

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/51839430>

# Screening of Exciplex Formation by Distant Electron Transfer

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · NOVEMBER 2011

Impact Factor: 2.69 · DOI: 10.1021/jp202920m · Source: PubMed

---

CITATION

1

---

READS

21

## 3 AUTHORS:



[S. G. Fedorenko](#)

Russian Academy of Sciences

26 PUBLICATIONS 204 CITATIONS

SEE PROFILE



[Svetlana Khokhlova](#)

Georgia Institute of Technology

10 PUBLICATIONS 22 CITATIONS

SEE PROFILE



[Anatoly Israel Burshtein](#)

Weizmann Institute of Science

216 PUBLICATIONS 3,131 CITATIONS

SEE PROFILE

## Screening of Exciplex Formation by Distant Electron Transfer

S. G. Fedorenko

Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russia

S. S. Khokhlova and A. I. Burshtein\*

Weizmann Institute of Science, 76100 Rehovot, Israel

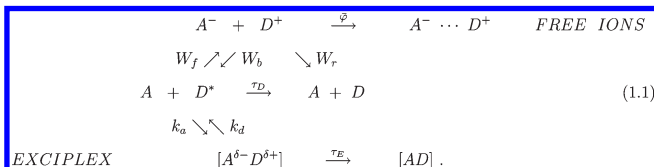
**ABSTRACT:** The excitation quenching by reversible exciplex formation, combined with irreversible but distant electron transfer, is considered by means of the integral encounter theory (IET). Assuming that the quenchers are in great excess, the set of IET equations for the excitations, free ions, and exciplexes is derived. Solving these equations gives the Laplace images of all these populations, and these are used to specify the quantum yields of the corresponding reaction products. It appears that diffusion facilitates the exciplex production and the electron transfer. On the other hand the stronger the electron transfer is, the weaker is the exciplex production. At slow diffusion the distant quenching of excitations by ionization prevents their reaching the contact where they can turn into exciplexes. This is a screening effect that is most pronounced when the ionization rate is large.

## 1. INTRODUCTION

The earliest theory of fluorescence quenching in liquid solutions goes back to the classical Smoluchowski model of contact reaction between excitations and quenchers during their diffusional encounters.<sup>1</sup> For a very long time and even now this is the most popular model of similar reactions.<sup>2–6</sup> However, in 1964 a few groups in Russia almost simultaneously proposed a new approach allowing us to account for the reactions proceeding at any distance  $r$  with the rate  $W(r)$ .<sup>7</sup> It proves itself to be very efficient in the study of distant energy and electron transfer and very soon became known as differential encounter theory (DET).<sup>8–10</sup> This theory and its numerous applications reviewed in ref 11 are considered either solely distant reactions (with reflecting boundary condition) or contact alone (with absorbing boundary conditions) but never both of them together. There were only a few exception from this rule published simultaneously in refs 12 and 13. There was obtained the analytical solution of the problems by means of DET but the most essential effect of parallel reactions interference was screened out. Only recently was this phenomenon titled "screening effect" disclosed in ref 14. The distant quenching of an excited electron donor,  $D^*$ , by charge transfer to an electron acceptor,  $A$ , which precedes the irreversible contact reaction between them, makes this reaction impossible provided the charge transfer is under diffusion control. The letter proceeds in reaction layer of radius  $R_Q$ , which exceeds the contact one ( $\sigma$ ), making impossible penetration of excited reactants inside this layer and their approach of contact where they can react. In such a situation one can ignore the contact reaction at all restricting to distant quenching alone, as was actually done many times.<sup>11</sup> Unfortunately, using DET, one can consider only irreversible reactions either distant or contact. The natural contact reaction of exciplex formation cannot be

included in such a consideration because it is reversible in principle (see chapter VD in ref 15). To make it possible, the unified theory (UT) was heuristically extended and employed to confirm the existence of the screening effect in the reaction of distant (though irreversible) electron transfer competing with contact (reversible) exciplex formation.<sup>16</sup>

To account also for the reversibility of distant reaction, one has to employ the more consistent integral encounter theory commonly used for such goals.<sup>15</sup> The most general reaction of energy quenching by distant electron transfer and contact exciplex formation, followed by charge recombination or separation and exciplex decay, has the following reaction scheme, borrowed from ref 17:



All position dependent electron transfer rates represented here are assumed to be the exponential function of distance, peculiar to the normal Marcus region:

$$\begin{aligned} W_f(r) &= W_0 e^{-2(r-\sigma)/L} & W_b(r) &= W_{b0} e^{-2(r-\sigma)/L} \\ W_r(r) &= W_{r0} e^{-2(r-\sigma)/l} \end{aligned} \quad (1.2)$$

where  $\sigma$  is the contact distance and  $L$  and  $l$  are tunneling lengths for reversible electron transfer and irreversible charge recombination.

**Received:** March 29, 2011

**Revised:** May 12, 2011

**Published:** November 29, 2011

The contact exciplex formation and dissociation are given by the corresponding rate constant,  $k_a$  and  $k_d$ . The lifetimes of excitation and exciplex are  $\tau_D$  and  $\tau_E$ , respectively. The yield of ion separation is  $\phi$ , and their recombination in the bulk (to the ground states) is determined by the rate constant  $k_r$ .

In the previous paper<sup>17</sup> we considered by means of IET the full reaction scheme (1.1) but lost the screening effect using the contact approximation for all distant reactions. In such an approximation all position dependent rates are represented by their kinetic rate constant:

$$k_f = \int dr W_f(r) \quad k_b = \int dr W_b(r) \quad k_r = \int dr W_r(r) \quad (1.3)$$

Here we are going to solve the same problem, but by employing in IET the exponential transfer rates (1.2), thus restoring the screening effect, which is rather pronounced in highly viscous solutions where the distant transfer is under diffusion control.

