Luminescence Quenching by Reversible Ionization or Exciplex Formation/Dissociation

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The kinetics of fluorescence quenching by both charge transfer and exciplex formation is investigated, with an emphasis on the reversibility and nonstationarity of the reactions. The Weller elementary kinetic scheme of bimolecular geminate ionization and the Markovian rate theory are shown to lead to identical results, provided the rates of the forward and backward reactions account for the numerous recontacts during the reaction encounter. For excitation quenching by the reversible exciplex formation, the Stern−Volmer constant is specified in the framework of the integral encounter theory. The bulk recombination affecting the Stern−Volmer quenching constant makes it different for pulse excited and stationary luminescence. The theory approves that the free energy gap laws for ionization and exciplex formation are different and only the latter fits properly the available data (for lumiflavin quenching by aliphatic amines and aromatic donors) in the endergonic region.

I. Introduction

The quantum yield of A^* fluorescence in liquid solutions is conventionally described by the Stern−Volmer law

$$\eta = \frac{1}{1 + c\kappa\tau_A} \qquad (1.1)$$

where c is the concentration of quenchers assumed to be reasonably small, while τ_A is the lifetime of the excitation in the absence of them. When the quenching is carried out by electron transfer from electron donor D to excited acceptor, A^*, it is expected that the Stern−Volmer constant dependence on the free energy of ionization, $\kappa(\Delta G_i)$ should reproduce the free energy gap (FEG) law established by Marcus for the elementary rate of electron transfer.[1] This expectation was not confirmed by a crucial experiment by Rehm and Weller[2] who found that the top of the predicted FEG parabola is cut by a plateau, later on recognized as a diffusional one.[3] Still it remained unclear why this plateau is extended so far in the exergonic region. This was the long standing Rehm−Weller paradox that was subjected to a number of hypothetical explanations. Finally it was proved that even the most exergonic reaction is really under diffusion control.[4] Since the Rehm−Weller paradox takes place in the highly exergonic region ($-\Delta G_i \ll k_BT$), the transfer there is actually irreversible and for that a non-Markovian theoretical description of the unified theory (UT) was actually used.[5]

Here we concentrate on another paradox in the opposite, near resonant and even endergonic region, where the reversibility of electron transfer can not be ignored. Here only the integral encounter theory (IET) should be employed since it is the only theory capable of accounting for the electron transfer reversibility and the transient effects.[6] The reversible charge separation can be interrupted by either recombination to the ground state or formation of exciplex, ruined by its luminescence. In both cases such processes control the reaction when it becomes too slow, shifting the descending branch of the curve left or right. Such an effect found recently in charge transfer reactions was called “the multiple Rehm−Weller” effect[7] first explained in ref.[8] Now we are going to do the same for quenching by the exciplex formation and compare both phenomena, having qualitatively different $\kappa(\Delta G_i)$ dependence. Assuming that the transfer in any case is contact, the problem is solved analytically, even taking into account the spin-conversion in radical-ion pairs and the reversible production of triplet excitations.

It is shown in section II that the elementary kinetic scheme of bimolecular geminate ionization (Weller) and the Markovian rate theory of the same give identical results, provided that the forward and backward rates similarly account for the numerous recontacts during the reactant encounter. The same relationship exists also for the rate constants of exciplex association/dissociation. It was first pointed out by Berg, studying reversible complex dissociation and extended to exciplex dissociation in section III by means of non-Markovian IET. There the exciplex separation into counterions or neutral (excited) particles was studied and the Berg results for stable complex dissociation were confirmed. In section IV the IET is applied to the quenching of excitation by reversible exciplex formation and the free energy dependence of the Stern−Volmer quenching constant is specified. The rest of this article is devoted to the quenching of photoexcitation by bimolecular ionization. In section V, it is just the geminate one which proceeds in diluted solutions and in restricted time interval after δ-pulse excitation. In the next section it is done taking into account the bulk recombination of photogenerated free ions, which takes place in more dense solutions and under stationary illumination. The Stern−Volmer constants are shown to be different for pulse excited and stationary luminescence. In the last section, VII, both the geminate and stationary reactions are considered taking into account the spin states of the ions and recombination products (either singlet or triplet). The yields of the products of the geminate reaction are analytically specified, assuming the incoherent spin conversion in ion pairs and the stationary Stern−Volmer constant is shown to be independent of whether there is or is not the reversible production of triplet excitation.

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II. Markovian (rate) theories

A. Reversible geminate ionization. The archaic reaction scheme for the reversible charge transfer from electron donor (D) to excited acceptor (A*) is usually written as follows:[2]

$$\underset{\downarrow\tau_A}{A^*} + D \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} [A^* \cdots D] \underset{k^*}{\overset{k_{\text{rip}}}{\rightleftharpoons}} [A^- \underset{\downarrow k_r}{\cdots} D^+] \tag{2.1}$$

The Stern−Volmer constant of the impurity quenching carried out by D is

$$\kappa = \frac{k_D}{1 + \dfrac{k_{-D}}{k_{\text{rip}}}\left[1 + \dfrac{k^*}{k_r}\right]} \tag{2.2}$$

Here k_D is the diffusional rate constant of bimolecular formation of the encounter complex [A*• • •D] subjected to monomolecular dissociation (k_{-D}) and charge separation (k_{rip}), as well as radical ion pair (RIP) recombination, to either the excited (k^*) or ground state (k_r) of neutral products. Unfortunately the interparticle distance in a pair [A^-• • •D^+] and its precursor [A*• • •D] remains an enigma and neither of these rates can be specified. As a matter of fact, this distance varies from the minimal (contact) up to infinity and all of the transfer rates are functions of this distance. An adequate description of the remote transfer can be only obtained with differential or integral encounter theories (DET or IET).[6]

The only exception is the contact transfer that can be described by the reduced scheme

$$\underset{I_0\uparrow\downarrow\tau_A}{A^*} + D \underset{k_b}{\overset{k_i}{\rightleftharpoons}} [A^- \underset{\downarrow k_r}{\cdots} D^+] \tag{2.3}$$

The corresponding set of rate equations with time-independent rate constants, constituting the formal basis of the conventional chemical kinetics

$$\frac{dN^*}{dt} = -\left(ck_i + \frac{1}{\tau_A}\right)N^* + k_bP + I_0N \tag{2.4a}$$

$$\frac{dP}{dt} = ck_iN^* - (k_b + k_r)P \tag{2.4b}$$

Here c = [D] is the concentration of donors, N^* = [A*] is the concentration of excited acceptors, I_0 is the rate of the stationary light pumping, N is the ground-state population being unchanged at low light intensity, and $P = [A^-] = [D^+]$ is the concentration of the counterions. This is the Markovian theory:

Getting N_s^* from the stationary solution of eqs 2.4 and using it for the conventional definition of the fluorescence quantum yield

$$\eta = \frac{N_s^*}{I_0N\tau_A} \tag{2.5}$$

we confirm the Stern−Volmer law with the following quenching constant:

$$\kappa = \frac{k_ik_r}{k_b + k_r} \tag{2.6}$$

Here the stationary (Markovian) rate constant of bimolecular ionization

$$k_i = \frac{k_D}{k_0 + k_D}k_0 \tag{2.7}$$

is expressed via the kinetic constant of bimolecular ionization $k_0 = k_{\text{rip}}v$ and the diffusional one, $k_D = 4\pi\sigma D$ (σ is the contact distance, D is the encounter diffusion coefficient, $v = 4\pi\sigma^2\Delta$ is the volume of the reaction layer with a width $\Delta \ll \sigma$). Equation 2.6 is equivalent to the expression 2.2, provided

$$k_D = k_{-D}v \tag{2.8}$$

and

$$k_b = \frac{k_D}{k_0 + k_D}k^* \tag{2.9}$$

The relation 2.8 presumes that there is no potential interaction between reactants reaching and leaving contact by a free diffusion. The nature of the backward rate, eq 2.9, is more complex. It accounts for the numerous recontacts of ions during a single encounter, i.e., for repeated attempts of recombination to the excited state (with rate k^*) which are separated by a diffusional motion in between.

B. Reversible Exciplex Formation. Only a consistent diffusional theory of a reversible contact reaction confirms and clarifies the definition of the multicontact backward transfer rate k_b. In the particular case of reversible exciplex formation, the reaction proceeds according to the following scheme

$$\underset{I_0\uparrow\downarrow\tau_A}{A^*} + D \underset{k_b}{\overset{k_i}{\rightleftharpoons}} [A^{-\delta}\underset{\downarrow\tau_{\text{exc}}}{}D^{+\delta}] \tag{2.10}$$

The rate equations similar to (2.4a) describe the time evolution of the excited-state and exciplex populations

$$\frac{dN^*}{dt} = -\left(ck_i + \frac{1}{\tau_A}\right)N^* + k_bN^e + I_0N \tag{2.11a}$$

$$\frac{dN^e}{dt} = ck_iN^* - (k_b + 1/\tau_{\text{exc}})N^e \tag{2.11b}$$

Here N^e is the concentration of exciplexes, while

$$k_i = k_a\frac{k_D}{k_a + k_D} \tag{2.12a}$$

$$k_b = k_d\frac{k_D}{k_a + k_D} \tag{2.12b}$$

where $k_a = k_{\text{exc}}v$ is the kinetic rate constant of exciplex formation (analog of k_0) but for association and k_d is the rate of a single exciplex dissociation (analog of k^*).

