Instantaneous and Permanent Photoionization

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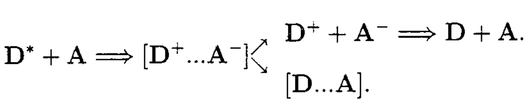
The bimolecular ionization of photoexcited molecules is theoretically investigated assuming the light pumping of moderate intensity is either instantaneous or permanent. The kinetics of energy quenching and ion−radical accumulation and recombination after δ-pulse excitation are studied beyond the rate concept, in the framework of Integral Encounter Theory (IET). The results are compared with those obtained within extended Unified Theory (UT), contact and Markovian approximations, and a widely accepted exponential model. When there is a shortage of acceptors the theory becomes nonlinear and discloses the striking effect of electron-transfer saturation. In such conditions and under permanent illumination IET is the sole formalism appropriate for a full time-scale (non-Markovian) description of system relaxation. The original program for solving nonlinear IET equations for particle concentrations was developed and first used to calculate the kinetics of relaxation to equilibrium and to a stationary regime. The non-Markovian corrections to the quantum yields of fluorescence and charge separation obtained numerically are in good correspondence with analytic estimates of these quantities.

I. Introduction

In the past decade of the century theoretical photochemistry experienced a real revolution as primitive models were replaced by fundamental and self-consistent theories of transfer reactions activated by light pumping.[1−10] There comes a time when different approaches should be compared between themselves to find out what and where is more powerful and accurate. Such an assessment has been made already for intermolecular energy transfer after instantaneous excitation.[11−14] Here we consider a more complex energy quenching mechanism and not only after instantaneous excitation but during permanent illumination as well. The latter has not been the focus of attention so far because only a few approaches are able to provide a non-Markovian description of the nonlinear response of a system to stationary pumping.

Energy quenching is often carried out by charge transfer from an excited electron donor **D*** to an electron acceptor **A**, according to the multi-stage reaction scheme:



$$\mathbf{D}^* + \mathbf{A} \Longrightarrow [\mathbf{D}^+ ... \mathbf{A}^-] \begin{cases} \mathbf{D}^+ + \mathbf{A}^- \Longrightarrow \mathbf{D} + \mathbf{A}. \\ [\mathbf{D} ... \mathbf{A}]. \end{cases} \qquad (1.1)$$

The forward electron-transfer ends either by backward transfer to the ground state in the geminate ion pair $[\mathbf{D}^+...\mathbf{A}^-]$ or by ion separation and subsequent bimolecular charge recombination in the bulk involving free ions $\mathbf{D}^+$ and $\mathbf{A}^-$. The recombination completes the cycle with nonexcited product **D**, making possible a stationary regime under permanent excitation $\mathbf{D} \rightarrow \mathbf{D}^*$. This is the self-consistent but oversimplified reaction scheme which ignores a few important factors of the process: the spin states of excited particles and ion pairs as well as the exciplex (contact ion pair) formation before or after charge separation. Both factors were recently included into extended reaction scheme and thoroughly investigated within Unified Theory.[8−10] However, for our present goal we need as simple scheme as possible to compare the different approaches which usually do not account for additional complications. The scheme (1.1) is the simplest one which allows such a comparison.

A number of time-resolved experiments have been done using very short light pulses considered as instantaneous. Under such idealization the rate of excitation, $I(t)$, is represented by the δ-pulse:

$$I = \gamma\delta(t) \qquad (1.2)$$

where $\gamma = N^*(0)/N_0$ is a fraction of the excited molecules immediately after the pulse ($N^* \equiv [\mathbf{D}^*]$, and N_0 is the total concentration of donor molecules in solution). When this fraction is rather small, the concentration of free ions which escape geminate recombination is also small. Their bimolecular recombination in the bulk, whose rate is quadratic in $N^+ \equiv [\mathbf{D}^+] = [\mathbf{A}^-] \equiv A^-$, is much slower than the preceding stage of ion accumulation and separation. This geminate stage was actually the subject of the original Unified Theory (UT), which completely ignored the bulk recombination.[15,16] Although valid in a limited time range, UT was nevertheless very successful in calculating the kinetics of ion accumulation, geminate

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recombination, and the free ion quantum yield. UT was successfully applied to a number of different phenomena after inclusion into consideration the spin states of excitations and ion pairs, inter-system crossing, and exciplex formation in magnetic field (see recent review[6]). The subsequent bimolecular recombination in the bulk was also taken into consideration in a properly extended unified theory (EUT).[17]

An essential limitation of original UT as well as EUT is the assumption that acceptors are present in such an excess that their concentration $A \equiv [\mathbf{A}]$ remains almost constant, approximately equal to its initial value c. This is possible if their number is not really exhausted due to partial ionization, that is under the condition

$$N^*(0) = \gamma N_0 \ll c \qquad (1.3)$$

In what follows we will eliminate this restriction and account for expendable neutral acceptors whose concentration, $A(t)$, decreases in the course of ionization. However, even extended in this way the unified theory is still somewhat limited.

It has been stressed already a few times that UT is not suitable for consideration of the system response to pulses of finite duration, especially for rather long or even infinitely long (permanent) excitation, represented by ζ-pulse:[18-20]

$$I = I_0\,\zeta(t) = \begin{cases} 0 & \text{at } t < 0 \\ I_0 & \text{at } t \geq 0 \end{cases} \qquad (1.4)$$

The pumping term IN_0 cannot be incorporated in any non-Markovian rate theory containing time-dependent rate coefficients.[21,22] Fortunately, there is an alternative when acceptors are very much in excess, so that $A(t) \equiv [\mathbf{A}] = c$ does not change over time. In this particular case the UT equations are linear in concentrations and their solution can be employed to calculate the system response to a pulse of arbitrary shape, $I(t)$. In fact, $N^*(t)$ can be obtained from the well-known convolution recipe generalized for arbitrary strong pumping in refs 3 and 20. We will show here that the same can be done for ion accumulation/recombination kinetics, $N^+(t)$, as well. However, the system response to a light pulse of nonzero duration is unattainable for the non-Markovian rate theory, if there is a deficiency of acceptors. In this case the second-order kinetic equations are essentially nonlinear due to the expenditure of neutral electron acceptors and the convolution recipe is inapplicable.

On the contrary, Integral Encounter Theory (IET) elaborated about 20 years ago in a few Russian works[24,25] does not discriminate between linear and nonlinear problems. This is a kind of memory function formalism applied to the chemical kinetics of bimolecular reactions in dilute solutions. The additive inclusion of the pumping term IN_0 into the IET equation for N^* provides the standard way for solving these problems involving arbitrary pulse shape.[7,18] The effect of nonlinearity increases with the intensity of light pumping because N^* eventually grows to the point that inequality (eq 1.3) no longer holds. This leads to a saturation of the electron transfer due to a lack of neutral acceptors of electron when $A \ll c$. This is in essence a Markovian effect accessible to a largely simplified Markovian version of the encounter theory that will be examined in line with EUT and IET.