## II. MECHANISM OF REACTION AND KINETIC EQUATIONS

In the kinetic limit (at the highest solute mobilities) the kinetic equations for all the reactant concentrations  $[X_i]_t$  do not depend on their diffusion but take the following simplest form:

$$\begin{aligned} \frac{d[D^*]_t}{dt} = & -(k_f + k_a)[D^*]_t[A]_t + k_b[D^+]_t[A^-]_t \\ & + k_d[E]_t - \frac{[D^*]_t}{\tau_D} \end{aligned} \quad (2.1a)$$

$$\frac{d[A]_t}{dt} = -(k_f + k_a)[D^*]_t[A]_t + (k_b + k_r)[D^+]_t[A^-]_t + (k_d + \tau_E^{-1})[E]_t \quad (2.1b)$$

$$\frac{d[D^+]_t}{dt} = \frac{d[A^-]_t}{dt} = k_f[D^*]_t[A]_t - (k_b + k_r)[D^+]_t[A^-]_t \quad (2.1c)$$

$$\frac{d[D]_t}{dt} = k_r[D^+]_t[A^-]_t + \frac{[D^*]_t}{\tau_D} + \frac{[E]_t}{\tau_E} \quad (2.1d)$$

$$\frac{d[E]_t}{dt} = k_a[D^*]_t[A]_t - (k_d + \tau_E^{-1})[E]_t \quad (2.1e)$$

There are two evident conservation laws for donors and accepts in all their modifications:

$$\begin{aligned} [D^*]_t + [D^+]_t + [D]_t + [E]_t &= \text{const} \\ [A^-]_t + [A]_t + [E]_t &= \text{const} \end{aligned} \quad (2.2)$$

Therefore, we can keep only three equations, for example, eqs 2.1a, 2.1c, and 2.1e, because others are dependent.

In the general case of moderate mobilities the multiparticle correlations have to be taken into consideration. Formally exact kinetic equations for the concentrations  $[X_i]_t$  we can get easily, by introducing the deviations of the pair distribution functions  $\rho_{ij}(r,t)$  from the chemical kinetics value<sup>18</sup> ( $\pi$ -forms):  $P_{ij}(r,t) = \rho_{ij}(r,t) - [X_i]_t[X_j]_t$ .

The formally exact equations for the independent reactants take the form

$$\begin{aligned} \frac{d[D^*]_t}{dt} = & -(k_f + k_a)[D^*]_t[A]_t - k_a P_{D^*A}(\sigma, t) \\ & - \int dr W_f(r) P_{D^*A}(r, t) + k_b[D^+]_t[A^-]_t \\ & + \int dr W_b(r) P_{D^+A^-}(r, t) + k_d[E]_t - \frac{[D^*]_t}{\tau_D} \end{aligned} \quad (2.3)$$

$$\begin{aligned} \frac{d[D^+]_t}{dt} = \frac{d[A^-]_t}{dt} = & k_f[D^*]_t[A]_t \\ & + \int dr W_f(r) P_{D^*A}(r, t) - (k_b + k_r)[D^+]_t[A^-]_t \\ & - \int dr [W_b(r) + W_r(r)] P_{D^+A^-}(r, t) \end{aligned} \quad (2.4)$$

$$\frac{d[E]_t}{dt} = k_a([D^*]_t[A]_t + P_{D^*A}(\sigma, t)) - (k_d + \tau_E^{-1})[E]_t \quad (2.5)$$

where the correlation forms,  $P_{ij}$ , obey the infinite set of coupling equations, describing the behavior of a many-particle reacting system. Initially, the reactants are randomly distributed, so  $P_{ij}(r, t=0) = 0$ . Later on, correlations are accumulated with time due to chemical reactions.

In the simplest approximation corresponding to IET,<sup>17</sup> all three-particle correlations in the equations for  $\pi$ -forms of the reacting pairs are neglected. As a result, we have the following coupled equations involving two-particle correlations only:

$$\begin{aligned} \frac{\partial}{\partial t} P_{D^*A}(r, t) = & D \nabla^2 P_{D^*A}(r, t) - (W_f(r) + \tau_D^{-1}) P_{D^*A}(r, t) \\ & + W_b(r) P_{D^+A^-}(r, t) - W_f(r) [D^*]_t[A]_t + W_b(r) [D^+]_t[A^-]_t \end{aligned} \quad (2.6)$$

$$\begin{aligned} \frac{\partial}{\partial t} P_{D^+A^-}(r, t) = & D \nabla^2 P_{D^+A^-}(r, t) + W_f(r) P_{D^*A}(r, t) \\ & - [W_b(r) + W_r(r)] P_{D^+A^-}(r, t) + W_f(r) [D^*]_t[A]_t \\ & - [W_b(r) + W_r(r)] [D^+]_t[A^-]_t \end{aligned} \quad (2.7)$$

where  $D$  is an encounter diffusion coefficient that is assumed to be the same for neutral and charged particles ( $D = D_{D^*A} = D_{D^+A^-}$ ) and the solvent polarity is so high that Coulomb attraction is neglected. The contact association–dissociation reactions are included in the boundary conditions for the contact:

$$4\pi\sigma^2 D \left. \frac{\partial P_{D^*A}}{\partial r} \right|_{r=\sigma} = k_a([D^*]_t[A]_t + P_{D^*A}(\sigma, t)) - k_d[E]_t \quad (2.8)$$

$$4\pi\sigma^2 D \left. \frac{\partial P_{D^+A^-}}{\partial r} \right|_{r=\sigma} = 0 \quad (2.9)$$

Hence, we have to solve two coupled eqs 2.6 and 2.7 with the boundary conditions (eqs 2.8 and 2.9) for  $P_{ij}(r=\sigma)$  and the condition of correlation vanishing at a large distance:  $P_{ij}(r \rightarrow \infty, t) = 0$ .

After solving the boundary problem (eqs 2.6–2.9), we can represent eqs 2.3–2.5 in a form of kinetic equations of the

integral encounter theory:

$$\begin{aligned} \frac{d[D^*]_t}{dt} = & - \int_0^t d\tau R_1(t-\tau)[D^*]_\tau[A]_\tau + \int_0^t d\tau R_2(t-\tau)[E]_\tau \\ & + \int_0^t d\tau R_3(t-\tau)[D^+]_\tau[A^-]_\tau - \frac{[D^*]_t}{\tau_D} \quad (2.10) \end{aligned}$$

$$\begin{aligned} \frac{d[D^+]_t}{dt} = & \int_0^t d\tau R_4(t-\tau)[D^*]_\tau[A]_\tau + \int_0^t d\tau R_5(t-\tau)[E]_\tau \\ & - \int_0^t d\tau R_6(t-\tau)[D^+]_\tau[A^-]_\tau \quad (2.11) \end{aligned}$$

$$\begin{aligned} \frac{d[E]_t}{dt} = & \int_0^t d\tau R_7(t-\tau)[D^*]_\tau[A]_\tau - \int_0^t d\tau R_8(t-\tau)[E]_\tau \\ & + \int_0^t d\tau R_9(t-\tau)[D^+]_\tau[A^-]_\tau - \frac{[E]_t}{\tau_E} \quad (2.12) \end{aligned}$$

where the kernels are defined by the solution of eqs 2.6 and 2.7. For the particular case of the contact transfer reaction, the corresponding kernels were calculated in ref 17.