The fluorescence quantum yield may be obtained from either the stationary experimental data, from eq 2.5, or from the δ-pulse excitation providing the quenching kinetics $N^*(t)$ is traced up to complete decay of A*. Setting $I_0 = 0$ in eqs 2.11 and solving them with the initial condition

$$N^*(0) = 1 \qquad N^e(0) = 0 \tag{2.13}$$

one can get the fluorescence quantum yield integrating $N^*(t)$ over time

$$\eta = \int_0^\infty N^*(t)\,dt/\tau_A = \tilde{N}^*(0)/\tau_A \tag{2.14}$$

where the tilde denotes the Laplace transformation

$$\tilde{N}(s) = \int_0^\infty e^{-st}N(t)\,dt \tag{2.15}$$

Expression 2.14 is actually the Stern−Volmer dependence 1.1 with

$$\kappa = \frac{k_i}{1 + k_\mathrm{b}\tau_\mathrm{exc}} = \begin{cases} k_i & \text{irreversible charge separation} \quad k_\mathrm{b}\tau_\mathrm{exc} \ll 1 \\ K/\tau_\mathrm{exc} & \text{reversible electron transfer} \quad k_\mathrm{b}\tau_\mathrm{exc} \gg 1 \end{cases} \tag{2.16}$$

where $K = k_i/k_\mathrm{b}$ is the equilibrium constant. The ionization rate constant k_i is defined in (2.12a) as usual, although the kinetic constant of ion association into the exciplex, k_a, has a different nature than that of electron transfer (k_0) and the recombination rate k_r is now substituted by the exciplex decay $1/\tau_\mathrm{exc}$. However, the full identity of expressions 2.16 and 2.6 is reached under the assumption that the backward transfer rate relates to the dissociation rate, as in eq 2.12b. There k_d is the monomolecular rate of a single exciplex dissociation. The dissociation repeats after any subsequent association, and eq 2.12b, similar to (2.9), accounts for all the recontacts.

This important relationship was first derived by Berg considering the dissociation/association equilibrium in a nonexcited system:[9]

$$\mathrm{A} + \mathrm{D} \underset{k_\mathrm{b}}{\overset{k_i}{\rightleftharpoons}} [\mathrm{AD}] \tag{2.17}$$

with the equilibrium constant

$$K = \frac{k_i}{k_\mathrm{b}} = \frac{k_\mathrm{a}}{k_\mathrm{d}} \tag{2.18}$$

The Berg relationship (2.12b) follows from the last equality. According to this equation k_b reaches its maximal value, k_d, if the restoration of the exciplex in recontacts is ineffective ($k_\mathrm{a} \to 0$). In the opposite limit, under diffusional control ($k_\mathrm{D} \ll k_\mathrm{a}$), the total rate of dissociation is much less.

III. The Non-Markovian Kinetics of Exciplex Dissociation

A. Reversible Dissociation into Ions. The kinetics of the exciplex dissociation can be investigated separately assuming that there is just a single exciplex that decays and dissociates reversibly into an ion pair which either recombines or separates into free ions that never meet afterward

$$\underset{I_0\uparrow\downarrow\tau_\mathrm{exc}}{\mathrm{A}^{-\delta}\mathrm{D}^{+\delta}} \underset{k_\mathrm{a}}{\overset{k_\mathrm{d}}{\rightleftharpoons}} [\mathrm{A}* \underset{\downarrow k_\mathrm{R}}{\cdots} \mathrm{D}] \rightarrow \mathrm{A}^- + \mathrm{D}^+ \tag{3.1}$$

Here $k_\mathrm{R} \simeq k_\mathrm{r}v$ and k_a are kinetic constants of charge recombination and association, respectively, while k_d is the rate of a single exciplex dissociation via charge separation.

The pioneering investigation of this phenomenon by Berg[9] showed that the dissociation of a stable complex ($\tau_\mathrm{exc} = \infty$) to neutral components is not exponential under diffusional control. The same is true for exciplex dissociation to an ion pair in a highly polar solvent (allowing to neglect the Coulomb attraction). In such a case, the exciplex population $N^\mathrm{e}(t)$ obeys the equation[10]

$$\frac{\mathrm{d}N^\mathrm{e}}{\mathrm{d}t} = -(k_\mathrm{d} + 1/\tau_\mathrm{exc})N^\mathrm{e} + k_\mathrm{d}\int_0^t \mathscr{F}(t-\tau)N^\mathrm{e}(\tau)\,\mathrm{d}\tau \tag{3.2}$$

For the absence of recombination ($k_R = 0$) such an equation was first obtained by Berg who specified $F(t)$ in the contact approximation (see eq 2.6 in ref [9]). The Laplace transformation of this kernel is rather simple even in the general case ($k_R \neq 0$):[10]

$$\tilde{\mathscr{F}}(s) = \frac{k_\mathrm{a}}{k_\mathrm{a} + k_\mathrm{R} + k_\mathrm{D}(1 + \sqrt{s\tau_\mathrm{d}})} \tag{3.3}$$

where $\tau_\mathrm{d} = \sigma^2/D$ is an encounter time of any neutral fragments as well as counterions in highly polar solvent. In the kinetic control limit ($k_\mathrm{D} \gg k_\mathrm{a}$) $F \to 0$ and the integral kernel approaches zero. Then eq 3.2 reduces to the following

$$\frac{\mathrm{d}N^\mathrm{e}}{\mathrm{d}t} = -(k_\mathrm{d} + 1/\tau_\mathrm{exc})N^\mathrm{e} \tag{3.4}$$

where

$$N^\mathrm{e}(0) = 1$$

from which follows the pure exponential decay

$$N^\mathrm{e} = e^{-k_\mathrm{d}t - t/\tau_\mathrm{exc}} \tag{3.5}$$

However, this is not the case when the diffusion is slow and controls the dissociation.

The Berg equation (3.2) was the first integral equation in chemical kinetics which substitutes the rate equation, eq 3.4. Later on, the well-grounded and matrix formulated IET did the same with reactions of arbitrary complexity, either contact or remote.[6] To the problem on hand, IET gives a similar kinetic equation[6,10]

$$\frac{\mathrm{d}N^\mathrm{e}}{\mathrm{d}t} = -\frac{N^\mathrm{e}}{\tau_\mathrm{exc}} - k_\mathrm{d}\int_0^t F(t-\tau)N^\mathrm{e}(\tau)\,\mathrm{d}\tau \tag{3.6}$$

which is identical to eq 3.2 provided

$$F(t) = \delta(t) - \mathscr{F}(t) \tag{3.7}$$

i.e.

$$\tilde{F}(s) = 1 - \tilde{\mathscr{F}}(s)$$

In the contact approximation the kernel has the form

$$\tilde{F}(s) = \frac{k_\mathrm{R} + k_\mathrm{D}(1 + \sqrt{s\tau_\mathrm{d}})}{k_\mathrm{a} + k_\mathrm{R} + k_\mathrm{D}(1 + \sqrt{s\tau_\mathrm{d}})} \tag{3.8}$$

The effect of the recontacts leading to the restoration of the exciplex makes the charge separation kinetics nonexponential.

B. Reversible Dissociation into Neutral Fragments. If the instantaneously created exciplex reversibly separates into excited acceptor and electron donor, the reaction follows the scheme (from right to left):

$$\underset{\downarrow\tau_\mathrm{A}}{\mathrm{A}}{*} + \mathrm{D} \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\rightleftharpoons}} [\underset{I_0\uparrow\downarrow\tau_\mathrm{exc}}{\mathrm{A}^{-\delta}\mathrm{D}^{+\delta}}] \tag{3.9}$$

The exciplex population obeys eq 3.2 with the same initial condition ($N^\mathrm{e}(0) = 1$) but with another kernel

$$F = k_\mathrm{a}G(\sigma, t) \tag{3.10}$$

expressed through the Green function of the relative diffusion and association of A* and D. The latter obeys the equation substituting eq 51 in ref[10]

$$\frac{\partial}{\partial t}G(r,t) = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}G(r,t) - \frac{G(r,t)}{\tau_\mathrm{A}} \tag{3.11}$$

at

$$G(r,0) = \delta(r-\sigma)/4\pi r^2$$

with the boundary condition

$$4\pi\sigma^2 D\frac{\partial}{\partial r}G(r,t)|_{r=\sigma} = k_a G(\sigma,t) \tag{3.12}$$

The solution of this equation can be easily obtained by its Laplace transformation[5]

$$\tilde{G}(\sigma,s) = \frac{\tilde{G}_0\left(\sigma, s+\frac{1}{\tau_A}\right)}{1 + k_a\tilde{G}_0\left(\sigma, s+\frac{1}{\tau_A}\right)} \tag{3.13}$$

where

$$\tilde{G}_0(\sigma,s) = \frac{1}{k_D(1+\sqrt{s\tau_D})}$$

From eqs 3.10 and 3.13 we obtain instead of eq 3.3

$$\mathscr{A}(s) = \frac{k_a}{k_a + k_D(1+\sqrt{(s+1/\tau_A)\tau_d})} \tag{3.14}$$

As has been noted, the exciplex population obeys eq 3.2 as well as the equivalent IET eq 3.6 but with a new kernel following from the last result

$$\tilde{F}(s) = 1 - \mathscr{A}(s) = \frac{k_D(1+\sqrt{(s+1/\tau_A/)\tau_d})}{k_a + k_D(1+\sqrt{(s+1/\tau_A)\tau_d})} \tag{3.15}$$

Using it in eq 3.6 we obtain

$$\tilde{N}^e(s) = \left[s + 1/\tau_{exc} + \frac{k_d}{1 + k_a/k_D(1+\sqrt{(s+1/\tau_A)\tau_d})}\right]^{-1}. \tag{3.16}$$

Since the exciplex created by a light excitation of precursor complex decays by either fluorescence or dissociation into fragments, the dissociation is the only quenching mechanism lowering the fluorescence quantum yield

$$\eta_e = \int_0^\infty N^e(t)\,dt/\tau_{exc} = \frac{\tilde{N}^e(0)}{\tau_{exc}} \tag{3.17}$$

Using here $\tilde{N}^e(0)$ 3.16, we obtain instead of the Stern−Volmer law:

$$\eta_e = \frac{1 + k_a/k_D(1+\sqrt{\tau_d/\tau_A})}{1 + k_a/k_D(1+\sqrt{\tau_d/\tau_A}) + k_d\tau_{exc}} \tag{3.18}$$

When $\tau_{exc} \to 0$, the fluorescence yield turns to 1, while at $\tau_{exc} \to \infty$ the exciplex fluorescence is fully quenched ($\eta_e \to 0$).

