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Stern−Volmer Law in Competing Theories and Approximations[†]

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The numerous theories of contact energy quenching are compared between themselves and with the theories of remote electron transfer. The Stern−Volmer constant used as a criterion is studied in the full range of quencher concentrations and diffusion. When any one of these parameters is increased, diffusion-controlled quenching gives way to kinetic control, although differently in the theories of contact and remote transfer.

I. Introduction

Fluorescence quenching in solutions is usually carried out by electron or energy transfer from excited donors to acceptors moving around, or vice versa. The main characteristic of the phenomenon is the relative quantum yield of the fluorescence, which obeys the famous Stern−Volmer law:[1−3]

$$\eta = \int_0^\infty N(t)\, dt/\tau = \frac{1}{1 + c\kappa\tau} \qquad (1.1)$$

Here $N(t)$ is the survival probability of the excitation instantaneously created at $t = 0$. It decays with a time τ and is quenched by transfer partners given in concentration c. The "Stern−Volmer constant" κ is not actually a constant but was shown to increase with quencher concentration c and encounter diffusion coefficient D, varying with solvent viscosity. This dependence, $\kappa(c, D)$, is deduced here from different theories of the same phenomenon and used for their comparison.

Roughly speaking, all the theories are divided in two groups. One group is based on the contact model, assuming that transfer occurs only at the closest approach distance σ with kinetic rate constant k_0. To another group belong all encounter theories using the distance-dependent rate of transfer $W(r)$. We will prove that there is practically no difference between the majority of contact theories. All of them describe the monotonic increase of $\kappa(c)$ with concentration from its lowest ("ideal") value, $\kappa_0 = \kappa(0, D)$ to the largest one, which is

$$k_0 = \int W(r)\, d^3r \qquad (1.2)$$

The contact value of the Stern−Volmer constant at zero concentration is well-known:[9−11]

$$\kappa_0 = \frac{k_0}{1 + k_0/[k_D(1 + \sqrt{u\tau_d})]} \qquad (1.3)$$

where $k_D = 4\pi\sigma D$ is the diffusional rate constant, $u = 1/\tau$, and $\tau_d = \sigma^2/D$ is the encounter time. The difference between these two constants is most pronounced at slow diffusion when $k_D \ll k_0$. Then the concentration increase causes the transition from small $\kappa_0 \approx k_D(1 + \sqrt{u\tau_d})$ to large k_0.

This transition is similar to the transition from diffusional to kinetic control of electron transfer, which the "ideal" Stern−Volmer constant $\kappa_0(D)$ experiences with an increase in diffusion. The latter is given by one and the same eq 1.3 in all contact approximations. Here we will demonstrate that in the encounter theory of remote transfer κ_0 changes similarly with diffusion, although it differs more from its contact estimate the larger the tunneling length is. Moreover, the concentration dependence of κ in theories of remote transfer is qualitatively the same as in its contact analogue whose k_0 is taken from eq 1.2. However, the true value of κ essentially exceeds its contact estimate, especially under diffusional control.

Sometimes the experimental κ values also are found to be higher than the maximal contact estimates. To explain them, the contact formulas were often supplemented by an additional factor accounting for the static quenching.[4] The latter is remote in principle and precedes the diffusion-accelerated quenching modeled as contact. As an alternative the "finite sink approximation" was proposed by Stevens and co-workers.[5−8] Unfortunately, this model is inconsistent and the phenomenon obtained with it is just an artifact bearing no relationship to static quenching and its parameters. However, the data obtained or used by Stevens indicates that only the theories of remote transfer can be successful in fitting them. From such a fit made with the oldest (differential) encounter theory, we get here quite realistic parameters of an exponential transfer rate.

The outline of the article is as follows. In the next section we will elucidate what are the basic encounter theories and compare with them a number of others, which are all contact and integral but will be discriminated by kernels (memory functions) of corresponding integral equations. In Section III the Stern−Volmer constant at a zero concentration limit will be considered as function of diffusion to demonstrate the essential difference between contact and remote quenching. Their difference will be examined in Section IV in the whole concentration range at given diffusional coefficient and different tunneling lengths. In Section V we will prove that only the theory of remote transfer provides the nonmodel explanation of real experimental data. The results will be summarized in the Conclusions.

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II. Kinetic Theories of Irreversible Energy Quenching

There are a number of multiparticle theories starting from different axiomatic constructions but deducing one and the same result: the average survival probability of the excitation, D^*, quenched by surrounding molecules, A. The general scheme of the reaction is $D^* + A \rightarrow D + A$, but for the electron or energy transfer mechanism it may be presented in more detail:

$$D^* + A \begin{array}{l} \nearrow \; [D^+ ... A^-] \;\rightarrow\; D + A \\ \searrow \; [D ... A^*] \;\rightarrow\; D + A \end{array} \tag{2.1}$$

In solid solutions the excitation jumps from one donor to another due to the resonance energy transfer approaching one of the immobile acceptors where energy is trapped and dissipates. This is the so-called "trapping problem" that was solved for small and large steps of the random walk leading to diffusional and hopping quenching of excitation. A few approximate and exact solutions of the trapping problem were used in ref 3 to calculate κ at any c and estimate the accuracy of each from their comparison.

Similar work was partially done in ref 13 but for an excited molecule quenched by electron transfer during diffusional encounters with acceptors in liquid solutions. However, the consideration there was restricted to encounter theories: differential (DET), integral (IET), and modified (MET), while the diversity of approaches to diffusion-assisted reactions in liquids is much wider and makes uncertain the appropriate choice of the theory for fitting the experimental data. Here we are going to make the comparison more general and universal by identifying some of the theories and discriminating between others, comparing them with the exact one.

