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Quenching of Singlets and Triplets by Reversible Ionization Followed by Charge Recombination

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The reversible electron transfer from donor to excited molecule (acceptor of electron) is shown to be the irreversible energy quenching, if it is completed by subsequent irreversible recombination radical-ions which are produced. The Stern−Volmer constant of fluorescence as well as the Markovian rate constant of triplet quenching are calculated analytically, assuming the electron transfer is contact. The multiple Rehm−Weller effect is shown to be peculiar to both constants.

I. Introduction

The modern integral encounter theory (IET) is the unique theoretical method for investigation of reversible transfer reactions between metastable reactants.[1] The earliest kinetic theories considered only the irreversible forward electron transfer. According to Figure 1A, it turns the neutral reactants into the radical-ion pair (RIP) subjected to irreversible recombination and charge separation (with a yield $\bar{\varphi}$):

$$\begin{array}{lcccc} A^* + D & \xrightarrow{W_f} & [D^+ \ldots A^-] & \xrightarrow{\bar{\varphi}} & D^+ \ + \ A^- \\ \downarrow \tau_A & & \Downarrow W_R & & \end{array} \qquad (1.1)$$

Here $W_f(r)$ and $W_R(r)$ are the rates of forward and backward electron transfer (ionization and recombination) in a pair of reactants separated by distance r, provided the electron acceptor is excited and decays with time τ_A.

The classical theories developed by Smoluchowski[2] and Collins and Kimball[3] for irreversible and contact reactions (proceeding at the closest approach distance σ) were used for very long for studying the quenching of luminescence. If the latter follows the δ-pulse excitation, then the luminescence quantum yield is defined via the kinetics of energy quenching $N^*(t)$

$$\eta = \int_0^\infty N^*(t)\,\mathrm{d}t/\tau_A = \frac{1}{1 + c\kappa_i\tau_A} \qquad (1.2)$$

Here $N^*(t) = [A^*]$ is the survival probability of excitations and $c = [D] =$ constant is the concentration of quenchers which are present in great excess. Under such condition the Stern−Volmer constant of luminescence quenched by irreversible and contact ionization is known to be[4]

$$\kappa_i = \frac{k_f}{1 + k_f/k_D\,(1 + \sqrt{\tau_d/\tau_A})} \qquad (1.3)$$

where the kinetic and diffusional constants of ionization are

$$k_f = \int W_f(r)\,\mathrm{d}^3r \text{ and } k_D = 4\pi\sigma D$$

whereas $D = D_A + D_D$ is the encounter diffusion coefficient. The last term in the denominator of eq 1.3 accounts for the non-Markovian transient effect (during encounter time $\tau_d = \sigma^2/D$).

Being extended to remote electron transfer, the classical theory became known as differential encounter theory and later on as the unified theory of ionization and recombination.[5] However, these theories as well as their contact precursors are inapplicable to reversible electron transfer (Figure 1B). The latter can only be considered by means of IET whose spin-less version was first applied to the geminate reaction, that follows reversible ionization switched on by instantaneous light excitation, $I \propto \delta(t)$[6]

$$\begin{array}{lcccc} A^* + D & \underset{W_B}{\overset{W_f}{\rightleftarrows}} & [D^+ \ldots A^-] & \xrightarrow{\bar{\varphi}} & D^+ \ + \ A^- \\ I \uparrow\downarrow \tau_A & & \Downarrow W_R & & \\ D & & [D \ldots A] & & \end{array} \qquad (1.4)$$

IET made possible the calculation of the fluorescence quantum yield (1.2) on a time scale where the bulk recombination of radical ions can be completely neglected. There the Stern−Volmer dependence on concentration remains the same except that the geminate quenching constant κ_g should be substituted for κ_i.[6,7] In the contact approximation

$$\kappa_g = \frac{\kappa_i}{1 + \kappa_i/K(k_D + k_c)} \qquad (1.5)$$

where the equilibrium constant

$$K = k_f/k_b = \exp(-\Delta G_i/T) \qquad (1.6)$$

while the constants of the forward and reverse electron transfer are

$$k_f = \int W_f(r)\,\mathrm{d}^3r = k_f^0 \mathrm{e}^{-\frac{(\Delta G_i + \lambda_c)^2}{4\lambda_c T}},$$

$$k_b = \int W_B(r)\,\mathrm{d}^3r = k_b^0 \mathrm{e}^{-\frac{(\Delta G_i - \lambda_c)^2}{4\lambda_c \mathrm{T}}} \qquad (1.7)$$

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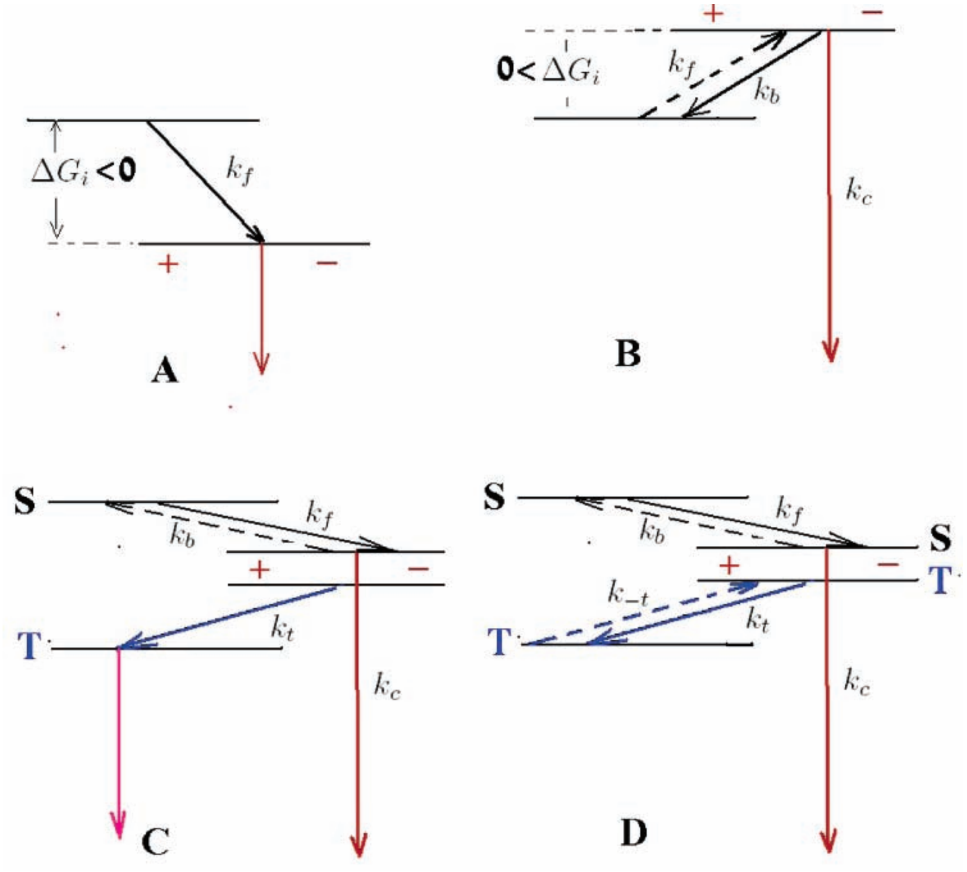

