

Integral encounter theories of multistage reactions. II. Reversible inter-molecular energy transfer

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The matrix Modified Encounter Theory (MET), developed in Part I of this work, is applied here to reversible inter-molecular energy transfer in liquid solutions. For fluorescence quantum yield at contact transfer the Stern–Volmer law is confirmed, but the concentration corrections to its constant are diffusion-dependent unlike those obtained earlier with Superposition Approximation. In the particular case of irreversible energy transfer, when the exact solution is available, the latter is used to discriminate between all competing approaches and establishes MET superiority. In the case of reversible energy transfer producing the long-lived or even stable products, the energy is stored there and dissipates due to backward energy transfer in re-encounters. The kinetics of this process, resulting in a delayed fluorescence, is shown to be qualitatively different in cases of short and long encounter times as compared to the excitation lifetime. © 2001 American Institute of Physics.
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I. INTRODUCTION

The theory of reversible diffusion-influenced reactions of metastable reactants is an important branch of modern chemical kinetics. Although the kinetics of the reactions in liquids was first studied by Smoluchowski¹ and Waite² a long time ago, seminal progress in this topic was achieved only in recent decades. In this paper we study the reactions of reversible energy transfer which play a crucial role in photochemical kinetics, being unavailable for most conventional theoretical approaches.

The formal reaction scheme of reversible inter-molecular energy transfer is the following:



The excitation transfers from A^* to B and backward in the course of encounter diffusion with coefficient D , which is assumed to be independent on the level of excitation: $D = D_{A^*} + D_B = D_A + D_{B^*}$. Besides, we account for the relaxation of the excited state to the ground state with the lifetimes τ_A and τ_B :



If B^* has longer lifetime than A^* the energy comes back after the decay of the latter, causing fluorescence decay from

a newly excited A^* .^{3,4} If the encounter time $\tau_d = \sigma^2/D$ (σ is the closest approach distance) is comparable with τ_A or τ_B , it affects the kinetics and quantum yield of the fluorescence.

Nowadays there are a number of theoretical approaches to the description of reversible reactions in liquids involving short-lived particles. The most general and consistent between them is Integral Encounter Theory (IET), developed in Refs. 5–7. It adequately describes the multistage reactions,^{3,8–11} as well as the magnetic field and spin effects in chemical reactions.¹² The kinetic equations of IET are of the integro-differential type, unlike the differential equations of conventional (Differential) Encounter Theory (DET). The very first application of matrix-form IET to reversible reactions of metastable reactants has shown that the usual chemical kinetics, based on the rate concept, fails to describe them properly.^{3,4} The same is true for the original Superposition Approximation (SA).¹³ When the excited reactants have different lifetimes, either the forward or backward rate constant diverges with time. In contrast, the integro-differential approach is free of this defect. It provides the correct description of energy transfer kinetics and the fluorescence quantum yield in dilute solutions, that remained unique for a long time.^{3,4}

However, IET is not free from some drawbacks. It fails to describe properly long-time quenching kinetics^{14,15} and gives incorrect values for Stern–Volmer constants at higher reactant densities.^{16,17} This happens because IET does not account for all the binary terms of the concentration expansion.^{18,19} To overcome this difficulty IET should be

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modified, as it was first pointed out by Kipriyanov *et al.* in Refs. 20,21. Modified Encounter Theory (MET) is also of the integro-differential type as well as recently developed fully renormalized YLS theory.²² MET provides more accurate expressions for the quantum yield of fluorescence¹⁶ and describes the quenching kinetics in a wider time interval than IET.¹⁴

In Part I of the present work,²³ we correctly derive IET (that was previously obtained semi-intuitively) and generalize MET, imparting the matrix-form to the latter. Matrix MET makes possible the theoretical treatment of reversible energy transfer at higher concentrations and in a wider time interval than those available for IET. The main goal of this paper is the detailed comparison of IET and MET with the competing SA approach. The latter was recently revised in such a way that the IET results were reproduced^{24,25} and even higher concentration corrections to the fluorescence quantum yield were obtained. This is actually a challenge for MET to either confirm or revise these corrections. They are obtained here and found to be different in both magnitude and diffusional (viscosity) dependence. The origin of such a discrepancy is established and the superiority of MET is confirmed by comparison with the exact results available for irreversible energy transfer from immobile donor to point acceptors. The outline of this paper is as follows. In the next section we briefly summarize the results of Part I and apply them to reversible reaction Eq. (1.1) between two-level systems representing *A* and *B*. In Sec. III we derive the kinetic equations of IET and modify them in Sec. IV. In Sec. V we confirm the Stern–Volmer law for fluorescence quantum yield and define its constant within IET and MET. The quantum yield of energy quenching by short-lived partners is considered in Sec. VI, while in Sec. VII the kinetics of energy storing for long-lived particles is analyzed, with or without accountings for bimolecular backward transfer.

II. IET AND MET EQUATIONS

The chemical processes of energy or charge transfer may be formally considered as reactions between the “skeleton” particles **A** and **B** composed from *p* and *s* components, respectively. The components of the skeletons represent the energy or charge states of the reactants and reaction products:

$$\begin{aligned} \mathbf{A} &= \{A_{ij}\} = \{A_1, A_2, \dots, A_p\}; \\ \mathbf{B} &= \{B_{kl}\} = \{B_1, B_2, \dots, B_s\}. \end{aligned} \quad (2.1)$$

The monomolecular decay or inter-conversion change the states of the particles but not the number of particles:

$$A_i \Leftrightarrow A_j \quad (i, j = 1, 2, \dots, p), \quad B_k \Leftrightarrow B_l \quad (k, l = 1, 2, \dots, s). \quad (2.2)$$

Besides, the different particles are partners in bimolecular transfer reactions which also conserve their total number:

$$A_i + B_k \Leftrightarrow A_j + B_l \quad (i, j = 1, 2, \dots, n; \quad k, l = 1, 2, \dots, m). \quad (2.3)$$

In Part I of this work we obtained for such reactions the hierarchy for the Reduced Density Vectors (RDVs) or related

Vector Correlation Patterns (VCPs). Making a truncation as in Ref. 21, we derived the IET and MET kinetic equations for the concentrations of all internal states of **A** and **B**, assigned as the elements of column Density Vectors (DV) $\hat{\sigma}_A$ and $\hat{\sigma}_B$.

The IET integro-differential equations are of the following form:

$$\frac{\partial \hat{\sigma}_A(t)}{\partial t} = \hat{Q}_A \hat{\sigma}_A(t) - \text{Tr}_B \int_0^t \dots$$

The concentration-dependent modifying operator $\hat{\mathcal{R}}$, which tends to zero at infinite dilution, acts on the effective Green function as follows:

$$\begin{aligned} \hat{\mathcal{R}}\hat{G}^{\text{eff}} = & \text{Tr}_{\mathbf{B}'} \int_0^t [\hat{R}_{\mathbf{A}\mathbf{B}'}(t-t') \otimes \exp\{\hat{Q}_{\mathbf{B}}(t-t')\}] \\ & \times [\hat{\sigma}_{\mathbf{B}'}(t') \otimes \hat{G}^{\text{eff}}(\mathbf{r}, t' | \mathbf{r}_0, t_0)] dt' \\ & + \text{Tr}_{\mathbf{A}'} \int_0^t [\hat{R}_{\mathbf{A}'\mathbf{B}}(t-t') \otimes \exp\{\hat{Q}_{\mathbf{A}}(t-t')\}] \\ & \times [\hat{\sigma}_{\mathbf{A}'}(t') \otimes \hat{G}^{\text{eff}}(\mathbf{r}, t' | \mathbf{r}_0, t_0)] dt'. \end{aligned} \quad (2.10)$$

Here we made use of operator $\hat{R}_{\mathbf{A}\mathbf{B}} = \hat{R}$ that was introduced in Eq. (2.5). In the simplest case both **A** and **B** particles are two-level systems whose population densities of excited and ground states are $a^* = [A^*]$, $b^* = [B^*]$ and $a = [A]$, $b = [B]$. These compose the density vectors of two particles participating in the reversible energy transfer Eq. (1.1):

$$\hat{\sigma}_{\mathbf{A}} = \begin{bmatrix} a \\ a^* \end{bmatrix}, \quad \hat{\sigma}_{\mathbf{B}} = \begin{bmatrix} b \\ b^* \end{bmatrix}. \quad (2.11)$$