The particular case of immobile excitation surrounded by independently moving point acceptors is known as a "target problem". The well-known solution to this problem is recognized as exact at any concentration of acceptors, $c = [A]$.[12] An important fact is that this solution coincides with that provided by differential encounter theory (DET) created long ago.[14−16] It is based on non-Markovian, but the differential (rate) equation for the survival probability of the excitation $N(t) = [D^*]$:

$$\dot{N} = -k(t)cN - uN \tag{2.2}$$

where the time-dependent "reaction constant" should be found from the following equations:

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

$$\dot{n} = -W(r)n(r, t) + D\Delta n \qquad \left.\frac{\partial n}{\partial r}\right|_{r=\sigma} = 0 \tag{2.3}$$

where $n(r, 0) = 1$. The input data are only D, σ, and $W(r)$. The most popular approximations of the latter are either exponential or contact:[17]

$$W(r) = W_c e^{-2(r-\sigma)/l} \tag{2.4a}$$

$$W(r) = \frac{k_0}{4\pi\sigma^2}\delta(r - \sigma) \tag{2.4b}$$

In the contact approximation, eqs 2.3 reduce to the classical Collins−Kimball model:[18]

$$k(t) = k_0 n(\sigma, t) \qquad \dot{n} = D\Delta n \qquad 4\pi D r^2 \left.\frac{\partial n}{\partial r}\right|_{r=\sigma} = k_0 n(\sigma, t) \tag{2.5}$$

When k_0 is calculated from eq 1.2 by using the exponential $W(r)$, then approximately $k_0 = W_c 2\pi\sigma^2 l$. If the tunneling length l is turned to 0, keeping $W_c l$ as well as k_0 constant, then the results obtained for the remote transfer should approach those in the contact approximation.

The integral encounter theory (IET) was deduced later[19−21] as the lowest-order approximation with respect to partner concentration. Although approximate in this sense it was shown to be ultimately better than DET when the excited reactants and products of reversible reactions have different lifetimes.[22] IET is a kind of a memory function formalism using integral kinetic equations instead of differential equations:

$$\dot{N} = -c\int_0^t \Sigma(t - t')N(t')\,\mathrm{d}t' - uN \tag{2.6}$$

$\Sigma(t) = R(t)$ is the simplest kernel (memory function) of the original IET, which takes the place of the rate constant. It is defined through $W(r)$ and the pair correlation function ν substituted for n:

$$R(t) = \int W(r)[\delta(t) + \dot{\nu} + u\nu]\,\mathrm{d}^3r$$

$$\dot{\nu} = -W(r)\nu + D\Delta\nu - u\nu \qquad \left.\frac{\partial n}{\partial r}\right|_{r=\sigma} = 0 \tag{2.7}$$

where $\nu(r, 0) = 1$. As seen from these definitions, R is concentration-independent. As a result the Laplace transformation of eq 2.7 used in eq 1.1 reproduces the original (linear in c) Stern−Volmer law:

$$1/\eta = 1 + c\kappa_0\tau \tag{2.8}$$

with the "ideal" (concentration-independent) Stern−Volmer constant

$$\kappa_0 = \tilde{R}(0) = \int_0^\infty R(t)\,\mathrm{d}t \tag{2.9}$$

However, it was proved long ago that the Stern−Volmer law is nonlinear and its real constant

$$\kappa = \kappa_0 + \beta c + ... \tag{2.10}$$

increases with concentration.[23−26] From this point of view the IET is just the lowest-order approximation with respect to c. To eliminate this demerit, modified encounter theory (MET) was developed, which redefines the kernel of the integral equation in the following way:[27,28]

$$\Sigma(t) = R(t)\exp(-ckt) \tag{2.11}$$

Here

$$k \equiv k(\infty) = \int_0^\infty R(t)e^{ut}\,\mathrm{d}t \tag{2.12}$$

is the stationary (asymptotic) value of $k(t)$. In the contact approximation it takes the well-known form:

$$k = \frac{k_0}{1 + k_0/k_D} \tag{2.13}$$

Unlike $R(t)$, the MET kernel (eq 2.11) is concentration-dependent and the corresponding Stern−Volmer constant was

TABLE 1

theory	$k_0/\tilde{\boldsymbol{\Sigma}}(\boldsymbol{s})$
LSA (= IET)	$1 + k_0g(s + u)$
LESA	$1 + k_0g(s + u + ck_0)$
CA, MPK1 (= DET)	$[ck_0\tilde{P}(s + u)]/[1 - (s + u)\tilde{P}(s + u)]$
MPK2	$1 + k_0g(s + u + ck_0\tilde{\Sigma}(s))$
MPK3 (= MET)	$1 + k_0g(s + u + ck_0/[1 + k_0g(s + u)])$
SCRTA	$1 + k_0g(s + u + ck_f)$, $k_f = k_0/[1 + k_0g(ck_f)]$

shown to increase with c:[13]

$$\kappa = \tilde{\Sigma}(0) = \tilde{R}(ck) \tag{2.14}$$

The similar dependence is inherent also with DET as well as other theories that compete with it. It is remarkable that all of them can be presented as integral theories, whose $N(t)$ obeys one and the same eq 2.6 but with different kernels. Sometimes the latter is explicitly defined in the original works, but more often the reduction to the integral form and extraction of the kernel was done ourselves. In a few cases this procedure was nontrivial and required rather long and sophisticated calculations that are not of interest in the present context, except the final results represented by the Laplace-transformed kernels $\tilde{\Sigma}$ in Table 1.

In Table 1 we used the Laplace transformation of the general solution of eq 2.2:

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

where

$$P(t) = \exp(-c\int_0^t k(t')\,dt') \tag{2.16}$$

Besides, the Green function of the free diffusion equation with reflecting boundary conditions, $G_0(r, r', t)$, was used to define the function $g(s) = \tilde{G}_0(\sigma, \sigma, s)$, which is well-known in the contact approximation:

$$1/g(s) = k_D(1 + \sqrt{s\tau_d}) \tag{2.17}$$

According to eq 2.14, the "ideal" Stern−Volmer constant expressed through this very function is actually

$$\kappa_0 = \kappa(c = 0) = \lim_{c\to 0}\tilde{\Sigma}(0) = \frac{k_0}{1 + k_0g(u)} \tag{2.18}$$

It coincides with eq 1.3 and is the same for all theories listed in Table 1.