Figure 1. Spin-less models of electron transfer: (A) highly exergonic irreversible transfer and (B) endergonic forward transfer, followed by backward transfer and charge recombination to the ground state. Spin sensitive models: irreversible (C) and reversible (D) triplet formation follow reversible electron transfer between the RIP and excited singlet state.

and the rate constant of RIP recombination to the ground state is

$$k_c = \int W_R(r)\,d^3r = k_c^0 e^{-\frac{(\epsilon + \Delta G_i - \lambda_c)^2}{4\lambda_c T}} \tag{1.8}$$

Here ΔG_i and λ_c are the contact free energy of ionization and the reorganization energy of the polar solvent, T is the thermal energy ($k_B = 1$), and ϵ is the energy of acceptor excitation, which is the sum of the ionization and recombination free energies, $|\Delta G_i|$ and $|\Delta G_r|$

$$\epsilon = -\Delta G_i - \Delta G_r$$

The rate of single channel electron transfer in any direction is defined by the Marcus formula[8]

$$W(r) = V_0^{\,2} \exp\left(-\frac{2(r-\sigma)}{L}\right) \frac{\sqrt{\pi}}{\sqrt{\lambda T}} \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda T}\right) \tag{1.9}$$

where ΔG and λ are known functions of reactants separation, r.[1,5] Equation 1.9 was generalized for the multichannel (phonon-assisted) transfer by Bixon at al.[9,10] However, we are concerned here only with the simplest phonon-less model of transfer (1.9) with electron coupling V_0 and tunneling length L. In contact formulas 1.7 and 1.8, $\Delta G_i = \Delta G_I(\sigma)$ and $\lambda_c = \lambda(\sigma)$, whereas the pre-exponents marked by the upper index 0 are the rates of the corresponding activation-less transfer

$$k^0 \approx \int W(r)|_{\Delta G = -\lambda}\,d^3r$$

With increasing exergonicity $K \to \infty$. As a result, $\kappa_g \to \kappa_i$, according to eq 1.5. That is, the reversible geminate ionization becomes irreversible. The same happens even for quasi-resonant transfer ($K \sim 1$, $k_f \approx k_b$), if the RIP state is exhausted faster by recombination (k_c) and/or separation (k_D) than populated by the forward electron transfer. In the endergonic case ($\Delta G_i > 0$, $K \ll 1$), the excited and RIP states are equilibrated and their decay is controlled by the RIP dissipation: $\kappa_g \to K(k_D + k_c)$.

The situation is qualitatively different if the stationary fluorescence is studied using permanent illumination $I = I_0 =$ constant. After charge separation, the free ions recombine in the bulk to either the ground state or backward, to the excited neutral products, which contribute again to the total fluorescence

$$\begin{array}{ccccccccc}
A^* + D & \underset{W_B}{\overset{W_f}{\rightleftarrows}} & [D^+ \ldots A^-] & \xrightarrow{\bar{\varphi}} & D^+ + A^- & \underset{W_f}{\overset{W_B}{\rightleftarrows}} & [D \ldots A^*] & \longrightarrow & D + A^* . \\
I_0 \uparrow\downarrow \tau_A & & \Downarrow W_R & & \Downarrow W_R & & \downarrow \tau_A & & \downarrow \tau_A \\
A & & [D \ldots A] & & D + A & & [D \ldots A] & & A
\end{array} \tag{1.10}$$

The quantum yield of such a luminescence is defined differently than the nonstationary one[1,11]

$$\eta = \frac{N_s^*}{I_0 N_G \tau_A} = \frac{1}{1 + c\kappa_0 \tau_A} \tag{1.11}$$

Here N_s^* and N_G are the stationary densities of the acceptors in their excited and ground states and the corresponding Stern−Volmer constant is[12]

$$\kappa_0 = \kappa_g[1 - \chi\bar{\varphi}] \tag{1.12}$$

It is smaller than the geminate Stern−Volmer constant because not all excitations are quenched forever at first encounter. Some of them are restored with an efficiency χ in the subsequent bulk encounters of the free ions, separated with the yield $\bar{\varphi}$. All of the components of eq (1.12) are well defined in IET and when calculated in the contact approximation, reduces this expression to the following one:[13]

$$\kappa_0 = \frac{\kappa_i}{1 + \kappa_i/Kk_c} \tag{1.13}$$

The principle difference between this result and the geminate one, eq 1.5, is an absence of k_D in the denominator. Diffusional RIP separation cannot make the stationary energy quenching irreversible. It does not put an end to the reversible reaction but just interrupt it for a while. Only the irreversible recombination to the ground state of the neutral product proceeding with the rate constant k_c causes this to happen. If $k_c = 0$, the ionization is fully reversible; that is, $\kappa_0 = 0$ and the fluorescence is not quenched at all. But as $k_c \to \infty$ the quenching becomes irreversible; that is, $\kappa_0 \equiv \kappa_i$. Almost the same is true when $K \gg \kappa_i/k_c$, whereas in the opposite case, the ionization is mainly reversible and proceeds with the rate constant $\kappa_0 \approx Kk_c$.

Considered as a function of ΔG_i, the Stern–Volmer constant demonstrates the typical stepwise behavior: at large negative ΔG_i, where $K \to \infty$, it is almost a constant, $\kappa_0 \approx \kappa_i \approx k_D$, but this diffusional plateau is cut abruptly when K reduces to 1 (at $\Delta G_i = 0$) and then turns to zero at the endergonic region (when $\Delta G_i \to \infty$). Such behavior first obtained by Rehm and Weller in ref 14 was considered as universal for a very long time, until it was found recently that in different families of reactants the cut off is placed at different ΔG_i.[15] Such a phenomenon was called by discoverers “the multiple Rehm–Weller effect”. We have already related it to the different rates of irreversible recombination of different singlet RIPs[1] or to different rates of triplet formation from triplet RIPs, provided this recombination is also irreversible.[12] The last condition is met if the triplets die soon after formation, due to their annihilation. This was shown to be the case in the system perylene + DMA where the triplet decay was studied and fitted well assuming the biexciton annihilation is the only quenching mechanism.[16] However, it was shown recently that the dominant quenching mechanism of other triplet molecules is the transfer of electrons to them from the same donors that execute the ionization of singlet excitations.[17] In such a case, the triplet RIPs recombination to neutral triplet products has to be considered as reversible when calculating the Stern–Volmer constant, as well as the triplet quenching rate. This is what we are going to do here, revising the free energy dependence of both and comparing them between themselves and with the available experimental data from ref 17.

First we will consider in the next section the irreversible triplet RIP recombination, which is so fast that the singlet one can be ignored, as in ref 12. The irreversibility of RIP recombination to the triplet acceptor state is conditioned by even faster exhausting of the latter due to biexciton annihilation or other triplet quenching. In the opposite case when triplets decay with their long life time, they may be considered as the stable particles ionized in encounters with donors (Figure 1D). In such a case, their formation being reversible affects differently the geminate production of ions and triplets, as well as the yields of the stationary luminescence. All of them are calculated in section III as well as the asymptotic (Markovian) rate constant of triplet quenching after the light is switched off.