Besides electron-transfer saturation, there is also an essentially non-Markovian effect of strong light pumping. The latter affects the kernels of integral terms in IET equations, changing the Stern−Volmer constant of fluorescence, when either $1/\tau$ or I_0 is greater than $1/\tau_d$. Here τ is the lifetime of excited reactant while $\tau_d = \sigma^2/D$ is the encounter time determined by the closest approach distance σ and the encounter diffusion coefficient D.[20] To study electron-transfer saturation in a pure form, we restrict ourselves to a moderate light intensity, assuming

$$I_0 \ll 1/\tau \lesssim 1/\tau_d \qquad (1.5)$$

This assumption ensures that D^* is not saturated, i.e., $N^* \ll N_0$ for any relationship between N^* and c.

The system response to a δ-pulse can be described not only within encounter theories, but also with their contact and Markovian analogues, as well as with an Exponential Model (EM). The latter is questionable but very popular among experimentalists. To make the comparison of the theories the most favorable for contact approximation, we take as input data the exponential rates of the distant-dependent forward and backward electron transfer:[26]

$$W_I(r) = W_i \exp[-2(r - \sigma)/L], \qquad W_R(r) = W_r \exp[-2(r - \sigma)/l] \qquad (1.6)$$

where σ is the closest approach distance. According to the classification given in ref 26 both rates are exponential in the rather rare situation when the free energies of ionization and recombination are so small that both the forward and backward transfer proceed in the Marcus normal region. Only “normal” transfer at small L and l may be considered as contact. Otherwise neither the contact approximation nor the exponential model is acceptable from the very beginning. We will use the rates (eq 1.6) in all theories of distant transfer and define through them all the parameters of the rest of the approaches.

Time-resolved experiments after δ-pulse aim to study the geminate recombination of ion pairs. They are usually done at relatively fast excitation decay so that charge transfer from D^* to A is essentially over before recombination begins. Therefore, the comparison of different theories of initial charge separation is made here at rather short decay time. The same is true regarding the study of the kinetics of the approach to the stationary regime under action of a ζ-pulse. On the contrary, the effect of electron-transfer saturation is better seen at longer times when there is no difference between the Markovian and non-Markovian theories. The last two problems are studied here for the first time.

The outline of this paper is as follows. In the next section we reproduce the original UT that will be extended and generalized later. In section III the IET formalism is applied to the reaction scheme (eq 1.1) as in ref 20 and slightly simplified in accordance with limitation established by eq 1.5. In section IV the system response to a δ-pulse is considered for each of the available theories. There the saturation of energy quenching due to electron transfer is demonstrated. In section V we turn to a description of the system response to ζ-pulse. There we generalize UT to determine the excitation decay as well as ion pair accumulation/recombination by a convolution recipe. The latter is valid when the electron acceptors are really in great excess. If the concentration is not large, only IET provides a valid description of the non-Markovian kinetics of approach to the stationary regime. In the conclusion, the importance of non-Markovian effects in kinetic and stationary phenomena will be inspected.

II. Unified Theory of Photochemical Charge Separation

If the light excitation is instantaneous and weak, the bimolecular charge recombination in a bulk can be ignored during a limited time interval. Nonetheless, this initial interval can exceed the larger of two times: the lifetime of the excited donor τ and the diffusional encounter time τ_d. Within such an interval the survival probability of the excited state, $P^*(t) = N^*(t)/N^*(0)$, and that of ions, $P^+ = N^+/N^*(0)$ obey the set of original UT equations first derived in refs 15 and 16:

$$\dot{P}^* = -k_I(t)cP^* - \frac{P^*}{\tau} \quad P^*(0) = 1 \tag{2.1a}$$

$$\dot{P}^+ = c\int \frac{\partial m(r,t)}{\partial t}\mathrm{d}^3r \quad P^+(0) = 0 \tag{2.1b}$$

The time-dependent "reaction constant"

$$k_I(t) = \int W_I(r)n(r,t)\mathrm{d}^3r$$

and ion pair distribution $m(r,t)$ are expressed in UT through the solutions of auxiliary differential equations

$$\frac{\partial n}{\partial t} = -W_I n + \hat{L}_1 n \tag{2.2a}$$

$$\frac{\partial m}{\partial t} = -W_R m + \hat{L}_2 m + W_I n P^* \tag{2.2b}$$

where $n(r,0) = 1$, $m(r,0) = 0$ and the operators

$$\hat{L}_1 = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} \quad \text{and} \quad \hat{L}_2 = \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r}r^2 e^{r_c/r}\frac{\partial}{\partial r}e^{-r_c/r}$$

represent the encounter diffusion in neutral and charged pairs [**D***...**A**] and [**D**$^+$...**A**$^-$], taking into account the Onsager radius r_c for Coulomb well between ions.

The set of UT equations above describes only geminate ion pair accumulation/recombination and separation. This is an initial stage of the system response to δ-pulse excitation that proceeds in a restricted time interval. However, within this interval the survival probability of ions approaches the plateau which is the free carriers quantum yield ϕ. The latter can be represented in the following form:[26,27]

$$\phi = P^+(\infty) = \psi\bar{\varphi} \tag{2.3}$$

Here $\bar{\varphi}$ is the charge separation quantum yield while ψ is the quantum yield of complete ionization, simply related to the fluorescence quantum yield:[28,29]

$$\eta = \int_0^\infty P^*(t)\mathrm{d}t/\tau = 1 - \psi \tag{2.4}$$

The geminate stage of ion accumulation/recombination is followed by a bimolecular recombination in the bulk, which is much slower when excitation is weak. The bulk recombination has been incorporated in Extended Unified Theory (EUT) which is formulated in terms of absolute concentrations of excited donors and ions, N^* and N^+, instead of their survival probabilities, P^* and P^+.[17]

III. Integral Encounter Theory for Moderate Pumping

At light intensity limited by inequality (1.5), we can obtain from the general theory published in ref 20 the reduced set of IET equations:

$$\dot{N}^* = -\int_0^t R^*(t-t')N^*(t')A(t')\mathrm{d}t' - \frac{N^*}{\tau} + IN_0 \tag{3.1a}$$

$$\dot{N}^+ = \int_0^t [R^*(t-t') - R^\dagger(t-t')]N^*(t')A(t')\mathrm{d}t' - \int_0^t R^\ddagger(t-t')[N^+(t')]^2\mathrm{d}t' \tag{3.1b}$$

where $A(t) = c - N^+(t)$. All kernels are defined through their Laplace transformations, denoted by tilde:

$$\tilde{R}^*(s) = (s + 1/\tau)\int \mathrm{d}^3r W_I(r)\tilde{\nu}_1(\rho,\sigma) \tag{3.2a}$$

$$\tilde{R}^\dagger(s) = (s + 1/\tau)\int \mathrm{d}^3r W_R(r)\tilde{\mu}(r,s) \tag{3.2b}$$

$$\tilde{R}^\ddagger(s) = s\int \mathrm{d}^3r W_R(r)\tilde{\nu}_2(r,s) \tag{3.2c}$$