The first group of theories was based on the superposition approximation used for truncation of an infinite hierarchy of equations for a reduced distribution function at the pair distribution level.[29,30] It was generalized and applied to reversible reactions by Lee and Karplus[31] and their successors.[32−34] After linearization over deviations from equilibrium,[35,36] the theory became simpler and finally was recognized as one identical to IET, provided the reduction to phenomenological equations is not done.[37,38] This is why the linearized superposition approach called LSA here provides exactly the same kernel as IET.

The superposition approximation was also applied to the reversible reactions

$$D^* + A \underset{k_d}{\overset{k_a}{\rightleftharpoons}} [D^*A]$$

for studying the asymptotic behavior of $N(t)$, when the system approaches equilibrium.[35,39] Since the results were not satisfactory, Naumann et al.[40] developed an extended superposition approach (ESA) that was later linearized and became known as LESA. Independently, similar linearization over deviations from equilibrium was also made in ref 41. Although the asymptotic description of the quenching kinetics is improved, it was recognized that LESA is not valid at a large equilibrium constant $K = k_a/k_d$,[41] because the superposition approach becomes worse when K increases.[40] This is especially true for earlier times when the deviations from equilibrium are not small. However, the authors who constructed LESA pretend that it is "applicable at all times".[40] Therefore, we took it for comparison in the irreversible limit where $K \to \infty$ and the kernels obtained in both works[40,41] coincide with the one listed as LESA in Table 1.

The largest body of research carried out by different authors[42−45] with different methods on closer inspection are noted to be identical to DET of contact-irreversible reactions, that is, to the classical Collins−Kimball theory.[18] This is equally true for a few works[35,46] based on convolution approximation (CA) and those published by Lee and co-workers[47,48] as many-particle kernel theory, named later MPK1. If the DET of irreversible quenching is presented as integral theory, it has the kernel listed in the table, which is common to all those works.

However, the upgrading of the theory designed for reversible reactions was not stopped. After the first attempt, MPK2[49] and MPK3[50] have arisen, which are not exact for irreversible target problem as was their precursor. Therefore, their kernels are different and the kernel for MPK2 is actually defined as a solution of transcendent equation. Another one, for MPK3, in the case of irreversible quenching appears to be identical to that provided by MET. For a very long time the latter was considered the most reasonable extension of IET for larger concentrations,[13,51] but very recently a new theory named self-consistent relaxation time approximation (SCRTA) has taken on this role.[52] In the irreversible case the inverse relaxation time of SCRTA, k_fc, is defined by the transcendent equation for k_f shown in Table 1. It is equivalent to the one expressed by the Laplace transform of $k(t)$: $c\tilde{k}(k_f) = 1$.[4] Despite this complication, SCRTA looks more reasonable than IET and MET when compared with other theories in Section IV.

III. Viscosity Dependence of the Ideal Stern−Volmer Constant

As follows from eqs 1.1 and 2.15, there is the following concentration expansion of quantum yield:

$$\eta = \frac{\tilde{N}(0)}{\tau} = u\int_0^\infty e^{-ut}P(t)\,dt = 1 - cu\int_0^\infty e^{-ut}\,dt\int_0^\infty k(t')\,dt' + ...\cdot \approx 1 - c\kappa_0\tau \tag{3.1}$$

where κ_0 is defined as in ref 4:

$$\kappa_0 = \frac{1}{\tau}\int_0^\infty e^{-t/\tau}k(t)\,dt = \frac{\tilde{k}(1/\tau)}{\tau} \tag{3.2}$$

This is the constant that appears in the ideal (linear in concentration) Stern−Volmer law (eq 2.8). Obtained from DET,it is exactly the same one that follows from the IET eqs 2.9 and 2.7:

$$\kappa_0 = \int_0^\infty dt\int W(r)[\delta(t) + \dot{\nu} + u\nu]\,d^3r = u\int W(r)\tilde{\nu}(r, 0)\,d^3r = u\int W(r)\tilde{n}(r, u)\,d^3r \tag{3.3}$$

where we took into account that $\nu = n\exp(-ut)$. In view of the definition of k through $n(r, t)$ given in eq 2.3, this IET result is exactly the same as in eq 3.2.

In the contact case of eq 2.4b, we get from the last equation

$$\kappa_0 = k_0 u\tilde{n}(\sigma, u) = k_0 u \int \tilde{G}(\sigma, r_0, u)\, \mathrm{d}^3 r_0 = \frac{k_0 u \int \tilde{G}_0(\sigma, r_0, u)\, \mathrm{d}^3 r_0}{1 + k_0 G_0(\sigma, \sigma, u)} \quad (3.4)$$

Here we used the well-known relationship (see eq 5.10 in recent review[17]) between the Green function of eq 2.3 for n and that for the free motion, $\tilde{G}_0(\sigma, r_0, u)$. Since the integral of the latter over space is $1/u$ while $\tilde{G}_0(\sigma,\sigma, u)$ is $g(u)$ from eq 2.17, the expression in eq 3.4 is identical to the ideal contact value of the Stern−Volmer constant given in eq 1.3.