The relaxation operators, representing the excited state decay, are the following:

$$\hat{Q}_{\mathbf{A}} = \begin{bmatrix} 0 & 1/\tau_A \\ 0 & -1/\tau_A \end{bmatrix}, \quad \hat{Q}_{\mathbf{B}} = \begin{bmatrix} 0 & 1/\tau_B \\ 0 & -1/\tau_B \end{bmatrix}. \quad (2.12)$$

For easier comparison with the previous results of Refs. 3, 4, we shall restrict our consideration to the contact energy transfer whose reactivity operator is simply defined in the collective basis of a pair, $|AA\rangle$, $|A^*B\rangle$, $|AB^*\rangle$, $|A^*B^*\rangle$ is nonzero at $r = \sigma$:

$$\begin{aligned} \hat{W} = & \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & -w_a(r) & w_b(r) & 0 \\ 0 & w_a(r) & -w_b(r) & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \\ = & \frac{\delta(r-\sigma)}{4\pi\sigma^2} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & -k_a & k_b & 0 \\ 0 & k_a & -k_b & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}. \end{aligned} \quad (2.13)$$

Here we introduced the kinetic rate constants of the forward and backward energy transfer $k_a = \int w_a d^3r$ and $k_b = \int w_b d^3r$. This matrix form is transferred to either \hat{R} or $\hat{\Sigma}$:

$$\hat{R} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & R_{22} & R_{23} & 0 \\ 0 & R_{32} & R_{33} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad \hat{\Sigma} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \Sigma_{22} & \Sigma_{23} & 0 \\ 0 & \Sigma_{32} & \Sigma_{33} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (2.14)$$

The relaxation operator in the same collective basis is easy to deduce from Eq. (2.12):

$$\hat{Q}_{\mathbf{A}\mathbf{B}} = \begin{bmatrix} 0 & 1/\tau_A & 1/\tau_B & 0 \\ 0 & -1/\tau_A & 0 & 1/\tau_B \\ 0 & 0 & -1/\tau_B & 1/\tau_A \\ 0 & 0 & 0 & -(1/\tau_A + 1/\tau_B) \end{bmatrix}. \quad (2.15)$$

First of all, we have to reproduce the known results of IET for reversible energy transfer.

III. INTEGRAL ENCOUNTER THEORY

Let us disclose the general IET equations (2.4a), (2.4b) by specifying the matrix kernel \hat{R} . In our four states basis, $|1\rangle = |AB\rangle$, $|2\rangle = |A^*B\rangle$, $|3\rangle = |AB^*\rangle$, $|4\rangle = |A^*B^*\rangle$, the kernel has only four nonzero elements which compose in Eq. (2.14) a block \hat{r} of 2×2 rank:

$$\hat{r} = \begin{bmatrix} R_{22} & R_{23} \\ R_{32} & R_{33} \end{bmatrix}. \quad (3.1)$$

Substituting Eq. (2.13) into Eq. (2.5) one can see that \hat{r} is related only to the corresponding block of the Green function $\hat{G}_{\mathbf{A}\mathbf{B}}$,

$$\hat{g} = \begin{bmatrix} G_{22} & G_{23} \\ G_{32} & G_{33} \end{bmatrix}. \quad (3.2)$$

On the first glance, there is no closed equation on \hat{g} , because the elements of this block are mixed with G_{42} and G_{43} by the equation of motion (2.6). Fortunately, $G_{42}(t) = G_{43}(t) = 0$, because they obey the homogeneous equations and their initial values are 0. Therefore, from Eq. (2.6) we obtain the closed equation for the reduced Green function

$$\begin{aligned} \left[\partial_t - \hat{q} - D\Delta + \frac{\delta(r-\sigma)}{4\pi\sigma^2} \hat{k} \right] \hat{g}(r|r_0, t-t_0) \\ = \frac{\delta(r-r_0)}{4\pi r_0^2} \delta(t-t_0) \hat{I}, \end{aligned} \quad (3.3)$$

where

$$\hat{q} = \begin{bmatrix} -1/\tau_A & 0 \\ 0 & -1/\tau_B \end{bmatrix}, \quad \hat{k} = \begin{bmatrix} k_a & -k_b \\ -k_a & k_b \end{bmatrix}. \quad (3.4)$$

It is more convenient to study the problem in the Laplace domain. Let us introduce the ‘‘free Green function’’ \hat{u} which represents free encounter diffusion in a pair (without reaction), accompanied by intra-molecular relaxation. This auxiliary Green function obeys the simple kinetic equation

$$[s - \hat{q} - D\Delta] \hat{u}(r|r_0, s) = \frac{\delta(r-r_0)}{4\pi r_0^2} \hat{I}, \quad (3.5)$$

where the tilde denotes the Laplace transformation of $\hat{u}(r|r_0, t)$. The contact value of this Laplace transformation, $\hat{u}(\sigma|\sigma, s)$, is the following:

$$\hat{u}(\sigma|\sigma, s) = \frac{1}{k_D} \begin{bmatrix} \frac{1}{1 + \sqrt{\tau_d(s + 1/\tau_A)}} & 0 \\ 0 & \frac{1}{1 + \sqrt{\tau_d(s + 1/\tau_B)}} \end{bmatrix}. \quad (3.6)$$

There is a convenient relationship between \hat{u} and \hat{g} :

$$\begin{aligned} \hat{g}(r|r_0, s) &= \hat{u}(r|r_0, s) - \int_{\sigma}^{\infty} dr_1 \hat{u}(r|r_1, s) \hat{k} \\ &\quad \times \delta(r_1 - \sigma) \hat{g}(r_1|r_0, s) \\ &= \hat{u}(r|r_0, s) - \hat{u}(r|\sigma, s) \hat{k} \hat{g}(\sigma|r_0, s). \end{aligned} \quad (3.7)$$

At $r=r_0=\sigma$ this equation can be resolved for \hat{g} whose contact value is:

$$\hat{g}(\sigma|\sigma, s) = [\hat{I} + \hat{u}(\sigma|\sigma, s) \hat{k}]^{-1} \hat{u}(\sigma|\sigma, s). \quad (3.8)$$

In the contact approximation we obtain from Eq. (2.5) the following relationship for the reduced quantities:

$$\hat{r}(t) = \hat{k} [\hat{I} - \hat{g}(\sigma|\sigma, t) \hat{k}]. \quad (3.9)$$

Making the Laplace transformation of this relationship and substituting $\hat{g}(\sigma|\sigma, s)$ from Eq. (3.8), we obtain the following result:

$$\hat{r}(s) = \hat{k} [\hat{I} - \hat{g}(\sigma|\sigma, s) \hat{k}] = \hat{k} [\hat{I} + \hat{u}(\sigma|\sigma, s) \hat{k}]^{-1}. \quad (3.10)$$

Substituting into this formula \hat{u} from Eq.(3.6) and \hat{k} from Eq.(3.4) we obtain the final expression for the kernel:

$$\hat{r}(s) = \tilde{F}(s) \hat{k} = \tilde{F}(s) \begin{bmatrix} k_a & -k_b \\ -k_a & k_b \end{bmatrix}, \quad (3.11)$$

where the Laplace transformation of the function $F(t)$ is given by the famous expression:

$$\tilde{F}(s) = \frac{1}{1 + k_a \chi(s + 1/\tau_A) + k_b \chi(s + 1/\tau_B)}, \quad (3.12)$$

where

$$\chi(x) = 1/[k_D(1 + \sqrt{x\tau_d})]. \quad (3.13)$$

Using these results one can recover the original, $\hat{r}(t)$, as well as $\hat{R}(t)$ from Eq. (2.14). After substitution of the latter into Eqs. (2.4a) and (2.4b) we obtain the following kinetic equations for a^* , b^* :

$$\begin{aligned} \frac{da^*}{dt} &= -\frac{a^*}{\tau_A} - k_a[B] \int_0^t F(t-\tau) a^*(\tau) d\tau + k_b[A] \\ &\quad \times \int_0^t F(t-\tau) b^*(\tau) d\tau, \end{aligned} \quad (3.14a)$$

$$\begin{aligned} \frac{db^*}{dt} &= -\frac{b^*}{\tau_B} + k_a[B] \int_0^t F(t-\tau) a^*(\tau) d\tau - k_b[A] \\ &\quad \times \int_0^t F(t-\tau) b^*(\tau) d\tau, \end{aligned} \quad (3.14b)$$

which exactly coincide with those obtained earlier.^{3,4} Hereafter, we will restrict ourselves to linear spectroscopy assuming that the fraction of excited molecules is small $[A^*], [B^*] \ll [A], [B]$. That is, the number of particles in the ground states, $[A]$ and $[B]$, remains practically unchanged under illumination and kinetic equations become linear in a^* and b^* . Now it should be remembered that this set of integral equations cannot be transformed into differential ‘‘rate’’ equations if $k_a, k_b \neq 0$ and $\tau_A \neq \tau_B$. The rate constant of energy transfer from short-lived particle to a more stable particle becomes negative and diverges with $t \rightarrow \infty$. This is evidence that there is no quasi-stationary (Markovian) energy transfer to the partner, which conserves the excitation and returns it back later, giving rise to delayed fluorescence.^{3,4}