The auxiliary pair distributions obey the following set of equations:

$$\left[\frac{\partial}{\partial t} - \hat{L}_1 + W_I(r) + 1/\tau\right]\nu_1(r,t) = 0 \tag{3.3a}$$

$$\left[\frac{\partial}{\partial t} - \hat{L}_2 + W_R(r)\right]\nu_2(r,t) = 0 \tag{3.3b}$$

$$\left[\frac{\partial}{\partial t} - \hat{L}_2 + W_R(r)\right]\mu(r,t) = W_I\nu_1 \tag{3.3c}$$

The initial conditions for these functions are

$$\nu_1(r,0) = \nu_2(r,0) = 1, \quad \mu(r,0) = 0$$

The bimolecular ionization producing the energy quenching and primary charge separation is represented by two integral terms in eqs 3.1a and 3.1b, containing kernel R^*. The integral term with kernel $R^\dagger$ accounts for geminate recombination of the created ion pairs. The final bimolecular recombination of free ions in the bulk is represented by a kernel $R^\ddagger$, from the last term in eq 3.1b, which is quadratic in ion concentration. If one employs such a weak δ-pulse that the initial concentrations of excited donors satisfies $N^*(0) = \gamma N_0 \ll c$ then acceptors are in great excess from the very beginning. Under such a condition the bimolecular recombination does not play any role in a relatively long time interval after excitation and can be neglected. Then one obtains the reduced version of IET similar to the original UT which also ignores the recombination in a bulk.

Neglect of bulk recombination is absolutely impossible if the illumination is permanent and the stationary concentrations of excited donors and ions, N_s^* and N_s^+, have to be obtained. The former determine the fluorescence quantum yield:[20]

$$\eta = \frac{N_s^*}{I_0\tau N_0} \tag{3.4}$$

while the latter contribute to the stationary photoconductivity:

$$\sigma = euN_s^+ \tag{3.5}$$

where e is the charge of free carriers whose mobility is u.

These two quantities, N_s^+ and η, are the main ones pertaining to the free ion production and energy quenching which are often available for analytic study. The kinetic information about the system response to δ-pulse usually comes from numerical investigations of IET equations partially reduced in Unified Theory to a differential form. For this adopted theory very powerful programs were elaborated[30,31] and used a number of times.[32] Here we develop a new program for solving IET eqs

3.1, 3.2, 3.3 and gaining for the first time the system response not only to δ-pulses, but to permanent excitation with ζ-pulse as well.

IV. Relaxation after δ-Pulse

The system response to a very short pulse excitation is a standard problem treated many times by different methods. In what follows we will compare some of these methods we are going to compare below by the example of reaction 1.1.

After instantaneous excitation (eq 1.2) the last term in eq 3.1a is zero and can be omitted, provided the initial conditions are set to the following:

$$N^*(0) = \gamma N_0 \qquad N^+(0) = 0$$

The remaining homogeneous equations can be now reduced to a semi-differential form inherent in UT using standard procedure recommended in classical works[33] and employed a number of times:[19,25,34]

$$\frac{dN^*(t)}{dt} = -k_I(t)N^*(t)A(t) - \frac{N^*(t)}{\tau} \tag{4.1a}$$

$$\frac{dN^+(t)}{dt} = \int \frac{\partial}{\partial t} p(r,t) d^3r - k_R(t)[N^+(t)]^2 = -\frac{dA(t)}{dt} \tag{4.1b}$$

where we took into account that $A(t) + N^+(t) = c =$ constant, and the time-dependent rate constant for ionization and recombination are

$$k_I(t) = \int d^3r w_i(r) n(r,t), \qquad k_R(t) = \int d^3r W_R(r) n'(r,t) \tag{4.2}$$

Here the auxiliary pair distributions obey the diffusional equations

$$\left[\frac{\partial}{\partial t} + W_I(r) - D\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\right] n(r,t) = 0 \qquad n(r,0) = 1 \tag{4.3a}$$

$$\left[\frac{\partial}{\partial t} + W_R(r) - \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 e^{r_c/r} \frac{\partial}{\partial r} e^{-r_c/r}\right] n'(r,t) = 0 \qquad n'(r,0) = 1 \tag{4.3b}$$

Here we accounted for the Coulomb attraction between ions with Onsager's radius r_c. The same should be done in an equation that governs the time behavior of charge distribution in a pair:

$$\left[\frac{\partial}{\partial t} + W_R(r) - \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 e^{r_c/r} \frac{\partial}{\partial r} e^{-r_c/r}\right] p(r,t) = W_I(r) n(r,t) N^*(t) A(t) \tag{4.4}$$

Initially $p(r,0) = 0$, but ions appear due to a pumping term on the right-hand side of this equation.

One of the most widespread models of reactions in solutions is known as contact approximation. It assumes the reaction to take place only at a contact distance σ with kinetic rate constant $k_0 = \int W_I(r) d^3r$ for ionization and $k_0' = \int W_R(r) d^3r$ for recombination. Under this assumption the charge-transfer rates (eq 1.6) can be substituted by their contact analogues:

$$W_I(r) = \frac{k_0}{4\pi\sigma^2}\delta(r - \sigma), \qquad W_R(r) = \frac{k_0'}{4\pi\sigma^2}\delta(r - \sigma) \tag{4.5}$$

To make use of the contact approximation let us first substitute $\partial p/\partial t$ from eq 4.4 into eq 4.1b and integrate it over r. In this way we arrive to the equation

$$\frac{dN^+(t)}{dt} = k_I(t)N^*(t)A(t) - \int W_R(r) p(r,t) d^3r - k_R(t)[N^+(t)]^2 \tag{4.6}$$

Using here the contact $W_R(r)$ from eq 4.5 and assuming a great excess of acceptors we obtain

$$\frac{dN^+(t)}{dt} = ck_I(t)N^*(t) - k_0' p(\sigma,t) - k_R(t)[N^+(t)]^2 \tag{4.7}$$

where $p(\sigma,t)$ should be found from the solution of the contact analogue of eq (4.4):

$$\frac{\partial p(r,t)}{\partial t} = W_I(r) n(r,t) c N^*(t) + \tilde{D}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 e^{r_c/r} \frac{\partial}{\partial r} e^{-r_c/r} p(r,t), \qquad 4\pi\sigma^2 \frac{\partial p}{\partial r}\Big|_{r=\sigma} = k_0' p(\sigma,t) \tag{4.8}$$

The general solution of this equation expressed through its Green function, $G_R(r,r',t)$, takes the form

$$p(r,t) = ck_0 \int_0^t G_R(r,\sigma,t - t') n(\sigma,t') N^*(t') dt' \tag{4.9}$$

Here we took into account, that ionization is contact as in eq 4.5. In this approximation $k_I = k_0 n(\sigma,t)$, where $n(r,t)$ obeys the contact equation equivalent to eq 2.2a:

$$\dot{n} = \hat{L}_1 n, \qquad 4\pi\sigma^2 \frac{\partial n}{\partial r}\Big|_{r=\sigma} = k_0 n(\sigma,t)$$

The contact solution of the problem given by eqs 4.7 and 4.9 is very suitable for analytic investigation because the properties of the Green function of geminate recombination, $G_R(r,r',t)$, are studied in great detail in a few fundamental works.[35,36] In particular, it is known that contact approximation does not work in a static limit, but is a reasonable approximation for moderate and fast diffusion, provided that the space dependence of the transfer rate is really exponential and sharp.[37] Here we should only add that in the contact approximation the static stage is also missed in bimolecular ionization. Therefore the initial rate of this process is significantly underestimated and the quantum yield of contact ionization should be less than that in theories of remote transfer (UT or IET), especially for the case of short excitation lifetime.