For remote transfer the analytic calculation of this quantity from eq 3.3 is hardly possible, but for the exponential quenching rate $W(r)$ given in eq 2.4 at least the Laplace transformation of n can be found from the equation, following from eq 2.3:

$$(s + W_c \mathrm{e}^{-2(r-\sigma)/l})\tilde{n} - D\Delta\tilde{n} = 1 \qquad \left.\frac{\partial \tilde{n}}{\partial r}\right|_{r=\sigma} = 0 \quad (3.5)$$

Following Pilling and Rice,[53] we get the general solution of this equation:

$$\tilde{n}(r, s) = \frac{1}{s}\left[1 + \frac{\Phi}{r} I_\nu(w) + \frac{\pi l}{2r \sin \nu\pi} F_{\nu\nu}(w)\right] \quad (3.6)$$

Here $w = w_0 \exp[-(r - \sigma)/l]$, $w_0 = l\sqrt{W_c/D}$, $\nu = l\sqrt{s/D}$, and

$$F_{\mu\nu}(w) = I_{-\mu}(w)G_\nu(w) - I_\mu(w)G_{-\nu}(w)$$
$$G_\nu(w) = \int_0^\omega x \ln(x/\lambda) I_\nu(x)\, \mathrm{d}x \quad (3.7)$$

where I_ν is the modified first-kind Bessel function of the order ν. However

$$\Phi = -\frac{\pi l}{2 \sin \nu\pi} \frac{[1 + \sqrt{s\tau_d}]F_{\nu\nu}(w_0) + \sqrt{W_c\tau_d}F_{\nu+1,\nu}(w_0)}{[1 + \sqrt{s\tau_d}]I_\nu(w_0) + \sqrt{W_c\tau_d}I_{\nu+1}(w_0)} \quad (3.8)$$

differs from that obtained by Pilling and Rice in eq 10 of their work.[53] The difference is originated from boundary conditions. They took the absorbing one, $n(\sigma, t) = 0$, assuming that the remote transfer is accompanied by very strong contact quenching. Contrary to this, we are assuming that there is only a single channel reaction, either remote or contact. If it is remote, no quenching at contact is possible, so that the reflecting boundary condition common for all encounter theories has to be used in eqs 2.3 and 3.5.

After the substitution of eq 3.6 into the definition of the ideal Stern−Volmer constant (eq 3.3), the integral was taken numerically at any diffusion coefficient except for very small values of it, where the quenching is quasi-static. However, for this very region there is an approximate expression derived in ref 54:

$$\kappa_0 = \int_\sigma^\infty \frac{W(r)4\pi r^2\, \mathrm{d}r}{1 + W(r)\tau} + D\int_\sigma^\infty \frac{(\tau\, \mathrm{d}W/\mathrm{d}r)^2 4\pi r^2\, \mathrm{d}r}{[1 + W(r)\tau]^4} \quad (3.9)$$

The Stern−Volmer constant increases monotonically with diffusion from the lowest static value $\kappa_0(0)$ up to the upper one, which is the kinetic rate constant $k_0 = \lim_{D\to\infty} \kappa_0(D)$. In the contact approximation represented by eq 1.3, this dependence is qualitatively the same except that there is no static quenching $[\kappa_0(0) = 0]$. At slowest diffusion it is proportional to $\sqrt{D}$ due to nonstationary diffusional quenching. To demonstrate this linearity, $\sqrt{D}$ is used as an abscissa in Figure 1. As seen from this figure at the same k_0, the remote transfer is more efficient for larger tunneling length l.

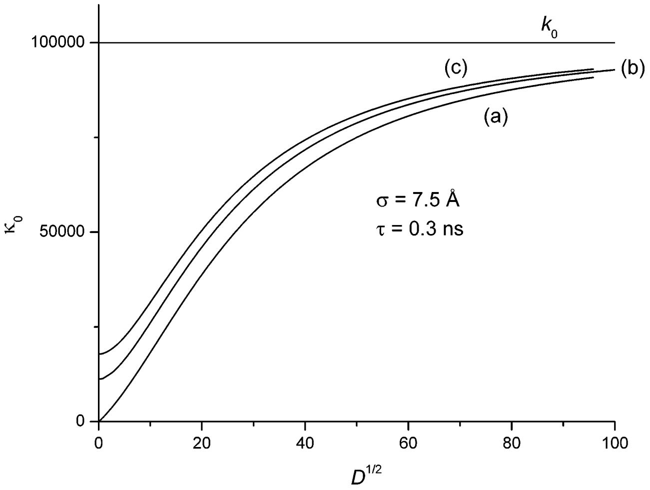

Figure 1. Ideal Stern−Volmer constant as a function of diffusion in contact approximation (a) and for the exponential transfer rate with different tunneling lengths: $l = 1.6$ Å (b) and $l = 2.5$ Å (c).

IV. Concentration Dependence of the Stern−Volmer Constant

As has been proved in eq 2.18, the lowest limit of the Stern−Volmer constant $\kappa_0 = \kappa(0)$ is the same for all contact theories. But there is also the upper limit of $\kappa(c)$ reached at largest c: this is k_0 defined in eq 1.2, which is the maximal value of the time-dependent rate constant $k(t)$ from eq 2.3. The latter starts from k_0 at $t = 0$ when $n(r, 0) = 1$ and goes down with time up to the stationary (steady-state) value k given in eq 2.13. Therefore, at the very beginning the quenching kinetics is always exponential:

$$P(t) = \exp(-ck_0 t + ...) \quad (4.1)$$

but it remains the same till almost the end of quenching if the concentration of quenchers, c, is high enough. With exponential $P(t)$ we obtain from eq 3.1 the classical Stern−Volmer law (eq 1.1) but with kinetic constant

$$k_0 = \lim_{c\to\infty} \kappa(c)$$

The problem is, what is the true Stern−Volmer constant behavior between these two limits, that is, in the interval $\kappa_0 \leq \kappa(c) \leq k_0$.