II. Irreversible Triplet Production

As is clear from the preceding, the photoionization produces not only the free ions, ${}^2D^+$ and ${}^2A^-$, but also the triplet products of their recombination, ${}^3A^*$, detectable by their characteristic absorption spectra. Since the ions are actually radical-ions, their pairs are formed in either the singlet or triplet states. Furthermore, the singlet RIP produced from the singlet precursor, ${}^1A^*$, is subjected not only to luminescence and recombination but also to spin-conversion into the triplet RIP, from where the recombination to a triplet excitation of neutral acceptor is allowed. If this recombination is completely irreversible, as well as the singlet one (Figure 1 C), then there are two parallel channels of RIP recombination competing between themselves: Instead of the distant dependent rates, $W(r)$, we are using in this scheme the corresponding rate constants, $k = \int W(r)\,d^3r$, including a new one, k_t, which determines the triplet RIPs recombination producing the neutral triplets, ${}^3A^*$.

$$\begin{array}{ccccc}
 & & {}^2D^+ + {}^2A^- & & \\
 & \nearrow\swarrow & \bar{\varphi} & \nwarrow\searrow & \\
{}^1A^* + D & \underset{k_b}{\overset{k_f}{\rightleftharpoons}} & {}^1[D^+ \ldots A^-] \quad \underset{k_s}{\longleftrightarrow} & {}^3[D^+ \ldots\ A^-] & \\
I \uparrow\downarrow \tau_A & & k_c \downarrow \varphi_S & \varphi_T \downarrow k_t & \\
A & & D + A & D + {}^3A^* &
\end{array} \tag{2.1}$$

It was shown that the spin-conversion proceeding with a rate k_s affects not only the kinetics of ionization, $N^*(t)$, but also the yields of ions, $\bar{\varphi}$, as well as the singlet and triplet products of geminate recombination, φ_S and φ_T.[18,19] Evidently, $\bar{\varphi} + \varphi_T + \varphi_S = 1$, but the partial values of these yields and their viscosity (diffusional) dependence are different. Even at equal rates of triplet and singlet RIPs recombination, the yield of the triplet excitations, φ_T, is usually much smaller than that of the ground state products, φ_S.[1] This is because the recombination of the triplet RIPs does not start from the beginning of the encounter but only after the triplet states are populated by spin conversion. This takes part of the encounter time τ_d while the recombination of the singlet RIP proceeds all of this time. This conclusion was recently confirmed with a more consistent theory using the coherent (Hamiltonian) description of spin-conversion instead of the incoherent one (with the rate k_s).[20]

A different situation arises when the stationary luminescence is studied. This phenomenon includes not only the geminate effects but the recombination of ions in the bulk as well. Since the spins of radical-ions meeting in the bulk are uncorrelated, the RIPs appear in either the singlet or triplet states with their stochastic weights, 1/4 and 3/4, respectively. On the contrary, the redistribution of the RIP spin states populations by spin-conversion during the encounter is negligible, if $k_s\tau_d \ll 1$. This is usually the case if it is carried out by an HFI-mechanism, when $k_s \sim 10^8$ s^{-1}, whereas the encounter time is $\tau_d \sim 10^{-10}$ s at normal viscosities.[14] Under such conditions one can set $k_s = 0$, looking for the stationary phenomena.

This is exactly what was done in ref 12 estimating the Stern–Volmer constant of reversible ionization. It was also assumed that the recombination of triplet RIPs, being irreversible, is also the strongest one. In the extreme case when the singlet recombination is negligible, it follows from eq 4. 1 of ref 12

$$\chi = \frac{k_b(1 + k_t/k_D)}{k_b(1 + k_t/k_D) + 3k_t[1 + k_f/k_D(1 + \sqrt{\tau_d/\tau_A}) + k_b/k_D]}$$

$$\text{provided } k_{-t} = k_c = 0$$

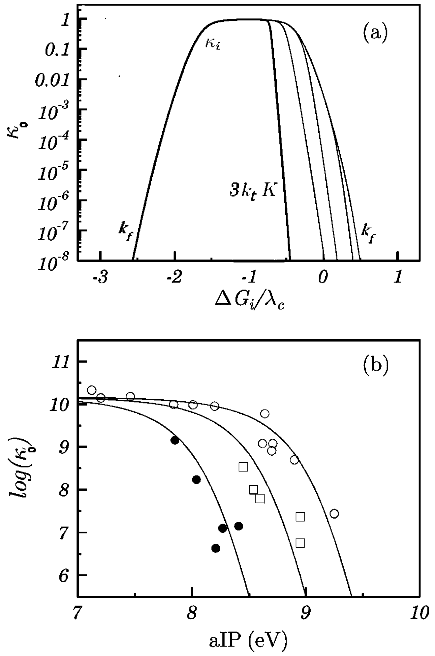

Figure 2. (a) Free energy dependence of the Stern−Volmer constant, κ_0, for different rates of irreversible triplet recombination $k_t^0/k_D = \infty$; 20; 0.1; 10^{-5}; 10^{-8} (from right to left) at $k_c = 0$. The external curve represents the Stern−Volmer constant of irreversible ionization, $\kappa_i(\Delta G_i)$, composed from the FEG parabola for forward electron transfer, $\kappa_f(\Delta G_i)$ and diffusional plateau $\kappa_i \approx k_D =$ constant which cuts the top of it. (b) Interpolation through the experimental points in acetonitrile (borrowed from Figure 10 of ref 12).

Since $\bar{\varphi} = 1$, in the absence of spin conversion (at $k_s = 0$), the Stern−Volmer constant is

$$\kappa_0 = \kappa_g(1 - \chi) = \frac{\kappa_i}{1 + \kappa_i(1 + 4k_t/k_D)/3k_tK} = \begin{cases} \dfrac{\kappa_i}{1 + \kappa_i/3k_tK} & \text{triplet production control} \\ \dfrac{\kappa_i}{1 + 4\kappa_i/3k_DK} & \text{RIP separation control} \end{cases} \tag{2.2}$$

There are evidently two limits: when triplet RIP recombination proceeds slower than its diffusional separation, the whole process is under triplet production control, and in the opposite case, it is controlled by RIP separation.

As seen from the comparison of eqs 2.2 and 1.13, the irreversible triplet RIP recombination plays the same role as the singlet RIP recombination, exhausting the RIP states. However, this concerns only the triplet states while the singlet population survives and contributes to the backward electron transfer. Therefore, the singlet ionization remains partially reversible even as $k_t \to \infty$, when the quenching, controlled by RIP dissociation, proceeds with the rate $(3/4)k_DK$. This is because only 75% of the separated ions recombine into the triplet product at the next encounter.