IV. MODIFIED ENCOUNTER THEORY

In the low excitation limit one can neglect all the concentration corrections related to excited particles, but must modify IET with respect to the ground state concentrations. In the contact approximation the general form of the modifying operator $\hat{\mathcal{R}}$ can be obtained from Eq. (2.10) with the use of Eqs. (2.9) and (2.12) as shown in the Appendix:

$$\hat{\mathcal{R}}(s) = \begin{bmatrix} 0 & -k_a[B] & -k_b[A] & 0 \\ 0 & k_a[B] & 0 & -k_b[A] \\ 0 & 0 & k_b[A] & -k_a[B] \\ 0 & 0 & 0 & k_a[B] + k_b[A] \end{bmatrix} \tilde{F}(s). \quad (4.1)$$

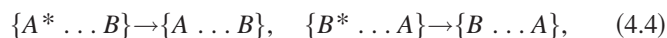
The structure of this matrix is the same as that for the relaxation operator Eq. (2.15). After its substitution into Eq. (2.9), the latter can be reduced to Eq. (2.6) by the simple redefinition of the relaxation times:

$$1/\tau_A \rightarrow 1/\tau_A + K_A(s), \quad 1/\tau_B \rightarrow 1/\tau_B + K_B(s). \quad (4.2)$$

The complex ‘‘rates’’

$$K_A(s) = k_a[B] \tilde{F}(s) \quad \text{and} \quad K_B(s) = k_b[A] \tilde{F}(s), \quad (4.3)$$

for additional quenching of excitation by any partner not belonging to a given couple (reactant pair). These ‘‘bachelors’’ are treated as a ‘‘background’’ of the event. They compete for an excitation with its partner in a couple when it moves away for a while between successive re-contacts. As energy transfer to ‘‘bachelors’’ does not contribute too much to a number of free products of transfer, the interaction with the ‘‘background’’ leads to effectively irreversible reactions:



which are similar to usual decay $A^* \rightarrow A$, $B^* \rightarrow B$. Therefore the modification leads to a simple redefinition of the decay rates Eq. (4.3).

Such a modification allows reducing the problem to that solved in the previous subsection. The kinetic equations for a^* and b^* remain practically the same though the modified kernel \mathcal{F} should be substituted for F :

$$\frac{da^*}{dt} = -\frac{a^*}{\tau_A} - k_a[B] \int_0^t \mathcal{F}(t-\tau)a^*(\tau)d\tau + k_b[A] \times \int_0^t \mathcal{F}(t-\tau)b^*(\tau)d\tau, \quad (4.5a)$$

$$\frac{db^*}{dt} = -\frac{b^*}{\tau_B} + k_a[B] \int_0^t \mathcal{F}(t-\tau)a^*(\tau)d\tau - k_b[A] \times \int_0^t \mathcal{F}(t-\tau)b^*(\tau)d\tau. \quad (4.5b)$$

The Laplace transform of \mathcal{F} follows from Eq. (3.12) after the redefinition of decay rates according to Eq. (4.2):

$$\tilde{\mathcal{F}}(s) = \frac{1}{1 + k_a\chi(s + 1/\tau_A + K_A(s)) + k_b\chi(s + 1/\tau_B + K_B(s))}. \quad (4.6)$$

Very recently a new many-particle theory of diffusion-influenced reactions was proposed by Sung, Chi, and Lee (SCL).²⁵ The SCL theory is based on the revised superposition approximation. The authors were the first, who managed to obtain the concentration corrections to the well-known IET result for the reversible energy transfer. They corrected the long-time asymptotics of transfer as well as the fluorescence quantum yield. However, making a truncation of the hierarchy, the authors intuitively neglected the three-particle correlations of the types A^*AB and B^*BA in comparison with A^*BB and B^*AA .²⁶ In contrast, we accounted explicitly for all the elements of the three-particle matrix correlation patterns which are the analogs of the correlation patterns (CPs) of the nonequilibrium statistical mechanics.^{27,21} In our approximation, which accurately reproduces whole binary kinetics, the CPs π_{A^*BB} and π_{B^*BA} , responsible for the correlations of types A^*BB , B^*BA , are expressed via the CP π_{A^*B} :

$$\tilde{\pi}_{A^*BB}(r, \sigma, s) = -\frac{1 - k_b g_b}{1 - k_a k_b g_a g_b} k_a g_a [B] \tilde{\pi}_{A^*B}(r, s), \quad (4.7a)$$

$$\tilde{\pi}_{B^*BA}(r, \sigma, s) = \frac{1 - k_a g_a}{1 - k_a k_b g_a g_b} k_a g_b [B] \tilde{\pi}_{A^*B}(r, s), \quad (4.7b)$$

where $g_a = [k_a + k_D(1 + \sqrt{\tau_d(s + 1/\tau_A)})]^{-1}$, $g_b = [k_b + k_D(1 + \sqrt{\tau_d(s + 1/\tau_B)})]^{-1}$. Similar expressions, which can be deduced from these formulae by the permutation of indexes, exist for the CPs π_{B^*AA} and π_{A^*AB} as well. It is clear that the quantities π_{A^*BB} , π_{B^*BA} and π_{B^*AA} , π_{A^*AB} are of the same order of magnitude and there is no reason to neglect the two of them keeping the others, as has been done in Ref. 25. As a result the concentration corrections obtained in SCL work are different from ours and improve the IET results only qualitatively. The authors recently overcome this drawback making the next revision of their approach which brought their results in full correspondence with MET.²⁶

V. QUANTUM YIELD OF FLUORESCENCE

The relative quantum yield of the fluorescence from A^* is conventionally defined as

$$\eta = \int_0^\infty a^*(t) dt / \tau_A = \tilde{a}^*(0) / \tau_A. \quad (5.1)$$

It can be represented in the form of the Stern–Volmer law

$$\eta = \frac{1}{1 + k_Q[B]\tau_A}, \quad (5.2)$$

with a quenching constant k_Q , first obtained by means of IET in Ref. 3:

$$k_Q^{\text{IET}} = \frac{k_a}{1/\tilde{F}(0) + k_b\tau_B[A]} = \frac{k_a}{1 + k_a\chi(1/\tau_A) + k_b\chi(1/\tau_B) + k_b\tau_B[A]}, \quad (5.3)$$

where $\chi(x)$ was defined in Eq. (3.13). The populations of the ground states, $[A]$ and $[B]$, are considered here as the total concentrations of corresponding particles.

From here on we should discriminate between qualitatively different situations:

- (1) **Energy quenching.** This is a case when either the transfer is irreversible $k_b = 0$ or $\tau_B \rightarrow 0$, that is nothing can be transferred back before B^* decays.
- (2) **Equal times.** This is a border case, $\tau_A = \tau_B = \tau$, when the decay of excited states and energy redistribution between them proceed independently.
- (3) **Energy storing.** At $\tau_A < \tau_B$ the initial quenching of A^* by forward energy transfer to B 's results in energy storing there and subsequent backward transfer to the short-lived A^* detected as their delayed fluorescence.