Even more popular than the contact approximation, until recently was the so-called exponential model (EM) of ion pair recombination. In this model the real diffusion from the reaction zone is replaced by a hopping escape from it with a rate k_{sep}. On the other hand, EM does not assume recombination to be contact, but suggests that it takes place with a uniform back electron-transfer rate k_{-et} within the reaction sphere of the volume $v = 4\pi\sigma^3/3$. As a result eq 4.4 is replaced by the following one:

$$\frac{\partial p(r,t)}{\partial t} = W_I(r) n(r,t) N^*(t) A(t) - k_{sep} p(r,t) - k_{-et} p(r,t) \qquad r \le \sigma \tag{4.10}$$

where the used parameters of EM are simply related to those of the contact approximation:[36]

$$k_{sep} = \frac{3r_c\tilde{D}}{\sigma^3[e^{r_c/\sigma} - 1]} \qquad k_0' = k_{-et} v \tag{4.11}$$

In addition, EM assumes that ionization also takes place only within the same reaction sphere as recombination, that is $W_I = 0$ at $r > \sigma$. Therefore, integrating eq 4.10 over space we obtain a similar equation for the total number of ions inside the reaction sphere, $p_c = p(\sigma,t)v$:

$$\frac{\mathrm{d}p_c}{\mathrm{d}t} = k_I(t)N^*(t)A(t) - (k_{sep} + k_{-et})p_c \tag{4.12}$$

This equation should be supplemented by eq 4.7 with k_0' taken from eq 4.11:

$$\frac{\mathrm{d}N^+(t)}{\mathrm{d}t} = k_I(t)N^*(t)A(t) - k_{-et}p_c - k_R(t)[N^+(t)]^2 \tag{4.13}$$

Linear equations of this sort (with $A_s \equiv c$) have been used a number of times,[38−41] but in their Markovian version when the time-dependent rate constants, $k_I(t)$ and $k_R(t)$, are substituted by their asymptotic (stationary) values:

$$k_i = \lim_{t\to\infty} k_I(t) = \int W_I(r)n_s(r)\mathrm{d}^3r,$$
$$k_r = \lim_{t\to\infty} k_R(t) = \int W_R(r)n_s'(r)\mathrm{d}^3r \tag{4.14}$$

where $n_s(r) = n(r,\infty)$ and $n_s'(r) = n'(r,\infty)$.

There is also an important difference in the way in which the bimolecular recombination is accounted for here, in eq 4.13, and in ref 39. There it is decomposed in two stages: diffusional formation of an ion pair with a rate constant $4\pi\sigma\tilde{D}$ and subsequent geminate recombination inside the reaction sphere with a conventional EM rate k_{-et}. Under these conditions there is an upper limit for the rate constant of the bimolecular recombination: $k_r \leq 4\pi\sigma\tilde{D}$, that was actually exceeded in experiments done in ref 39. Authors considered this fact as a reason for the suggestion that this is an additional reaction channel (proton transfer) which facilitates ion recombination. In eqs 4.12 and 4.13 we did not account for proton transfer in the ion pair, although it can be done in the same way as in refs 38 and 39. There is no need to complicate the reaction scheme. The stationary values of k_r represented as $4\pi R_Q\tilde{D}$ can significantly exceed the contact estimate of the diffusional rate constant, because the effective radius R_Q is in general larger than σ. The effective radius for ionization was experimentally shown to be twice as large at high solution viscosity.[42] For recombination it can be even larger, reaching the value of the Onsager radius r_c in solvents of low polarity.[43] From the theoretical point of view there is also no reason to discriminate between the similar processes of forward and backward electron transfer, which can be treated uniformly as distant bimolecular reactions.

To avoid further discussion of this point we restrict ourselves to the initial geminate stage of the reaction, neglecting bimolecular recombination during this time interval. Then all EM theories become identical, including that proposed by the authors of ref 39. Summing their two equations for charges inside and outside the reaction sphere, we get our equation for the total ion concentration N^+ at $k_I = k_i$ and $k_R = k_r = 0$. With a large excess of acceptors the full set of EM equations can be rewritten for the survival probabilities of excitations and ions:

$$\frac{\mathrm{d}P^*}{\mathrm{d}t} = -ck_iP^* - \frac{P^*}{\tau}, \quad \frac{\mathrm{d}P^+}{\mathrm{d}t} = ck_iP^* - k_{-et}p_c \tag{4.15}$$

where $P^*(0) = 1$, $P^+(0) = p_c(0) = 0$ and

$$\frac{\mathrm{d}p_c}{\mathrm{d}t} = ck_iP^* - (k_{sep} + k_{-et})p_c \tag{4.16}$$

They were really useful for the rough interpretation of some experimental data,[40,41] but in principle EM is much worse than even the contact approximation. The escape from the reaction zone and more from the Coulomb well, does not proceed by a single jump described as an exponential (rate) process even if k_{sep} is given a reasonable estimate (eq 4.11). This simplification ignores all subsequent re-contacts and an essential nonexponentiality of the whole geminate process.[36] It was shown a number of times that EM fails to describe not only long time kinetics,[41] but also the free energy dependence of geminate recombination[26] and magnetic field effects in the charge separation quantum yield.[10] This is a linear unified theory that was actually used in all aforementioned works to solve these and other problems.[6]

Equations 4.1−4.4 constitute the formal basis of the extended unified theory. Unlike the original theory, represented by the set (eq 2.1)−(eq 2.2), extended UT accounts for nonlinear effects, including the bimolecular recombination of ions. Only one step remains to be taken to go from UT to its simplified, Markovian version which describes the asymptotic relaxation of the system long after the pulse. Using the Green-function of eq 4.4, $G_R(r,r',t)$, one can make in this time limit the following approximation:

$$\int p(r,t)\mathrm{d}^3r = \int_0^t \int \mathrm{d}^3r' \int G_R(r,r',t-t')\mathrm{d}^3r W_I(r')n(r',t') \times N^*(t')A(t')\mathrm{d}t' \approx \int \mathrm{d}^3r'\varphi(r')W_I(r')n_s(r') \int_0^t N^*(t')A(t')\mathrm{d}t' = k_i\bar{\varphi}_m \int_0^t N^*(t')A(t')\mathrm{d}t' \tag{4.17}$$

where $n_s(r') = n(r',\infty)$ and

$$\varphi(r') = \int G_R(r,r',\infty)\mathrm{d}^3r \tag{4.18}$$

is the survival probability of ions initially separated by a distance r'. The Markovian charge separation quantum yield