If under triplet production control the triplet RIP recombination is rather fast $\kappa_0 = \kappa_i \ll 3k_t$. In the opposite case, when the recombination is the slowest one ($3k_t \ll \kappa_0$), the highly irreversible ionization gives way to its reversible analog with $\kappa_0 = 3k_tK$. The former is indicated by the diffusional plateau $k_D[1 + (\tau_d/\tau_A)^{1/2}]$ reached by κ_i at strong $k_f \gg k_D$, whereas the latter shifts with k_t to the higher free energies, making the resonant and even endergonic reaction irreversible (Figure 2a). This can be the origin of the multiple Rehm−Weller effect revealing itself in a number of the descending branches (Figure 2b) particular to different families of reactants.[15]. At least this was the explanation given to such a phenomenon in ref 12, assuming that the recombination of triplet RIPs proceeding with the rate constant

$$k_t = k_t^0 \exp\left[-\frac{(\Delta G_t - \lambda_c)^2}{4\lambda_c T}\right] \tag{2.3}$$

is irreversible. Generally speaking, this is not true. According to the detailed balance principle, the backward transfer (ionization of triplet excitations) has the rate constant

$$k_{-t} = k_tK_t, \text{ where } K_t = e^{-\Delta G_t/T} \tag{2.4}$$

At $\Delta G_t < 0$, the ionization of the triplets is faster than their production and cannot be ignored unless the triplets are very unstable. This instability may be due to reaction with solvent or biexcitonic quenching which is rather fast under strong light illumination. This was implied in ref 12, and our other works addressed mainly the quenching of Perylene by DMA. In such a system, the triplet ionization is highly endergonic ($\Delta G_t = +0.72$ eV) but triplets were shown to be quenched by a biexcitonic annihilation (as in Chapter XIII of a recent review[1])

$${}^1A^* + A \leftarrow {}^3A + {}^3A \rightarrow {}^3A^* + A. \tag{2.5}$$

This reaction which is mainly responsible for the quenching of triplets, when they are copiously produced by a strong light pulse, was studied in ref 16. Not only the triplet quenching kinetics was well fitted in this work but the delayed luminescence of singlets produced by their annihilation (2.5) was detected and fitted as well. The annihilation of triplets prevents their ionization and allows one to neglect the ionization during the geminate stage of the reaction. However, this becomes more problematic for stationary fluorescence because the light illumination is weaker and consequently the stationary triplet concentration is lower, as well as the annihilation rate quadratic in it.

III. Reversible Triplet Production

Recently reported experiments indicate that in a few systems studied the triplets are mainly quenched by electron transfer from the same donors as the singlets: their quenching rate was found to be proportional to donor concentration.[17] Also a close similarity was found to exist between the free energy dependencies of the Stern−Volmer constant and the triplet quenching rate constant. Here we will calculate both of them, neglecting completely the biexcitonic annihilation but accounting for triplet ionization.

In the general reaction scheme of such a reaction $\tau_A \equiv \tau_S$ and τ_T is the triplet life time

$$\begin{tikzcd} & & {}^2D^+ + {}^2A^- \arrow[dl, shift left] \arrow[dr, shift left] & & \\ D + {}^1A^* \arrow[r, shift left, "k_f"] \arrow[d, "\tau_S"] & {}^1[D^+ \ldots A^-] \arrow[l, shift left, "k_b"] \arrow[ur, shift left] \arrow[r, leftrightarrow, "k_s"] \arrow[d, Rightarrow, "k_c"] & & {}^3[D^+ \ldots A^-] \arrow[ul, shift left] \arrow[r, shift left, "k_t"] & D + {}^3A^* \arrow[l, shift left, "k_{-t}"] \arrow[d, "\tau_T"] \\ {} & {} & & & {} \end{tikzcd} \tag{3.1}$$

The scheme allows 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. Assuming $k_s = 0$, we will demonstrate that the reversible ionization of quasistable triplets does not affect the stationary fluorescence.

Only the recombination of the singlet RIP to the ground state makes the luminescence quenching irreversible. Therefore, not k_t as in eq 2.2 but k_c controls the endergonic energy quenching as in eq 1.13 of the spin-less theory in ref 13. The variation of this very rate constant must be responsible for the multiple Rehm−Weller effect in luminescence, at a reasonably weak stationary illumination.

The general IET equations for the densities of the excited singlet acceptors $N_S \equiv N^*$, the radical ions of both signs, $P = [D^+] = [A^-]$, and the excited triplet product of their recombination, N_T, are taken from the Appendix to ref 12

$$\dot{N}_S = -\frac{N_S}{\tau_S} - c\int_0^t R^*(t-\tau)N_S(\tau)\,d\tau + \int_0^t R^{\#}(t-\tau)P^2(\tau)\,d\tau + c\int_0^t R^{\S}(t-\tau)N_T(\tau)\,d\tau \quad (3.2a)$$

$$\dot{P} = c\int_0^t R^{\dagger}(t-\tau)N_S(\tau)\,d\tau - \int_0^t R^{\ddagger}(t-\tau)P^2(\tau)\,d\tau + c\int_0^t R^{\diamond}(t-\tau)N_T(\tau)\,d\tau \quad (3.2b)$$

$$\dot{N}_T = -\frac{N_T}{\tau_T} + c\int_0^t R^{\Delta}(t-\tau)N_S(\tau)\,d\tau + \int_0^t R^{\blacksquare}(t-\tau)P^2(\tau)\,d\tau - c\int_0^t R^{\bigstar}(t-\tau)N_T(\tau)\,d\tau \quad (3.2c)$$

If there is an effective quenching of triplet acceptors making N_T small, the last terms in the eqs 3.2a−c can be neglected and the whole set reduces to that used in ref 12 and in the previous section for studying the irreversible triplet formation.

Assuming that any transfer reaction proceeds at contact the following exact definitions for the Laplace transformations of all the kernels of the integral eqs 3.2a−c are obtained

$$\tilde{R}^* = k_f[4 + g_0^{\,2}k_ck_{-t} + g_1(3k_c + k_t) + g_0(k_c + 3k_t + 4k_{-t} + 3g_1k_ck_{-t} + 4g_1k_ck_t)]/Y \quad (3.3a)$$

$$\tilde{R}^{\#} = k_b(1 + g_0k_{-t} + g_1k_t)/Y, \quad \tilde{R}^{\S} = (g_0 - g_1)k_bk_{-t}/Y, \quad \tilde{R}^{\dagger} = 4k_f(1 + g_0k_{-t} + g_1k_t)/Y \quad (3.3b)$$

$$\tilde{R}^{\ddagger} = [k_b(1 + g_0k_{-t} + 4g_1k_t) + (1 + g_sk_f)(3k_t + k_c + g_0k_ck_{-t} + 4g_1k_ck_t)]/Y \quad (3.3c)$$

$$\tilde{R}^{\diamond} = 4k_{-t}[(1 + g_sk_f)(1 + g_1k_c) + g_1k_b]/Y, \quad \tilde{R}^{\Delta} = 3(g_0 - g_1)k_fk_t/Y \quad (3.3d)$$

$$\tilde{R}^{\blacksquare} = 3k_t[(1 + g_sk_f)(1 + g_1k_c) + g_1k_b]/Y \quad (3.3e)$$

$$\tilde{R}^{\bigstar} = k_{-t}[(1 + g_sk_f)(4 + g_0k_c + 3g_1k_c) + k_b(g_0 + 3g_1)] \quad (3.3f)$$