Note that in contrast to the kinetic equations (2.1a), (2.1c), and (2.1e) the general equations contain the additional second term in the right-hand side of eq 2.11 and a third term in the right-hand side of eq 2.12. The former represents the exciplex dissociation into ions due to ionization of the neutral products of its initial dissociation. The slow diffusion leaves no time for the immediate separation of neutral products, thus allowing for their ionization during the same encounter. The latter term represents the inverse process of fast association into the exciplex of the neutral products of the initial charge recombination. This is an essential feature of a reversible multistage reaction running under diffusional control.

Thus we have obtained the closed mathematical formulation of the problem corresponding to reaction scheme 1.1. The solution of the boundary problem (eqs 2.6–2.9) allows one to express the  $\pi$ -forms of the reacting pairs  $P_{ij}(r,t)$  in terms of concentrations  $[X_i]_t$ . Then, the substitution of these expressions into eqs 2.3–2.5 and the necessary integration yields the closed kinetic equations. Their solution determine the required change in  $[X_i]_t$  concentration with time.

### III. IRREVERSIBLE PHOTO-IONIZATION VERSUS EXCIPLEX FORMATION

In this section we set  $W_b = 0$ , making remote ionization irreversible and looking for its competition with the reversible contact exciplex formation. We will also consider the ions accumulation (yield) neglecting their recombination ( $W_r = 0$ ).

For further consideration, the following dimensionless variables are introduced:

$$\begin{aligned} N^*(t) &= \frac{[D^*]_t}{[D^*]_0} & N_P(t) &= \frac{[D^+]_t}{[D^*]_0} = \frac{[A^-]_t}{[D^*]_0} \\ N_E(t) &= \frac{[E]_t}{[D^*]_0} \end{aligned} \quad (3.1)$$

where  $[D^*]_0$  is the initial concentration of  $[D^*]_t$ . It is also assumed that the concentration of the ground state acceptors is time independent ( $[A]_t \approx [A]_0 = c$ ) because they are present in great excess.

After that, we obtain from eqs 2.3–2.5 the set of linearized kinetic equations

$$\dot{N}^* = -c(k_f + k_a)N^* - k_a P(\sigma, t) - \int dr W_f(r) P(r, t) + k_d N_E - \frac{N^*}{\tau_D} \quad (3.2)$$

$$\dot{N}_P = ck_f N^* + \int dr W_f(r) P(r, t) \quad (3.3)$$

$$\dot{N}_E = k_a(cN^* + P(\sigma, t)) - (k_d + \tau_E^{-1})N_E \quad (3.4)$$

They contain a single  $\pi$ -form,  $P(r, t) = P_{D^*A}(r, t)/[D^*]_0$ , which obeys the equation

$$\begin{aligned} \frac{\partial}{\partial t} P(r, t) = & D \nabla^2 P(r, t) - (W_f(r) + \tau_D^{-1})P(r, t) \\ & - cW_f(r) N^*(t) \end{aligned} \quad (3.5)$$

Making the Laplace transformation of eqs 3.2–3.4 and introducing notation for the tunneling flux,

$$J_W(s) = \int dr W_f(r) \tilde{P}(r, s)$$

we obtain the set of algebraic equations:

$$\begin{aligned} s\tilde{N}^*(s) - 1 = & -c(k_f + k_a)\tilde{N}^*(s) - k_a\tilde{P}(\sigma, s) - J_W(s) \\ & + k_d\tilde{N}_E(s) - \frac{\tilde{N}^*(s)}{\tau_D} \end{aligned} \quad (3.6a)$$

$$s\tilde{N}_P(s) = ck_f\tilde{N}^*(s) + J_W(s) \quad (3.6b)$$

$$s\tilde{N}_E(s) = k_a(c\tilde{N}^*(s) + \tilde{P}(\sigma, s)) - (k_d + \tau_E^{-1})\tilde{N}_E(s) \quad (3.6c)$$

where  $\tilde{P}(r, s)$  is a solution for the following boundary problem:

$$\begin{aligned} s\tilde{P}(r, s) = & \frac{D}{r} \frac{d^2}{dr^2} r\tilde{P}(r, s) - [W_f(r) + \tau_D^{-1}]\tilde{P}(r, s) - cW_f(r) \tilde{N}^*(s) \end{aligned} \quad (3.7)$$

$$\begin{aligned} 4\pi\sigma^2 D \left. \frac{d\tilde{P}(r, s)}{dr} \right|_{r=\sigma} &= k_a(c\tilde{N}^*(s) + \tilde{P}(\sigma, s)) - k_d\tilde{N}_E(s) \\ \tilde{P}(r \rightarrow \infty, s) &= 0 \end{aligned} \quad (3.8)$$

**A. Contact  $\pi$ -Form and Tunneling Flux.** To define the functions  $J_W(s)$  and  $\tilde{P}(\sigma, s)$  appearing in the right-hand side of eq 3.6, it is necessary to solve the boundary problem (eqs 3.7–3.8). Equation 3.7 can be converted into an inhomogeneous Bessel equation whose solution can be represented in terms of the modified Bessel functions  $I_\nu(x)$  and  $K_\nu(x)$  (see Appendix):

$$\tilde{P}(r, s) = \frac{\sigma}{r} \left[ AI_\nu(x) + c\tilde{N}^*(s) \frac{L}{\sigma} \varphi_\nu(x) \right] \quad (3.9)$$

here  $x = x_0 \exp(-(r - \sigma)/L)$ , where  $x_0 = L(W_0/D)^{1/2}$ . The integration constant  $A$  is

$$A = \frac{1}{I_\nu(x_0)Z} [k_d \tilde{N}_E(s) - c \tilde{N}^*(s) Z_1] \quad (3.10)$$

where  $k_D = 4\pi\sigma D$  in

$$Z = k_a + k_D \left( 1 + \frac{\sigma x_0}{L} \frac{I'_\nu(x_0)}{I_\nu(x_0)} \right) \quad \text{and} \quad (3.11)$$

$$Z_1 = k_a + (k_a + k_D) \frac{L}{\sigma} \varphi_\nu(x_0) + k_D x_0 \varphi'_\nu(x_0)$$

The function  $\varphi_\nu(x)$  is defined in the Appendix, and the prime denotes its derivation over  $x$  whereas  $I'_\nu(x_0) = (\partial I_\nu(x)/\partial x)|_{x=x_0}$ .