In the semilogarithmic plot of Figure 2 the concentration dependence $\kappa(c)$ is represented by the S-like curves related to different theories. The main one is that of DET, which is expected to be exact for target problem for independently moving point quenchers. This is also true for all equivalent theories of irreversible transfer (CA, MPK1, Vogel[43,44]). From the comparison of this result with others it is clear that LESA is just a bad interpolation between border limits. This is partially true also for MET/MPK3, although it is rather good for small concentrations as was actually expected.[27,28,55,56] At least it is better than IET and LSA, which reproduce the original Stern−Volmer law with the concentration-independent constant (horizontal dashed line) and are suitable for calculation of only this ideal value. Two remaining theories, MPK2 and SCRTA, give

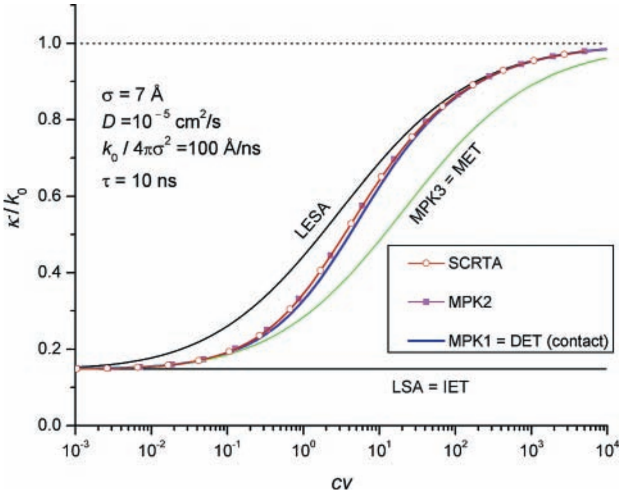

Figure 2. Concentration dependence of the Stern−Volmer constant κ in units of k_0 for a number of contact theories, provided $k_0 = 3.7 \times 10^{10}$ M^{-1} s^{-1} is the same for all of them.

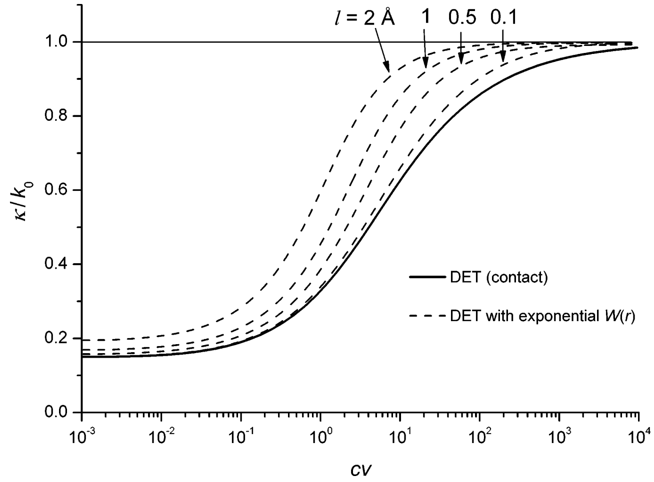

Figure 3. Same comparison as in Figure 2 but for the exponential transfer rates at different tunneling lengths indicated in the figure. The contact approximation ($l \to 0$) is represented by a solid line.

results that are very close to each other and to the exact one. We believe that this comparison is instructive to those who like to employ one of the existing contact theories for the particular problem of interest.

Even more important is the comparison of contact and remote electron transfer shown in Figure 3. The calculations were performed for a few realistic tunneling lengths l (dashed lines). The smaller l is, the closer the results obtained are to those gained in the contact approximation. The latter is actually justified for only the smallest $l = 0.1$ Å, which is reasonable for proton transfer but rather bad for electron transfer, where usually $l = 1 \div 2$ Å. We will make this point clear by a straightforward fitting of the remote transfer theory to the data presented in the recent work of Stevens and Biver.[57]

Neither contact nor exponential approximation of W is good for real fitting. Instead, one should use the true Marcus rate of electron transfer, accounting for the energy balance and the properties of the solution. In the simplest case of a single-channel reaction in highly polar solvent, this rate is represented by the following expression:

$$W(r) = V_0^{\,2} \exp\left[-\frac{2(r-\sigma)}{L}\right]\frac{\sqrt{\pi}}{\sqrt{\lambda(r)T}}\exp\left[-\frac{(\Delta G + \lambda(r))^2}{4\lambda(r)T}\right] \tag{4.2}$$

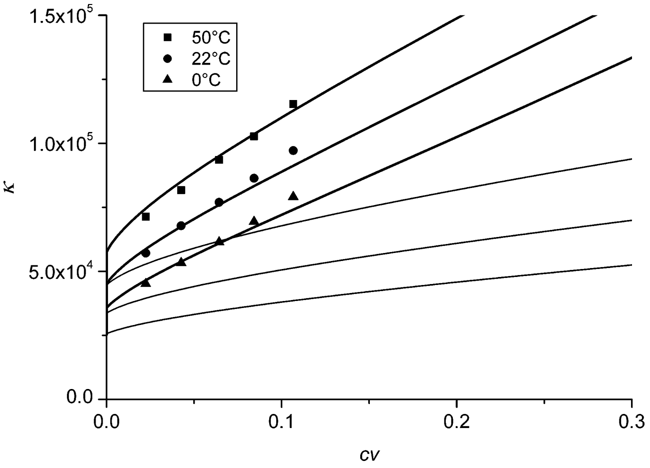

Figure 4. Concentration dependence of the Stern−Volmer constant for three different temperatures fitted by DET with the Marcus transfer rate (thick lines) and parameters listed in Table 2. Thin lines represent contact analogues of the above curves for the same temperatures (decreasing from top to bottom) and diffusion-controlled quenching ($k_0 = \infty$).