1. Irreversible energy transfer (quenching) was studied many times within encounter theory and alternative methods thoroughly compared in Ref. 16. There is a unique opportunity to inspect any theoretical innovations by comparison with exact results, available only in case 1 when A 's are immobile and B 's move independently.

2. In case 2 one can separate the state decay from energy redistribution, making a change in the variables in Eqs. (3.14a) and (3.14b): $a^*(t) = a_0(t)\exp(-t/\tau)$, $b^*(t) = b_0(t)\exp(-t/\tau)$. The energy redistribution turns the initial values $a_0(0) = 1$, $b_0(0) = 0$ to the stationary ones a_{0s} , b_{0s} whose ratio is

$$Q = \frac{b_{0s}}{a_{0s}} = \frac{k_a[B]\tilde{F}(-1/\tau)}{k_b[A]\tilde{F}(-1/\tau)} = K_{eq} \frac{[B]}{[A]}.$$

Here $K_{eq} = k_a/k_b = \exp(-\epsilon/k_B T)$ is the equilibrium constant expressed through the free energy difference between two excitations, ϵ . It follows from Eqs. (5.2) and (5.3) that

$$\eta = \frac{1 + Q\eta_0 - \eta_0}{1 + Q - \eta_0}, \quad (5.4)$$

where

$$\eta_0 = \frac{1}{1 + \kappa[B]\tau},$$

has the form of the conventional Stern–Volmer law for irreversible energy quenching by $[B]$'s, but with constant $\kappa = k_a \tilde{F}(0)$, which accounts for both forward and backward transfer. Our result Eq. (5.4) is similar to that obtained for the reversible intra-molecular transfer, $A+B \rightleftharpoons C+B$, in Ref. 13 for the same case of equal times. For the particular case of diffusion controlled transfer

$$\kappa \approx \frac{\kappa_{irr}}{1 + k_b/k_a}, \quad (5.5)$$

where

$$\kappa_{irr} = \frac{k_a k_D}{k_D + k_a(1 + \sqrt{\tau_d/\tau})}$$

is the Stern–Volmer constant for really irreversible energy transfer.

3. It is the most intriguing, when the excitation lives longer on the acceptor of energy than on the donor. In the extreme case $\tau_B \rightarrow \infty$ the excited acceptors may be considered as stable products of a reversible reaction. If nevertheless $\tau_B[A] \rightarrow 0$ the quantum yield of such products is

$$\begin{aligned} \phi &= b^*(\infty) = k_a[B] \int_0^\infty dt \int_0^t F(t-\tau) a^*(\tau) d\tau \\ &= k_a[B] \tilde{F}(0) \tilde{a}^*(0). \end{aligned} \quad (5.6)$$

Here $\tilde{a}^*(0) = \{1/\tau_A + k_a[B] \tilde{F}(0)\}^{-1}$ as follows from Eq. (4.5a) at initial condition $a^*(0) = 1$. Finally we have

$$\phi = \frac{\kappa[B]\tau_A}{1 + \kappa[B]\tau_A} = 1 - \eta, \quad (5.7)$$

where the quantum yield of fluorescence η obeys the conventional law Eq. (5.2), but with the concentration independent Stern–Volmer constant

$$\kappa = \lim_{\tau_B[A] \rightarrow 0} k_Q = k_a \tilde{F}(0). \quad (5.8)$$

As a matter of fact, at short τ_B and a low concentration of A particles, one can always ignore the bimolecular backward energy transfer. When

$$\tau_B[A] \ll \chi(1/\tau_B) = [k_D(1 + \sqrt{\tau_d/\tau_B})]^{-1}, \quad (5.9)$$

the terms proportional to $[A]$ may be neglected in Eq. (4.5a), (4.5b) as well as in the denominators of Eqs. (5.3). Under this condition the general k_Q turns to be the usual Stern–Volmer constant (5.8). Inserting Eq. (5.3) into Eq. (5.8) we reproduce the widely known result of IET:³

$$k_a/\kappa^{\text{IET}} = 1 + k_a\chi(1/\tau_A) + k_b\chi(1/\tau_B). \quad (5.10)$$

The MET result is obtained by substitution of $\tilde{F}(0)$ from Eq. (4.6) for $\tilde{F}(0)$ in Eq. (5.3):

$$\begin{aligned} k_a/\kappa^{\text{MET}} &= 1 + k_a\chi(1/\tau_A + k_a\tilde{F}(0)[B]) \\ &\quad + k_b\chi(1/\tau_B + k_b\tilde{F}(0)[A]). \end{aligned} \quad (5.11)$$

Unlike Eq. (5.10) this result contains concentration corrections to both decay rates. The same conclusion was drawn by

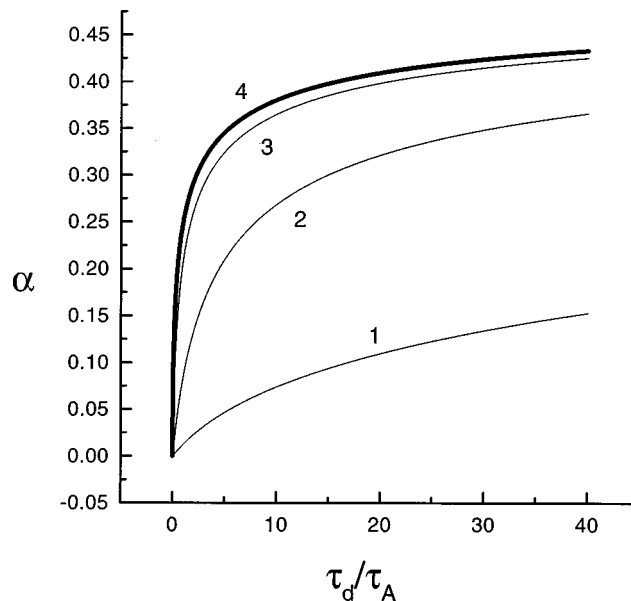


FIG. 1. Dependence of correcting coefficient α for the irreversible energy transfer ($k_b=0$) on encounter diffusion measured in $\tau_d/\tau_A = \sigma^2/D\tau_A$ at different reactivities: $k_a\tau_A/4\pi\sigma^3=0.1$ (1), 1.0 (2), 10.0 (3), and ∞ (thick line).

Sung, Chi, and Lee within their SCL theory.²⁵ However, they obtained, instead of Eq. (5.11), an essentially different result which is in their notations $\hat{F}(0) = k_a/\kappa^{\text{SCL}}$:

$$k_a/\kappa^{\text{SCL}} = k_a/\kappa^{\text{IET}} - k_a\tau_A[B] - k_b\tau_B[A]. \quad (5.12)$$

This result, valid in the lowest order approximation with respect to particle concentrations, is in principle better than that of IET because it contains linear corrections in $[A]$ and $[B]$. To compare it with our MET formula Eq. (5.11), the latter should be expanded also in the power series of concentrations, keeping only the lowest terms. To stress the difference we present the result in the same form,

$$k_a/\kappa^{\text{MET}} \approx k_a/\kappa^{\text{IET}} - \alpha k_a\tau_A[B] - \beta k_b\tau_B[A], \quad (5.13)$$

but with coefficients α and β correcting the last terms:

$$\alpha = \frac{k_a\sqrt{\tau_A\tau_d}}{2k_D(\sqrt{\tau_A} + \sqrt{\tau_d})^2} \tilde{F}(0), \quad \beta = \frac{k_b\sqrt{\tau_B\tau_d}}{2k_D(\sqrt{\tau_A} + \sqrt{\tau_d})^2} \tilde{F}(0). \quad (5.14)$$

Unfortunately, we did not find conditions when α and β are equal to 1 and remain the same at any D as in SCL theory. In the kinetic control limit ($D \rightarrow \infty$) $\alpha = \beta = 0$, but not 1. It is reasonable, that in such an essentially Markovian limit all concentration corrections to IET vanish. In the opposite diffusion control limit, when $k_a \rightarrow \infty$, the difference is not as drastic, but also essential: α approaches the upper limit equal 1/2. The set of curves representing diffusional dependence of α at different values of k_a is shown in Fig. 1.