The value of  $\tilde{P}(r,s)$  at the contact radius  $\sigma$  can be obtained after some transformations:

$$\tilde{P}(\sigma,s) = \frac{1}{Z} \left[ k_d \tilde{N}_E(s) - c \tilde{N}^*(s) \left( k_a - k_D \frac{G_\nu(x_0)}{I_\nu(x_0)} \right) \right] \quad (3.12)$$

whereas the tunnelling flux  $J_W(s) = \int dr W_1(r) \tilde{P}(r,s)$  can be obtained after straightforward integration:

$$J_W(s) = -\tilde{N}_E(s) \frac{k_d k_D}{Z} \frac{G_\nu(x_0)}{I_\nu(x_0)} - c \tilde{N}^*(s) k_D \left[ \frac{L}{\sigma} \Phi_\nu(x_0) - \frac{G_\nu(x_0)}{I_\nu(x_0)} \frac{Z_1}{Z} \right] \quad (3.13)$$

where the function  $\Phi_\nu(x_0)$  is

$$\Phi_\nu(x_0) = \int_0^{x_0} y \ln \left( \frac{y}{\lambda} \right) \varphi_\nu(y) dy \quad (3.14)$$

whereas the definition of the function  $G_\nu(x)$  is given in the Appendix.

**B. IET Equations.** After substituting eqs 3.12 and 3.13 into eq 3.6 and collecting like terms, it is easy to obtain the Laplace presentation of the IET kinetic equations at  $N^*(0) = 1$ ,  $N_E(0) = N_P(0) = 0$ :

$$s \tilde{N}^*(s) - 1 = -c \tilde{R}_1(s) \tilde{N}^*(s) + \tilde{R}_2(s) \tilde{N}_E(s) - \frac{\tilde{N}^*(s)}{\tau_D} \quad (3.15a)$$

$$s \tilde{N}_E(s) = c \tilde{R}_7(s) \tilde{N}^*(s) - \tilde{R}_8(s) \tilde{N}_E(s) - \frac{\tilde{N}_E(s)}{\tau_E} \quad (3.15b)$$

$$s \tilde{N}_P(s) = c [\tilde{R}_1(s) - \tilde{R}_7(s)] \tilde{N}^*(s) + [\tilde{R}_8(s) - \tilde{R}_2(s)] \tilde{N}_E(s) \quad (3.15c)$$

Note that only two first equations are independent. Here the kernels defining the contact processes exciplex association/dissociation are

$$\tilde{R}_2(s) = \frac{k_d}{Y} \quad \tilde{R}_7(s) = \frac{k_a}{Y} \quad \tilde{R}_8(s) = \frac{k_d}{Y} \left[ 1 - \frac{G_\nu(x_0)}{Z_2 I_\nu(x_0)} \right] \quad (3.16)$$

where

$$Y = 1 + \frac{k_a - k_D G_\nu(x_0)/I_\nu(x_0)}{k_D Z_2}$$

$$Z_2 = 1 + \frac{\sigma x_0}{L} \frac{I'_\nu(x_0)}{I_\nu(x_0)} + \frac{G_\nu(x_0)}{I_\nu(x_0)} \quad (3.17)$$

The kernel  $\tilde{R}_1(s)$  takes into account both processes of the remote ionization and the contact exciplex association:

$$\tilde{R}_1(s) = k_f + k_D \left[ \frac{Z_1}{Z} \frac{G_\nu(x_0)}{I_\nu(x_0)} - \frac{L}{\sigma} \Phi_\nu(x_0) \right] + \tilde{R}_7(s) \quad (3.18)$$

Finally, the solution of the system (3.15) can be represented in the following form:

$$\tilde{N}^*(s) = \frac{1}{s + \tau_D^{-1} + c \tilde{\Sigma}(s)} \quad (3.19a)$$

$$\tilde{N}_E(s) = \frac{c \tilde{R}_7(s)}{s + \tau_E^{-1} + \tilde{R}_8(s)} \tilde{N}^*(s) \quad (3.19b)$$

$$\tilde{N}_P(s) = \frac{c}{s} \left[ \tilde{R}_1(s) - \tilde{R}_7(s) \frac{s + \tau_E^{-1} + \tilde{R}_2(s)}{s + \tau_E^{-1} + \tilde{R}_8(s)} \right] \tilde{N}^*(s) \quad (3.19c)$$

where

$$\tilde{\Sigma}(s) = \tilde{R}_1(s) - \frac{\tilde{R}_2(s) \tilde{R}_7(s)}{s + \tau_E^{-1} + \tilde{R}_8(s)} \quad (3.20)$$

For the recovery of the reaction kinetics  $N^*(t)$ ,  $N_E(t)$ , and  $N_P(t)$  one has to make the inverse Laplace transformation of eqs 3.19.

In the limit of contact ionization, ( $L \rightarrow 0$ ,  $W_0 \rightarrow \infty$ ,  $k_f = 2\pi\sigma^2 L W_0 = \text{const}$ ), all the kernels (3.16) and (3.18) can be rewritten in the following form

$$\tilde{R}_1(s) = \frac{k_f + k_a}{Y} \quad \tilde{R}_2(s) = \frac{k_d}{Y} \quad \tilde{R}_7(s) = \frac{k_a}{Y}$$

$$\tilde{R}_8(s) = \frac{k_d}{Y} \left( 1 + \frac{k_f}{s_1 \tilde{k}_D(s_1)} \right) \quad (3.21)$$

obtained earlier in ref 17 where

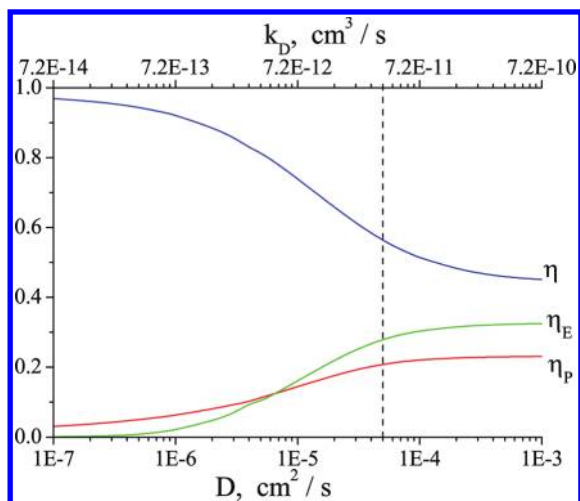
$$Y = 1 + \frac{k_f + k_a}{s_1 \tilde{k}_D(s_1)} \quad \tilde{k}_D(s) = \frac{k_D}{s} \left( 1 + \sigma \sqrt{\frac{s}{D}} \right)$$

$$s_1 = s + \tau_D^{-1} \quad (3.22)$$

Note that the last term in the right-hand side of eq 3.15c for  $\tilde{N}_P(s)$  describes the transformation of exciplex into ion products, via preliminary exciplex dissociation into the neutral reactants  $D^*$  and A. The rate of this reaction in contact approximation,

$$\tilde{R}_8(s) - \tilde{R}_2(s) = \frac{k_d}{Y} \frac{k_f}{s_1 \tilde{k}_D(s_1)} \quad (3.23)$$

tends to zero in a high mobility limit, only when the fast separation of  $D^*$  and A prevents their ionization. The same is true for remote ionization eq 3.16.



