. \quad (2.10)$$

Being much simpler than its analog for intermolecular energy transfer studied in Ref. 2, this equation contains a single term in the right-hand side. Another one turns identically to zero. As a result, not only IET, but also MET of intramolecular energy transfer is greatly simplified and easier available for precise investigation and comparison with other approaches.

III. WEAK PUMPING IN IET

A. Kernels

We have to first specify the IET kernels for our particular problem. Since the ground state G is not involved in bimolecular reactions that appeared in operator (2.5), the same is true for a kernel whose shape is the same. In other words, the kernel elements $R_{13}, R_{23}, R_{31}, R_{32}, R_{33}$ are equal to zero. Therefore the ground state may be excluded from consideration when solving Eq. (2.6) provided I_0 is also omitted in the relaxation operator \hat{Q} . Thus, the rank of the operators is reduced to 2×2 and the problem becomes very similar to that considered in part II of this article.² To solve it we have to use the same method of introducing the Green function of free diffusion \hat{u} in the reduced basis of only two states, A and B . Its Laplace-transformation denoted with \hat{u} obeys the equation,

$$(s - \hat{q} - D\Delta_r) \hat{u}(\mathbf{r}|\mathbf{r}_0, s) = \frac{\delta(\mathbf{r}-\mathbf{r}_0)}{4\pi r_0^2} \hat{I}, \quad (3.1)$$

where \hat{q} is the reduced relaxation matrix with pumping neglected,

$$\hat{q} = \begin{pmatrix} -1/\tau_A & 0 \\ 0 & -1/\tau_B \end{pmatrix}. \quad (3.2)$$

The contact value of \hat{u} found from Eq. (3.1) is

$$\hat{u}(\sigma|\sigma, s) = \frac{1}{k_D} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 + \sqrt{\tau_d(s + 1/\tau_A)} & \\ & 1 + \sqrt{\tau_d(s + 1/\tau_B)} \end{pmatrix}^{-1}. \quad (3.3)$$

The relationship between \hat{u} and the IET kernel in the reduced basis of two states, \hat{r} , was established in part II.² In contact approximation it has the following form:

$$\hat{r}(s) = \hat{k}[\hat{I} + \hat{u}(\sigma|\sigma, s)\hat{k}]^{-1}, \quad (3.4)$$

where \hat{k} is defined through the kinetic rate constants of forward and backward transfer,²

$$\hat{k} = \begin{pmatrix} k_f & -k_r \\ -k_f & k_r \end{pmatrix}. \quad (3.5)$$

In the reduced basis one can obtain $\hat{r}(s)$ from Eq. (3.4) by exactly the same way as in part II because the shape of \hat{u} and \hat{k} remains the same. Thus, using the results of part II² we easily deduce the kernel for the present problem,

$$\hat{R}(t) = \begin{pmatrix} k_f & -k_f & 0 \\ -k_f & k_r & 0 \\ 0 & 0 & 0 \end{pmatrix} F(t), \quad (3.6)$$

where F is given by its Laplace transform,

$$\tilde{F}(s) = \left[1 + \frac{k_f/k_D}{1 + \sqrt{\tau_d(s + 1/\tau_A)}} + \frac{k_r/k_D}{1 + \sqrt{\tau_d(s + 1/\tau_B)}} \right]^{-1}. \quad (3.7)$$

The latter result coincides with that obtained many times earlier for the intermolecular energy transfer and was confirmed for the present problem in Ref. 7.

B. Integral equations

The corresponding IET equations take the linear form in the excited state concentrations N_A and N_B ,

$$\begin{aligned} \frac{dN_A}{dt} &= -\frac{N_A}{\tau_A} - k_{fC} \int_0^t F(t-\tau) N_A(\tau) d\tau \\ &\quad + k_{rC} \int_0^t F(t-\tau) N_B(\tau) d\tau, \\ \frac{dN_B}{dt} &= -\frac{N_B}{\tau_B} + k_{fC} \int_0^t F(t-\tau) N_A(\tau) d\tau \\ &\quad - k_{rC} \int_0^t F(t-\tau) N_B(\tau) d\tau. \end{aligned} \quad (3.8)$$