This result is concentration independent and can be deduced at $c = 0$ from the more general one obtained in ref[11] but presented in a different way

$$1 - \eta_e = \frac{k_d}{k_a}\kappa\tau_{exc} \tag{3.19}$$

where

$$\kappa = \frac{k_a'}{1 + \frac{k_a'}{k_D(1+\sqrt{\tau_d/\tau_A})}}$$

and

$$k_a' = \frac{k_a}{1 + k_d\tau_{exc}} \tag{3.20}$$

In the kinetic control limit

$$\kappa = k_a' \tag{3.21}$$

$$1 - \eta_e = \frac{k_d\tau_{exc}}{1 + k_d\tau_{exc}}$$

while under diffusional control

$$\kappa = k_D(1 + \sqrt{\tau_d/\tau_A}) \tag{3.22}$$

$$1 - \eta_e = \frac{k_D\tau_{exc}}{K}(1 + \sqrt{\tau_d/\tau_A})$$

where $K = k_a/k_d$ and the correction factor $(1 + (\tau_d/\tau_A)^{1/2})$ accounts for the transient effect in the diffusional ionization of the excitation discovered by Smoluchowski.[12]

The particular case $\tau_{exc} = \tau_A = \infty$ is the most often studied phenomenon of complex dissociation, scheme 2.17, when all the reactants are stable and the corresponding IET equation has the simplest form

$$\frac{dN_c}{dt} = -k_d\int_0^t F(t-\tau)N_c(\tau)\,d\tau \tag{3.23}$$

where N_c is the concentration of [AD], initially equals 1 while the kernel is

$$\tilde{F}(s) = \frac{k_D(1+\sqrt{s\tau_d})}{k_a + k_D(1+\sqrt{s\tau_d})} = \frac{1}{1 + k_a/k_D(1+\sqrt{s\tau_d})} \tag{3.24}$$

Making the Laplace transformation of eq 3.23, one can easily find

$$\tilde{N}_c = \left[s + \frac{k_d}{1 + k_a/k_D(1+\sqrt{s\tau_d})}\right]^{-1} \tag{3.25}$$

The same follows from eq 3.16 at $\tau_{exc} = \tau_A = 0$. Making the inverse Laplace transformation of this result, we obtain the dissociation kinetics $N_c(t)$ shown in Figure 1A for a few different values of the diffusion coefficient. When the association rate constant is equal to zero ($k_a = 0$, the lowest solid line), the population decay is exponential with the kinetic rate $k_d + 1/\tau_{exc}$. For nonzero k_a, the dissociation is not exponential (all upper curves). The deviation from the exponent is greater when the diffusion coefficient is smaller. For the smallest values of the diffusion coefficient, when dissociation is under diffusional control ($k_D \ll k_a$) the decay is the slowest and its nonlinearity in the ln N_c/t plot is huge. The asymptote of this decay is known to obey the power law[11]

$$N_c(t) = \frac{K}{(4\pi Dt)^{3/2}} \tag{3.26}$$

This conclusion is confirmed by presenting the same result in the ln N_c/ln t plot (Figure 1B). It clearly shows that the linear asymptote (dashed line) has a slope −3/2 as predicted in eq 3.26 for reversible dissociation ($K \neq 0$).

The situation is more complex when the fragments of dissociation are not stable. In particular, the dissociation following reaction scheme 3.9 is represented by its Laplace transformation in eq 3.16, which depends on both lifetimes, τ_{exc} and τ_A. The former just facilitates the decay of the exciplex, while the latter significantly affects its kinetics, as shown in Figure 2. At $\tau_A = \infty$ it coincides with that obtained for complex dissociation at the diffusion coefficient D = 5 Å^2/ns. With

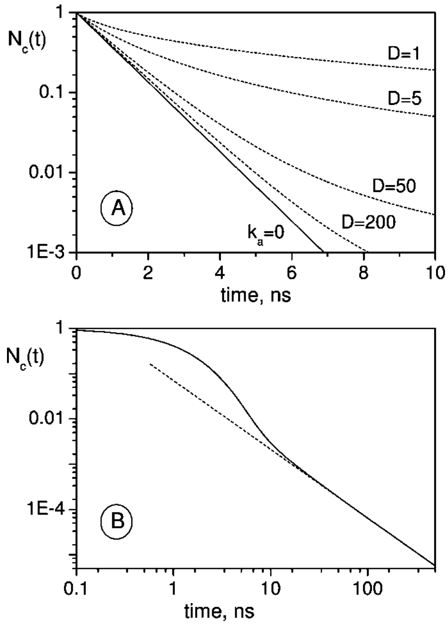


Figure 1. (A) Complex dissociation kinetics for different encounter diffusion, D, of its fragments. The other parameters are $k_r = 0$, $k_d = 1$ ns^{-1}, $\sigma = 7$ Å, $\tau_d = \sigma^2/D$, $k_D = 4\pi\sigma D$, $k_a = 0$ (solid line), $k_a = 1000$ Å^3/ns for all the rest of the curves. The values of the diffusion coefficient, D, are given in the figure in Å^2/ns. (B) The power law asymptotical dependence of reversible complex dissociation, presented by the dashed straight line (for $D = 50$ Å^2/ns and $K = k_a/k_d = 1000$ Å^3, the rest of the parameters are the same as in (A).

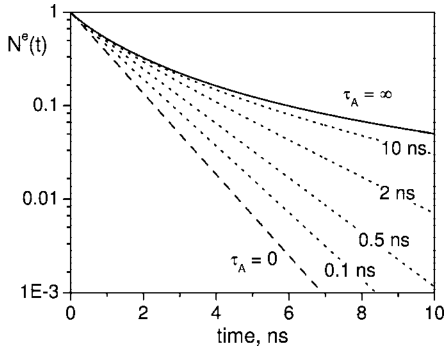


Figure 2. The kinetics of the exciplex dissociation at different τ_A and $D = 5$ Å^2/ns ($\tau_d = \sigma^2/D = 9.8$ ns).

shortening of τ_A the number of recontacts restoring the exciplex decreases, accelerating its decay. At $\tau_d/\tau_A \gg 1$ it becomes highly irreversible and turns to be kinetically controlled at $\tau_A = 0$. Such a transient effect is absent in the Markovian theories as well as the nonexponential asymptotic law 3.26.

IV. Excitation Quenching by Exciplex Formation

The Markovian description of this reaction schematically represented in eq 2.10 is given by the set of equations 2.11, whose IET analog is[11]

$$\frac{dN^*}{dt} = \frac{N^*}{\tau_A} - ck_a\int_0^t F(t-\tau)N^*(\tau)\,d\tau + k_d\int_0^t F(t-\tau) \times N^e(\tau)\,d\tau + I_0N \quad (4.1a)$$

$$\frac{dN^e}{dt} = \frac{N^e}{\tau_{exc}} - ck_a\int_0^t F(t-\tau)N^*(\tau)\,d\tau + k_d\int_0^t F(t-\tau) \times N^e(\tau)\,d\tau \quad (4.1b)$$

Here the kernel $F(t)$ is defined by its Laplace transformation 3.15. The last integrals representing exciplex dissociation are the same as before, while those proportional to the donor concentration $c = [D]$ correspond to the bulk formation of the exciplex. When $c \rightarrow 0$, these terms disappear and eq 4.1b becomes eq 3.6.

If the light pumping is permanent (as well as fluorescence), then I_0 = constant and the stationary populations of A* and exciplexes are obtained from eqs 4.1a, setting $dN^*/dt = dN^e/dt = 0$. In particular, the stationary density of excitations is

$$N_s^* = \frac{1 + k_d\tilde{F}(0)\tau_{exc}}{1 + k_d\tilde{F}(0)\tau_{exc} + ck_a\tau_A\tilde{F}(0)} I_0N\tau_A \quad (4.2)$$

Using this result in the quantum yield definition 2.5 together with $\tilde{F}(0)$ from eq 3.15, we confirm the Stern−Volmer law, $\eta = (1 + c\kappa\tau_A)^{-1}$, having the constant

$$\kappa = \frac{k_a'}{1 + \dfrac{k_a'}{k_D(1 + \sqrt{\tau_d/\tau_A})}} \equiv \frac{\kappa_i}{1 + \kappa_i\tau_{exc}/K} \quad (4.3)$$

where k_a' is the same as in eq 3.20 while the Stern−Volmer constant of irreversible quenching

$$\kappa_i = \frac{k_a}{1 + k_a/k_D(1 + \sqrt{\tau_d/\tau_A})} \quad (4.4)$$

Although the quantum yields of A* and exciplex fluorescence are different, both of them depend on one and the same quenching constant κ (see eqs 3.19 and 4.3).

This constant depends on both lifetimes, τ_A and τ_{exc}. The former accounts for the transient effect while the shortening of the latter makes the fluorescence quenching more effective, since the energy transfer to exciplexes becomes irreversible. The quantum yield of exciplex fluorescence $\eta_e = 1 - \eta$ because in the scheme 3.9 there is no recombination to the ground state: the energy dissipation is possible only via fluorescence, through either one or another channel. It should be noted that the same results were obtained in ref 11 from the alternative definition of η, eq 2.14, where the total nonstationary solution of eq 4.1a (after δ-pulse excitation) is really integrated in an infinite time interval (up to $t = \infty$). In the same way the yields of fluorescence after pumping the exciplex were also calculated in ref 11, as well as the equilibration of the system at $\tau_A = \tau_{exc} = \infty$.