Hereafter tilde will denote the Laplace transformation with s being the Laplace variable. Here

$$Y = (1 + g_0k_{-t})[(1 + g_sk_f)(4 + g_0k_c + 3g_1k_c) + k_b(g_0 + 3g_1)] + [(1 + g_sk_f)(g_1 + 3g_0 + 4g_0g_1k_c) + 4g_0g_1k_b]k_t$$

$$g_0(s) = \frac{1}{k_D[1 + \sqrt{s\tau_d}]}, \quad g_1(s) = \frac{1}{k_D[1 + \sqrt{(s + 4k_s)\tau_d}]}, \quad g_s(s) = \frac{1}{k_D[1 + \sqrt{(s + 1/\tau_S)\tau_d}]}. \quad (3.4)$$

There are two different ways to study the quenching of the fluorescence initiated by the light of intensity $I(t)$. The oldest and most common way is to study the stationary illumination $I(t) = I_0$ which allows measuring the permanent fluorescence quantum yield (1.11). A similar yield could be found from eq 1.2 studying only the geminate reaction during a short time interval, following the instantaneous light excitation of the N_0 acceptors, $I(t) = N_0\delta(t)$.

A. Geminate Reaction. The geminate production of ions and triplet excitations, shortly after instantaneous excitation, has to be investigated ignoring the bulk reactions: charge recombination and ionization of triplet products. This can be done setting $P = N_T = 0$ in the right-hand side of eqs 3.2a−c which reduce to the following set:

$$\dot{N}_S = -\frac{N_S}{\tau_S} - c\int_0^t R^*(t-\tau)N_S(\tau)\,d\tau \quad N_S(0) = N_0 \quad (3.5a)$$

$$\dot{P} = c\int_0^t R^{\dagger}(t-\tau)N_S(\tau)\,d\tau \quad P(0) = 0 \quad (3.5b)$$

$$\dot{N}_T = -\frac{N_T}{\tau_T} + c\int_0^t R^{\Delta}(t-\tau)N_S(\tau)\,d\tau \quad N_T(0) = 0 \quad (3.5c)$$

This set was studied in section III.B in ref 12 assuming that the triplet recombination is irreversible ($k_{-t} = 0$). This is impossible in principle due to the detailed balance relationship (2.4) but can be used as an approximation, provided τ_T is abnormally short (or $\Delta G_t \gg T$).

In reality τ_T is the longest time, that may be set infinite, when the geminate reaction is studied. In such a case, one can easily find from the Laplace transformed eqs 3.5

$$\tilde{N}_S(0) = \frac{N_0\tau_S}{1 + c\tau_S\tilde{R}^*(0)} \quad (3.6a)$$

$$P(\infty) = \lim_{s\to 0} s\tilde{P}(s) = c\tilde{R}^{\dagger}(0)\tilde{N}_S(0) = N_0\psi\bar{\varphi} \quad (3.6b)$$

$$N_T(\infty) = \lim_{s\to 0} s\tilde{N}_T(s) = c\tilde{R}^{\Delta}\tilde{N}S(0) = N_0\psi\varphi_T \quad (3.6c)$$

where the total yield of ions $\psi = 1 - \eta$.

Using the result (3.6a) in an equation identical to (1.2), we reproduce the Stern−Volmer law

$$\eta = \frac{\tilde{N}_S(0)}{N_0\tau_S} = \frac{1}{1 + c\kappa_g\tau_S}, \quad \psi = \frac{c\kappa_g\tau_S}{1 + c\kappa_g\tau_S} \quad (3.7)$$

whose constant is

$$\kappa_g = \tilde{R}^*(0) \quad (3.8)$$

By using the last results and $\tilde{N}_S(0)$ in other eqs (3.6), we get the quantum yields of the separated ions and triplet products

$$\bar{\varphi} = \frac{\tilde{R}^{\dagger}(0)}{\tilde{R}^*(0)}, \quad \varphi_T = \frac{\tilde{R}^{\Delta}(0)}{\tilde{R}^*(0)} \quad (3.9)$$

In the present article, we are concerned with the reversible ionization of triplets whose appearance on the geminate stage of the reaction (2.1) is conditioned by the spin-conversion. If the latter is negligible ($k_s = 0$) then

$$g_0(0) = g_1(0) = 1/k_D, \quad g_s(0) = \frac{1}{k_D[1 + \sqrt{\tau_d/\tau_S}]} = 1/k_D^* \tag{3.10}$$

and for any k_t and k_{-t}, we obtain in the contact approximation

$$\tilde{R}^*(0) = 4k_f(1 + k_c/k_D)[1 + (k_t + k_{-t})/k_D]/Y \tag{3.11a}$$

$$\tilde{R}^\dagger(0) = 4k_f[1 + (k_t + k_{-t})/k_D]/Y \tag{3.11b}$$

$$\tilde{R}^\ddagger(0) = \{[k_b + k_c(1 + k_f/k_D^*)][1 + (k_{-t} + 4k_t)/k_D] + 3k_t(1 + k_f/k_D^*)\}/Y \tag{3.11c}$$

$$\tilde{R}^\#(0) = k_b[1 + (k_t + k_{-t})/k_D]/Y \tag{3.11d}$$

$$\tilde{R}^\diamond(0) = 4k_{-t}[(1 + k_f/k_D^*)(1 + k_c/k_D) + k_b/k_D]/Y = \tilde{R}^\bigstar(0) = \frac{4k_{-t}}{3k_t}\tilde{R}^\blacksquare(0) \tag{3.11e}$$

where

$$Y = 4(1 + k_f/k_D^*)[1 + k_c/k_D + k_b/k_D(1 + k_f/k_D^*)][1 + (k_{-t} + k_t)/k_D]$$

The geminate Stern−Volmer constant

$$\kappa_g = \tilde{R}^*(0) = \frac{k_f(1 + k_c/k_D)}{[1 + k_f/k_D^*][1 + k_c/k_D + k_b/k_D(1 + k_f/k_D^*)]} = \frac{\kappa_i}{1 + \frac{\kappa_i}{K(k_D + k_c)}} \tag{3.12}$$

is identical to that given in the spin-less eq (1.5). The other yields

$$\bar{\varphi} = \frac{1}{1 + k_c/k_D} \text{ and } \varphi_T = 0 \tag{3.13}$$

also are exactly the same as in the spin-less unified theory.[5]

B. Stationary Fluorescence. When the system is under permanent illumination, $I = I_0$, the luminescence quantum yield should be calculated from the definition (1.11) using there $N_s^* \equiv \hat{N}_S = N_S(\infty)$, obtained from the stationary solution of eqs 3.2a−c

$$\hat{N}_S = \frac{I_0 N_G \tau_S}{1 + c\kappa_0\tau_S} \tag{3.14a}$$

$$\hat{P}^2 = c\frac{\tilde{R}^\dagger(0)}{\tilde{R}^\ddagger(0)}\left[\hat{N}_S + \frac{\tilde{R}^\diamond(0)}{\tilde{R}^\dagger(0)}\hat{N}_T\right] \tag{3.14b}$$

$$\hat{N}_T = \hat{N}_S \cdot \frac{\tilde{R}^\Delta(0)\tilde{R}^\ddagger(0) + \tilde{R}^\blacksquare(0)\tilde{R}^\dagger(0)}{\tilde{R}^\bigstar(0)\tilde{R}^\ddagger(0) - \tilde{R}^\blacksquare(0)\tilde{R}^\diamond(0)} \tag{3.14c}$$