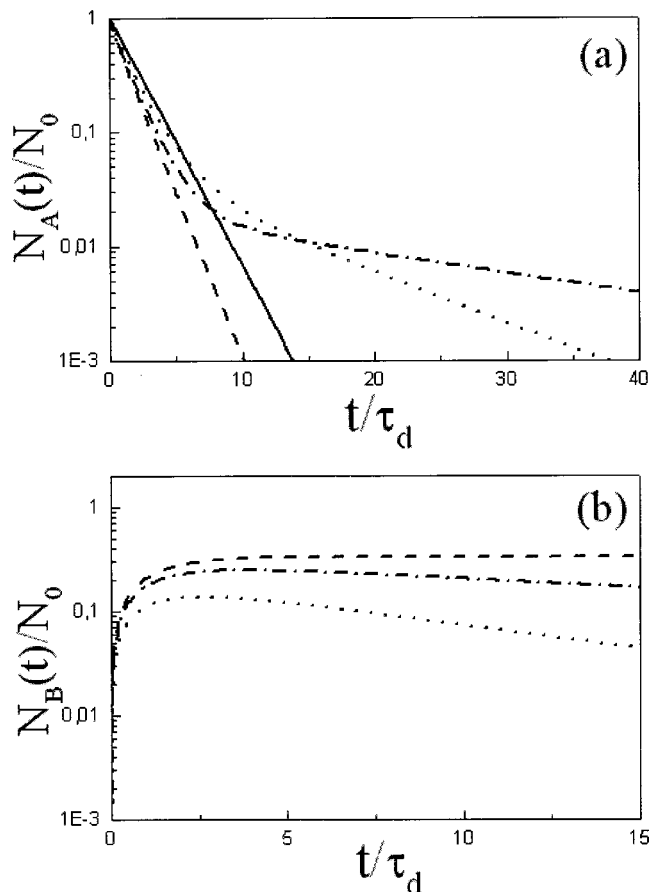


FIG. 1. Relaxation of state populations after instantaneous excitation of A at $\tau_B = \infty$, $k_f = 5.0k_D$, and $ck_f\tau_d = 1.0$. (a) Spontaneous (exponential) decay of A with the lifetime $\tau_A = 2\tau_d$ (thick straight line) and its dissipation accompanied by intersystem crossing with backward rates $k_r = 5.0k_D$ (dotted line), $k_r = k_D$ (dashed-dotted line), and $k_r = 0$ (dashed line). (b) Accumulation and dissipation of initially empty state B which decays through A the faster the higher is k_r or does not decay at all if $k_r = 0$.

Numerical solution of these equations after instantaneous (δ -pulse) excitation of state A has to be obtained with initial conditions $N_A(0) = N_0$, $N_B(0) = 0$. The results are shown in Fig. 1. The intramolecular energy transfer to B first facilitates the decay of A in comparison with a spontaneous monomolecular process in the absence of C [solid line in Fig. 1(a)]. If the transfer is irreversible ($k_r = 0$) this is a pure quenching process which lasts up to the end [dashed line in Fig. 1(a)]. Otherwise the energy comes back due to collisions with C and supports the delayed fluorescence from state A. Initially the density of this state also decreases due to forward energy transfer, but later on crosses the solid line and goes down much slower than the exponential curve with the lifetime τ_A . The smaller k_r the later, weaker and slower should be delayed fluorescence. This qualitative picture is supplemented with a corresponding kinetics of B particles accumulation during quenching and their decay even at $\tau_B = \infty$ through the bimolecular backward transfer to A [Fig. 1(b)]. Such a decay is absent only at $k_r = 0$ and is the faster the higher k_r . In general, at any $\tau_A < \tau_B \neq 0$ the energy comes back to the short living excited state A from a more

stable B , causing the delayed fluorescence of A . This is an additional channel of B decay which competes with its own, given by τ_B .

C. Reduction to the rate equations

In fact, the integral equations of the same kind were first obtained with the “fully renormalized” kinetic theory of Yang, Lee, and Shin (YLS).⁸ This theory correctly reproduces the binary kinetics and has the same accuracy as the MET for a number of simple problems.^{17,18} However, the authors had not confined themselves to original integral equations, but reduced them to a differential form convenient for comparison with some earlier theories and intuitive rate equations. Such a reduction is reasonable to some extent, but this particular one is not the best because of inappropriate transformation of the integral terms. The population densities N_A and N_B were factored outside the integral signs without making an account for excited states decay,

$$\begin{aligned} k_f \int_0^t F^{\text{YLS}}(t-\tau) N_A(\tau) d\tau &\approx k_f N_A(t) \int_0^t F^{\text{YLS}}(\tau) d\tau \\ &= k_f^{\text{ph}}(t) N_A(t), \\ k_r \int_0^t F^{\text{YLS}}(t-\tau) N_B(\tau) d\tau &\approx k_r N_B(t) \int_0^t F^{\text{YLS}}(\tau) d\tau \\ &= k_r^{\text{ph}}(t) N_B(t), \end{aligned} \quad (3.9)$$

where F^{YLS} is the kernel of the YLS-theory. By this means the authors really got the usual kinetic equations,

$$\begin{aligned} \frac{dN_A}{dt} &= -\frac{N_A}{\tau_A} - k_f^{\text{ph}}(t) c N_A + k_r^{\text{ph}}(t) c N_B, \\ \frac{dN_B}{dt} &= -\frac{N_B}{\tau_B} + k_f^{\text{ph}}(t) c N_A - k_r^{\text{ph}}(t) c N_B, \end{aligned} \quad (3.10)$$

but with wrong time-dependent (“phenomenological”) rate constants,

$$k_f^{\text{ph}} = k_f \int_0^t F^{\text{YLS}}(\tau) d\tau, \quad k_r^{\text{ph}} = k_r \int_0^t F^{\text{YLS}}(\tau) d\tau. \quad (3.11)$$