$$\bar{\varphi}_m = \int \varphi(r')f_m(r')\mathrm{d}^3r' \tag{4.19}$$

is averaged over the initial distribution of ions calculated in the Markovian approximation:

$$f_m(r) = \frac{W_I(r)n_s(r)}{\int W_I(r')n_s(r')\mathrm{d}^3r'} \tag{4.20}$$

Using these results in eq 4.1b we obtain from it and eq 4.1a the following set of Markovian equations valid for long times:

$$\frac{\mathrm{d}N^*(t)}{\mathrm{d}t} = -k_iN^*(t)A(t) - \frac{N^*(t)}{\tau} \tag{4.21a}$$

$$\frac{\mathrm{d}N^+(t)}{\mathrm{d}t} = k^+N^*(t)A(t) - k_r[N^+(t)]^2 = -\frac{\mathrm{d}A(t)}{\mathrm{d}t} \tag{4.21b}$$

where the important definition for the rate constant of free carrier production, k^+, is given:

$$k^+ = k_i\bar{\varphi}_m \tag{4.22}$$

The latter differs from the ionization rate constant by a multiplier equal to charge separation quantum yield $\bar{\varphi}_m$ obtained in the Markovian approximation. This difference indicates that a

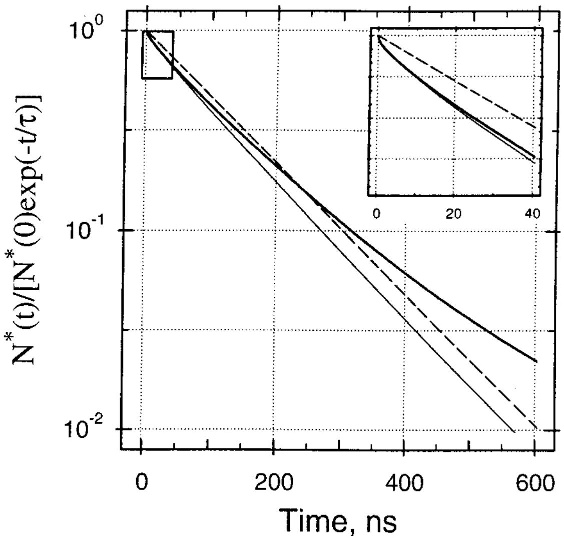

Figure 1. Semilogarithmic plot of quenching kinetics at a large excess of acceptors ($N^*(0) = 10^{-4}$ M $\ll 10^{-2}$ M $= c$) calculated with IET (thick line), UT considered as an exact (thin line), and Markovian theory (dashed line). The remaining of parameters are the following: $\sigma = 6$ Å, $W_i = 1000$ ns^{-1}, $D = 1.2 \times 10^{-6}$ cm^2/s, $L = 1.0$ Å, $k_i = 1271$ Å^3/ns. The initial nonstationary quenching is shown in the insert.

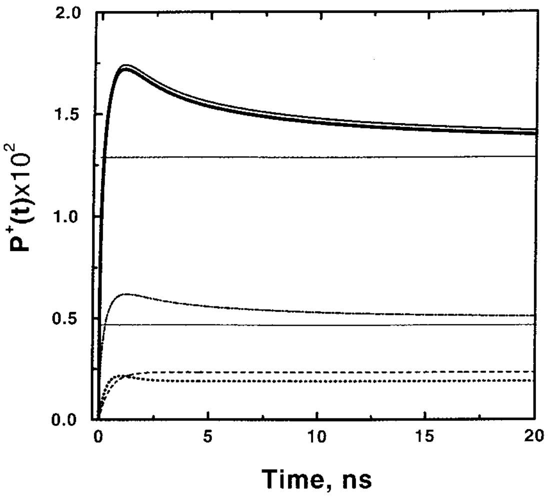

Figure 2. Ion survival probability as a function of time at $\tau = 0.5$ ns with great excess of acceptors. In line with GUT, IET, and Markovian theory, the contact approximation (dashed−dotted line) and exponential model with $k_{sep} = k_{-et} = 1.0$ ns^{-1} (dotted line) are also shown. The horizontal thick lines indicate the free ion quantum yield ϕ for upper curves. The concentrations and ionization parameters are the same as in Figure 1, while $W_r = 3.4$ ns^{-1}, $\tilde{D} = D = 1.2 \times 10^{-6}$ cm^2/s, $k^+ = 784$ Å^3/ns, and $k_r = 486$ Å^3/ns.

TABLE 1: Quantum Yields of Ionization (ψ), Charge Separation ($\bar{\varphi}$), and Free Ion Production ($\phi = \psi\bar{\varphi}$)

theories	$\psi \times 10^3$	$\bar{\varphi}$	$\phi \times 10^3$
UT	21.7	0.59	12.8
IET	21.5	0.59	12.7
Contact	9.3	0.50	4.6
Markovian	3.7	0.61	2.3
EM	3.7	0.50	1.9

definite part of photogenerated ions react in a geminate ion pair, so that the fraction of those which survive geminate recombination and become free is less than their total amount: $\bar{\varphi}_m < 1$.

Unfortunately, the Markovian theory has a number of drawbacks when applied to an essentially non-Markovian problem like that in hand. It is well-known that the transformation of IET into UT is sometimes an improvement (see ref 11 and references therein). On the contrary, reduction of UT to its Markovian version deprives UT of all its advantages and misrepresents the kinetics of energy quenching and charge accumulation at short τ. In Figure 1 we compare the kinetics of excited-state quenching in all these theories. The results of UT, known to be exact in the case of immobile **D*** and an independently moving point particles **A**, is taken as a primary standard. IET well reproduces the initial quenching, including its nonstationary stage, but deviates from the long time asymptotics of UT. This is due to a false tail inherent in IET that can be removed if Modified Encounter Theory (MET) is used instead of IET.[1] We will not make this modification here, but simply restrict our consideration to the time interval where the difference between UT and IET is not pronounced.

If the interval is short enough that the bimolecular recombination can be neglected, then the kinetics of ion accumulation and their geminate recombination can be expressed in terms of the survival probabilities, $P^+(t)$, available in all theories at a large excess of acceptors. In Figure 2 we show almost the identical results obtained with IET and UT which demonstrate the well-pronounced maximum. According to ref 15, this maximum appears only in the course of fast ionization when τ is shorter than the characteristic time of subsequent geminate recombination.

In the contact approximation the results are qualitatively the same but the ionization quantum yield ψ is half as much as in distant theories (see Table 1). It was expected because at such a short τ a significant fraction of ions are produced during the initial static ionization which is missed in the contact approximation.