Here $\hat{N}_S$, $\hat{N}_T$, and $\hat{P}$ are the stationary concentrations of the excited states and ions, whereas κ_0 is the Stern−Volmer constant of the quantum yield defined in eq 1.11

$$\kappa_0 = \tilde{R}^*\left\{1 - \frac{\tilde{R}^\#(0)}{\tilde{R}^\ddagger(0)}\cdot\frac{\tilde{R}^\dagger(0)}{\tilde{R}^*(0)} - \frac{[\tilde{R}^\S(0)\tilde{R}^\ddagger(0) + \tilde{R}^\#(0)\tilde{R}^\diamond(0)][\tilde{R}^\Delta(0)\tilde{R}^\ddagger(0) + \tilde{R}^\blacksquare(0)\tilde{R}^\dagger(0)]}{\tilde{R}^\ddagger(0)\tilde{R}^*(0)[\tilde{R}^\bigstar(0)\tilde{R}^\ddagger(0) - \tilde{R}^\blacksquare(0)\tilde{R}^\diamond(0)]}\right\}$$

Everything becomes much simpler if we neglect the spin conversion setting $k_s = 0$. Then according to eq 3.10 in such a case

$$\tilde{R}^\S(0) = \tilde{R}^\Delta(0) = 0$$

and the last expression for the Stern−Volmer constant takes the form of eq 1.12, with the following microscopic definitions of all its components:

$$\kappa_g = \tilde{R}^*(0), \quad \chi = \frac{\tilde{R}^\#(0)}{\tilde{R}^\ddagger(0)}\cdot\frac{\tilde{R}^\bigstar(0)\tilde{R}^\ddagger(0)}{\tilde{R}^\bigstar(0)\tilde{R}^\ddagger(0) - \tilde{R}^\blacksquare(0)\tilde{R}^\diamond(0)}, \quad \bar{\varphi} = \frac{\tilde{R}^\dagger(0)}{\tilde{R}^*(0)} \tag{3.15}$$

It should be noted that $\hat{N}_T \neq 0$ in this case, unlike φ_T in eq 3.13, because triplets are produced from the triplet RIPs formed in each encounter of the spin uncorrelated free radical ions.

In the contact approximation and absence of spin conversion, there is the relationship (3.11e) which makes the probability of singlet restoration much simpler

$$\chi = \frac{\tilde{R}^\#(0)}{\tilde{R}^\ddagger(0) - \tilde{R}^\blacksquare(0)} \tag{3.16}$$

Taking into account other kernels (3.11), eq 3.16 appears to be even simpler

$$\chi = \frac{k_b}{k_b + k_c(1 + k_f/k_D^*)} = \frac{\kappa_i/k_cK}{1 + \kappa_i/k_cK} \tag{3.17}$$

It coincides with that for a spin-less theory which is independent of k_t and k_{-t}.[13] This is because the stable triplets do not participate in the fluorescence quenching, although there are permanently a definite number of them, given by eq 3.14c. They can be detected by either light absorption or phosphorescence, as well as the stationary density of ions $\hat{P}$ given in (3.14b) could 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. If the latter is absent ($k_c = 0$) then according to eqs 3.17 and 3.13, $\chi = \bar{\varphi} = 1$ and $\kappa_0 = \kappa_g(1 - \chi\bar{\varphi}) = 0$, that is the luminescence quenching is not possible at all.

As a matter of fact, the general spin-less equation for the Stern−Volmer constant (1.13) remains also valid at $k_c \neq 0$, that is regardless of whether the stable triplets are formed or not. One can find from there that

$$\kappa_0 = \frac{\kappa_i}{1 + \kappa_i/Kk_c} = \begin{cases} \kappa_i = \dfrac{k_f}{1 + k_f/k_D^*} & \text{as } k_c \to \infty \text{ ionization control} \\ k_cK & \text{as } k_c \to 0 \text{ recombination control} \end{cases} \tag{3.18}$$

Under ionization control, the free energy dependence of κ_0 reproduces that of κ_i, which coincides with the bell-shaped curve $k_f(\Delta G_i)$ from eq 2.3, except that the top of the latter is cut by

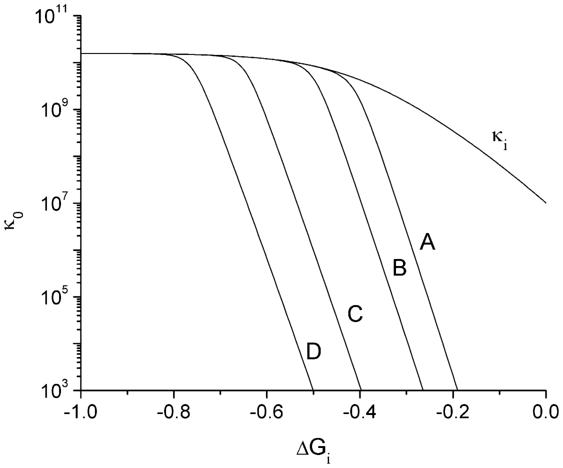

Figure 3. Free energy dependence of the Stern−Volmer constant at different RIP recombination rate constants, whose Arrhenius prefactor $k_c^0 = \infty$ for the upper curve and for the rest k_c^0/k_D is 20 (A), 0.1 (B), 10^{-5} (C), and 10^{-8} (D). The singlet excitation energy is 2.83 eV, $k_D = 10^{10}$ 1/Ms, $\tau_d = 2.8$ ns, $\tau_A = 5.5$ ns, $\lambda = 1$ eV.

the diffusional plateau $k_D^* = k_D/[1 + (\tau_d/\tau_A)^{1/2}]$ = constant (Figure 3). With increasing ΔG_i, the singlet ionization becomes quasireversible and occurs earlier when the RIP recombination is slower (Figure 3). As soon as the diffusional ionization gives way to recombination control, the latter abruptly cuts the right branch of the free energy dependence of $\kappa_i \approx k_f$.