**Figure 1.** Diffusional dependence of the fluorescence, exciplex and ions quantum yields at  $\tau_D = 10$  ns,  $\tau_E = 2\tau_D$ , and  $c = 0.01$  M. The other parameters are mentioned in the text.

**C. Quantum Yields of the Quenching Products.** The excitation quantum yield,  $\eta$ , exciplex quantum yield,  $\eta_E$ , and the share (fraction) of ions,  $\eta_P$ , can be specified from eqs 3.19:

$$\eta = \frac{\tilde{N}^*(0)}{\tau_D} = \frac{1}{1 + c\tau_D\kappa} \quad (3.24)$$

$$\eta_E = \frac{\tilde{N}_E(0)}{\tau_E} = \tau_D \eta \frac{\phi_E}{\tau_E} \quad (3.25)$$

$$\eta_P = \lim_{s \rightarrow 0} s\tilde{N}_P(s) = \tau_D \eta \{c[\tilde{R}_1(0) - \tilde{R}_7(0)] + \phi_E[\tilde{R}_8(0) - \tilde{R}_2(0)]\} \quad (3.26)$$

Here

$$c\kappa = c\tilde{\Sigma}(0) = c\tilde{R}_1(0) - \phi_E\tilde{R}_2(0) \quad (3.27)$$

where  $\kappa$  is the Stern–Volmer constant, whereas the share of exciplexes generated from the excitations related to their total amount is defined as follows:

$$\phi_E = \frac{\tilde{N}_E(0)}{\tilde{N}^*(0)} = \frac{c\tilde{R}_7(0)}{\tau_E^{-1} + \tilde{R}_8(0)} \quad (3.28)$$

When calculating all these quantities, we have to choose some particular values of the main variables, which are in our case

$$\tau_D = 10 \text{ ns} \quad \text{and} \quad k_a = 37700 \text{ Å}^3/\text{ns} \quad (3.29)$$

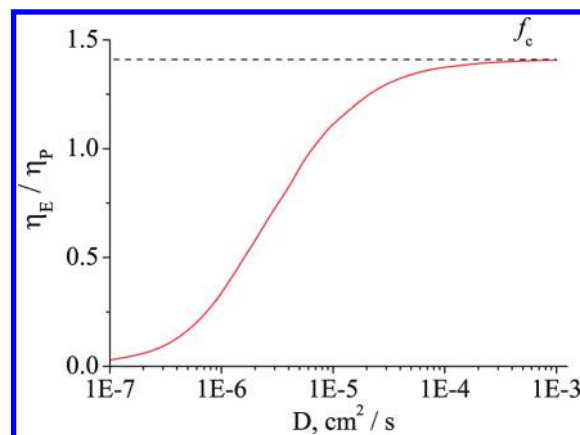
Then<sup>20,21</sup>

$$\frac{1}{\tau_E} = \frac{1}{\tau_D} \frac{1}{1 + (\Delta E_-/V)^2} \quad (3.30)$$

where the energy of the exciplex  $\Delta E_-$  is related to the ionization energy  $\Delta G_i$  as follows

$$\Delta E_- = \Delta G_i/2 - \sqrt{(\Delta G_i/2)^2 + V^2} \quad (3.31)$$

and  $V$  is an interaction between the exciplex and ion pair states.



**Figure 2.** Diffusional dependence of the ratio of exciplex and ion quantum yields at  $\tau_D = 10$  ns. The rest of the parameters are the same as in Figure 1 ( $f_c \approx 1.41$ ).

The equilibrium constant of exciplex formation in a spherical reaction layer of radius  $\sigma$  and the width  $\Delta$  is

$$K = k_a/k_d = 4\pi\sigma^2\Delta e^{-\Delta E_-/T} \quad (3.32)$$

It allows us to find  $k_d$  corresponding to chosen value of  $k_a$ , as  $\Delta E_-$  is known (we use the system of units assuming  $k_B = 1$ ,  $T = 0.025$  eV). Assuming  $\Delta G_i = 0$ ,  $V = 0.2$  eV,  $\Delta = 0.6$  Å, and  $\sigma = 6$  Å, we obtain

$$\tau_E = 20 \text{ ns} \quad \text{and} \quad k_d = 0.1 \text{ ns}^{-1} \quad (3.33)$$

For distant electron transfer in the normal Marcus region (at  $\Delta G_i = 0$ ) we accept the exponential transfer rate  $W_f(r)$  given in eq 1.2 assuming  $L = 1.5$  Å and  $W_0 = 20 \text{ ns}^{-1}$ .

The relationship between the contact and remote products of the excitation quenching reaction,

$$\frac{\eta_E}{\eta_P} = \frac{1}{\tau_E} \{c[\tilde{R}_1(0) - \tilde{R}_7(0)]/\phi_E + [\tilde{R}_8(0) - \tilde{R}_2(0)]\}^{-1} \quad (3.34)$$

depends on the encounter diffusion  $D$ , whereas in the model considered in ref 17, where both competing reactions were assumed to be contact, the similar ratio,