TABLE 2: Parameters of DCA Quenching by TMPD in Acetonitrile[57]

D (0°)	D (22°)	D (50°)	σ	τ	ΔG	λ_0[58]
2.4×10^{-5} cm^2/s	3.2×10^{-5} cm^2/s	4.3×10^{-5} cm^2/s	7.5 Å	12.6 ns	1.81 eV	1.3 eV

Here ΔG is the free energy of electron transfer whose reorganization energy

$$\lambda(r) = \lambda_0(2 - \sigma/r) \tag{4.3}$$

increases with interparticle distance, making the Arrhenius factor r-dependent and $W(r)$ nonexponential and even nonmonotonic at high exergonicity.[17] If such a complex dependence is approximated by a pure exponential formula (eq 2.4a), then l acquires the sense of effective decrement, unlike L, which is the true tunneling length for an electron. For the case of transfer in the normal Marcus region ($-\Delta G < \lambda_0$), l may be essentially smaller than L, sometimes twice as small.[58] No such reduction occurs in the inverted Marcus region where $-\Delta G > \lambda_0$. This is the case investigated in ref 57. The other parameters of the system studied at three different temperatures ($T = 0$, 22, and 50 °C) in acetonitrile solutions are listed in Table 2. All the data are taken from the original article,[57] except contact reorganization energy λ_0, which is borrowed from another work.[58]

In Figure 4 the results of our best fit to the experimental points from ref 57 are shown as functions of the dimensionless concentration cv where $v = {}^4/_3\pi\sigma^3 c$. The agreement is rather satisfactory and could be even better if a number of additional factors were taken into account. Instead of a single-channel transfer rate (eq 4.2), one could better use its multichannel analogue to account for the vibrational excitation of the inner quantum modes of reaction products.[17,59,60] The reorganization energy attributed to quantum channels comprises an additional λ_i, which is sometimes around 0.3 eV.[61] Besides, we did not take into account the liquid structure near the contact and the spatial dependence of the diffusional coefficient as is sometimes done.[62−64] Also, we did not even mention chemical anisotropy, which is essential sometimes.[65]

Due to these simplifications we have only two varying parameters: the tunneling length L and its matrix element V_0.

TABLE 3: Kinetic Constants and Contact Rates

	T (°C)		
	0	22	50
$k_0 \times 10^{-6}$ (Å^3/ns)	0.979	1.004	1.03
W_c (ns^{-1})	484	546	619

Found from the best fit, they are

$$L = 1.6\ \text{Å} \qquad V_0 = 4.07 \times 10^{-2}\ \text{eV} \tag{4.4}$$

With these parameters known, the kinetic rate constant (eq 1.2) and the contact value of the rate, $W_c = W(\sigma)$, have definite although different values for all three temperatures studied.

All the k_0 values listed in Table 3 are much larger than the contact diffusional constants $k_D = 4\pi\sigma D$, so that the reactions are strongly in the diffusional control limit, as was expected.[57] Calculated in this limit, contact $\kappa(c)$ is maximally available in this approximation, as well as $k_D(1 + \sqrt{\tau_d/\tau})$ is the maximal κ_0 resulting from eq 1.3 at $k_0 \to \infty$. The diffusional $\kappa(c)$ obtained in the contact approximation and shown in Figure 4 indicates that the experimental points are far above their contact estimates. Likewise, the steady-state rate constant for the remote transfer, $k = 4\pi R_Q D$, is always higher than k_D if the reaction is under diffusional control because in this region $R_Q > \sigma$ for certain.[16,17]

However, not only are the contact lines beneath all the points but also their slope is too small to explain the true concentration dependence. Perhaps these troubles stimulated Stevens to propose the original "finite sink approximation" instead of the existing theory.[5,6] The inconsistency of this model is seen from the very fact that it does not discriminate between the Stern–Volmer and the steady-state constants, κ and k, and ascribes to the latter the concentration dependence that is not inherent to $k = \lim_{t\to\infty} k(t)$ in principle.[66] At the same time, the model predicts the linear dependence of the results in coordinates $1/\kappa$ versus $c^{1/3}$. Moreover, it was shown a number of times[6–8,57] that the straight lines representing this dependence for different temperatures intersect at a common point where "the static quenching limit is unambiguously located" according to ref 57.

To inspect this statement we redrew the previous figure in similar but dimensionless coordinates, k_0/κ versus $(cv)^{1/3}$ (Figure 5), adding one more curve representing the true static quenching. As has been known for a very long time, the kinetics of static quenching following from eqs 2.16 and 2.3 at $D = 0$ is given by the following expression:[67,68]

$$P(t) = \exp\{-c\int_\sigma^\infty [1 - e^{-W(r)t}] 4\pi r^2\, dr\} \tag{4.5}$$

This expression was applied to dipole–dipole quenching by Förster himself[67] and employed to "exchange" (exponential) rate transfer by Inokuti and Hirayama.[69] It is clear that for earliest times $P \approx \exp(-ck_0t)$, so that for the largest concentrations $\kappa \to k_0$. That is why all the curves approach 1 at the largest concentrations. Where they are close to this limit the quenching is quasi-static, that is, almost viscosity-independent. But the experimental points are far from this region. Just occasionally they are near the bend of the S-like curves where the straight line with viscosity-dependent slope is rather a good approximation. The intersection of these lines at a common point is just artificial and the point itself has nothing in common with the static quenching. This artifact would be easily removed if the experimental region were extended a little bit either to the right or to the left.

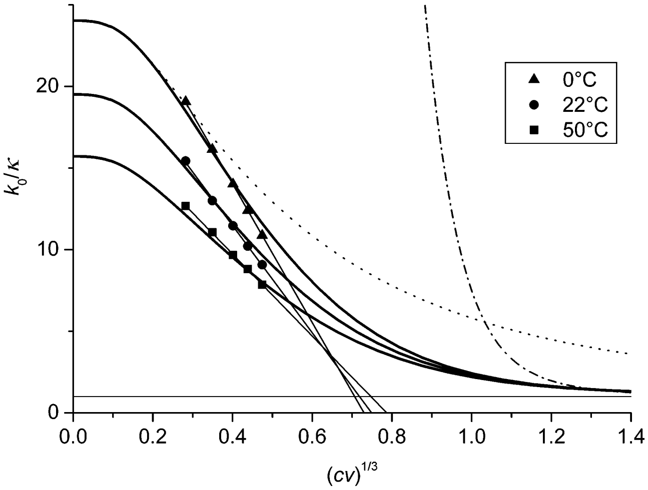

Figure 5. Same DET curves (solid lines) and experimental data (points) as in Figure 4 but in Stevens' coordinates. The static quenching (– • –) and the MET analogue of DET with the same parametrization (•••) are shown for only the lowest temperature. The straight lines intersecting at the common point are Stevens' interpolation of the experimental results.