C. Triplet Quenching by Ionization. The triplet decay can be easily obtained after the geminate reaction, following δ-pulse excitation, or after suddenly switching off the permanent illumination. Soon after the singlet life time, the vast majority of excitations are triplets that decay much longer, unless they are not quenched by ionization (the electron transfer from donors). Since the triplets live long, the concentration of ions, produced quasistationary, follows them as well as the singlet concentration. All of them obey equations following from the general set (3.2), which are at $k_s = 0$ the following ones:

$$0 = -c\tilde{R}^*(0)N_S + \tilde{R}^{\#}(0)P^2 - \frac{N_S}{\tau_S} \tag{3.19a}$$

$$0 = c\tilde{R}^{\dagger}(0)N_S - \tilde{R}^{\ddagger}(0)P^2 + c\tilde{R}^{\diamond}(0)N_T \tag{3.19b}$$

$$\dot{N}_T = \tilde{R}^{\blacksquare}(0)P^2 - c\tilde{R}^{\bigstar}(0)N_T - \frac{N_T}{\tau_T} \tag{3.19c}$$

Solving them, we obtain

$$N_S = \frac{c\tau_S\tilde{R}^{\#}(0)\tilde{R}^{\diamond}(0)}{\tilde{R}^{\ddagger}(0) + c\tau_S[\tilde{R}^*(0)\tilde{R}^{\ddagger}(0) + \tilde{R}^{\#}(0)\tilde{R}^{\dagger}(0)]}N_T \tag{3.20a}$$

$$P^2 = c\frac{\tilde{R}^{\diamond}(0)}{\tilde{R}^{\ddagger}(0)}\left[1 + \frac{c\tau_S\tilde{R}^{\#}(0)\tilde{R}^{\dagger}(0)}{\tilde{R}^{\ddagger}(0) + c\tau_S[\tilde{R}^*(0)\tilde{R}^{\ddagger}(0) + \tilde{R}^{\#}(0)\tilde{R}^{\dagger}(0)]}N_T\right. \tag{3.20b}$$

$$\dot{N}_T = -\frac{N_T}{\tau_T} - ck_QN_T \tag{3.20c}$$

As was expected at low concentrations, N_S is small compared to N_T and the second term in the square brackets in eq 3.20b can be neglected in the first order approximation with respect to c. In this approximation, the rate constant of triplet quenching is

$$k_Q = \tilde{R}^{\bigstar}(0)[1 - \tilde{R}^{\blacksquare}(0)/\tilde{R}^{\ddagger}(0)] \tag{3.21}$$

In the contact approximation

$$k_Q = k_{-t}\frac{1 + k_b/k_c(1 + k_f/k_D^*)}{1 + k_b/k_c(1 + k_f/k_D^*) + (k_{-t} + 4k_t)/k_D + 3k_t/k_c} \tag{3.22}$$

The general overview of the free energy dependence of k_Q at different charge recombination rates is given in Figure 4.

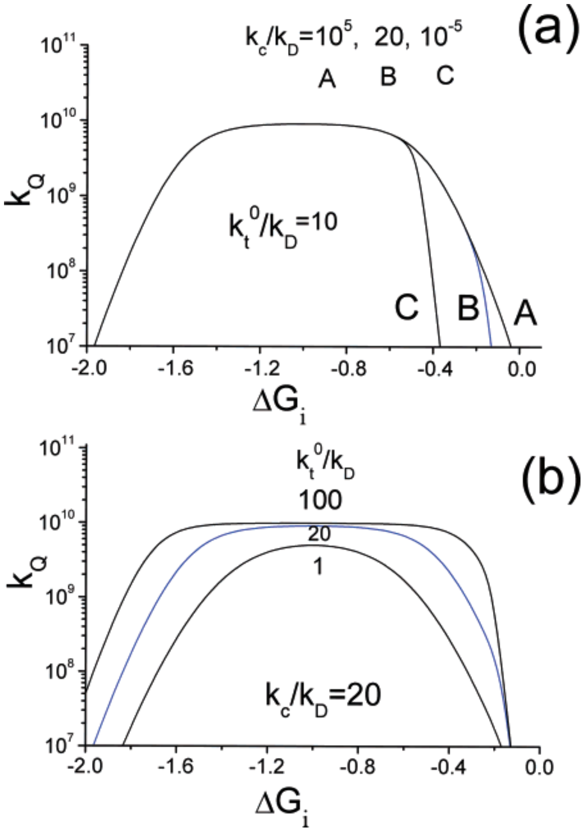

Figure 4. Rate constant of the triplet quenching via triplet ionization: (a) at $k_t^0/k_D = 10$ and $k_c^0/k_D = 10^5$ (A), 20 (B), and 10^{-5} (C); (b) at different k_t^0/k_D = 1, 20, and 100 (from bottom to top) and $k_c^0/k_D = 20$. The singlet excitation energy $\epsilon = 2.83$ eV, whereas the singlet−triplet splitting is taken as 0.28 eV and $k_t^0/k_D = 20$. The rest of parameters are the same as before.

The free energy dependence of either κ_0 or k_Q is usually studied at negative ΔG_i, where according to the Marcus free energy gap (FEG) law[8] k_b is expected to be small unlike k_c passing through the maximum at $\Delta G_i = -\epsilon + \lambda$. In this area, expression 3.22 can be simplified assuming $k_b \ll k_c$

$$k_Q = \frac{k_{-t}k_c}{k_c[1 + (k_{-t} + 4k_t)/k_D] + 3k_t} = \begin{cases} \dfrac{k_{-t}k_D}{k_D + k_{-t} + 4k_t} & \text{as } k_c \gg k_t \text{ (ionization control)} \\ \dfrac{k_c}{3}K_t & \text{as } k_c \ll k_t \text{ (recombination control)} \end{cases} \tag{3.23}$$

In the last expression, $K_t = k_{-t}/k_t$ introduced in eq 2.4 is an equilibrium constant for reversible transitions between the triplet RIPs and neutral triplets. The origin of the coefficient 1/3 is also easy to trace. The recombination of RIPs proceeding through only one, from their four sublevels, has the rate $(k_c/4)P$. Since there is an equilibrium between the four-level RIP and its three-level neutral product, $P = (4/3)K_tN_T$. Hence, the rate of quenching under recombination control is $(k_c/4)(4/3)K_tN_T = (k_c/3)K_t\,N_T$.

If the charge recombination proceeding from the singlet RIP is the fastest one, then

$$k_Q = \frac{k_{-t}}{1 + (k_{-t} + 4k_t)/k_D} = \begin{cases} k_{-t} & \text{under kinetic control} \\ \dfrac{k_D}{1 + 4/K_t} & \text{under diffusion control} \end{cases} \tag{3.24}$$

Under kinetic control, the free energy dependence of k_Q follows the parabolic FEG law inherent to k_{-t} but the top of $k_Q(\Delta G_i)$ is cut by the diffusional plateau. This is the region of diffusional control where $k_Q = k_D$ because $K_t \gg 1$.

The Stern−Volmer constant also levels off there, reaching the maximum value inherent in its own plateau: $\kappa_0 = k_D^* = k_D[1 + (\tau_d/\tau_A)^{1/2}]$. The latter lies a bit higher than that for $k_Q \leq k_D$ (Figure 4). This is the theoretical confirmation of the fact obtained experimentally in ref 17 and particularly emphasized in this work. As a matter of fact, the ratio of the plateau's heights

$$\frac{\kappa_0}{k_Q} = k_D^*/k_D = 1 + \sqrt{\tau_d/\tau_A} > 1 \text{ under diffusional control,}$$

due to the non-Markovian contribution to κ_0. This difference can be varied by changing τ_d, which is proportional to the solvent viscosity.