The free energy dependence of the Stern−Volmer constant 4.3 is different for irreversible and reversible formation of the exciplex

$$\kappa = \begin{cases} \kappa_i & \text{at} \quad \kappa_i\tau_{exc} \ll K \quad \text{(irreversible)} \\ K/\tau_{exc} & \text{at} \quad \kappa_i\tau_{exc} \gg K \quad \text{(reversible)} \end{cases} \quad (4.5)$$

The irreversible one, given by eq 4.4, depends on the association rate constant k_a representing not electron transfer but heavy atom penetration into the first coordination sphere of the partner. This is an elementary step of the encounter diffusion accompanied by adiabatic rearrangement of the excited state of the solvent separated pair into the exciplex ground state.[13] In the "black sphere" approximation

$$k_a \gg k_D \quad (4.6)$$

the irreversible quenching constant 4.4 reduces to the diffusional one accounting for the transient effect:

$$\kappa_i \approx k_D\left(1 + \sqrt{\tau_d/\tau_A}\right) \quad (4.7)$$

In the opposite limit, the Stern−Volmer constant dependence on the free energy is determined mainly by the equilibrium constant of reversible association/dissociation

$$K = k_a/k_d = k_{exc}\upsilon/k_d = 4\pi\sigma^2\Delta e^{-\Delta E_-/T} \tag{4.8}$$

where ΔE_- is the energy gap between the excited acceptor and exciplex (the Boltzmann constant $k_B = 1$). This gap depends on both the free energy of complete ionization, ΔG_i, and the coupling V between the A^-D^+ state and A*D:[14]

$$\Delta E_\pm = \Delta G_i/2 \pm \sqrt{(\Delta G_i/2)^2 + V^2} \tag{4.9}$$

Two solid curves representing these dependencies in Figure 3 show the transition of the contact ion pair to the neutral excited complex and vice versa. Only in the narrow strip $|\Delta G_i| < V$ are they essentially mixed, and the lower curve within these limits represents the energy of the lower exciplex state. It should be stressed that this is the simplest approach to the problem The particular shape of these curves can be essentially corrected accounting for the mutually correlated medium reorganization and charge shift as was sometimes done.[15−17]

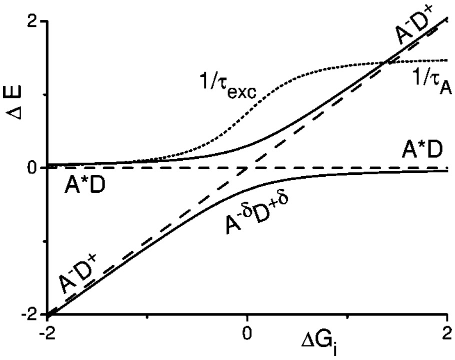


Figure 3. The energies of the adiabatic collective states, ΔE_+ and ΔE_- (solid lines), and their diabatic precursors (at $V = 0$, dashed lines), as well as the free energy dependence of the excitation decay rate $1/\tau_{exc}$ (dotted line).

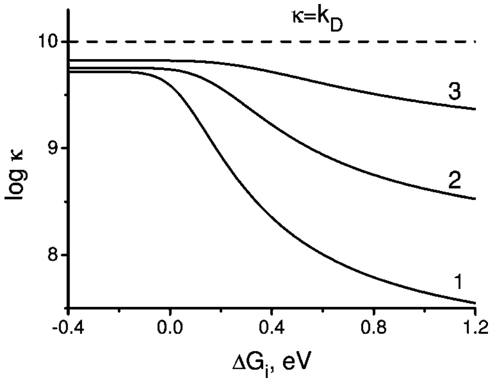


Figure 4. The free energy dependence of the Stern−Volmer constant (in 1/M) from eq 4.3. The values of the varying parameter are as follows: $\tau_A = 100\tau_d$ (1), $10\tau_d$ (2), τ_d (3). The rest of the parameters are $k_D = 4\pi\sigma D = 10^{10}$ M^{-1} s^{-1} $=1.66 \times 10^4$ Å^3 ns^{-1} as $\sigma = 7.5$ Å and $D = 176$ Å^2 ns^{-1}; $\tau_d = \sigma^2/D = 0.32$ ns; $V = 8T = 0.2$ eV and $\upsilon = 4\pi\sigma\Delta$, where $\Delta = 0.1\sigma$ is the reaction layer width.

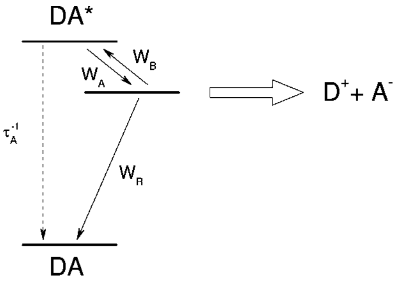


Figure 5. The energetic scheme of the reversible geminate photoionization.

The energy shift of the upper exciplex state, ΔE_+, determines the extent of the charge separation in the exciplex, $A^{-\delta}D^{+\delta}$

$$\delta = \frac{V^2}{V^2 + \Delta E_+^{\,2}} \tag{4.10}$$

The less the charge separation, the stronger the exciplex fluorescence affording the exciplex decay[18]

$$\frac{1}{\tau_{exc}} = \frac{1}{\tau_A}\frac{1}{1 + (\Delta E_-/V)^2} \tag{4.11}$$

However, $|\Delta E_-| \approx |\Delta G_i|$ should not be so large that $K \gg 1$. Assuming c = constant, the present theory excludes the saturation effect (when all D transform to exciplexes) which is inevitably the case when $K \to \infty$.

The free energy dependence of the Stern−Volmer constant for quenching by the exciplex is specified in eq 4.3 and depicted in Figure 4 for a few values of the exciplex lifetime. At negative ΔG_i, it approaches a plateau a bit lower than its Markovian height k_D (due to a transient effect), while at positive ΔG_i goes down smoothly approaching the value υ/τ_A. A similar behavior was established earlier by means of the elementary Markovian theory[19]

$$\kappa = \frac{k_i}{1 + k_i\tau_{exc}/K} \tag{4.12}$$

where

$$k_i = k_D\frac{k_a}{k_a + k_D}$$

is substituted for the Stern−Volmer constant in eq 4.3. In the Markovian limit ($\tau_A \gg \tau_d$) our result (4.7) is hardly distinguishable from the Markovian one. The experimental data provide evidence that $\kappa_i \approx k_i \approx k_D$ since they were well fitted with this accuracy in ref 19 for a number of reactant families, having a descending branch of κ_i in essentially endergonic region $\Delta G_i > 0$.

V. Reversible Geminate Photoionization

The rate description of photoionization presented by the reaction scheme 2.3 not only excludes the transient effect but does not account for ion pair diffusional separation according to the general scheme of the geminate reaction:

$$\begin{array}{lcccc} \mathrm{A}^* + \mathrm{D} & \underset{W_B}{\overset{W_A}{\rightleftharpoons}} & [\mathrm{A}^-\cdots\mathrm{D}^+] & \xrightarrow{\bar{\varphi}} & \mathrm{A}^- + \mathrm{D}^+ \\ I_0 \uparrow\downarrow \tau_A & & \Downarrow W_R & & \\ \mathrm{A} & & [\mathrm{A}\cdots\mathrm{D}] & & \end{array} \tag{5.1}$$

The kinetics of this process as well as the yield of the free ions, $\bar{\varphi}$, were first calculated by means of UT which is also the encounter theory.[5,20]

A. Remote Electron Transfer in IET. Another great advantage of all encounter theories compared to their Markovian analogs (section II.A) is their capability of dealing with the remote electron transfer presented by the position-dependent rates $W_A(r)$, $W_B(r)$, and $W_R(r)$, instead of the bimolecular constants of forward and backward transfer and charge recombination

$$k_0 = \int W_A(r) d^3r$$

$$k_B = \int W_B(r) d^3r$$

and

$$k_R = \int W_R(r) d^3r \approx k_r v$$

These rates are pointed out in Figure 5 which is equivalent to scheme 2.1. Such a reaction was first considered by means of IET in ref 21 where the following equations were obtained (instead of the Markovian set 2.4)

$$\frac{dN^*}{dt} = -c\int_0^t R^*(\tau)N^*(t-\tau)\, d\tau - \frac{N^*}{\tau_A} \qquad (5.2a)$$

$$\frac{dP}{dt} = c\int_0^t R^\dagger(\tau)N^*(t-\tau)\, d\tau \qquad (5.2b)$$

The kernels (memory functions) of these equations are specified by their Laplace transformations

$$\tilde{R}^*(s) = \left(s + \frac{1}{\tau_D}\right)\int [W_A(r)\tilde{v}(r,s) - W_B(r)\tilde{\mu}(r,s)]\, d^3r \qquad (5.3a)$$

$$\tilde{R}^\dagger(s) = \left(s + \frac{1}{\tau_A}\right)\int [W_A(r)\tilde{v}(r,s) - W_B(r)\tilde{\mu}(r,s) - W_R(r)\tilde{\mu}(r,s)]\, d^3r \qquad (5.3b)$$

while the originals of ν and μ obey the following auxiliary equations

$$\dot{\nu} = -W_A(r)\nu + W_B(r)\mu - \frac{1}{\tau_A}\nu + D\Delta\nu \qquad (5.4a)$$

$$\dot{\mu} = W_A(r)\nu - W_B(r)\mu - W_R(r)\mu + D\Delta\mu \qquad (5.4b)$$

with initial conditions $\nu(r, 0) = 1$ and $\mu(r, 0) = 0$ and reflecting boundary conditions at contact. Solving these equations at the initial conditions for $N(0) = 1$, $P(0) = 0$, one can find the total ion yield ψ and the yield of free ions ϕ[21−23]

$$\eta = \tilde{N}^*(0)/T_A = \frac{1}{1 + c\kappa_g T_A} = 1 - \psi \qquad (5.5)$$

and

$$\phi = P(\infty) = \lim_{s\to\infty} s\tilde{P}(s) = \psi\bar{\varphi}$$

Here the Stern−Volmer constant is

$$\kappa_g = \tilde{R}^*(0) \qquad \text{and} \qquad \bar{\phi} = \tilde{R}^\dagger(0)/\tilde{R}^*(0) \qquad (5.6)$$

is the charge separation quantum yield, the most often studied quantity.