Unfortunately, such a reduction of integral equations to their differential analogs is incorrect even in a short time domain. The conventional way of doing the same is well known from a number of works¹⁴⁻¹⁶ which recommend excluding first the decay of A and B by making the substitution,

$$N_A(t) = A(t) e^{-t/\tau_A}, \quad N_B(t) = B(t) e^{-t/\tau_B}. \quad (3.12)$$

Only then the slowly changing variables $A(t)$ and $B(t)$ can be factored outside the integral signs in IET equations,

$$\begin{aligned} k_f \int_0^t F(t-\tau) N_A(\tau) d\tau &= k_f e^{-t/\tau_A} \int_0^t F(t') e^{t'/\tau_A} A(t-t') dt' \\ &\approx k_f(t) N_A(t), \\ k_r \int_0^t F(t-\tau) N_B(\tau) d\tau &= k_r e^{-t/\tau_B} \int_0^t F(t') e^{t'/\tau_B} B(t-t') dt' \\ &\approx k_r(t) N_B(t), \end{aligned} \quad (3.13)$$

where the true reaction constants of the DET are time-dependent quantities,

$$k_f(t) = k_f \int_0^t F(\tau) e^{\tau/\tau_A} d\tau \quad \text{and} \quad k_r(t) = k_r \int_0^t F(\tau) e^{\tau/\tau_B} d\tau. \quad (3.14)$$

As a result, we come to the same differential equations (3.10), but with proper rate constants $k_f(t)$ and $k_r(t)$ substituted for $k_f^{\text{ph}}(t)$ and $k_r^{\text{ph}}(t)$. The time evolution of the true rate constants is identical to that described in Ref. 10, where the intermolecular energy transfer was studied between A and B . In Figs. 4 and 5 of this work, the time behavior of $k_f(t)$ is shown for the case when an initially excited molecule decays much faster than the transfer product. In an application to a problem in hands A may be a short living (say singlet) excitation while B (say triplet) lives much longer or even infinitely long. Initially A is quenched by interconversion with $k_f > 0$ as long as energy flows from singlet to triplet. Then, after singlet decay is accomplished the energy goes back from triplet to singlet, resulting in a delayed fluorescence from the latter. At this last stage $k_f(t)$ changes the sign (becomes negative) as well as the energy flux, that changed the direction. This physically clear effect is lost in the YLS theory due to its reduction to the differential form. The “phenomenological” constants are always positive and approach their stationary values at $t > \tau_d$ as in classical Smoluchowski theory.

The same is true for a backward DET constant $k_r(t)$ [Fig. 2(b)], but its forward analog, $k_f(t)$, is sign-alternating and diverges as $t \rightarrow \infty$ [Fig. 2(a)]. This effect, peculiar to the intermolecular transfer as well, indicates that even a proper DET description is seriously restricted in time when $\tau_A \neq \tau_B$. As was always stressed in our previous works⁹⁻¹¹ the long time (quasistationary) or Markovian rate constants,

$$\begin{aligned} k_f^s &= \lim_{t \rightarrow \infty} k_f(t) = k_f \tilde{F}(-1/\tau_A) \\ &= k_f \left[1 + \frac{k_f}{k_D} + \frac{k_r}{k_D [1 + \sqrt{-\tau_d \delta}]} \right]^{-1}, \\ k_r^s &= \lim_{t \rightarrow \infty} k_r(t) = k_r \tilde{F}(-1/\tau_B) \\ &= k_r \left[1 + \frac{k_r}{k_D} + \frac{k_f}{k_D [1 + \sqrt{\tau_d \delta}]} \right]^{-1}, \end{aligned} \quad (3.15)$$

do not exist simultaneously if $\delta = 1/\tau_A - 1/\tau_B \neq 0$. One of them, which describes transfer from a short living state to more stable, becomes complex making the Markovian (rate) approach inapplicable.

D. Comparison with IET “effective constants”

To the contrary, there are no such troubles in IET. The effective rate constants, introduced by the relationships

$$k_f^{\text{eff}}(t) N_A(t) = k_f \int_0^t F(t-\tau) N_A(\tau) d\tau, \quad (3.16)$$



FIG. 2. Time evolution of the YLS “phenomenological rate constants” (dotted lines) approaching their stationary values (thin horizontal lines) and “true rate constants” of DET (thick solid lines) in comparison with the “effective rate constants” of IET (dashed lines) for forward (a) and backward transfer (b). $k_f = k_r = 5k_D$; $k_{fc} \tau_d = 0.1$; $\tau_A = 2\tau_d$, $\tau_B = \infty$.

$$k_r^{\text{eff}}(t) N_B(t) = k_r \int_0^t F(t-\tau) N_B(\tau) d\tau,$$

and calculated from IET equations (3.8), are real and finite. When $\tau_B > \tau_A$, $k_f^{\text{eff}}(t)$ changes the sign with time, but then levels off, while corresponding DET constant diverges: $\lim_{t \rightarrow \infty} k_f(t) = -\infty$ [Fig. 2(b)].