$$f_c = \frac{k_a}{k_f(1 + k_d\tau_E)} \quad (3.35)$$

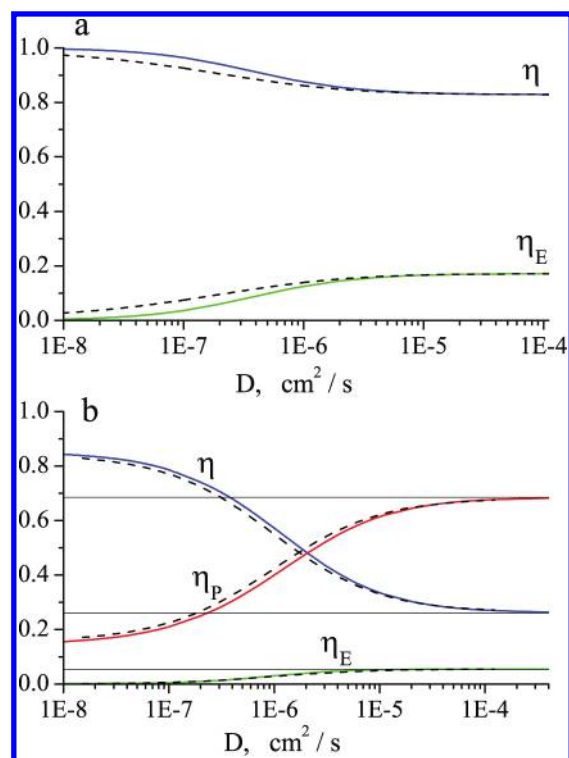
is diffusion independent. In fact, this is the upper limit of the true ratio achieved at infinitely fast diffusion:  $f_c = \lim_{D \rightarrow \infty} (\eta_E/\eta_P)$ . At so fast and even moderate diffusion where the reaction is under kinetic control (to the right of the vertical dashed line in Figure 1) the yield of the exciplexes at chosen parameters is larger than that of ions. In the limit  $D \rightarrow \infty$  the values  $\eta$ ,  $\eta_E$ , and  $\eta_P$  tend to their kinetic limits:

$$\eta \rightarrow [1 + c\tau_D k_f(1 + f_c)]^{-1} \quad (3.36a)$$

$$\eta_E \rightarrow c\tau_D k_f f_c \eta \quad (3.36b)$$

$$\eta_P \rightarrow c\tau_D k_f \eta \quad (3.36c)$$





**Figure 3.** Quantum yields of competing reactions of contact exciplex formation and fluorescence in the absence (a) and presence (b) of excitation quenching by distant ionization. The present theory is represented by solid lines, and the dashed lines were obtained with UT.<sup>16</sup> The rest of the parameters are  $\sigma = 6 \text{ \AA}$ ,  $L = 1.5 \text{ \AA}$ ,  $c = 0.1 \text{ M}$ ,  $k_a = 500 \text{ \AA}^3/\text{ns}$ ,  $k_d = 0.03 \text{ ns}^{-1}$ ,  $W_0 = 10 \text{ ns}^{-1}$ ,  $k_f \approx 4347 \text{ \AA}^3/\text{ns}$ ,  $\tau_E = 15 \text{ ns}$ , and  $\tau_D = 10 \text{ ns}$ .

where

$$k_f = 2\pi W_0(L\sigma^2 + L^2\sigma + L^3/2)$$

In the opposite case, under diffusion control, the distant ionization exhausts the near-contact region, thus screening it from the excitations that can turn into the exciplex. As a result, the yield of the latter approaches zero when  $D \rightarrow 0$  as well as the ratio ( $\eta_E/\eta_P$ ) in Figure 2. In the opposite limit this value reaches the upper limit (3.35). The high diffusion limits of all the yields (3.36) are shown in Figure 3b by the horizontal straight lines, which are approached asymptotically by the corresponding quantities. As far as there is no ionization, only exciplexes are born (at contact) and in greater amounts at faster diffusion. Besides, only they are responsible for the corresponding reduction of the fluorescence yield with diffusion, shown in Figure 3a. This reduction is greatly pronounced when ionization contributes to the excitation quenching (Figure 3b). Simultaneously, the exciplex yield is also reduced, due to the above-described screening effect.

Unlike the previous figures, the parameters of the problem were taken here the same as in our previous paper,<sup>16</sup> where the unified theory (UT) was developed for getting an easier solution to the same problem. The results obtained there are shown in Figure 3 by the dashed lines either for the case of only exciplex formation (a) or in the presence of parallel

ionization by distant electron transfer (b). They appear to be in reasonable agreement with the new ones getting here. The remaining difference can be attributed to the well-known distinction between integral and differential encounter theories stressed in chapter IV of the review<sup>15</sup> and references herein. The former (IET) is employed here whereas the latter (DET) is the base of our UT used for comparison.<sup>16</sup>

#### IV. KINETICS OF EXCITATION QUENCHING AND EXCIPLEX ACCUMULATION–DISSIPATION

It has been shown that the reciprocal yields of reaction products appear to be different at different encounter diffusion. The same is true for the kinetics of their accumulation and dissipation that will be analyzed below for two alternative cases of slow and fast diffusion:  $D = 2 \times 10^{-7} \text{ cm}^2/\text{s}$  and  $D = 2 \times 10^{-5} \text{ cm}^2/\text{s}$ . As a matter of fact, one can obtain this kinetics from the numerical solution of the basic eqs (3.2)–(3.5).

**A. Only Exciplex Formation.** We begin from the simplest case known as Weller scheme I<sup>22,23</sup> when the distant energy quenching is excluded ( $W_f = W_b = 0$ ) as well as ion recombination ( $W_r = k_r = 0$ ). It was considered analytically in section IV.B1 of the preceding work.<sup>17</sup> It was shown there that one has to discriminate between two alternative limits:

- Fast exciplex/excitation equilibration compared to their natural decays (high diffusion, kinetic limit).
- Fast natural decay compared to association and dissociation (slow diffusion, governing the reaction).

The corresponding kinetics is shown in Figure 4a,b, respectively. In the former case the equilibration of reactant populations is reached very soon (during exciplex accumulation) and whereupon both populations decay with the common rate

$$w_0 = \frac{\mathcal{N}}{\tau_D} + \frac{\mathcal{N}_E}{\tau_E} \quad (4.1)$$

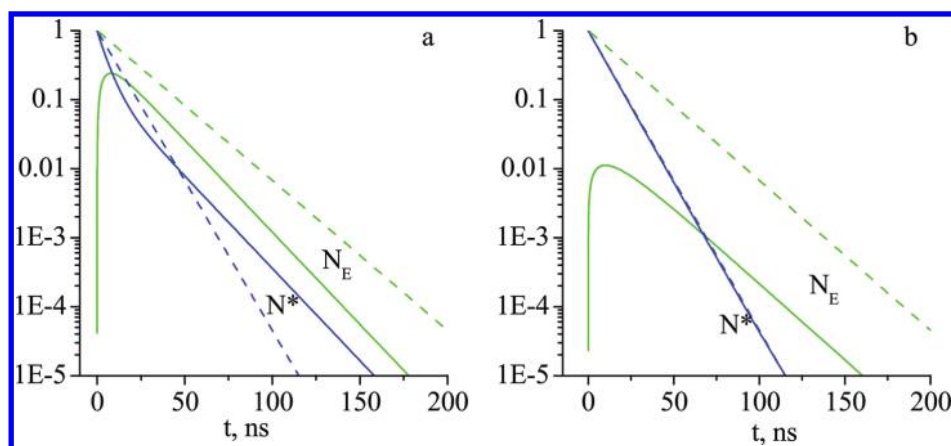
where their decays are weighted with corresponding equilibrium amplitudes,  $N$  and  $N_E$ :

$$\mathcal{N} = \frac{\gamma}{1 + \gamma} \quad \mathcal{N}_E = \frac{1}{1 + \gamma} \quad \gamma = k_d/c k_a \quad (4.2)$$