Neither the maximum nor the descending branches of the upper curves, representing geminate recombination, are reproduced in Markovian theory. It predicts the monotonic ion accumulation and still further decrease in the ionization quantum yield ψ. This is because the Markovian theory cannot account for static and the subsequent nonstationary electron transfer. These are faster than the stationary (Markovian) transfer when ionization is under diffusional control. EM is a bit better in this respect. As a non-Markovian theory it accounts at least for static ionization and qualitatively reproduces the maximum in the charge accumulation kinetics. However, the subsequent geminate recombination develops exponentially in the EM because in this model the kinematics of ion separation is oversimplified. It is not compatible with the actual diffusional motion of ions responsible for their numerous re-contacts and the power dependence of long time separation kinetics studied in a number of works.[36,37,41]

It is interesting that in the Markovian theory, the charge separation quantum yield $\bar{\varphi}$ is largest when the lifetime is as short as in Figure 2 ($\tau = 0.5$ ns). As was shown in ref 11, in the short time limit the initial charge distributions in UT and IET are practically the same, but significantly different from a Markovian one. Due to the ignorance of nonstationary ionization, the Markovian density is smaller or even zero near the contact, where the recombination is most probable. Therefore in the framework of Markovian theory the ions have greater survival probability. On the contrary, in EM they are initially entirely inside the reaction zone where there are minimum chances to escape.

In conclusion, let us consider the opposite case when deficiency of acceptors leads to electron-transfer saturation. This case is more likely at large τ. In the limit of infinite τ all the theories here discussed, Markovian theory including, become equivalent. As seen from Figure 3 saturation results when $N^*(t)$

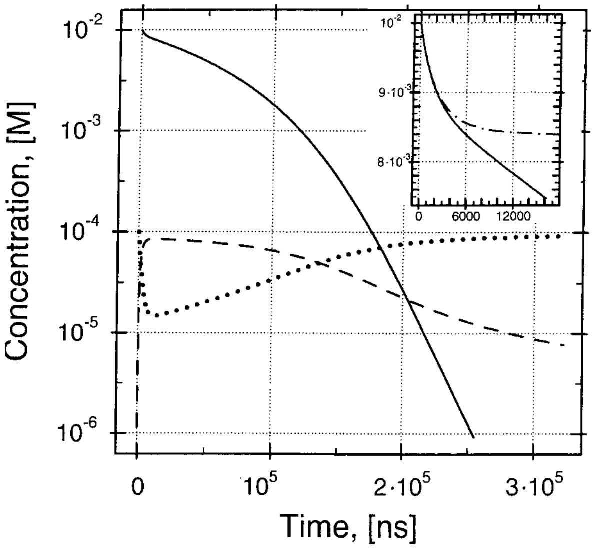

Figure 3. Decay of excited donor concentration (solid line) accompanied by ion accumulation/recombination (dashed line) and depletion of neutral acceptors (dotted line) at $W_i = W_r = 1000.0$ ns^{-1} and $\tau = \infty$ (the remaining parameters are the same as in the previous figures). The shortest stage of electron-transfer saturation due to deficiency of acceptors is shown in the insert in comparison to the excitation decay without bimolecular recombination in the bulk (dashed−dotted line). The charge separation quantum yield $\bar{\varphi} = 6.2\%$, $N^*(0) = 10^{-2}$ M, $c = 10^{-4}$ M.

is greater than $A(t)$ and is removed when $N^*(t)$ becomes smaller than $A \approx c$. Within the saturation region there are two stages: the initial one, when ions are accumulated and the subsequent quasi-stationary stage, when their concentration remains approximately constant. Initially, the concentration of excited molecules goes down approximately to the level shown in the insert by a dashed−dotted line, which is obtained by ignoring the bimolecular recombination. This level does not equal $N^*(0) - c$ as one might expect, but is much lower. The reason is that only a $\bar{\varphi}$ fraction of c ions produced at first transfer are separated. The rest of them recombine, restoring the $c(1 - \bar{\varphi})$ neutral particles which are ready to accept electrons once again. Hence, in the absence of bimolecular recombination the concentration of excitations approaches the following limit:

$$N^*(\infty) = N^*(0) - c - c(1 - \bar{\varphi}) - c(1 - \bar{\varphi})^2 - ... = N^*(0) - \frac{c}{\bar{\varphi}} \quad (4.23)$$

where each term of the expansion accounts for first, second, etc., electron transfer to neutral acceptors. In the next stage bimolecular recombination is important and maintains a quasi-stationary concentration of charged and neutral acceptors. This stage continues until the concentrations of excited donors and acceptors become approximately equal. Then the former disappear while the latter are totally discharged.

V. Evolution during ζ-Pulse

If electron acceptors are in great excess, one can express the relaxation of the excited-state population $N^*(t)$ during and after arbitrary light excitation through the survival probability of excited donors after δ-pulse, $P^*(t)$, that was introduced in section II. As is known,[28,29] $N^*(t)$ is simply given by the convolution of $P^*(t)$ with the time-dependent irradiation intensity $I(t)$:

$$N^*(t) = N_0 \int_0^t I(t - \tau)P^*(\tau)\mathrm{d}\tau \quad (5.1)$$

Equation 5.1 is just a consequence of linear response theory applied to our reaction. The physical interpretation of it is as follows. Let us consider the system response to an arbitrary pulse as a sequence of responses resulting from absorption of separate photons.[29] If the time evolution after each excitation is the same due to the linearity of the problem, one can sum them up to get the total response to the original pulse. In the case of ζ-pulse eq 5.1 simplifies to

$$N^*(t) = I_0N_0 \int_0^t P^*(\tau)\mathrm{d}\tau \quad (5.2)$$

Extension of this procedure to the ion relaxation $N^+(t)$ is not as straightforward, if the bulk recombination is not negligible. The latter makes the problem nonlinear:

$$\dot{N}^+ = \Pi(t) - k_R(t)(N^+)^2 \quad (5.3)$$

The source term $\Pi(t)$ of the above equation is in fact linear in I_0, if acceptors are present in great excess. Therefore it can be obtained by application of the same convolution procedure as in eq 5.2:

$$\Pi(t) = I_0N_0 \int_0^t \dot{P}^+(\tau)\mathrm{d}\tau = I_0N_0P^+(t) \quad (5.4)$$

Finally for ion accumulation we have the following equation:

$$\dot{N}^+ = I_0N_0P^+(t) - k_R(t)(N^+)^2 \quad (5.5)$$

Equations 5.2 and 5.5 together with the original UT eqs 2.1 and 2.2 constitute the formal basis of the Generalized Unified Theory (GUT). The latter can be used to find the system response to ζ-pulse, provided the acceptor concentration is sufficiently large. In this way one can obtain the accumulation kinetics of excitations and free ions and their stationary concentrations:

$$N^*_s = I_0N_0\tilde{P}^*(0), \quad N_s^+ = \sqrt{I_0N_0\phi/k_r} \quad (5.6)$$

where the free ion quantum yield ϕ was defined in eq 2.3. Substituting N_s^* into eq 3.4, we confirm the conventional definition of the fluorescence quantum yield (eq 2.4) while substitution of N_s^+ into eq 3.5 gives the conductivity as a function of light strength and electron-transfer parameters.

Figure 4 illustrates the kinetics of excitation and ion accumulation obtained from the numerical solution of the GUT eqs 5.2 and 5.5 using our standard programs for calculating P^* and P^+. For comparison, the same result was obtained from the IET equations of section III, with a large excess of electron acceptors. The difference between the results is not essential but becomes larger when c increases. This difference is in favor of GUT because this theory as well as UT account for higher order corrections in c which are not accounted for in IET.