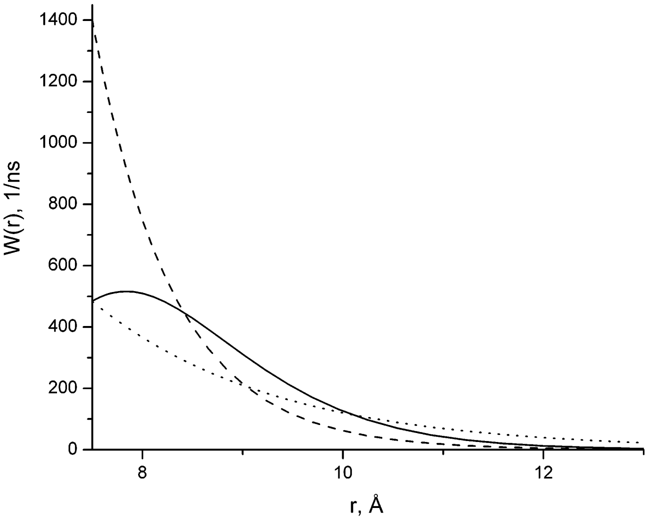

Figure 6. Single-channel Marcus transfer rate obtained from the best fitting and its exponential approximations: (a) with a true tunneling length $l = L = 1.6$ Å and effective contact rate $W_c = 1400$ ns^{-1} (– – –) and (b) with a true contact rate 484 ns^{-1} but effective $l = 3.59$ Å (•••).

However, even the existing data are unique. We already demonstrated that their fitting is inaccessible for all contact theories. From Figure 5 we see that this is equally correct for MET, whose results cannot be advanced so far in the high-concentration region without losing accuracy. Only the old classical DET is good enough for the appropriate fitting and interpretation of these data. Making use of the parameters obtained from this fitting at 0 °C (Table 3), we reconstructed the true Marcus rate (eq 4.2) as a function of the interparticle distance (Figure 6). As usual in the inverted region, it has a maximum near the contact, but at very large distances it has an exponential asymptote with a true tunneling length L. If one models this rate by exponential function (eq 2.4a) with effective length $l = L$, keeping k_0 the same, then the pre-exponent appears to be much larger than the true contact rate. If quite the reverse, the pre-exponent is equalized to the true contact value of the Marcus rate, and then l becomes more than twice as large as L and cannot be associated with a true tunneling length. This alternative does not exclude all the intermediate choices of W_c and l. Even when fitting with the exponential model is successful, it leaves a great uncertainty in the model parameters and their identification with the true ones.

V. Conclusions

By comparing all the existing theories between themselves and with the available experimental data, we arrived at the following conclusions:

(i) All contact theories provide the nonlinear concentration dependence of the Stern−Volmer constant, which is either identical or very close to that of DET but insufficient to fit the real data.

(ii) Among the theories that are suitable to work with distant quenching, DET is the best while the "finite sink approximation" is inappropriate.

(iii) The successful fitting of DET with the Marcus transfer rate to the experimental data provides a unique tunneling length, while the exponential models of this rate used for the same goal are unable to get an unambiguous result.

The comparison of different theories by their application to irreversible energy quenching is not exhaustive because most of them were designed for reversible transfer reactions. This is the more general and complex case that will be put to the test soon.