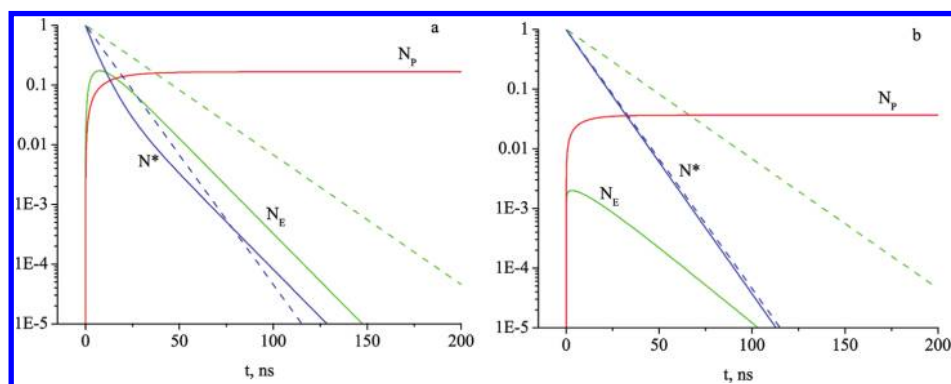
This decay is faster than that of the exciplex but slower than the excitation decay (dotted lines). It is represented by two parallel straight lines (green and blue).

Under diffusion control, both excited reactants decay with their own times after accumulation of exciplexes is accomplished (Figure 4b), but the latter is in a lesser amount than in the kinetic limit (Figure 4a). This is because the rate of diffusional exciplex production though time-dependent is always slower than the initial one, which is kinetic in essence.

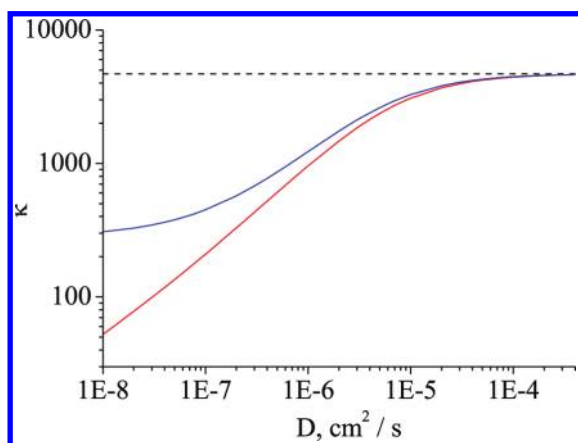
**B. Irreversible Distant Ionization Competing with the Exciplex Formation.** When the irreversible distant electron transfer occurs parallel to the contact exciplex formation, the results are also different at fast and slow encounter diffusion, as shown in Figure 5a,b respectively. In the former case, there is the fast mixing between the excitations and exciplex populations that finally decay with their common rate. In the latter case, each of them vanishes with its own rate though the excitation decay is slightly accelerated by the weak diffusional quenching. As to the ions whose recombination is neglected, their accumulation is faster and larger when diffusion is higher. In the opposite limit



**Figure 4.** Kinetics of excitation quenching  $N^*$  (blue lines) and exciplex formation/dissipation  $N_E$  (green lines) obtained by a numerical Laplace transformation of eq 3.19 with the kernels (3.16) at  $k_f = k_b = 0$  and different diffusion coefficients (a)  $D = 200 \text{ \AA}^2/\text{ns}$  (fast diffusion) and (b)  $D = 2 \text{ \AA}^2/\text{ns}$  (slow diffusion). The rest of the parameters are the same as in Figure 1. The natural decays of excitation and exciplex are represented by corresponding dashed straight lines.



**Figure 5.** Kinetics of excitation quenching  $N^*$  (blue lines), irreversible ion accumulation  $N_P$  (red lines), and exciplex formation/dissipation  $N_E$  (green lines) obtained by a numerical Laplace transformation of eq 3.19 with the kernels (3.16) at different diffusion coefficients (a)  $D = 200 \text{ \AA}^2/\text{ns}$  (fast diffusion) and (b)  $D = 2 \text{ \AA}^2/\text{ns}$  (slow diffusion). The rest of the parameters are the same as in Figure 1. The natural decays are also shown by dashed straight lines.



**Figure 6.** Diffusional dependence of the Stern–Volmer constant in the present theory (blue curve) and in its contact analog calculated from eq 4.9 of ref 17 (red curve). The horizontal dashed line represents the kinetic limit where both the theories are indistinguishable. The rest of the parameters are the same as in Figure 3.

not only the ion density is smaller but also the number of exciplexes is greatly reduced due to screening effect. It is so much

pronounced because there is almost no excitations near the contact at stationary diffusional quenching which is carried out far away.

## V. CONCLUDING REMARKS

The account of the space dependence of the irreversible ionization rate is the major advantage of the present work compared to its precursor,<sup>17</sup> where the electron transfer was considered as a contact one. The difference between distant and contact electron transfer is especially pronounced when it is under diffusion control. In this case, the effective radius of diffusional ionization  $R_Q$  is larger than the contact one,  $\sigma$ , increasing the contribution of ionization into fluorescence quenching. The slower the diffusion, the larger is  $R_Q$  but smaller  $\kappa$  and the predominance of the distant quenching  $\kappa$  over the contact one is maximal (Figure 6).

Another important consequence of the distant irreversible ionization is the screening effect under diffusion control. The quenching of excitation at distance  $R_Q$  far from the contact, prevents them from approaching  $\sigma$  where the exciplex has to be created from the excitations. As a result, the long distance ionization executes the fluorescence quenching, preventing simultaneously the excitation approach to contact.