These non-Markovian results can be compared with those obtained with Markovian theory. The light pumping can be incorporated in its eqs 4.21 as an additive term, as in IET:

$$\frac{\mathrm{d}N^*}{\mathrm{d}t} = -k_iN^*A - \frac{N^*}{\tau} + I_0N_0 \quad (5.7a)$$

$$\frac{\mathrm{d}N^+}{\mathrm{d}t} = k_i\bar{\varphi}_mN^*A - k_r(N^+)^2 = -\frac{\mathrm{d}A}{\mathrm{d}t} (5.7b) \quad (5.7b)$$

where $A = c - N^+$. The difference seen in Figure 4 between Markovian and other results is due to the usage of stationary parameters k_i and $\bar{\varphi}_m$ which do not account for the initial

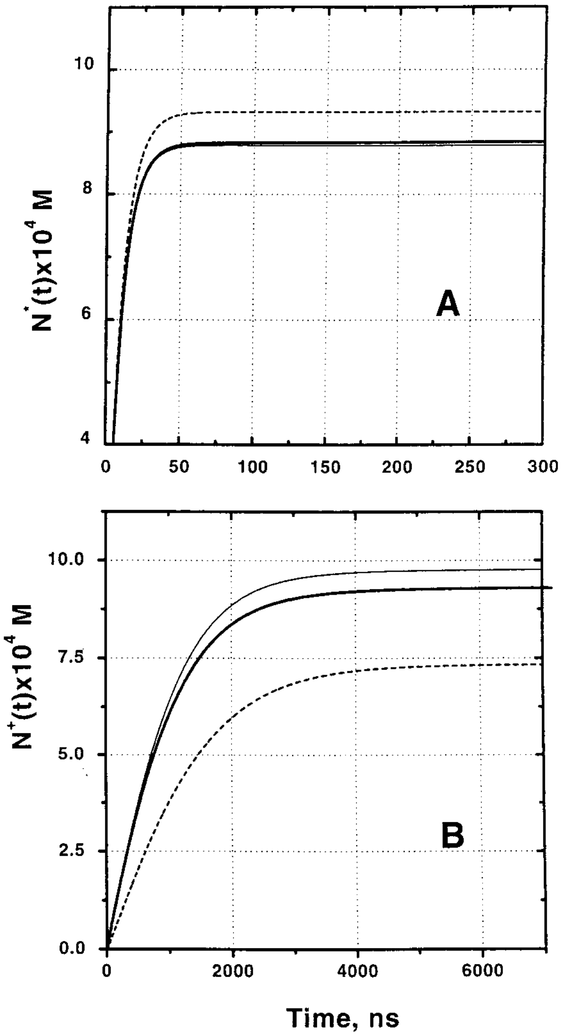

Figure 4. Concentration of excitations (A) and of ions (B) as functions of time under permanent illumination ($I_0N_0 = 10^{-4}$ M ns^{-1}) and a great excess of acceptors, as in Figure 1. Thick line, IET; thin line, GUT; dashed line, Markovian theory. The parameters are the following: $\tau = 10$ ns, $W_i = W_r = 1000$ ns^{-1}, $k_i = 1271$ Å^3/ns, $k^+ = 78.8$ Å^3/ns, $k_r = 1271$ Å^3/ns. The other parameters are the same as in Figure 1.

nonstationary development of the process. This difference exists at any finite lifetime and is larger the shorter τ.

At short lifetime the difference is seen even at c smaller than N_s^*, when electron transfer is saturated. Since this situation is essentially nonlinear, GUT does not hold, so that only IET provides a proper non-Markovian solution. However, the nonlinear effect of acceptor depletion is accounted for in Markovian theory as well. Using these two theories we estimated the difference in the non-Markovian and Markovian description of accumulation kinetics under saturation conditions (Figure 5). As before, it is larger for charged products than for excitations and stronger the shorter the lifetime τ.

A scale of non-Markovian corrections can be easily estimated in the stationary regime available for analytic investigation. The stationary solution of eqs 5.7 is trivial:

$$N_s^* = \frac{I_0 N_0 \tau}{1 + k_i A_s \tau}, \qquad N_s^+ = \sqrt{\frac{I_0 N_0 \psi \bar{\varphi}_m}{k_r}} \tag{5.8}$$

where according to eq 3.4 we have

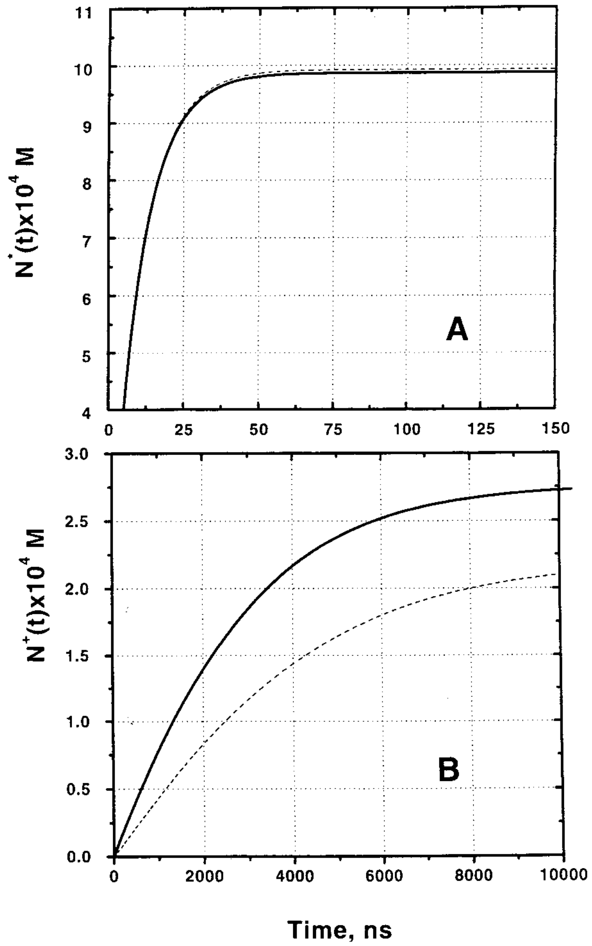

Figure 5. Accumulation kinetics of excitations (A) and ions (B) under the same permanent illumination as in Figure 4, but at a much lower acceptor concentration, 10^{-3} M, responsible for the electron-transfer saturation. Thick line, IET; dashed line, Markovian theory; the remaining parameters are the same as in the previous figure.

$$\eta = \frac{1}{1 + k_i A_s \tau} = 1 - \psi \tag{5.9}$$

which is actually the Stern–Volmer law modified as in ref 30. An important relationship between the stationary concentration of neutral acceptors A_s and their total concentration c is specified by the cubic equation which follows from the set of eqs 5.7:

$$k_r(c - A_s)^2(1 + k_i \tau A_s) = I_0 N_0 \tau k_i \bar{\varphi}_m A_s \tag{5.10}$$

Due to such a complex dependence $A_s(c)$ the inverse quantum yield (eq 5.9) is linear in A_s, but not in c (Figure 6). From eq 5.10 one sees that the condition for linearity in c is given by

$$k_i \bar{\varphi}_m N_s^* \ll k_r c \tag{5.11}$$

Otherwise, the depletion of neutral acceptors results in the quadratic dependence of $1/\eta$ on c. This violation of the Stern–Volmer law cannot be reproduced with GUT which is valid only if inequality (eq 5.11) holds. Contrary to the Markovian result the concentration dependence following from eq 2.4 is linear at small c (Figure 6).