B. Contact Approximation. In the case of proton transfer or electron transfer in the normal Marcus region, the reactions occur at the closest approach of the reactants making quite reasonable the contact approximation of their rates. This simplification allows the analytical solution of the problem, specifying the kernel of IET

$$\tilde{R}^*(s) = k_0\tilde{F}^*(s) \qquad (5.7)$$

where

$$\tilde{F}^*(s) = \frac{1 + k_R/k_D(1 + \sqrt{s\tau_d})}{[1 + k_0/k_D(1 + \sqrt{(s + 1/\tau_A)\tau_d})](1 + k_R/k_D(1 + \sqrt{s\tau_d})) + k_B/k_D(1 + \sqrt{s\tau_d})}$$

Using this result in eq 5.6 the following Stern−Volmer constant is obtained

$$\kappa_g = \frac{k_0'}{1 + k_0'/k_D(1 + \sqrt{\tau_d/\tau_A})} \equiv \frac{\kappa_i}{1 + \dfrac{\kappa_i}{K_{eq}(k_D + k_R)}} \qquad (5.8)$$

where

$$k_0' = \frac{k_0}{1 + k_B/(k_D + k_R)} \qquad (5.9)$$

while

$$\kappa_i = \frac{k_0}{1 + k_0/k_D(1 + \sqrt{\tau_d/\tau_A})}$$

is the Stern−Volmer constant for the irreversible charge transfer, including the transient effect accessible for only non-Markovian theories. The sum $k_D + k_R$ is the rate constant of transfer interruption by either ion pair separation (k_D) or their geminate recombination (k_R). It plays the same role as the exciplex decay $1/\tau_{exc}$ in eq 3.20, where k_d is the analog of k_B.

An exclusive advantage of IET is accounting for the backward transfer in eq 5.8, either through $k_0' \neq k_0$ or via the equilibrium constant

$$K_{eq} = k_0/k_B = e^{-\Delta G_i/T}$$

At highly exergonic ionization $\Delta G_i \rightarrow -\infty (K_{eq} \rightarrow \infty)$ and in the opposite limit of endergonic electron transfer ($\Delta G_i \rightarrow \infty$, $K_{eq} \rightarrow 0$) the Stern−Volmer constant is given by the alternative expressions

$$\kappa_g = \begin{cases} \kappa_i & \text{exergonic transfer} \\ K_{eq}(k_D + k_R) & \text{endergonic transfer} \end{cases} \qquad (5.10)$$

The usually considered irreversible ionization is peculiar to only exergonic transfer while the endergonic one is not controlled by ionization but either ion pair separation (k_D) or recombination (k_R). This Stern−Volmer constant increases with exergonicity due to K_{eq} The kinetics of geminate ionization can be studied by inversion of its Laplace transformation obtained from eq 5.2a and eq 5.7

$$\tilde{N}^* = \frac{N^*(0)}{s + ck_0\tilde{F}^*(s) + 1/\tau_A} \qquad (5.11)$$

The inversion is easier and simpler for analysis in the absence of geminate recombination ($k_R = 0$) when

$$\tilde{F}^*(s) = \frac{1}{[1 + k_0/k_D(1 + \sqrt{(s + 1/\tau_A)\tau_d})] + k_B/k_D(1 + \sqrt{s\tau_d})}$$

In this case only backward electron transfer (with subsequent excitation decay) competes with diffusional ion pair separation. In the highly exergonic limit there is no backward transfer at all and the irreversible quenching proceeds exponentially (with the rate $1/\tau_0 + ck_0$) after short transient effect (the lower dotted line in Figure 6). At moderate exergonicity (curve a) the fast quenching of luminescence is followed by a delayed fluorescence backed by the reverse electron transfer from the survived (nonseparated) ion pairs. Due to this transfer, the quenching becomes less efficient at resonance (b) and even more in the

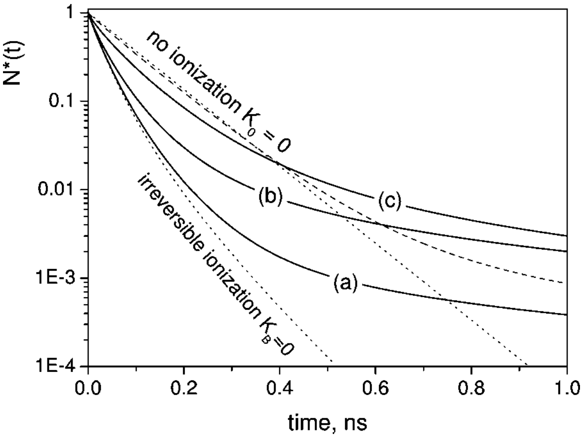


Figure 6. Kinetics of the excited-state dissipation (at $N^*(0) = 1$) due to reversible geminate ionization followed ion pair separation. The lowest dotted quasi-exponential curve represents the irreversible (though nonstationary) quenching while the upper dotted straight line is the exponential natural decay (no ionization). The lowest solid line (a) represents ionization at modest exergonicity ($\Delta G_i = -2T$), the middle one (b) describes the resonant transfer ($\Delta G_i = 0$), and the upper solid curve relates to the endergonic ionization ($\Delta G_i = 2T$). Even more endergonic transfer is represented by the dashed curve ($\Delta G_i = 4T$) which is straightening approaching the natural decay. The rest of the parameters are as follows: $c = 1$ M, $\tau_d = 0.4$ ns, $\tau_A = 0.1$ ns, $k_D = 3 \times 10^4$ Å^3/ns, $k_0 = 5 \times 10^4$ Å^3/ns, $\sigma = 10$ Å, $D = 250$ Å^2/ns.

endergonic region (c) while delayed luminescence is more pronounced. At further increase of endergonicity the quenching practically disappears leaving only natural decay. Hence the quasi-resonance region ($\Delta G_i \approx 0$) is an exceptional situation where the curvature of transfer kinetics is the maximal one. As has been shown in this very region the exciplexes creation becomes possible when the electron coupling V is large enough.

The kernels of eqs 5.2 are related to each other as follows:[21]

$$\tilde{R}^*(s) = \tilde{R}^\dagger(s)[1 + k_R/k_D(1 + \sqrt{s\tau_d})] \qquad (5.12)$$

Consequently the averaged charge separation yield from eq 5.6 is

$$\bar{\varphi} = \tilde{R}^\dagger(0)/\tilde{R}^*(0) = \frac{1}{1 + k_R/k_D} \qquad (5.13)$$

as in the elementary Markovian theory.[5,6] Unlike $\psi = c\kappa_g\tau_A/(1 + c\kappa_g\tau_A)$, this yield does not depend on whether the ionization is reversible or irreversible until it is contact.

All the results of the present section, which follow from eq 5.5, relate to the fluorescence measured after δ-pulse excitation in a limited time interval. At a low initial concentration of A* and low concentration of counterions, their recombination in the bulk occurs after detection of fluorescence is finished. In other words, only the geminate backward transfer is accounted for while the bulk recombination contributed into long delayed fluorescence is cut off.

VI. Bulk Recombination following Ion Separation

At. Stationary fluorescence. The situation is different when the fluorescence is detected stationary and its yield is calculated from eq. 3.17. The corresponding reaction scheme accounting for the bulk recombination was first considered in ref [24].

$$\begin{array}{cccccccc} \mathrm{A}^* + \mathrm{D} & \underset{W_B}{\overset{W_A}{\rightleftarrows}} & [\mathrm{A}^- \cdots \mathrm{D}^+] & \xrightarrow{\bar{\varphi}} & \mathrm{A}^- + \mathrm{D}^+ & \xrightarrow{W_B} & \mathrm{A}^* + \mathrm{D}. & (6.1) \\ I_0 \uparrow\downarrow \tau_A & & \Downarrow W_R & & \Downarrow W_R & & \downarrow \tau_A & \\ \mathrm{A} & & [\mathrm{A} \cdots \mathrm{D}] & & \mathrm{A} + \mathrm{D} & & \mathrm{A} & \end{array}$$

The following set of corresponding IET equations was obtained there

$$\dot{N}^* = -c\int_0^t R^*(\tau)N^*(t-\tau)\,\mathrm{d}^3r + \int_0^t R^\#(\tau)[P(t-\tau)]^2\,\mathrm{d}^3r - \frac{N^*}{\tau_A} + I_0N \qquad (6.2a)$$

$$\dot{P} = -c\int_0^t R^\dagger(\tau)N^*(t-\tau)\,\mathrm{d}^3r - \int_0^t R^\ddagger(\tau)[P(t-\tau)]^2\,\mathrm{d}^3r \qquad (6.2b)$$

Here we imply that the light excitation is weak enough to not affect the ground-state population, which remains approximately equal to the total number of acceptors, N.

The Laplace transformations of the two additional kernels, representing the bimolecular recombination to the ground and excited states, are

$$\tilde{R}^\ddagger(s) = s\int [W_R(r)\tilde{f}(r,s) + W_B(r)\tilde{f}(r,s) + W_A(r)\tilde{g}(r,s)]\,\mathrm{d}^3r \qquad (6.3a)$$

$$\tilde{R}^\#(s) = s\int [W_B(r)\tilde{f}(r,s) + W_A(r)\tilde{g}(r,s)]\,\mathrm{d}^3r \qquad (6.3b)$$

where the auxiliary pair distributions obey the following set of equations:

$$\dot{f} = W_A(r)g - W_B(r)f - W_R(r)f + \mathbf{L}'f \qquad (6.4a)$$

$$\dot{g} = -W_A(r)g + W_B(r)f - \frac{1}{\tau_A}g + \mathbf{L}g \qquad (6.4b)$$

Here $\mathbf{L}'$ and $\mathbf{L}$ are the diffusional operators for ions ($\mathrm{D}^+\cdots\mathrm{A}^-$) and the neutral products of their recombination, ($\mathrm{D}\cdots\mathrm{A}^*$). The initial conditions are $f(r,0) = 1$, $g(r,0) = 0$.