On the other hand, the IET is also not ideal as it is seen from Fig. 2(b). The kernel of the IET has power dependence on time resulting from diffusional separation of the reacting pair. This property is passed on to the long time asymptotics of $N_A(t)$ or $N_B(t)$ when the corresponding lifetime is infinite.¹⁰ In this case the backward constants of DET and YLS exactly coincide and approach the asymptotic Markovian value at $t \rightarrow \infty$, while the effective constant of the IET declines from this limit downwards. This difference is initially not pronounced, but then increases with time. This is a principle demerit of the IET which does not account for all binary terms of concentration expansion and predicts the false asymptotic behavior for a long time decay.¹ The non-exponential behavior of the time-dependent rate coefficients was also revealed for the case of the intermolecular transfer.¹⁰ As a matter of fact, the real asymptotics should be exponential in a proper binary theory due to intervention of the third particles (“bachelors”) to the pair events.² This

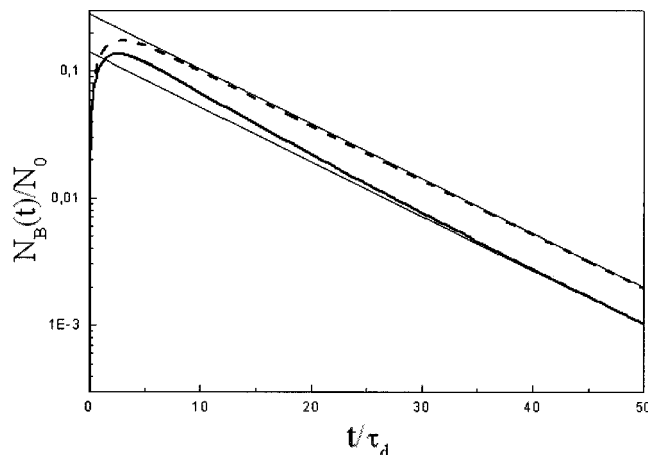


FIG. 3. The same as in Fig. 1(b) but in a wider dynamic region and for $k_r = k_f = 5k_D$. The solid line represents the results of the IET which accounts for an initial geminate process and bimolecular quasiexponential asymptotics (thin straight line) approached from above. The dashed line is the same kinetics obtained from the phenomenological YLS theory (dotted lines) which also approaches the bimolecular asymptotics (thin line), but from below.

drawback has been overcome when the MET (Refs. 17, 19–21) or equivalent theories^{8,22} are used instead of the IET.

E. Geminate and bimolecular backward transfer

One more feature of the kinetic behavior, which is completely lost in the YLS rate approach is represented in Fig. 3. The descending branches of the kinetics become exponential at long times representing the backward transfer in the bulk. They have the same slope in both IET and YLS-theory and are shown by parallel thin lines in Fig. 3. However, the IET-curve approaches this asymptotics from above, after a hump demonstrating the geminate backward transfer to state A. The geminate stage, which arises immediately after accumulation of some population in state B was studied with the IET in Ref. 11 for the intermolecular energy transfer. Such a phenomenon is completely lost in the YLS rate theory whose curve reaches the exponential asymptotics from below, ignoring the backward geminate transfer. This evident drawback demonstrates that the reduction to the rate description made in Eq. (3.11) is inappropriate when the lifetimes of the excited states are different.

IV. IET FOR A STRONG LIGHT PUMPING

In the presence of strong pumping light one should account for I_0 in the relaxation operators. It is impossible in this case to calculate the IET kernel in the reduced basis. For specifying the shape of a total IET kernel one should use instead of $\hat{u}(r|r_0, t-t_0)$ the general “free Green function” $\hat{G}_0(r|r_0, t-t_0)$ in the complete three state basis. The latter obeys the kinetic equation similar to Eq. (3.1),

$$(\partial_t - D\Delta_r - \hat{Q})\hat{G}_0(r|r_0, t-t_0) = \frac{\delta(r-r_0)}{4\pi r_0^2} \delta(t-t_0) \hat{I}. \quad (4.1)$$