Unlike GUT, IET has no restrictions of validity at small c. The fluorescence quantum yield calculated from the general eq 3.4 by means of IET does not differ qualitatively from the Markovian result (eq 5.9):

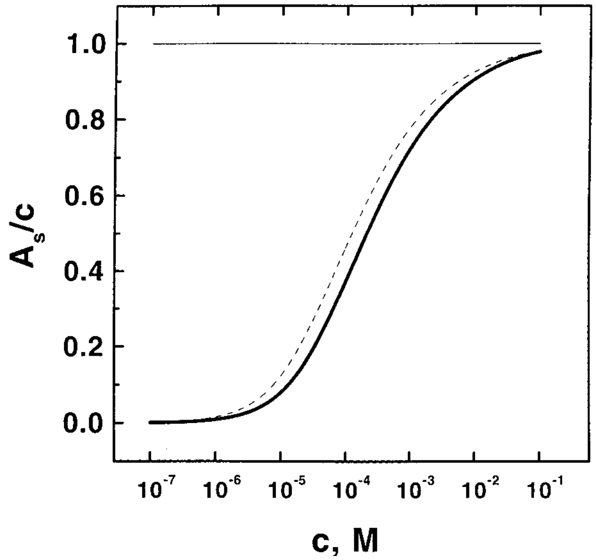

Figure 6. Stationary fraction of neutral acceptors as a function of their total density c in IET (thick line), UT (thin horizontal line), and Markovian theory (dashed line). The parameters are the following: $I_0N_0 = 10^{-4}$ M ns^{-1}, $\tau = 10$ ns, $W_i = W_r = 1000$ ns^{-1}; $k_i = 1271$ Å^3/ns, $\bar{\varphi}_m = 0.062$, $k_r = 1271$ Å^3/ns.

$$\eta = \frac{1}{1 + \kappa_i A_s \tau} \tag{5.12}$$

However, in this relationship as well as in the corresponding cubic equation for A_s a slightly different parameter

$$\kappa_i \equiv \tilde{R}^*(0) = \int W_I(r)\,\frac{\tilde{n}(r,1/\tau)}{\tau}\mathrm{d}^3r \tag{5.13}$$

is substituted for the Markovian (stationary) rate constant, $k_i = \lim_{\tau\to\infty}\kappa_i$, while another (recombination) rate constant remains the same: $\kappa_r \equiv \tilde{R}^{\ddagger}(0) = k_r$. Tilde over n indicates the Laplace transformation of the quantity, which is a solution of eq 4.3a: $\tilde{n}(r,s) = \int_0^\infty n(r,t)\,\exp(-st)\mathrm{d}t$.

Another noticeable difference is between

$$\bar{\varphi}_{IET} = \int \varphi(r) f_{IET}(r)\mathrm{d}^3r$$

and $\bar{\varphi}_m = \lim_{\tau\to\infty}\bar{\varphi}_{IET}$. The charge separation quantum yield is averaged in IET over the initial charge distribution, which has a more appropriate shape than the Markovian distribution given by eq 4.20:[11]

$$f_{IET} = \frac{W_I(r)\tilde{n}(r,1/\tau)}{\int W_I(r)\tilde{n}(r,1/\tau)\mathrm{d}^3r}$$

However, even this distribution is not quite as good as that obtained in UT, because the latter accounts for higher order corrections in the acceptor concentration which are ignored in IET.[11]

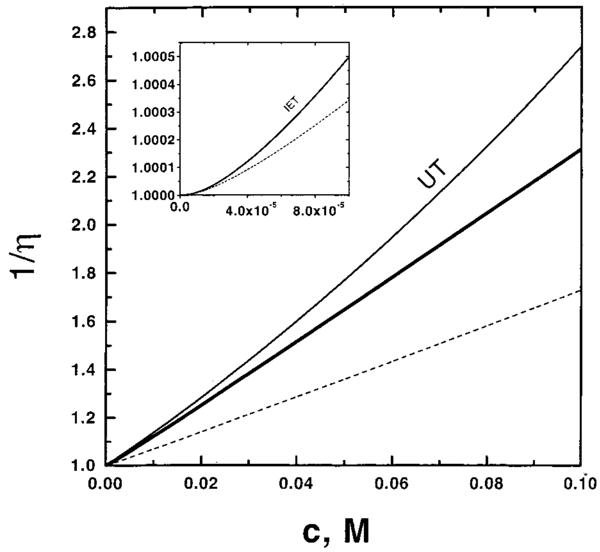

Figure 7. Quantum yield of fluorescence as a function of acceptor concentration c in IET (thick line), UT (thin line), and Markovian theory (dashed line). The nonlinearity of IET and the Markovian results at very low concentrations which are shown in the insert is caused by the saturation of electron transfer in this region. The parameters are the same as in Figure 6.

In Figure 7 we illustrate the difference between two competing non-Markovian theories, UT and IET, and their Markovian analogue. Inspecting the Stern−Volmer plot from IET, one can see that it is nonlinear at low concentrations where the saturation of electron transfer takes place. The Markovian theory well reproduces this effect, but for finite τ it is less accurate than IET at all values of c. On the contrary, UT is not good at low concentrations where it misses the saturation effect. On the other hand, it is better than the two others at high concentrations because it reproduces the nonlinear increase of η^{-1} with c. This super-linearity results in the widely recognized concentration dependence of the Stern−Volmer constant.[11,44−46]

VI. Markovian versus Non-Markovian Theories

Both the IET and Markovian theory provide the lowest order approximation for the fluorescence quantum yield with respect to acceptor concentration. This approximation is the only limitation of the validity of IET. Due to this limitation it is unable to describe the long time asymptotics of the system response to instantaneous excitation and the nonlinearity of the Stern−Volmer law at high concentrations. On the other hand, it accounts for the effect of electron-transfer saturation and all non-Markovian effects, such as nonstationary energy quenching and geminate charge recombination. They are seen in quenching kinetics and ion relaxation, as well as in the principal characteristics of the stationary regime, κ_i and $\bar{\varphi}$, which are different from their Markovian analogues, k_i and $\bar{\varphi}_m$. This difference is significant at short excitation lifetimes,[18] especially in nanosecond and picosecond range which is now intensively studied experimentally. Moreover, there is a non-Markovian effect arising at higher light intensities, that was not considered in the present work but highlighted in two others.[20,47] It affects the Stern−Volmer constant and makes it sensitive to light power at reasonable intensities.

Hence, IET is everywhere preferable to the Markovian theory, but at a large excess of acceptors it is less accurate than GUT. Fortunately, this drawback of IET can be easily removed by MET,[1] but this improvement is outside the scope of the present work.

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