VI. ENERGY QUENCHING

To recognize what is right and wrong in the diffusional limit, we turn to a well investigated particular case of energy quenching, $\tau_B \rightarrow 0$, when Eq. (5.13) reduces to the following:

TABLE I. Function $A(z)$ in different theories.

Theories	$A(z)$
DET	$3 \left[\frac{1}{2} \sqrt{\frac{\tau_A}{\tau_d}} + 1 - \frac{2}{\pi} \right]$
KGD	$3 \left[\frac{1}{2} \sqrt{\frac{\tau_A}{\tau_d}} \right]$
MET	$3 \left[\frac{1}{2} \sqrt{\frac{\tau_A}{\tau_d} + \frac{1}{2}} \right]$
YLS	$3 \left[\frac{1}{2} \sqrt{\frac{\tau_A}{\tau_d} + \frac{1}{2}} \right]$
SCL	$3 \left[2 \sqrt{\frac{\tau_A}{\tau_d} + \frac{\tau_A}{\tau_d} + 1} \right]$

$$\kappa^{\text{MET}} = \frac{k_a}{1 + k_a \{ \chi(1/\tau_A) - \alpha \tau_A [B] \}} \quad (6.1)$$

This result coincides with that provided by conventional DET. It can be compared with a famous exact solution of the same problem, which is valid at any concentrations if A particles are immobile and B s move independently.^{28,29} Such a comparison has already been made in Ref. 16 for testing the accuracy of the binary approach of Kipriyanov, Gopich, and Doktorov (KGD)²⁰ and the popular SA.^{30–33} Here we have to do the same for the MET and SCL theory²⁵ as well as for some others: KGD²⁰ and YLS theory.²² From Eqs. (5.14) and (3.12) we obtain in the diffusional limit

$$\lim_{k_a \rightarrow \infty} \alpha = \frac{\sqrt{\tau_d/\tau_A}}{2(1 + \sqrt{\tau_d/\tau_A})}, \quad (6.2)$$

and from Eq. (6.1)

$$\kappa^{\text{MET}} = \kappa^{\text{IET}} + \frac{k_D^2 \tau_A [B]}{2} \left\{ \sqrt{\frac{\tau_d}{\tau_A} + \frac{\tau_d}{\tau_A}} \right\}, \quad (6.3)$$

where $\kappa^{\text{IET}} = k_D(1 + \sqrt{\tau_d/\tau_A})$. The alternative result for κ^{SCL} can be obtained similarly from Eq. (6.1) with $\alpha = 1$.

To make the comparison easier, let us represent any Stern–Volmer constant of irreversible diffusion controlled transfer as follows:

$$\kappa = \kappa^{\text{IET}} + A k_D \xi,$$

where $\xi = (4\pi/3) \sigma^3 [B]$ is the dimensionless concentration of quenchers. We see that in the lowest concentration limit, $\xi \rightarrow 0$, all the theories reproduce the concentration independent IET result, $\kappa = \kappa^{\text{IET}}$. Likewise, all the results are linear in ξ , though with different slopes $A k_D$, which is determined by a single parameter $z = \sqrt{\tau_A/\tau_d}$. The slope, measured in k_D , is placed in Table I as a function $A(z)$ which is different in different theories. It is remarkable that A is linear in z and almost the same in all theories except the last one. The latter has a larger coefficient at $\sqrt{\tau_A/\tau_d}$ than that in DET which is considered as exact. Moreover, there is the odd term in SCL theory, τ_A/τ_d , which makes the corresponding $A(z)$ dependence nonlinear and qualitatively different from all the rest.

However, these theories, including “exact” solution available in DET, describe only the irreversible energy

quenching. In case of reversible energy transfer, i.e., Eq. (5.13), derived from MET, that provides an appropriate linear correction to the Stern–Volmer constant, obtained earlier with IET in Refs. 3, 4. This result, first announced a year ago,³⁴ was recently reproduced with a new improved version of SCL theory.²⁶

VII. ENERGY STORING

When $\tau_A < \tau_B$ the terms of the bimolecular backward transfer in kinetic Eqs. (3.14a) and (3.14b) can be transformed into the differential rate terms according to the conventional procedure, used a number of times.^{35–37,4}

$$\frac{da^*}{dt} = -\frac{a^*}{\tau_A} - k_a [B] \int_0^t F(t-\tau) a^*(\tau) d\tau + k_b(t) [A] b^*, \quad (7.1a)$$

$$\frac{db^*}{dt} = -\frac{b^*}{\tau_B} + k_a [B] \int_0^t F(t-\tau) a^*(\tau) d\tau - k_b(t) [A] b^*, \quad (7.1b)$$

where the time-dependent rate constant of bimolecular backward transfer is

$$k_b(t) = k_b \int_0^t F(t-t') e^{t'/\tau_B} dt'. \quad (7.2)$$

At $t \gg \tau_d$ this pseudo-constant approaches the stationary value

$$k_s = k_b(\infty) = k_b \tilde{F}(-1/\tau_B), \quad (7.3)$$

which is a real Markovian rate constant, independent of time. At $\tau_A > \tau_d$ the Markovian description of bimolecular backward transfer is possible at any times: at $t < \tau_d$ the corresponding terms in Eqs. (7.1a) and (7.1b) are negligible because of small $b^*(t)$ while at $t > \tau_d$ the Markovian limit of $k_b(t)$ has been already reached. Even at $\tau_A \leq \tau_d$ this Markovian description is approximately valid and can be represented as follows:

$$\frac{da^*}{dt} = -\frac{a^*}{\tau_A} - k_a [B] \int_0^t F(t-\tau) a^*(\tau) d\tau + k_s [A] b^*, \quad (7.4a)$$

$$\frac{db^*}{dt} = -\frac{b^*}{\tau_B} + k_a [B] \int_0^t F(t-\tau) a^*(\tau) d\tau - k_s [A] b^*. \quad (7.4b)$$

The storing of energy in B particles and its subsequent dissipation can be easily described by the straightforward integration of Eq. (7.4b):

$$b^* = k_a [B] e^{-(1/\tau_B + k_s [A])t} \int_0^t dt' e^{(1/\tau_B + k_s [A])t'} \times \int_0^{t'} F(t' - \tau) a^*(\tau) d\tau. \quad (7.5)$$

When B decays much slower than A the exponential factor in the integrand changes negligibly in the initial time interval,

while the integral multiplier soon turns to zero. Therefore, this exponent can be taken as 1 when estimating the long-time asymptotic behavior of b^* :

$$b^* \approx \phi e^{-(1/\tau_B + k_s[A])t} \quad \text{at } t \gg \tau_A, \tau_d, \quad (7.6)$$

where ϕ was defined in Eq. (5.7).

In Ref. 4 we studied the kinetics of product accumulation at $[A] \rightarrow 0$ and found that at $\tau_B = \infty$ the plateau $b^*(\infty) = \phi$ is approached from above. The quantum yield of free product ϕ is less than the maximal value of b^* , especially at $w_b > w_a$ due to the backward transfer of energy in a geminate pair before separation. In the contact approximation one can decompose the free B^* production in the series of contributions from a single encounter, one re-encounter, two re-encounters, etc.:

$$\begin{aligned} \phi &= \psi_0 \varphi(\sigma) \{ 1 + [1 - \varphi(\sigma)] \psi_0 + [1 - \varphi(\sigma)]^2 \psi_0^2 + \dots \} \\ &= \frac{\varphi(\sigma) \psi_0}{1 - \psi_0 [1 - \varphi(\sigma)]}. \end{aligned} \quad (7.7)$$

Here ψ_0 is the quantum yield of irreversible energy transfer from A^* to B :

$$\psi_0 = \frac{\kappa_0 [B] \tau_A}{1 + \kappa_0 [B] \tau_A} \quad \kappa_0 = \kappa |_{k_b=0}, \quad (7.8)$$

while $\varphi(\sigma)$ represents the fraction of excited B^* separated from A (see Appendix B). Substituting ψ_0 and $\varphi(\sigma)$ into Eq. (7.7), we reproduce the result which follows directly from Eqs. (5.7) and (5.8):

$$\phi = \frac{k_a [B] \tau_A}{1 + k_a / (k_D (1 + \sqrt{\tau_d / \tau_A})) + k_b / k_D + k_a [B] \tau_A}. \quad (7.9)$$

At any finite $[A]$ the geminate stage has to be followed by the final and longest stage of bimolecular backward transfer substituting for the plateau. This must be slow exponential decay with the rate $k_b [A] \tilde{F}(0)$. Making numerical calculations of a^* and b^* with the same programs as in Ref. 4, we confirmed these expectations. At $\tau_A < \tau_d$ the fast accumulation gives way to a geminate backward transfer, which steps down the plateau of free excited products at $[A] \rightarrow 0$, but at finite $[A]$ the plateau is substituted by an exponential decay with bimolecular rate $k_s [A]$, as shown in Fig. 2. In contrast, at $\tau_A > \tau_d$ this decay follows the relatively slow and almost monotonous accumulation of energy to a relatively higher level.