The solution to this equation can be easily found. Its contact value may be represented as follows:

$$\hat{G}_0(\sigma|\sigma, t) = \mathcal{G}(t) \exp(\hat{Q}t)/k_D, \tag{4.2}$$

where $\mathcal{G}(s) = [1 + \sqrt{s\tau_d}]^{-1}$. Making the Laplace transformation of this equation we obtain

$$\hat{G}_0(\sigma|\sigma, s) = \frac{1}{k_D} \begin{pmatrix} \frac{I_0 g_0 + g_1/\tau_A}{I_0 + 1/\tau_A} & I_0 \frac{(g_0 - g_1)/\tau_B}{(I_0 + 1/\tau_A)(I_0 + 1/\tau_A - 1/\tau_B)} & I_0 \frac{g_0 - g_1}{I_0 + 1/\tau_A} \\ 0 & g_2 & 0 \\ \frac{(g_0 - g_1)/\tau_A}{I_0 + 1/\tau_A} & \frac{g_0 \left(I_0 + \frac{1}{\tau_A} - \frac{1}{\tau_B} \right) - \frac{g_1 I_0}{\tau_B} - g_2 \left(\frac{1}{\tau_A} - \frac{1}{\tau_B} \right) \left(I_0 + \frac{1}{\tau_A} \right)}{(I_0 + 1/\tau_A)(I_0 + 1/\tau_A - 1/\tau_B)} & \frac{I_0 g_1 + g_0/\tau_A}{I_0 + 1/\tau_A} \end{pmatrix}, \tag{4.3}$$

where

$$g_0 = \tilde{\mathcal{G}}(s), \quad g_1 = \tilde{\mathcal{G}}(s + I_0 + 1/\tau_A), \quad g_2 = \tilde{\mathcal{G}}(s + 1/\tau_B).$$

The IET kernel can be calculated from the following relationship in the three state basis,

$$\hat{R}(s) = \hat{K} [\hat{I} + \hat{G}_0(\sigma|\sigma, s) \hat{K}]^{-1}, \tag{4.4}$$

where \hat{K} is the matrix composed of the kinetic rate constants in the complete basis

$$\hat{K} = \begin{pmatrix} k_f & -k_r & 0 \\ -k_f & k_r & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{4.5}$$

The relationship (4.4) is a generalization of Eq. (3.4) for the case of strong pumping.

The rather straightforward calculations yield the following expression for \hat{R} :

$$\hat{R}(t) = \begin{pmatrix} k_f & -k_f & 0 \\ -k_f & k_r & 0 \\ 0 & 0 & 0 \end{pmatrix} M(t), \tag{4.6}$$

where M is given by its Laplace transform,

$$\begin{aligned} \tilde{M}(s) &= \frac{I_0 + 1/\tau_A - 1/\tau_B}{(1/\tau_A - 1/\tau_B)(1 + k_f g_1 + k_r g_2) + I_0(1 + k_f g_2 + k_r g_2)}. \end{aligned} \tag{4.7}$$

In fact Eq. (4.6) follows from Eq. (3.6) if there is a substitution $M(t)$ for $F(t)$ in the latter.

As a result, we obtain a complete set of generalized IET equations instead of reduced Eqs. (3.8),

$$\begin{aligned} \frac{dN_A}{dt} &= -\frac{N_A}{\tau_A} - k_f c \int_0^t M(t-\tau) N_A(\tau) d\tau \\ &+ k_r c \int_0^t M(t-\tau) N_B(\tau) d\tau + I_0 N_G, \end{aligned} \tag{4.8a}$$

$$\begin{aligned} \frac{dN_B}{dt} &= -\frac{N_B}{\tau_B} + k_f c \int_0^t M(t-\tau) N_A(\tau) d\tau \\ &- k_r c \int_0^t M(t-\tau) N_B(\tau) d\tau, \end{aligned} \tag{4.8b}$$

$$\frac{dN_G}{dt} = \frac{N_A}{\tau_A} + \frac{N_B}{\tau_B} - I_0 N_G. \tag{4.8c}$$