It is remarkable that all diffusional dependencies of the yields obtained here and represented by the solid curves in Figure 3 are practically the same as those obtained earlier with UT and shown by the dashed lines. This is a manifestation that both theories are similar to each other, provided that the ionization is really an irreversible reaction.

However, in the opposite, endergonic region ( $\Delta G_i \geq 0$ ) the backward electron transfer is comparable or even faster than the forward one ( $W_b \geq W_f$ ). In such a case the efficiency of ionization is greatly reduced together with the screening effect. The present theory allows us to account for the reversible ionization as well as for the irreversible one. This can be done by a numerical solution of eqs 2.3–2.9.

## VI. APPENDIX

Equation 3.7 can be rewritten as an inhomogeneous Bessel equation:

$$x^2 \frac{d^2 z}{dx^2} + x \frac{dz}{dx} - (x^2 + \nu^2)z = -c\tilde{N}^*(s)(s + \tau_D^{-1})Lx^2 \ln \frac{x}{\lambda} \quad (6.1)$$

where

$$\begin{aligned} z &= r(s + \tau_D^{-1})\tilde{P}(r,s) & x &= \lambda e^{-r/L} \\ \lambda &= L\sqrt{\frac{W_0}{D}}e^{\sigma/L} & \nu &= L\sqrt{\frac{s + \tau_D^{-1}}{D}} \end{aligned} \quad (6.2)$$

The solution to the eq 6.1 may be obtained using the method of the parameters variation and written in the form:

$$z(r,s) = A_1 I_\nu(x) + A_2 K_\nu(x) + c\tilde{N}^*(s)(s + \tau_D^{-1})L\varphi_\nu(x) \quad (6.3)$$

where

$$\varphi_\nu(x) = K_\nu(x) G_\nu(x) - I_\nu(x) H_\nu(x) \quad (6.4)$$

and

$$\begin{aligned} G_\nu(x) &= \int_0^x y \ln\left(\frac{y}{\lambda}\right) I_\nu(y) dy \\ H_\nu(x) &= \int_0^x y \ln\left(\frac{y}{\lambda}\right) K_\nu(y) dy \end{aligned} \quad (6.5)$$

The arbitrary constants,  $A_1$  and  $A_2$ , were found from the boundary conditions: the boundary condition at  $r \rightarrow \infty$  gives  $A_2 = 0$ , whereas the value of  $A_1$  is defined from the contact boundary condition ( $r = \sigma$ ). Using the solution 6.3 in the expression  $\tilde{P}(r,s) = z(r,s)/r(s + \tau_D^{-1})$  given in eq 6.2, the latter can be represented in the form given earlier in eqs 3.9–3.11.

It is easy to show that the derivative  $\varphi'_\nu(x)$  used in eq 3.11 can be presented as follows:

$$\varphi'_\nu(x) = K'_\nu(x) G_\nu(x) - I'_\nu(x) H_\nu(x)$$

## REFERENCES

- (1) Smoluchowski, M. V. Z. *Phys. Chem.* **1917**, 92, 129–168.
- (2) Collins, F. C.; Kimball, G. E. *J. Colloid Sci.* **1949**, 4, 425–437.
- (3) Waite, T. R. *J. Chem. Phys.* **1958**, 28, 103–106.
- (4) Noyes, R. M. In *Progress of reaction kinetics*; Porter, G., Ed.; Pergamon Press: London, 1961; Vol. 1, pp 129–160.
- (5) Gosele, U. M. In *Progress of reaction kinetics*; Jennings, K. R., Cundall, R. B., Margerum, D. W., Eds.; Pergamon Press: New York, 1984; Vol. 13, pp 63–161.
- (6) Rice, S. A. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1985; Vol. 25, p 404.
- (7) Tunitskii, N. N.; Bagdasar'yan, Kh. S. *Opt. Spectrosc.* **1963**, 15, 303. Kilin, S. F.; Mikhelashvili, M. S.; Rozman, I. M. *Opt. Spectrosc.* **1964**, 16, 576. Vasil'ev, I. I.; Kirsanov, B. P.; Krongaus, V. A. *Kinet. Kataliz* **1964**, 5, 792.
- (8) Steinberg, I. Z.; Katchalsky, E. *J. Chem. Phys.* **1968**, 48, 2404–2410.
- (9) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1973**, 58, 4009–4019.
- (10) Doktorov, A. B.; Burshtein, A. I. *Sov. Phys. JETP* **1975**, 41, 671–677.
- (11) Burshtein, A. I. *Adv. Chem. Phys.* **2000**, 114, 419–587.
- (12) Pilling, M. J.; Rice, S. A. *J. Chem. Soc., Faraday Trans. 2* **1975**, 71, 1563–1571.
- (13) Berlin, Yu. A. *Dokl. Akad. Nauk SSSR* **1975**, 223, 625.
- (14) Khokhlova, S. S.; Burshtein, A. I. *Chem. Phys.* **2010**, 376, 69.
- (15) Burshtein, A. I. *Adv. Chem. Phys.* **2004**, 129, 105.
- (16) Khokhlova, S. S.; Burshtein, A. I. *J. Chem. Phys. A* **2010**, 114, 11506–11512.
- (17) Fedorenko, S. G.; Burshtein, A. I. *J. Phys. Chem. A* **2010**, 114, 4558–4569.
- (18) Kipriyanov, A. A.; Igoshin, O. V.; Doktorov, A. B. *Physica A* **1999**, 268, 567–606.
- (19) Gopich, I. V.; Szabo, A. *J. Chem. Phys.* **2002**, 117, 507–517.
- (20) Ivanov, A. I.; Burshtein, A. I. *J. Phys. Chem. A* **2008**, 112, 11547–11558.
- (21) Kuzmin, M. G. *J. Photochem. Photobiol. A* **1996**, 102, 51–57.
- (22) Weller, A. Z. *Phys. Chem. Neue Folg.* **1982**, 130, 129–138.
- (23) Weller, A.; Staerk, H.; Treichel, R. *Faraday Discuss. Chem.* **1984**, 78, 271–278.

## ACKNOWLEDGMENT

S.S.K. gratefully acknowledges the Chemical Physics Faculty of the Weizmann Institute of Science for its hospitality and the Russian Ministry of Education and Science for financial support (contract nos. P1145 and 14.740.11.0374). S.G.F. is very grateful to the Russian Foundation of Fundamental Research (project 09-03-00456) for the support of this work.