Setting $\dot{N}^* = \dot{P} = 0$, we obtain from eqs 6.2a and 6.2b two algebraic equations for the stationary populations N_s^* and P_s. Resolving them for N_s^* and using the result in eq 2.5, we confirm the Stern–Volmer law 1.1 with the quenching constant

$$\kappa = \kappa_g[1 - \chi\bar{\varphi}] \qquad (6.5)$$

where the geminate Stern–Volmer constant, κ_g, and the charge separation yield, $\bar{\varphi}$, were defined in eq 5.6, while the restoration of the acceptor excitation in the bulk occurs with a probability

$$\chi = \frac{\tilde{R}^\#(0)}{\tilde{R}^\ddagger(0)} \qquad (6.6)$$

at any reencounter. If the recombination to the ground state is impossible ($W_R = 0$), then the excitation decays only via fluorescence with $\eta = 1$. If the recombination proceeds as usual but the backward transfer is not possible ($W_B = 0$), then the quenching is irreversible and η is minimal, i.e.

$$\kappa = \begin{cases} 0 & \text{at} \quad W_R = 0 \\ \kappa_g & \text{at} \quad W_B = 0 \end{cases} \qquad (6.7)$$

To get more detailed information about the Stern–Volmer constant, one has to specify all four kernels of integral eqs 6.2. This has been done analytically in the contact approximation.[25]

B. Contact Approximation. In addition to the kernels considered earlier, eqs 5.8 and 5.13, two others were also calculated in the contact approximation, assuming the solvent to be highly polar, i.e., $\mathbf{L}' = \mathbf{L} = D\Delta$:[25]

$$\tilde{R}^{\#}(0) = \frac{k_B}{(1 + k_0/k_D(1 + \sqrt{\tau_d/\tau_A}))(1 + k_R/k_D) + k_B/k_D} \qquad (6.8a)$$

$$\tilde{R}^{\ddagger}(0) = \frac{k_B + k_R + k_0 k_R/k_D(1 + \sqrt{\tau_d/\tau_A})}{(1 + k_0/k_D(1 + \sqrt{\tau_d/\tau_A}))(1 + k_R/k_D) + k_B/k_D} \qquad (6.8b)$$

Using these kernels in eq 6.6, we obtain

$$\chi = \frac{k_B}{k_B + k_R[1 + k_0/k_D(1 + \sqrt{\tau_d/\tau_A})]} \qquad (6.9)$$

Substituting this result together with κ_g and $\bar{\varphi}$ from eq 5.6 into the general definition eq 6.5, the following Stern–Volmer constant is obtained

$$\kappa = \frac{k_0''}{1 + k_0''/k_D(1 + \sqrt{\tau_d/\tau_A})} \equiv \frac{\kappa_i}{1 + \dfrac{\kappa_i}{K_{eq} k_R}} \qquad (6.10)$$

where κ_i is the same as in eq 5.9 but

$$k_0'' = \frac{k_0}{1 + k_B/k_R} \qquad (6.11)$$

and

$$K_{eq} = \frac{k_0}{k_B} = e^{-\Delta G_i/T}$$

Contrary to geminate k_0' from eq 5.9, there is no k_D in k_0'' or in the last expression in eq 6.10. The diffusional separation of ion pairs does not stop the backward electron transfer but just interrupts it, until the ions reencounter in the bulk. Thus the whole energy stored in the free ions returns back to the luminophore which is stationary quenched only by recombination to the ground state

$$k_R = k_R^{\,0} \exp\left\{-\frac{(-\Delta G_i - \varepsilon + \lambda)^2}{4\lambda T}\right\} \qquad (6.12)$$

where ε is the energy of acceptor excitation equal to the sum of the ionization and recombination free energies

$$\varepsilon = -\Delta G_i - \Delta G_r$$

As a matter of fact, stationary quenching by formation of unstable exciplex has Stern–Volmer constant 4.3 equivalent to that for ionization quenching, eq 6.10, provided k_B/k_R in the latter is substituted by $k_d\tau_{exc}$. In both cases IET accounts for the reversibility of transfer (via k_B or k_d) as well as for the transient effect which becomes stronger as τ_A becomes shorter.

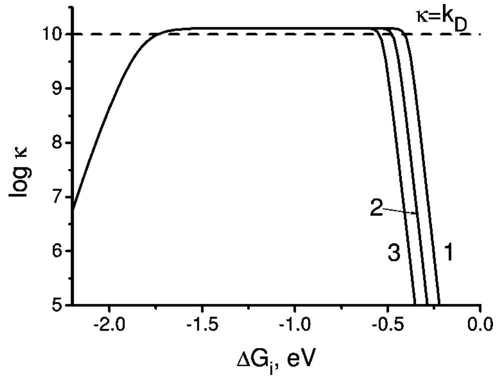


Figure 7. The free energy dependence of quenching by charge separation at different rates of their subsequent recombination given by eq 6.12 with $k_R{}^0 = 10^{12}$ M^{-1} s^{-1} (1), $k_R{}^0 = 10^{10}$ M^{-1} s^{-1} (2), and $k_R{}^0 = 10^8$ M^{-1} s^{-1} (3) at $\varepsilon = 2.8$ eV and $k_0 = 10^{13}\exp\{-(\Delta G_i + \lambda)^2/4\lambda T\}$ M^{-1} s^{-1}.

VII. Spin-Assisted Transfer

A. Geminate Recombination of RIPs. Up to now we were concerned with only the spin-less theory, although the real ion pairs gain the same spin state as their excited precursor. Being subjected to spin conversion, the geminate ion pairs either recombine into singlet or triplet neutral products or separate into free ions.

$$\begin{array}{ccccc} & & & {}^2\mathrm{D}^+ + {}^2\mathrm{A}^- & \\ & & \nearrow & \bar{\varphi} & \nwarrow \\ {}^1\mathrm{A}^* + \mathrm{D} & \underset{k_B}{\overset{k_0}{\rightleftharpoons}} & {}^1[\mathrm{D}^+ \ldots \mathrm{A}^-] & \underset{k_s}{\overset{3k_s}{\rightleftharpoons}} & {}^3[\mathrm{D}^+ \ldots \mathrm{A}^-] \\ \downarrow\ \tau_A & & k_S \downarrow \bar{\varphi}_S & & \bar{\varphi}_T \downarrow k_T \\ \mathrm{A} & & \mathrm{D} + \mathrm{A} & & \mathrm{D} + {}^3\mathrm{A}^* \end{array} \qquad (7.1)$$

The yields of neutral and charged products of geminate recombination were calculated with IET,[8,26,27] as well as with UT,[28,29] which is an excellent alternative to IET but only for irreversible ionization ($k_B = 0$). The incoherent model of spin conversion (proceeding with the rate k_s between the spin sublevels of the singlet and triplet RIP) is most often used in both theories, but in UT it was finally substituted by the coherent (HFI) mechanism.[30–32]

The RIP recombination to the ground or triplet states of the neutral products proceeds with rates k_S and k_T, respectively. The quantum yields of all products are equal to 1 in the sum:

$$\bar{\phi}_T + \bar{\phi}_S + \bar{\phi} = \frac{Z_T}{D + Z} + \frac{Z_S}{D + Z} + \frac{D}{D + Z} = 1 \qquad (7.2)$$

For contact electron transfer, all of them were calculated analytically, as well as the singlet and triplet recombination efficiencies (Z_S, Z_T) and $Z = Z_S + Z_T$. The diffusional dependences of all of them were specified with UT and well fitted to the experimental ones.[29]

The set of IET equations for singlet and triplet excitations, $N_S = [{}^1A^*]$ and $N_T = [{}^3A^*]$, together with charge population, P, is given below[8]

$$\dot{N}_s = -c\int_0^t R^*(t - \tau)N_s(\tau)\,d\tau - \frac{N_S}{\tau_A} \qquad (7.3a)$$

$$\dot{P} = c\int_0^t R^{\dagger}(t - \tau)N_S(\tau)\,d\tau \qquad (7.3b)$$

$$\dot{N}_T = c\int_0^t R^{\bigcirc}(t - \tau)N_S(\tau)\,d\tau \qquad (7.3c)$$

There is one more equation and integral kernel compared to eqs 5.2, but all of them were given the generalized definitions and specified in the contact approximation.

Instantaneous light pumping creates the usual initial conditions

$$N_S(0) = N_0; \qquad P(0) = N_T(0) = 0 \qquad (7.4)$$

Solving with them eqs 7.3, one can find the yields of fluorescence and ions (ψ), as well as of free ions (ϕ) and triplets

$$\eta = \int_0^\infty N_S(t)\,dt/\tau_A = \frac{1}{1 + c\kappa_g\tau_A} = 1 - \psi \qquad (7.5a)$$

$$P(\infty) = \psi\bar{\varphi} = \phi \qquad (7.5b)$$

$$N_{\mathrm{T}}(\infty) = \psi\bar{\varphi}_{\mathrm{T}} \tag{7.5c}$$

The last yield, $\bar{\varphi}_{\mathrm{S}}$, follows from the relationship 7.2, as well as all recombination efficiencies.