The great advantage of IET equations in comparison with

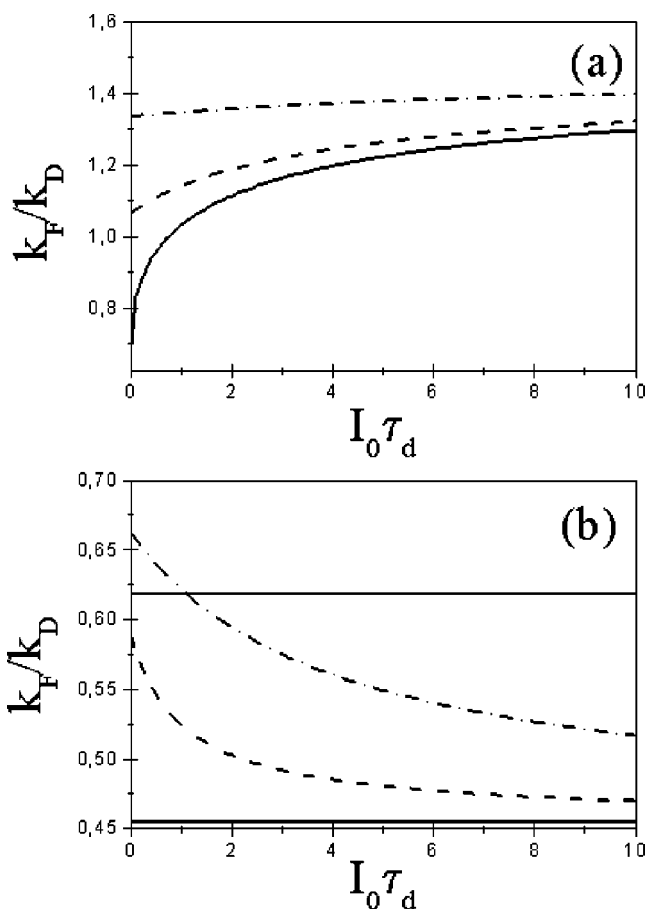


FIG. 4. The field dependence of k_F in the diffusion control limit ($k_f = k_r = 5k_D$) at a different ratio of encounter time to the lifetimes of the fluorescent state: $\tau_d/\tau_A = 0$ (solid line), 1 (dashed line), 5 (dashed-dotted line) at (a) $\tau_d/\tau_B = 10$ and (b) $\tau_B = \infty$.

similar non-Markovian equations of differential or unified theories is that they incorporate the pumping term $I_0 N_G$ additively with others. This makes possible their stationary solution at $dN_A/dt = dN_B/dt = dN_G/dt = 0$.

This solution can be used to specify the relative fluorescence quantum yield which is given by general formula,^{12,21}

$$\eta = \frac{N_A^{\text{st}}}{I_0 \tau_A N_G^{\text{st}}}, \quad (4.9)$$

where N_A^{st} and N_G^{st} are the stationary populations of fluorescent and ground states at permanent light pumping. Finding them from Eqs. (4.8) and using in Eq. (4.9) we generalize the famous Stern–Volmer Law,

$$\eta^{-1} = 1 + \tau_A c \kappa. \quad (4.10)$$

$$\tilde{M}(0) = \frac{I_0 + 1/\tau_A - 1/\tau_B}{(1/\tau_A - 1/\tau_B)(1 + \alpha k_f/k_D + \beta k_r/k_D) + I_0(1 + \beta k_f/k_D + \beta k_r/k_D)}, \quad (4.12)$$

where $\alpha^{-1} = 1 + \sqrt{\tau_d(I_0 + 1/\tau_A)}$, $\beta^{-1} = 1 + \sqrt{\tau_d/\tau_B}$. In the kinetic controlled limit this dependence is insignificant because the terms k_f/k_D and k_r/k_D are small and can be neglected together with the light dependent coefficients α and β . However, in the opposite, diffusion control limit the Stern–Volmer constant is significantly affected at high light intensity. For illustration of this statement we will analyze the field dependence of forward energy transfer represented by $k_f(I_0)$.

At zero field only the non-Markovian effect inherent to $\tilde{M}(0)$ is seen; κ increases with reduction of lifetime. At short τ_A the irreversible transfer ($\tau_B \rightarrow 0$) is interrupted long before a large dip near the energy acceptor is formed. Hence, the distribution of donors remains more uniform and the rate constant is not much less than the kinetic one. The light pumping serves the same goal as the donor decay by filling out the dip with free excitations. The stronger the pumping the more homogeneous is the reactant distribution and faster the quenching [Fig. 4(a)].

Roughly speaking, the strong pumping switches off the decay of A . As a result, it removes the non-Markovian acceleration of forward transfer, making it slower. In case of energy conservation ($\tau_B > \tau_A$) this changes the relationship between the forward and reverse transfer in favor of the latter. The quenching is damped by strong light [Fig. 4(b)]. The same was with irreversible intermolecular transfer at long τ_B , although the reason was different.¹³ The field dependence disappears at $\tau_A \rightarrow \infty = \tau_B$ because the non-Markovian effect in quenching is completely removed.

V. THE INTRAMOLECULAR ENERGY TRANSFER IN THE MET

Let us now take into account the 3-particle correlations of the reactants. From the general formula (2.10) we can deduce the expression for the modifying operator $\hat{\mathcal{R}}$,

The IET holds at relatively low concentration and within its limits the quenching constant

$$\kappa = \frac{k_F}{1 + \tau_B c k_R} \quad (4.11)$$

is expressed via stationary constants of forward and backward transfer,

$$k_F = k_f \tilde{M}(0) \quad \text{and} \quad k_R = k_r \tilde{M}(0).$$

This expression has essentially the same structure as the Stern–Volmer constant for reversible intermolecular transfer,^{9,10} but both forward and reverse transfer constants are corrected by a factor $\tilde{M}(0)$ which substitutes $\tilde{F}(0)$ from Eq. (3.7). A new factor is field dependent,

$$\hat{\mathcal{R}} = c \tilde{F}(s) \begin{pmatrix} k_f & -k_f & 0 \\ -k_f & k_r & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (5.1)$$

We suggest the following explanation of such a modification. The pair $[A \dots C]$ can be converted into $[B \dots C]$ and backward due to the reaction with ‘‘bachelors,’’ C particles belonging to the ‘‘background.’’ These processes are proportional to the rates of $A \rightleftharpoons B$ transitions and concentration of C . The product of them constitutes the elements of the modifying operator $\hat{\mathcal{R}}$.