As to the descending branches of $\kappa_0(\Delta G_i)$ and $k_Q(\Delta G_i)$, they are very similar under recombination control. It follows from eqs 3.18 and 3.23 that

$$\kappa_0 = k_c(\Delta G_i)e^{-\Delta G_i/T},$$
$$k_Q = \frac{1}{3}k_c(\Delta G_i)e^{-\Delta G_t/T} = \frac{1}{3}k_c(\Delta G_t - \epsilon)e^{-\Delta G_t/T} \tag{3.25}$$

since $\Delta G_i = \Delta G_t - \epsilon$. Here ϵ is the energy splitting between the singlet and triplet energy levels, $^1A^*$ and $^3A^*$, equal to 0.31 eV in the system studied in ref 17. This splitting is responsible for the parallel shift of the descending branch to the right, when going from $\kappa_0(\Delta G_0)$ to $k_Q(\Delta G_0)$ in Figure 5. Following the authors of ref 17, we set $\Delta G_0 = \Delta G_i$ in κ_0 but $\Delta G_0 = \Delta G_t$ in k_Q when depicting them in this figure as functions of the common coordinate, ΔG_0. Two black $\kappa_0(\Delta G_0)$ curves join together at large ΔG_0, as well as two red $k_Q(\Delta G_0)$ curves because in the recombination control limit nothing depends on the ionization rates k_f or k_t. However, the splitting between these linearized descending branches of κ_0 and k_Q stabilizes when ΔG_0 approaches 0. It can be characterized by the difference between the κ_0 and k_Q arguments, whereby these functions are equal, $\kappa_0(\Delta G_0) = k_Q(\Delta G_0 + x)$. In view of eqs 3.25, this difference, x, is defined by the equality

$$k_c(\Delta G_0) = \frac{1}{3}k_c(\Delta G_0 + x - \epsilon)e^{-x/T}$$

Using the definition of k_c given in eq 1.8, we obtain from here the quadratic equation for $z = x - \epsilon$

$$z^2 - 2(\epsilon + \Delta G_0 + \lambda_c)z + 4\lambda_c(\epsilon - T\ln 3) = 0$$

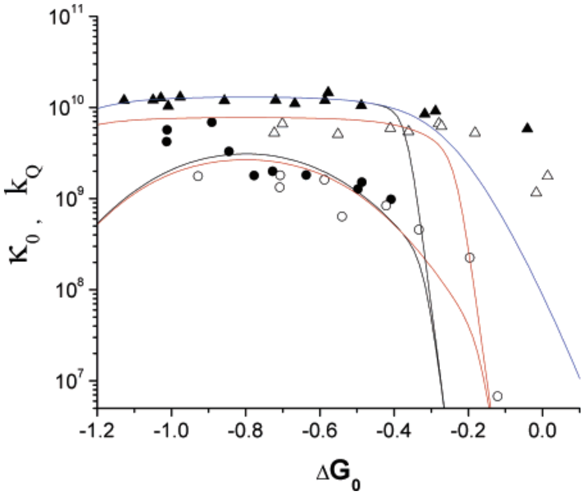

Figure 5. Experimental results from Figure 2 of ref 17 for the Stern−Volmer constants κ_0 (▲, ●) and triplet quenching constants k_Q (△, ○) fitted with our theory. Black lines are κ_0, and red ones are k_Q. The upper curves and triangles are related to lumicrome (LC) quenched by aromatic donors in methanol, whereas the lower curves and circles belong to the LC quenched by aliphatic amines in the same solvent. The upper curves are calculated for strong electron transfer, ($k_f = k_t = 30k_D$), whereas the lower ones are obtained for much weaker, kinetic controlled transfer, ($k_f = k_t = 0.5k_D$). It is assumed that $\lambda_c = 0.8$ eV, $k_D = 8 \times 10^9$ M^{-1} s^{-1} and $k_c = 10^3k_D$ are the same in both cases, as well as the singlet excitation energy $\mathcal{E} = 2.48$ eV and singlet−triplet splitting, 0.31 eV, particular to this system. The blue line shows the Stern−Volmer constant for irreversible ionization of LC singlet, $\kappa_i(\Delta G_0)$, at the very same parameters.

Solving it, we obtain for reasonably small ϵ

$$x = \epsilon\left(1 - \frac{2\lambda_c}{\mathcal{E} + \Delta G_0 + \lambda_c}\right) - \frac{2\lambda_c T\ln 3}{\mathcal{E} + \Delta G_0 + \lambda_c} \tag{3.26}$$

Hence, the splitting of the descending lines is approximately the linear function of ϵ and should be about 0.14 for our parameters (at $\Delta G_0 \approx 0$, $\mathcal{E} = 2.48$ eV, $\lambda_c = 0.8$ eV, $\epsilon = 0.31$ eV) as it is.

There is the qualitative difference between the two families of quenchers, aromatic donors (upper curves) and aliphatic amines (lower curves). These latter are well fitted, assuming that ionization of either the singlet or triplet is almost kinetic: $k_f = k_t = 0.5k_D$. Therefore, the points lay on the bell shaped curves similar to those peculiar to the Marcus electron-transfer rate, which obeys the famous free energy gap (FEG) law. On the contrary, the transfer to aromatic donors are expected to be much faster ($k_f = k_t = 30k_D \gg k_D$) so that the top of the corresponding FEG curve is cut by the diffusional plateau discussed above. However, the experimental points are located not only within the plateau but also far to the right of it, out of the region restricted by the descending branches of theoretical curves. It looks like the diffusional plateau extends up to $\Delta G_0 = 0$. This is hardly possible because even the Stern−Volmer constant for irreversible transfer, $\kappa_i(\Delta G_0)$, shown by the blue line, does not extend so far. Moreover, $\kappa_0 \leq \kappa_i$ cannot approach the experimental points located so high unless k_f and k_c are hundred times larger. Since our values for them ($30k_D$ and 10^3k_D) are already rather high, this is scarcely possible. Most likely the free energy is overestimated in the experimental work under study[17]. If the free energy was only 0.2 eV less, the theory and experiment would be in better agreement.

IV. Conclusions

The RIP formation by reversible electron transfer to or from the excited molecules performs the quenching of the excitation provided that the RIP itself recombines irreversibly from either its singlet or triplet state. However, the recombination of the triplet RIP to the neutral triplet molecules is irreversible if only the triplets are also quenched, say, by fast biexcitonic annihilation. If this is not the case, the triplet production is reversible, and the singlet RIP recombination to the ground state remains the only mechanism making the primary electron-transfer irreversible.

In such a case, the Stern−Volmer constant of luminescence quenching and the rate constant of triplet quenching have similar free energy dependencies. At negative free energies and fast recombination, they are controlled by the excited states ionization and remain constant as long as ionization is diffusional. However, as soon as the free energy approaches zero, the diffusional plateau is cut off due to slower recombination which limits the whole process.

It was shown that the production of quasistable triplet excitations does not affect the stationary luminescence quantum yield whose Stern−Volmer constant (1.13) universally depends on the single quenching parameter k_c, the constant of the RIP recombination to the ground state. At slow ionization, the free energy dependence of both the Stern−Volmer and triplet quenching constants are well fitted with the bell-shaped FEG curve, whereas at faster ionization, the experimental data lay on the diffusional plateau which is unfortunately longer than theoretically predicted.

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