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References and Notes

(1) Stern, O.; Volmer, M. *Physik. Z.* **1919**, *20*, 183.
(2) Vavilov, S. I. *Microstruct. Light (Moscow)* **1974**, *1*, 303.
(3) Fedorenko, S. G.; Burshtein, A. I. *J. Chem. Phys.* **1992**, *97*, 8223.
(4) Szabo, A. *J. Phys. Chem.* **1989**, *93*, 6929.
(5) Stevens, B. *Chem. Phys. Lett.* **1987**, *134*, 519.
(6) Stevens, B.; McKeithan, D. N. *J. Photochem. Photobiol. A: Chem.* **1987**, *40*, 1.
(7) Stevens, B.; McKeithan, D. N. *J. Photochem. Photobiol. A: Chem.* **1989**, *47*, 131.
(8) Stevens, B.; Biver, C. J., III; McKeithan, D. N. *Chem. Phys. Lett.* **1991**, *187*, 590.
(9) Burshtein, A. I.; Naberukhin, Yu. I. *Preprint 74-160P*; Institute of Theoretical Physics, Ukraina Academy: Kiev, 1974.
(10) Lukzen, N. N.; Doktorov, A. B.; Burshtein, A. I. *Chem. Phys.* **1986**, *102*, 289.
(11) Burshtein, A. I.; Sivachenko, A. Yu. *J. Photochem. Photobiol. A: Chem.* **1997**, *109*, 1.
(12) Allinger, K.; Blumen, A. *J. Chem. Phys.* **1980**, *72*, 4608.
(13) Burshtein, A. I.; Gopich, I. V.; Frantsuzov, P. A. *Chem. Phys. Lett.* **1998**, *289*, 60.
(14) Steinberg, I. Z.; Katchalsky, E. *J. Chem. Phys.* **1968**, *48*, 2404.
(15) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1973**, *58*, 4009.
(16) Doktorov, A. B.; Burshtein, A. I. *Sov. Phys. JETP* **1975**, *41*, 671.
(17) Burshtein, A. I. *Adv. Chem. Phys.* **2000**, *114*, 419.
(18) Collins, F. C.; Kimball, G. E. *J. Colloid Sci.* **1949**, *4*, 425.
(19) Sakun, V. P. *Physica A* **1975**, *80*, 128.
(20) Doktorov, A. B. *Physica A* **1978**, *90*, 109.
(21) Kiprianov, A. A.; Doktorov, A. B.; Burshtein, A. I. *Chem. Phys.* **1983**, *76*, 149, 163.
(22) Burshtein, A. I. *J. Lumin.* **2001**, *93*, 229.
(23) Ware, W. R.; Novros, J. S. *J. Phys. Chem.* **1966**, *70*, 3246.
(24) Nemzek, Th. L.; Ware, W. R. *J. Chem. Phys.* **1975**, *62*, 479.
(25) Eftink, M. R.; Ghiron, C. R. *J. Phys. Chem.* **1975**, *80*, 486.
(26) Murata, S.; Nishimura, M.; Matsuzaki, S. Y.; Tachiya, M. *Chem. Phys. Lett.* **1994**, *219*, 200.
(27) Kipriyanov, A. A.; Gopich, I. V.; Doktorov, A. B. *Chem. Phys.* **1994**, *187*, 241; **1995**, *191*, 101.
(28) Kipriyanov, A. A.; Gopich, I. V.; Doktorov, A. B. *Physica A* **1998**, *255*, 347.
(29) Monchick, L.; Magee, J. L.; Samuel, A. H. *J. Chem. Phys.* **1957**, *26*, 935.
(30) Waite, T. R. *Phys. Rev.* **1957**, *107*, 463.
(31) Lee, S.; Karplus, M. *J. Chem. Phys.* **1987**, *86*, 1883.
(32) Molski, A.; Keizer, J. *J. Chem. Phys.* **1992**, *96*, 1391.
(33) Naumann, W.; Molski, A. *J. Chem. Phys.* **1995**, *103*, 3474.
(34) Molski, A.; Naumann, W. *J. Chem. Phys.* **1995**, *103*, 10050.
(35) Szabo, A. *J. Chem. Phys.* **1991**, *95*, 2481.
(36) Naumann, W. *J. Chem. Phys.* **1994**, *101*, 10953.
(37) Naumann, W. *J. Chem. Phys.* **1999**, *111*, 2414; **2000**, *112*, 7152.
(38) Burshtein, A. I. *J. Chem. Phys.* **2002**, *117*, 7640.
(39) Szabo, A.; Zwanzig R. *J. Stat. Phys.* **1991**, *65*, 1057.
(40) Naumann, W.; Shokhirev, N. V.; Szabo, A. *Phys. Rev. Lett.* **1997**, *79*, 3074.
(41) Sung, J.; Shin, K. J.; Lee, S. *J. Chem. Phys.* **1997**, *107*, 9418.
(42) Berg, O. G. *Chem. Phys.* **1978**, *31*, 47.
(43) Vogelsang, J.; Hauser, M. *J. Phys. Chem.* **1990**, *94*, 7488.
(44) Vogelsang, J. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 15.
(45) Berberan-Santos, M. N.; Martinho, J. M. G. *Chem. Phys. Lett.* **1991**, *178*, 1.
(46) Agmon, N.; Szabo, A. *J. Chem. Phys.* **1990**, *92*, 5270.
(47) Sung, J.; Chi, J.; Lee, S. *J. Chem. Phys.* **1999**, *111*, 804.
(48) Sung, J.; Lee, S. *J. Chem. Phys.* **1999**, *111*, 796.
(49) Sung, J.; Lee, S. *J. Chem. Phys.* **1999**, *111*, 10159.
(50) Sung, J.; Lee, S. *J. Chem. Phys.* **2000**, *112*, 2128.
(51) Gopich, I. V.; Doktorov, A. B. *J. Chem. Phys.* **1996**, *105*, 2320.
(52) Gopich, I. V.; Szabo, A. *J. Chem. Phys.* **2002**, *117*, 507.
(53) Pilling, M. J.; Rice, S. J. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1563.
(54) Kipriyanov, A. A.; Karpushin, A. A. Preprint 23, 1988; Siberian Branch of Academy of Science, Novosibirsk (in Russian).
(55) Ivanov, K. L.; Lukzen, N. N.; Doktorov, A. B.; Burshtein, A. I. *J. Chem. Phys.* **2001**, *114*, 1754 (I), 1763(II).
(56) Ivanov, K. L.; Lukzen, N. N.; Doktorov, A. B.; Burshtein, A. I. *J. Chem. Phys.* **2001**, *114*, 5682 (III).
(57) Stevens, B.; Biver, C., III J. *Chem. Phys. Lett.* **1994**, *226*, 268.
(58) Gladkikh, V. S.; Burshtein, A. I.; Tavernier, H. L.; Fayer, M. D. *J. Phys. Chem.* **2002**, *A 106*, 6982.
(59) Burshtein, A. I.; Sivachenko, A. Yu. *Chem. Phys.* **1998**, *235*, 257.
(60) Burshtein, A. I.; Neufeld, A. A. *J. Phys. Chem. B* **2001**, *105*, 12364.
(61) Kikuchi, K.; Takahashi, Y.; Koike, K.; Wakamatsu, K.; Ikeda, H.; Miyashi, T. *Z. Phys. Chem. Neue Folge* **1990**, *167*, 27.
(62) Swallen, S. F.; Weidemaier, K.; Fayer, M. D. *J. Chem. Phys.* **1996**, *104*, 2976.
(63) Tavernier, H. L.; Kalashnikov, M. M.; Fayer, M. D. *J. Chem. Phys.* **2000**, *113*, 10191.
(64) Tavernier, H. L.; Fayer, M. D. *J. Chem. Phys.* **2001**, *114*, 4552.
(65) Burshtein, A. I.; Khudyakov I. V.; Yakobson, B. I. In *Progresses in Reaction Kinetics*; Pergamon Press: Oxford, U.K., 1984; Vol. 13, p 221.
(66) Angulo, G. Private communication, 2002.
(67) Förster, Th. *Z. Naturforsch.* **1949**, *4a* 321.
(68) Burshtein, A. I. *J. Lumin.* **1985**, *34*, 167.
(69) Inokuti, M.; Hirayama, F. *J. Chem. Phys.* **1965**, *43*, 1978.
(70) Krissinel, E. B.; Agmon, N. *J. Comput. Chem.* **1996**, *17*, 1085.