All the phenomenology of the process in MET is very similar to that in IET, because the kinetic equations remain essentially the same, but with substitution of \mathcal{F} for F . This difference can affect some of the results since \tilde{F} is constant,

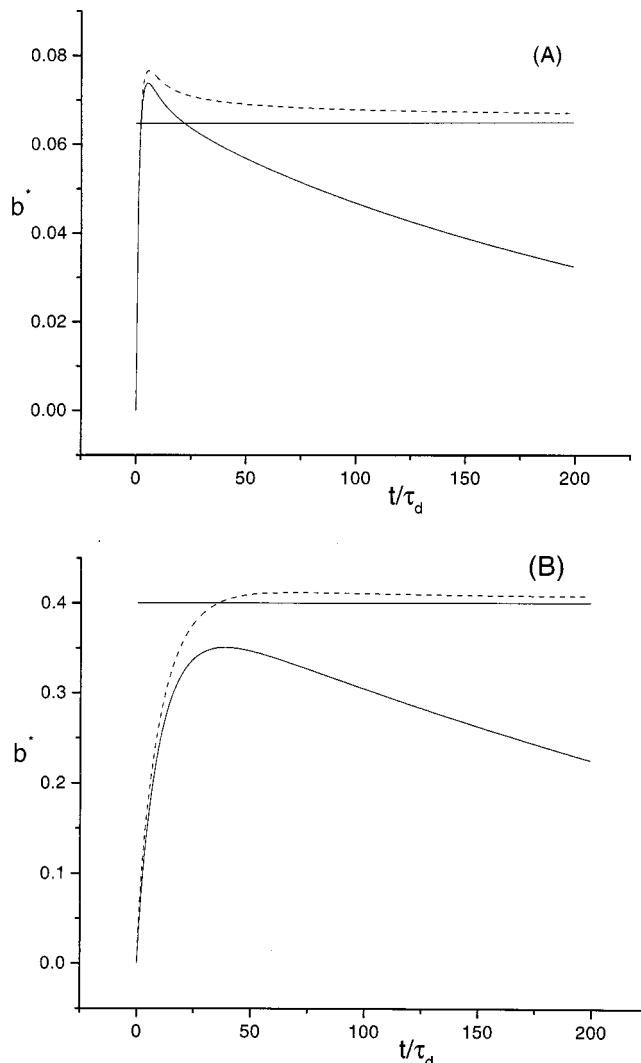


FIG. 2. Kinetics of energy storing and dissipation at short (A) and long (B) excitation lifetimes: $\tau_A = 2\tau_d$ (A) and $\tau_A = 20\tau_d$ (B). The rest of the parameters are: $k_a [B] \tau_d = 1.0, k_a = 5k_D, k_b = 25k_D$. The dashed lines show the energy storing kinetics $b^*(t)$ at $[A] \rightarrow 0$, while the horizontal lines indicate the stable product quantum yield $\phi = b^*(\infty)$ in this case. The solid lines show the product accumulation and dissipation (due to bimolecular backward transfer) at finite $[A]$, particularly, for $k_b [A] \tau_d = 0.1$.

while \tilde{F} is concentration dependent. For instance, the quenching constant Eq. (5.3) should be redefined as follows:

$$k_Q^{\text{MET}} = \frac{k_a}{1/\tilde{F}(0) + k_b \tau_B [A]}. \quad (7.10)$$

To get an expression for $\tilde{F}(0)$ valid at any τ_B , only the general result Eq. (4.6) must be used:

$$\tilde{F}(0) = \frac{1}{1 + k_a \chi (1/\tau_A + k_a [B] \tilde{F}(0)) + k_b \chi (1/\tau_B + k_b [A] \tilde{F}(0))}, \quad (7.11)$$

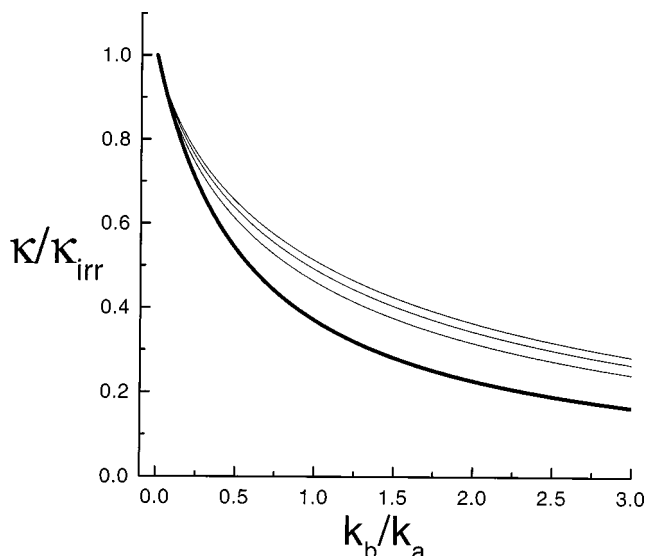


FIG. 3. Stern–Volmer constant dependence on the rate of backward energy transfer from the quasi-stable product ($\tau_B \rightarrow \infty$) in IET (thick line) and in MET (thin lines) at relatively small concentrations of A: $4\pi\sigma^3[A]/3 = 0.05, 0.15, 0.3$ (from bottom to top). The rest of the parameters are: $\tau_A = 2\tau_d$, $4\pi\sigma^3[B]/3 = 0.15$, $k_a, k_b \gg k_D$ (Diffusional control).

where

$$\tilde{F}(0) = \frac{1}{1 + k_a/[k_D(1 + \sqrt{\tau_d/\tau_A})] + k_b/[k_D(1 + \sqrt{\tau_d/\tau_B})]}.$$

The power expansion of χ in concentrations made in Eq. (5.13) does not hold at $\tau_B = \infty$. The same is true for the whole YLS theory, restricted itself to a similar expansion Eq. (5.12).

Substituting Eq. (7.11) into Eq. (5.11), we obtain the concentration corrected Stern–Volmer constant at $\tau_B \rightarrow \infty$, but $\tau_B[A] \rightarrow 0$:

$$\kappa^{\text{MET}} = \frac{k_a k_D}{k_D + k_a/(1 + \sqrt{x}) + k_b/(1 + \sqrt{y})}, \quad (7.12)$$

where

$$x = \tau_d/\tau_A + k_a[B]\tau_d\tilde{F}(0) \quad \text{and} \quad y = k_b[A]\tau_d\tilde{F}(0).$$

The expressions reduce to those of IET when $[A] = [B] = 0$. Otherwise, we obtain the nonlinear dependence of the Stern–Volmer constant on both concentrations. In a particular case of irreversible energy transfer ($k_b = 0$), the concentration correction enhances the role of non-stationary quenching by accelerating the rate of decay. This well known effect is only essential in the diffusion controlled limit when

$$\kappa_{\text{irr}}^{\text{MET}} = \frac{k_a k_D}{k_D + k_a/(1 + \sqrt{x})} \approx k_D(1 + \sqrt{x}) \ll k_a. \quad (7.13)$$

The larger the decay rate the closer is $\kappa_{\text{irr}}^{\text{MET}}$ to its upper limit k_a . If the backward transfer is taken into consideration, κ becomes smaller and the fluorescence quantum yield becomes larger than in the irreversible case (Fig. 3). However,

this effect is hindered if the concentration of $[A]$ particles increases:

$$\kappa^{\text{MET}} \approx \kappa_{\text{irr}}^{\text{MET}} \left\{ 1 + \frac{k_b(1 + \sqrt{x})}{k_a(1 + \sqrt{y})} \right\}^{-1}, \quad (7.14)$$

where

$$y \approx \frac{k_D \tau_d}{1 + k_a/[k_b(1 + \sqrt{\tau_d/\tau_A})]} [A], \quad \text{at} \quad k_D \ll k_a, k_b.$$

The restoration of the Stern–Volmer constant with inclusion of the MET concentration corrections is illustrated in Fig. 3. In the particular case of equal decay rates of the excited states, $x = y$, Eq. (7.14) reduces to a previously obtained Eq. (5.5), derived for this very case.