In the present context we are mainly interested in how the spin conversion affects the Stern−Volmer constant. Although the general dependence $\kappa_{\mathrm{g}}(k_{\mathrm{s}})$ was actually specified in ref 8, only the opposite limits of fast ($k_{\mathrm{s}}\tau_{\mathrm{d}} \gg 1$) and slow ($k_{\mathrm{s}}\tau_{\mathrm{d}} \ll 1$) spin conversion are worthy of analysis. Coming to the extreme, we get

$$\kappa_{\mathrm{g}} = \begin{cases} \dfrac{\kappa_i}{1 + \kappa_i/K_{\mathrm{eq}}(k_{\mathrm{D}} + k_{\mathrm{S}} + 3k_{\mathrm{T}})} & \text{at} \quad k_{\mathrm{s}} \to \infty \\ \dfrac{\kappa_i}{1 + \kappa_i/K_{\mathrm{eq}}(k_{\mathrm{D}} + k_{\mathrm{S}})} & \text{at} \quad k_{\mathrm{s}} \to 0 \end{cases} \tag{7.6}$$

In the absence of backward transfer, $K_{\mathrm{eq}} = k_0/k_{\mathrm{B}} \to \infty$, that makes κ_{g} (at any k_{s}) identical to the irreversible Stern−Volmer constant κ_i from eq 5.9. In the absence of spin conversion ($k_{\mathrm{s}} = 0$) the result is also identical to that obtained in eq 5.8 with the spinless theory. No geminate production of triplets is possible in such a condition: $\bar{\varphi}_{\mathrm{T}} = 0$ at $k_{\mathrm{s}} = 0$.

B. Stationary Fluorescence. The situation changes dramatically if the bulk charge recombination follows the geminate one. The kinetic equations substituting eq 7.3a, include six more integral terms and corresponding kernels

$$\dot{N}_{\mathrm{S}} = -c\int_0^t R^*(t-\tau)N_{\mathrm{S}}(\tau)\,\mathrm{d}\tau + \int_0^t R^{\#}(t-\tau)P^2(\tau)\,\mathrm{d}\tau + c\int_0^t R^{\S}(t-\tau)N_{\mathrm{T}}(\tau)\,\mathrm{d}\tau - \frac{N_{\mathrm{S}}}{\tau_{\mathrm{A}}} \tag{7.7}$$

$$\dot{P} = c\int_0^t R^{\dagger}(t-\tau)N_{\mathrm{S}}(\tau)\,\mathrm{d}\tau - \int_0^t R^{\ddagger}(t-\tau)P^2(\tau)\,\mathrm{d}\tau + c\int_0^t R^{\diamond}(t-\tau)N_{\mathrm{T}}(\tau)\,\mathrm{d}r$$

$$\dot{N}_T = -c\int_0^t R^{\triangle}(t-\tau)N_{\mathrm{S}}(\tau)\,\mathrm{d}\tau + \int_0^t R^{\blacksquare}(t-\tau)P^2(\tau)\,\mathrm{d}\tau - c\int_0^t R^{\bigstar}(t-\tau)N_{\mathrm{T}}(\tau)\,\mathrm{d}\tau - \frac{N_{\mathrm{T}}}{\tau_{\mathrm{T}}}$$

All the kernels expressed generally via the transfer rates, and pair correlation functions were also specified in the contact approximation (see ref 8 and Appendix available online: http://www.rsc.org/suppdata/cp/b2/b201784a/).

Looking for stationary luminescence, one has to add the light pumping term I_0N to the upper equation right-hand side and find the stationary solution of the whole set[27]

$$\hat{N}_{\mathrm{S}} = \frac{I_0 N_{\mathrm{G}}\tau_{\mathrm{S}}}{1 + c\kappa_0\tau_{\mathrm{S}}} \tag{7.8a}$$

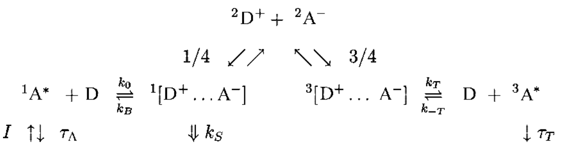
$$\hat{P}^2 = c\frac{\widetilde{R}^{\dagger}(0)}{\widetilde{R}^{\ddagger}(0)}\left[\hat{N}_{\mathrm{S}} + \frac{\widetilde{R}^{\diamond}(0)}{\widetilde{R}^{\dagger}(0)}\hat{N}_{\mathrm{T}}\right] \tag{7.8b}$$

$$\hat{N}_{\mathrm{T}} = \hat{N}_{\mathrm{S}}\frac{\widetilde{R}^{\triangle}(0)\widetilde{R}^{\ddagger}(0) + \widetilde{R}^{\blacksquare}(0)\widetilde{R}^{\dagger}(0)}{\widetilde{R}^{\bigstar}(0)\widetilde{R}^{\ddagger}(0) - \widetilde{R}^{\blacksquare}(0)\widetilde{R}^{\diamond}(0)} \tag{7.8c}$$

Here N_{S}, N_{T}, and P are the stationary concentrations of the excited states and ions while κ is the Stern−Volmer constant of the quantum yield 1.1 defined in eq 2.5 via $N_{\mathrm{S}}^* \equiv \hat{N}_{\mathrm{S}}$

$$\kappa = \widetilde{R}^*\left\{1 - \frac{\widetilde{R}^{\#}(0)}{\widetilde{R}^{\ddagger}(0)}\frac{\widetilde{R}^{\dagger}(0)}{\widetilde{R}^*(0)} - \frac{[\widetilde{R}^{\S}(0)\widetilde{R}^{\ddagger}(0) + \widetilde{R}^{\#}(0)\widetilde{R}^{\diamond}(0)][\widetilde{R}^{\triangle}(0)\widetilde{R}^{\ddagger}(0) + \widetilde{R}^{\blacksquare}(0)\widetilde{R}^{\dagger}(0)]}{\widetilde{R}^{\ddagger}(0)\widetilde{R}^*(0)[\widetilde{R}^{\bigstar}(0)\widetilde{R}^{\ddagger}(0) - \widetilde{R}^{\blacksquare}(0)\widetilde{R}^{\diamond}(0)]}\right\}$$

Everything becomes much simpler if we neglect the spin conversion setting $k_{\mathrm{s}} = 0$. The geminate production of a triplet in such a limit becomes impossible, but they appear nevertheless due to bulk encounters of uncorrelated radical ions forming the triplet ion pair with a stochastic weight 3/4.



(7.9)

This scheme enables studying the luminescence quenching (and its Stern−Volmer constant) proceeding from left to right, as well as the triplet quenching going from right to left.[27]

In the absence of a spin conversion in the ion pairs

$$\widetilde{R}^{\S}(0) = \widetilde{R}^{\triangle}(0) = 0$$

and the expression for the Stern−Volmer constant takes the form of eq 6.5, with the following microscopic definitions of all its components

$$\kappa_{\mathrm{g}} = \widetilde{R}^*(0) \tag{7.10}$$

$$\chi = \frac{\widetilde{R}^{\#}(0)}{\widetilde{R}^{\ddagger}(0)}\frac{\widetilde{R}^{\bigstar}(0)\widetilde{R}^{\ddagger}(0)}{\widetilde{R}^{\bigstar}(0)\widetilde{R}^{\ddagger}(0) - \widetilde{R}^{\blacksquare}(0)\widetilde{R}^{\diamond}(0)}$$

$$\varphi = \frac{\widetilde{R}^{\dagger}(0)}{\widetilde{R}^*(0)}$$

It should be noted that $\hat{N}_{\mathrm{T}} \neq 0$ at $k_{\mathrm{s}} = 0$ unlike $\bar{\varphi}_{\mathrm{T}}$, because the triplet excitations are produced from triplet RIPs during bulk encounters of the spin uncorrelated free radical ions.

The contact approximation makes the probability of singlet restoration in the absence of spin conversion much simpler[27]

$$\chi = \frac{\widetilde{R}^{\#}(0)}{\widetilde{R}^{\ddagger}(0) - \widetilde{R}^{\blacksquare}(0)} = \frac{k_{\mathrm{B}}}{k_{\mathrm{B}} + k_{\mathrm{S}}[1 + k_0/k_{\mathrm{D}}(1 + \sqrt{\tau_{\mathrm{d}}/\tau_{\mathrm{A}}})]} \tag{7.11}$$

It is remarkable that all three kernels in this expression accounting for the forward and backward transfer between the triplets are much more complex than their spin-less analogs in eq 6.6. However, the result is nevertheless exactly the same as in the spin-less theory, eq 6.9, which is k_{t} and $k_{-\mathrm{t}}$ independent. This is because the stable triplets do not participate in the fluorescence quenching, although there are permanently a lot of them: $\hat{N}_{\mathrm{T}}$ in eq 7.8c. They can be detected by either light absorption or phosphorescence, as well as the stationary density of ions given in eq 7.8b can be found from the electric current measurements.

Hence, the reversible triplet production does not affect the luminescence quenching which proceeds only through the singlet RIP recombination. The Stern−Volmer constant 6.10 with $k_{\mathrm{R}} \equiv k_{\mathrm{S}}$ remains valid, regardless of whether stable triplets are formed or not

$$\kappa = \frac{\kappa_i}{1 + \kappa_i/K_{eq}k_S} = \begin{cases} \kappa_i = \dfrac{k_0}{1 + k_0/k_D(1 + \sqrt{\tau_d/\tau_A})} & \text{as } K_{eq}k_S \gg \kappa_i \text{ (ionization control)} \\ K_{eq}k_S & \text{as } K_{eq}k_S \ll \kappa_i \text{ (recombination control)} \end{cases} \quad (7.12)$$

Under ionization control, the electron transfer being irreversible is either diffusional or kinetic. The kinetic rate constant $k_0 = \int W_A(r)\, d^3r$ is free energy dependent (unlike k_a). In the contact approximation,[5,27]

$$k_0 = k_0^{\ 0} e^{-(\Delta G_i + \lambda_c)^2/4\lambda_c T} \quad (7.13)$$

where λ_c is the solvent reorganization energy at contact.