The modified kinetic equations for N_A and N_B are

$$\begin{aligned} \frac{dN_A}{dt} = & -\frac{N_A}{\tau_A} - c k_f \int_0^t \mathcal{F}(\tau) N_A(t-\tau) d\tau \\ & + c k_r \int_0^t \mathcal{F}(\tau) N_B(t-\tau) d\tau, \end{aligned} \quad (5.2)$$

$$\begin{aligned} \frac{dN_B}{dt} = & -\frac{N_B}{\tau_B} + c k_f \int_0^t \mathcal{F}(\tau) N_A(t-\tau) d\tau \\ & - c k_r \int_0^t \mathcal{F}(\tau) N_B(t-\tau) d\tau, \end{aligned}$$

where the modified kernel $\mathcal{F}(t)$ is obtained in the Appendix and represented by its Laplace transformation, $\tilde{\mathcal{F}}(s)$.

In case of infinite lifetimes $\tau_A = \tau_B = \infty$ the expression for \mathcal{F} is much simpler,

$$\begin{aligned} \tilde{\mathcal{F}}(s) = & [1 + (k_f + k_r)U_1]^{-1} \\ = & \left[1 + \frac{(k_f + k_r)/k_D}{1 + \sqrt{\tau_d \left(s + \frac{(k_f + k_r)k_D}{k_f + k_r + k_D} c \right)}} \right]^{-1}. \end{aligned} \quad (5.3)$$

This formula coincides with the known result.¹⁷ Here we took into account that in the binary approximation the Laplace variable s can be omitted in the “modifying” terms,^{17,19,20} that is $\tilde{F}(s)$ in Eqs. (A9), (A10) has been substituted by $\tilde{F}(0) = k_D / (k_f + k_r + k_D)$. The analysis of these results will be made elsewhere.

The result (5.3) was also obtained in Ref. 18 from the hierarchical set of evolution equations in a rather transparent though semi-intuitive way. From our point of view, while the same result was derived here and in Ref. 17 in a more general and consistent manner. However, Sung and Lee believe that their MPK1 theory¹⁸ is more accurate than the MET. This is hardly true, although in a particular case of immobile A/B particles MPK1 reproduces the exact result²³ valid for only this case. In fact, MPK1 is essentially a binary theory, which operates only with encounter diffusion of the reactants $D = D_{A/B} + D_C$. It was shown earlier by diagrammatic summation¹⁹ that the MET reproduces only that part of the kinetics, which universally depends on D , but not separately on $D_{A/B}$ and D_C . Any theory, which pretends to correct the MET should be expressed via these absolute mobilities instead of their relative value. This is definitely not MPK1 which does not provide such a nonbinary corrections to the MET in any case except the single one, when the absolute and encounter diffusion coefficients coincide.

VI. CONCLUSION

We successfully applied the new method suggested in parts I and II to the impurity catalyzed intersystem crossing. The essential feature of intra- as well as of intermolecular transfer is that the Markovian or “rate equations” formalism using permanent or time dependent rate constants is inconsistent when reactants are metastable particles. To the contrary, the integral formalism employed by IET, MET or equivalent theories provides much better treatment of bimolecular reactions using memory functions obtained in binary approximation with respect to reactants. Our newly developed method allows us to regularly specify the IET and MET integral equations and examine the conditions of their reduction to differential rate equations providing an approximate description of the same phenomena. The difference between exact results and their approximate analogs based on the rate concept is illustrated here by an example of catalyzed interconversion between two states with different lifetimes. We calculated *ab initio* the kernels (memory functions) of the IET and MET equations, obtained numerically for their solutions of energy quenching or conservation kinetics and analyzed the non-Markovian effects originated by finite life-

times and strong light pumping. The comparison of our results with those obtained with other methods demonstrates the great advantage of the new photochemistry that is valid beyond the rate concept.