VIII. CONCLUSION

We successfully applied the new method suggested in Part I to the kinetic problem: the reversible energy transfer between metastable reactants with different lifetimes. The essential feature of such a reaction is that the conventional Markovian or ‘rate equation’ approaches are inconsistent, using either permanent or time dependent rate constants. They fail to describe properly the fluorescence quantum yield and kinetics of delayed fluorescence. On the contrary, the integral formalism using memory functions obtained in the binary approximation with IET, MET, or equivalent theories, provides much better treatment of these problems. Our newly developed method enables one to regularly specify the IET and MET integral equations or substitute them by a set of equivalent differential equations. The former approach is suitable for analytic calculations of fluorescence quantum yields and other stationary characteristics while the latter is more convenient for numerical calculations of reaction kinetics. The comparison of our results with those obtained with other methods has been illustrated by the examples of irreversible and reversible inter-molecular energy transfer, between the states with different lifetimes.

ACKNOWLEDGMENTS

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APPENDIX A: THE DERIVATION OF MET MODIFICATION OPERATOR

To obtain MET equations one needs the modifying operator $\hat{\mathcal{R}}$, which acts on the two-particle matrix correlation pattern σ_{AB} as follows:

$$\begin{aligned} \hat{\mathcal{R}}\sigma_{AB} = & \text{Tr}_{B'} \int_0^t [\hat{R}_{AB'}(t-t') \otimes \exp\{\hat{Q}_B(t-t')\}] \\ & \times [\sigma_{B'}(t') \otimes \sigma_{AB}(r, t')] dt' \\ & + \text{Tr}_A \int_0^t [\hat{R}_{A'B}(t-t') \otimes \exp\{\hat{Q}_A(t-t')\}] \\ & \times [\sigma_{A'}(t') \otimes \sigma_{AB}(r, t')] dt'. \end{aligned} \quad (\text{A1})$$

We will calculate only the first term of Eq. (A1), because the second one can be obtained in an analogous way. The operator $\hat{R}_{AB'}$ in the contact approximation in the two particle basis $\{AB', A^*B', AB'^*, A^*B'^*\}$ has the following form:

$$\hat{R}_{AB'}(t) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & k_a & -k_b & 0 \\ 0 & -k_a & k_b & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} F(t). \quad (\text{A2})$$

The matrix exponent $\exp\{\hat{Q}_B t\}$ in the individual basis $\{B, B^*\}$ is

$$\begin{aligned} \exp\{\hat{Q}_B t\} &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 0 & (1 - e^{-t/\tau_B}) \\ 0 & -(1 - e^{-t/\tau_B}) \end{pmatrix} \\ &= \hat{E} + \alpha(t) \begin{pmatrix} 0 & 1 \\ 0 & -1 \end{pmatrix}, \end{aligned} \quad (\text{A3})$$

$$\alpha(t) = 1 - \exp(-t/\tau_B).$$

Thus the operator $\hat{R}_{AB'}(t-t') \otimes \exp\{\hat{Q}_B(t-t')\}$ in the three-particle basis $\{AB'B, A^*B'B, AB'^*B, A^*B'^*B, AB'B^*, A^*B'B^*, AB'^*B^*, A^*B'^*B^*\}$ is a sum of two parts:

$$\begin{aligned} \hat{R}_{AB'}(t-t') \otimes \exp\{\hat{Q}_B(t-t')\} \\ = Z_1(t-t') + \alpha(t-t') Z_2(t-t'), \end{aligned} \quad (\text{A4})$$

where

$$Z_1(t-t') = \begin{pmatrix} R_{AB'}(t-t') & 0 \\ 0 & R_{AB'}(t-t') \end{pmatrix} \quad \text{and} \quad (\text{A5})$$

$$Z_2(t-t') = \begin{pmatrix} 0 & R_{AB'}(t-t') \\ 0 & -R_{AB'}(t-t') \end{pmatrix}.$$

Here $R_{AB'}(t)$ is given by Eq. (A2), and the zeroes in both matrices imply blocks of zeroes of 4×4 rank.

The product $\sigma_{B'}(t') \otimes \sigma_{AB}(r, t')$ in the abovementioned three-particle basis is equal to

$$\sigma_{B'}(t') \otimes \sigma_{AB}(r, t') = \begin{pmatrix} \sigma_{AB}(r, t') \sigma_{B'}(t') \\ \sigma_{A^*B}(r, t') \sigma_{B'}(t') \\ \sigma_{AB}(r, t') \sigma_{B'}^*(t') \\ \sigma_{A^*B}(r, t') \sigma_{B'}^*(t') \\ \sigma_{AB^*}(r, t') \sigma_{B'}(t') \\ \sigma_{A^*B^*}(r, t') \sigma_{B'}(t') \\ \sigma_{AB^*}(r, t') \sigma_{B'}^*(t') \\ \sigma_{A^*B^*}(r, t') \sigma_{B'}^*(t') \end{pmatrix}. \quad (\text{A6})$$

Substituting Eq. (A4) into Eq. (A1) and making the trace operation over B' we have the two following components of the kernel:

$$\begin{aligned} \text{Tr}_{B'} Z_1(t-t') [\sigma_{B'}(t') \otimes \sigma_{AB}(r, t')] \\ = \begin{pmatrix} k_a \sigma_{A^*B}(r, t') \sigma_{B'}(t') - k_b \sigma_{AB}(r, t') \sigma_{B'}^*(t') \\ -k_a \sigma_{A^*B}(r, t') \sigma_{B'}(t') + k_b \sigma_{AB}(r, t') \sigma_{B'}^*(t') \\ -k_a \sigma_{A^*B^*}(r, t') \sigma_{B'}(t') + k_b \sigma_{AB^*}(r, t') \sigma_{B'}^*(t') \\ k_a \sigma_{A^*B^*}(r, t') \sigma_{B'}(t') - k_b \sigma_{AB^*}(r, t') \sigma_{B'}^*(t') \end{pmatrix} \\ \times F(t-t'), \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} \text{Tr}_{B'} Z_2(t-t') [\sigma_{B'}(t') \otimes \sigma_{AB}(r, t')] \\ = \begin{pmatrix} k_a \sigma_{A^*B^*}(r, t') \sigma_{B'}(t') - k_b \sigma_{AB^*}(r, t') \sigma_{B'}^*(t') \\ k_a \sigma_{A^*B^*}(r, t') \sigma_{B'}(t') - k_b \sigma_{AB^*}(r, t') \sigma_{B'}^*(t') \\ k_a \sigma_{A^*B^*}(r, t') \sigma_{B'}(t') - k_b \sigma_{AB^*}(r, t') \sigma_{B'}^*(t') \\ -k_a \sigma_{A^*B^*}(r, t') \sigma_{B'}(t') + k_b \sigma_{AB^*}(r, t') \sigma_{B'}^*(t') \end{pmatrix} \\ \times F(t-t'). \end{aligned} \quad (\text{A8})$$