The quenching by reversible transfer is controlled by recombination, when the latter becomes too slow. Its rate constant is also free energy dependent. When calculated in the contact approximation, it is

$$k_S = \int W_R(r)\, d^3r = k_S^{\ 0} e^{-(\varepsilon + \Delta G_i - \lambda_c)^2/4\lambda_c T} \quad (7.14)$$

The recombination is enhanced by the equilibrium constant $K_{eq} = e^{-\Delta G_i}/T$.

If the product $K_{eq}k_S$ is large enough, then $\kappa = \kappa_i$ and ln κ reproduces the parabolic free energy dependence of ln k_0 (the Marcus FEG law) the top of which is cut off by a diffusional plateau.[3] This plateau reduces with slowing recombination giving way to a rapid decrease of ln κ = ln $K_{eq}k_S$. This can happen earlier or later depending on the value of k_S which is different in different ion pairs. This was the explanation given in ref 27 to the multiple Rehm−Weller effect discovered experimentally.[7]

VIII. Fitting to the Singlet and Triplet Quenching by Aliphatic Amines and Aromatic Donors

In this section we apply the theory we developed to fit the experimental data on the electron transfer quenching of the excited molecules of lumichrome (LC) and lumiflavin (LF), by a series of aliphatic amines and aromatic donors in methanol, presented in Figures 1 and 2 of ref 35. Before proceeding to a fitting, let us compare the excitation quenching rate constant dependence on the ionization free energy presented in Figures 4 and 7. One may see a very important feature. For the photoionization mechanism, a decrease in the quenching rate, with the rise of the ionization free energy, universally starts in the region of negative values of ΔG_i. At $\Delta G_i = 0$ the quenching rate constant becomes much smaller than its maximum value at the plateau. For excitation quenching by exciplex formation, the rate constant decrease appears much later and mainly proceeds in the region of positive ΔG_i.

Addressing the experimental data on quenching of LC and LF by aromatic donors, we may anticipate that these data can be fitted only to the exciplex formation mechanism (see Figures 8 and 9). An earlier attempt to fit this data to the ionization theory was unsuccessful near the endergonic edge of the FEG law. For the sake of similarity the excess of the free energy in cases of singlet and triplet ionization was denoted in ref 35 and article 27 by a single argument, ΔG_0. For the ionization of singlets $\Delta G_0 \equiv \Delta G_i$, while for the triplets $\Delta G_0 \equiv \Delta G_{trip} = \Delta G_i + \varepsilon$, where ε is the singlet−triplet splitting. The excellent reproduction of the FEG law for both singlet and triplet quenching was reached, assuming that exciplex formation is a dominant mechanism of energy quenching (see triangles in Figures 8 and 9). For singlet quenching the known values of the excited acceptor lifetimes (τ_A = 1 ns for LC and τ_A = 6.8 ns for LF) were used.[35] In such a case the electronic coupling was the only variable parameter of the fitting. Unfortunately, we could not find in the literature the lifetimes of triplet LC and LF, but those obtained from our fitting are 3 × 10^5 to 1.5 × 10^4 times as much as the singlet ones and look very reasonable.

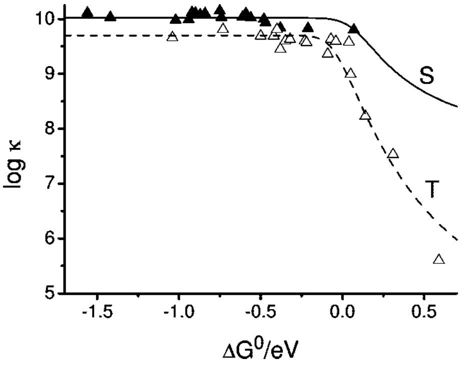


Figure 8. The dependence of the quenching rate constants, κ in M^{-1} s^{-1}, for excited states of LC on the ionization free energy, ΔG_i, in methanol. The experimental data:[35] (▲) singlet quenching by aromatic donors; (△) triplet quenching by aromatic donors. Solid and dashed lines are the fitting to eqs 4.3, 4.7, and 4.11 with the following parameters: singlet quenching, $k_D = 2 \times 10^{10}$ M^{-1} s^{-1}, V = 0.2 eV, τ_A/τ_d = 6; triplet quenching, $k_D = 10^{10}$ M^{-1} s^{-1}, V = 0.35 eV, $\tau_A/\tau_d = 3 \times 10^5$.

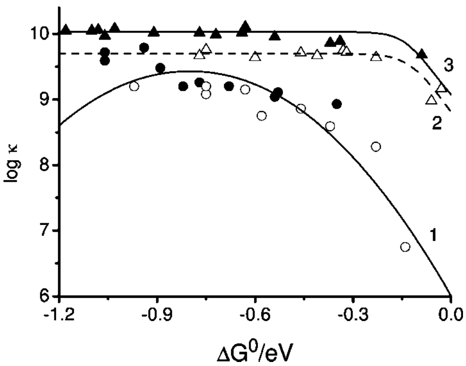


Figure 9. Dependence of the quenching rate constants, κ in M^{-1} s^{-1}, for the excited states of LF on the ionization free energy, ΔG_i, in methanol. The experimental data:[35] (▲) singlet quenching by aromatic donors; (△) triplet quenching by aromatic donors; (●) singlet quenching by aliphatic amines; (○) triplet quenching by aliphatic amines. Line 1 is the fitting to eqs 6.10, 5.9, and 7.13 with the parameters: $k_D = 2 \times 10^{10}$ M^{-1} s^{-1}, λ = 0.8 eV, $k_R = 3 \times 10^9$ M^{-1} s^{-1}, $k_0^{\ 0} = 3 \times 10^9$ M^{-1} s^{-1}. Lines 2 and 3 are the fittings to eqs 4.3, 4.7, and 4.11 with the following parameters: singlet quenching, $k_D = 2 \times 10^{10}$ M^{-1} s^{-1}, V = 0.1 eV, τ_A/τ_d = 41; triplet quenching, $k_D = 10^{10}$ M^{-1} s^{-1}, V = 0.25 eV, $\tau_A/\tau_d = 15 \times 10^3$.

It should be mentioned that for singlet and triplet quenching the same mechanism was assumed. The differences concern only the values of the excitation lifetimes and electronic couplings. In addition, we neglected the singlet−triplet conversion in the exciplexes that can considerably affect the reversible photoionization kinetics.[27] In the systems under study, the spin and magnetic interactions inducing conversion are too weak in comparison with the singlet−triplet splitting in exciplexes which is approximately the same as in neutral acceptors (ε ~ 0.4 eV).

The quenching by aliphatic amines is well fitted (see line 1 in Figure 9), assuming that it is carried out by a weak ionization of either the singlet or triplet states of LF. In this case the reaction proceeds under kinetic control and the experimental points lay on the bell-shaped curve, obeying the famous Marcus free energy gap law. The curve is very weakly sensitive to variation of k_R when it alters from 10^{12} up to 10^8 M^{-1} s^{-1}, thus confirming that the quenching is executed by the kinetic controlled electron transfer.

IX. Conclusions

If the excitation quenching by bimolecular charge separation is rather exergonic, it is usually irreversible and under diffusional control but gives way to a kinetic one at moderate exergonicity, provided the recombination of charged products is fast enough. In the opposite case the charge separation becomes reversible and the quenching is controlled by their recombination. On the other hand the quasi-resonance and weakly endergonic transfer lead to a reversible formation of the exciplexes resulting in quenching of excited reactants.

These alternative mechanisms of the luminescence quenching are compared here, as well as the corresponding Stern−Volmer constants and their free energy dependencies. The noncontact electron tunneling responsible for the charge separation is usually weak at least at large distances. This allows employing perturbation theory over electron coupling V, to estimate the rates of electron transfer and the corresponding kinetic constants. On the other hand, the exciplexes are created only at a contact due to penetration of heavy particles (reactants) into the first coordination sphere. There V is much larger, and the resulting collective states and their energies have to be specified far beyond perturbation theory.

The most delicate question is how these mechanisms relate to each other. The answer can be obtained only looking at the spectroscopic manifestation of the excitations and exciplexes. Only at large V is their luminescence represented by two split lines and the yields of luminescence can be measured separately for both, η_A and η_{exc}. Here, everywhere we looked only for $\eta = \eta_A$, but at $V \rightarrow 0$ this is $\eta = \eta_A + \eta_{exc}$ because the lines cannot be distinguished any more and the exciplex does not work as a specific quencher. It transforms to a usual ion pair whose creation and recombination, even at $\Delta G_i \approx 0$ is described by an alternative charge transfer mechanism, using conventional perturbation theory.

The key question still remains: why from some reactants the exciplexes are formed helping their quenching, while from other they do not form and the charge separation mechanism is the only one working? Most probably the answer to this question is not possible in the framework of the chemically (spherically) isotropic model of the elementary act, which is used in this paper as in most others. The creation of exciplexes demands the special orientation of its fragments making active only the limited black spot on the white (inactive) reaction sphere. Such a chemical anisotropy discovered long ago in a wide class of fast radical reactions was thoroughly investigated and reviewed.[33] The numerous recontacts during encounter and mutual rotation of reactants, average partially the anisotropy of the reactions, making them “pseudodiffusional” with a constant

$$k_a = \alpha k_D$$

which is less than the diffusional one, as $\alpha < 1$. Just recently the first experimental evidence appeared that even remote charge transfer reactions can be pseudodiffusional.[34] The same should be even more true for contact exciplex formation, but here we are the concerned with only the isotropic case, where k_a is a maximal one, eq 4.6, and the quenching by exciplexes dominates. In the opposite case ($\alpha \ll 1$) the exciplex formation does not contribute essentially in the excitation quenching, leaving the charge transfer to operate alone.

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