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APPENDIX: DERIVATION OF THE MET KERNEL

To obtain the expression for the MET kernel we will employ the same method as previously used for calculations of the IET kernel in the case of weak pumping. As previously, this problem can be solved in the reduced basis of two states A and B . To do it we should first calculate the contact value of the “free” Green function \hat{U} which is the solution of the following equation:

$$(s - \hat{Q}' - D\Delta_r)\hat{U}(r|r_0, s) = \frac{\delta(r - r_0)\hat{I}}{4\pi r_0^2}, \quad (\text{A1})$$

where \hat{Q}' is the “relaxation” matrix of the reaction pair in the reduced basis,

$$\hat{Q}' = \begin{pmatrix} -1/\tau_A - k_f c \tilde{F}(s) & k_r c \tilde{F}(s) \\ k_f c \tilde{F}(s) & -1/\tau_B - k_r c \tilde{F}(s) \end{pmatrix}. \quad (\text{A2})$$

This Green function describes the free evolution of the reaction pair accompanied by relaxation and reactions of A and B with the “bachelors.” To solve this problem we have to change the basis making operators \hat{Q}' and \hat{U} diagonal,

$$\hat{Q}' = T\hat{Q}_d T^{-1}, \quad \hat{U}(r|r_0, s) = T\hat{U}_d(r|r_0, s)T^{-1}, \quad (\text{A3})$$

where the matrix T is composed from the eigenvectors of \hat{Q}' . In the new basis \hat{Q}_d is the diagonal matrix of the form,

$$\hat{Q}_d = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}, \quad (\text{A4})$$

where

$$\lambda_{1,2} = [1/\tau_A + 1/\tau_B + c\tilde{F}(s)(k_f + k_r) \pm N]/2$$

are the eigenvalues of \hat{Q}' and

$$N = \sqrt{(1/\tau_A - 1/\tau_B)^2 + \tilde{F}^2(s)[B]^2(k_f + k_r)^2 + 2\tilde{F}(s)[B](k_f - k_r)(1/\tau_A - 1/\tau_B)}.$$

In the new basis the equation for \hat{U}_d contains only diagonal matrices and can be easily solved analytically. Again, we are interested only in the contact value of this Green function,

$$\hat{U}_d(\sigma|\sigma, s) = \frac{1}{k_D} \begin{pmatrix} \tilde{G}(s + \lambda_1) & 0 \\ 0 & \tilde{G}(s + \lambda_2) \end{pmatrix} = \begin{pmatrix} U_1 & 0 \\ 0 & U_2 \end{pmatrix}. \quad (\text{A5})$$

Substituting this result into formula $\hat{U} = T^{-1} \hat{U}_d T$ allows us to calculate the contact value of the “free” Green function,

$$\hat{U}(\sigma|\sigma,s) = \begin{pmatrix} \frac{[1/\tau_A - 1/\tau_B + (k_f - k_r)c\tilde{F}(s)][U_1 - U_2] + N[U_1 + U_2]}{2N} & \frac{k_r c\tilde{F}(s)[U_2 - U_1]}{N} \\ \frac{k_f c\tilde{F}(s)[U_2 - U_1]}{N} & \frac{[1/\tau_A - 1/\tau_B + (k_f - k_r)c\tilde{F}(s)][U_2 - U_1] + N[U_1 + U_2]}{2N} \end{pmatrix}. \quad (\text{A6})$$

The relationship between the kernel of the MET in the reduced basis $\hat{\Sigma}'$ and this Green function is essentially the same as Eq. (3.4),

$$\hat{\Sigma}'(s) = \begin{pmatrix} \Sigma_{11} & \Sigma_{12} \\ \Sigma_{21} & \Sigma_{22} \end{pmatrix} = \hat{k}[\hat{I} + \hat{U}(\sigma|\sigma,s)\hat{k}]^{-1}. \quad (\text{A7})$$

Substitution of $\hat{U}(\sigma|\sigma,s)$ from Eq. (A6) into Eq. (A7) leads to the following expression for the MET kernel in the full basis of three states:

$$\hat{\Sigma}(t) = \begin{pmatrix} k_f & -k_f & 0 \\ -k_f & k_r & 0 \\ 0 & 0 & 0 \end{pmatrix} \mathcal{F}(t), \quad (\text{A8})$$

where the function \mathcal{F} is given by its Laplace-transform,

$$\tilde{\mathcal{F}}(s) = \frac{2N}{(U_1 - U_2)[(k_f - k_r)(1/\tau_A - 1/\tau_B) + c\tilde{F}(s)(k_f + k_r)^2] + N[2 + (U_1 + U_2)(k_f + k_r)]}. \quad (\text{A9})$$

Here we introduced

$$N = \sqrt{(1/\tau_A - 1/\tau_B)^2 + c^2\tilde{F}^2(s)(k_f + k_r)^2 + 2c\tilde{F}(s)(k_f - k_r)(1/\tau_A - 1/\tau_B)}, \quad (\text{A10})$$

$$U_{1,2} = \tilde{\mathcal{G}}(s + \lambda_{1,2})/k_D, \quad \lambda_{1,2} = \frac{1}{2}[1/\tau_A + 1/\tau_B + c\tilde{F}(s)(k_f + k_r) \pm N].$$

This result was first obtained by Sung and Lee.¹⁸ One should note that at infinite dilution ($c \rightarrow 0$) $\mathcal{F}(t)$ certainly reduces to the IET kernel $F(t)$ given by Eq. (3.7).

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