To estimate which terms in these matrices can be neglected, one should know the order of the magnitude of elements σ_{AB} . For this goal we should use the equations for the σ_A , σ_B , σ_{AB} obtained in Part I [Eqs. (6.19a)–(6.19c)]:

$$\begin{aligned} \partial_t \hat{\sigma}_A(t) &= \hat{Q}_A \hat{\sigma}_A(t) + \text{Tr}_B \int d\vec{r} \hat{W}_{AB}(\vec{r}) \\ &\times \{\hat{\sigma}_A(t) \otimes \hat{\sigma}_B(t) + \hat{\sigma}_{AB}(\vec{r}, t)\}, \end{aligned} \quad (\text{A9a})$$

$$\begin{aligned} (\partial_t - \hat{\mathcal{L}}_r - \hat{W}_{AB}(\vec{r})) \hat{\sigma}_{AB}(\vec{r}, t) \\ = \{\hat{Q}_{AB} - \hat{\mathcal{R}}\} \hat{\sigma}_{AB}(\vec{r}, t) + \hat{W}_{AB}(\vec{r}) \hat{\sigma}_A(t) \otimes \hat{\sigma}_B(t), \end{aligned} \quad (\text{A9b})$$

$$\begin{aligned} \partial_t \hat{\sigma}_B(t) &= \hat{Q}_B \hat{\sigma}_B(t) + \text{Tr}_A \int d\vec{r} \hat{W}_{AB}(\vec{r}) \\ &\times \{\hat{\sigma}_A(t) \otimes \hat{\sigma}_B(t) + \hat{\sigma}_{AB}(\vec{r}, t)\}. \end{aligned} \quad (\text{A9c})$$

For our particular $\hat{W}_{AB}(\vec{r})$ and \hat{Q}_{AB} equations for the elements of σ_{AB} without modification of $\hat{\mathcal{R}}$ are

$$\begin{aligned}
& (\partial_t - \hat{\mathcal{L}}_r) \begin{pmatrix} \sigma_{AB}(\mathbf{r}, t) \\ \sigma_{A^*B}(\mathbf{r}, t) \\ \sigma_{AB^*}(\mathbf{r}, t) \\ \sigma_{A^*B^*}(\mathbf{r}, t) \end{pmatrix} + \begin{pmatrix} 0 \\ -w_a(\vec{r})\sigma_{A^*B} + w_b(\vec{r})\sigma_{AB^*} \\ w_a(\vec{r})\sigma_{A^*B} - w_b(\vec{r})\sigma_{AB^*} \\ 0 \end{pmatrix} \\
&= \begin{pmatrix} \frac{1}{\tau_A}\sigma_{A^*B} + \frac{1}{\tau_B}\sigma_{AB^*} \\ -\frac{1}{\tau_A}\sigma_{A^*B} + \frac{1}{\tau_B}\sigma_{A^*B^*} \\ -\frac{1}{\tau_B}\sigma_{AB^*} + \frac{1}{\tau_A}\sigma_{A^*B^*} \\ -\left(\frac{1}{\tau_A} + \frac{1}{\tau_B}\right)\sigma_{A^*B^*} \end{pmatrix} \\
&+ \begin{pmatrix} 0 \\ -w_a(\vec{r})\sigma_{A^*B} + w_b(\vec{r})\sigma_{A^*B^*} \\ w_a(\vec{r})\sigma_{A^*B} - w_b(\vec{r})\sigma_{A^*B^*} \\ 0 \end{pmatrix}. \quad (\text{A10})
\end{aligned}$$

It is easy to see that σ_{AB} term is in the same order as σ_{A^*B} and σ_{AB^*} , and this conclusion remains valid for modified $\hat{\mathcal{R}}$ as well. At a low level of excitation we can neglect all terms in Eqs. (A7),(A8) containing the multiplier σ_{B^*} , as second order terms in the concentration of excited molecules. The result can be represented as follows:

$$\begin{aligned}
& \text{Tr}_{\mathbf{B}'} Z_1(t-t') [\sigma_{\mathbf{B}'}(t') \otimes \sigma_{\mathbf{AB}}(r, t')] \\
& \approx \begin{pmatrix} 0 & -k_a[B] & 0 & 0 \\ 0 & k_a[B] & 0 & 0 \\ 0 & 0 & 0 & -k_a[B] \\ 0 & 0 & 0 & k_a[B] \end{pmatrix} \begin{pmatrix} \sigma_{AB}(r, t') \\ \sigma_{A^*B}(r, t') \\ \sigma_{AB^*}(r, t') \\ \sigma_{A^*B^*}(r, t') \end{pmatrix} \\
& \times F(t-t'), \quad (\text{A11})
\end{aligned}$$

where we set $\sigma_{\mathbf{B}'}(t') = [B]$ because at weak excitation the concentration of nonexcited molecules is approximately equal to their total density $[B]$. Similarly,

$$\begin{aligned}
& \text{Tr}_{\mathbf{B}'} Z_2(t-t') [\sigma_{\mathbf{B}'}(t') \otimes \sigma_{\mathbf{AB}}(r, t')] \\
& \approx \begin{pmatrix} 0 & 0 & 0 & -k_a[B] \\ 0 & 0 & 0 & k_a[B] \\ 0 & 0 & 0 & k_a[B] \\ 0 & 0 & 0 & -k_a[B] \end{pmatrix} \begin{pmatrix} \sigma_{AB}(r, t') \\ \sigma_{A^*B}(r, t') \\ \sigma_{AB^*}(r, t') \\ \sigma_{A^*B^*}(r, t') \end{pmatrix} F(t-t'). \quad (\text{A12})
\end{aligned}$$

The last column in the modifying matrices acts only on the $\sigma_{A^*B^*}$ element, which obeys homogeneous equations with the initial condition $\sigma_{A^*B^*} = 0$. Therefore this element is zero ($\sigma_{A^*B^*} \equiv 0$) and we can neglect the last row elements in the corresponding matrices setting them to zero, as well as the whole expression Eq. (A12). All the corrections responsible for the interaction with A's "bachelors" can be calculated in the similar manner.

Then, the final expression for the Laplace transformation $\hat{\mathcal{R}}(s)$ of the modifying operator is defined by the sum of Z_1 's originating from the two terms of the right hand side of Eq. (A1) and is of the form:

$$\hat{\mathcal{R}}(s) = \begin{pmatrix} 0 & -k_a[B] & -k_b[A] & 0 \\ 0 & k_a[B] & 0 & -k_b[A] \\ 0 & 0 & k_b[A] & k_a[B] \\ 0 & 0 & 0 & k_a[B] + k_b[A] \end{pmatrix} \tilde{F}(s). \quad (\text{A13})$$

APPENDIX B: CALCULATION OF φ

Let $\nu(r, t)$ and μ be the probabilities to find pair $[A^* \dots B]$ and $[A \dots B^*]$ at distance r , at time t provided initially, there was only the latter, at distance σ . The kinetics for these densities are

$$\frac{\partial \nu}{\partial t} = D\Delta\nu - \frac{1}{\tau_A}\nu \quad \text{and} \quad \frac{\partial \mu}{\partial t} = D\Delta\mu, \quad (\text{B1})$$

where $\Delta = (1/r^2)(d/dr)(r^2(d/dr))$. For the contact reaction we have to use the following boundary conditions:

$$\begin{aligned}
& (\sigma k_D) \frac{d\nu(r, t)}{dr} \Big|_{r=\sigma} = k_a\nu(\sigma, t) - k_b\mu(\sigma, t), \\
& (\sigma k_D) \frac{d\mu(r, t)}{dr} \Big|_{r=\sigma} = -k_a\nu(\sigma, t) + k_b\mu(\sigma, t). \quad (\text{B2})
\end{aligned}$$

The initial conditions are

$$\nu(r, t=0) = 0 \quad \text{and} \quad \mu(r, t=0) = \frac{1}{4\pi\sigma^2} \delta(r-\sigma). \quad (\text{B3})$$

Then, solving the set of algebraic equations for Laplace transformations $\tilde{\nu}(r, s)$ and $\tilde{\mu}(r, s)$, following from Eqs. (B1), (B2), (B3), we obtain the survival probability for a pair AB^* at time $t \rightarrow \infty$:

$$\begin{aligned}
\varphi(\sigma) &= \int 4\pi r^2 \mu(r, \infty) dr \\
&= \lim_{s \rightarrow 0} \int 4\pi r^2 s \tilde{\mu}(r, s) dr \\
&= \frac{1 + k_a/(k_D/(1 + \sqrt{\tau_d/\tau_A}))}{1 + k_b/k_D + k_a/(k_D/(1 + \sqrt{\tau_d/\tau_A}))}, \quad (\text{B4})
\end{aligned}$$

where $\tau_d = \sigma^2/D$.

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