On the Coherent Description of Diffusion-Influenced Fluorescence Quenching Experiments II: Early Events


Abstract: In a previous article we showed how to perform and analyze steady-state and nanosecond time-resolved experiments on fluorescence quenching by electron transfer in a coherent manner. Now, by making use of a superior time resolution, we explore the first stages of this kind of reaction. The novel information gained enables us to merge the results on the viscosity and the driving-force dependencies of the reaction rate. A unique set of parameters for a single reaction channel suffices to describe all the results in the frame of differential encounter theory for diffusion-influenced, bimolecular, remote electron-transfer reactions. The inclusion of the solvent structure is crucial for the understanding of the reaction kinetics. To the authors’ best knowledge, this is the first time that such a comprehensive set of data has been successfully and jointly explained in the field, with physically sound parameters for electron-transfer reactions.

Keywords: diffusion · differential encounter theory · electron transfer · fluorescence · quenching

Introduction

Electron transfer is one of the simplest and most important chemical reactions. Triggering the reaction by light reveals detailed information on the reaction dynamics down to the femtosecond timescale. This implies that photoinduced electron-transfer reactions can be studied on the same timescale as that of vibrational motion. For bimolecular reactions, the Brownian motion of freely diffusing species in liquid solution strongly affects the observed kinetics.[1] Therefore, freezing the relative motion of the reaction partners by chemical linking[2–4] or by studying the reaction in rigid media[5,6] have been common strategies to overcome the unmitigated electron-transfer events. Unfortunately, these approaches either modify the reactants or the reaction medium. In order to study the behavior of the bimolecular reaction directly in liquid media, the use of very short (with respect to the timescale of translational diffusion) laser pulses is compulsory. For example, the excited-state dynamics can be monitored by means of the fluorescence decay of one of the reactants, which is a very sensitive technique. Thus, the diffusion at very short times should not mask the dynamics of the reaction that proceeds during the so-called static quenching regime of fluorescence. So far, several attempts have been made with this aim.[7–13] The valuable results obtained are often difficult or even impossible to compare with the quenching experiments performed on the nanosecond timescale[7] or additional reaction channels have to be invoked.[12,13] Especially troublesome is the task of merging the reaction kinetics obtained on different timescales and under different conditions: it has been puzzling to compare the ultrafast techniques with slower ones, as well as with the steady-state measurements (or time-integrated kinetics). Furthermore, the dependence of the kinetics on the medium properties or on the driving force of the reaction has also been a matter of discussion.[10]
Only recently we used a diffusion-reaction theory, the "encounter theory",[1] which allows for a joint description of any kind of reaction and the influence of diffusion, regardless of the characteristics of the elementary reaction event, such as its distance dependence.[20] Making use of the differential version of the encounter theory we showed in a preceding paper[21] that the subtle details of the solvent structure and the hydrodynamic effect on the diffusion coefficient were needed to describe coherently the fluorescence decays on the nanosecond timescale and the steady-state quenching experiments in a wide range of viscosities and quencher concentrations. The importance of these two effects was first pointed out by Fayer et al.[9] In reference[22] we expanded our studies to the influence of the electron-transfer driving force, and were able to give a reasonable explanation for the so-called Rehm–Weller (RW) plateau.[19] Unfortunately, the two electron-transfer parameter sets obtained in references[21,22] are not the same. Besides that, even the reaction rate models were not identical. Moreover, some additional problems with the stationary rate constant (obtained from the fluorescence decay traces after the diffusion regime had become stationary) remained unsolved: we studied fluorescence up-conversion data (FU)) and reduction for the donor and the acceptor in electron transfers was first pointed out by Fayer et al.[8] The great advantage of the solvent mixtures used is that the reorganization energy is kept constant, whereas the viscosity is adjustable over a very wide range by adding increasing amounts of glycerol to dimethylsulfoxide (DMSO).

In the present study, we have performed time-resolved experiments on the femto- to picosecond timescales by means of fluorescence up-conversion, with the aim of gaining insight into the static quenching and nonstationary quenching regimes. As explained above, this should, ideally, allow access to the diffusionless quenching reaction, thus enabling us to extract directly the electron-transfer parameters. We will relate the present findings to those presented in our two previous reports. Eventually, by re-evaluating some of our previous results, we will obtain a fully coherent picture of the non-Markovian quenching kinetics on time, concentration, driving force, and viscosity scales.

Theoretical Description and Approximations

With respect to our previous work,[21] we will introduce three modifications concerning the analysis of the data in order to explain the three sets of data simultaneously (the Stern–Volmer (SV) plots, the long-time asymptotes or nanosecond-resolved single-photon counting data (SPC), and the initial static and nonstationary quenching or picosecond-resolved fluorescence up-conversion data (FU)).

Firstly, a more comprehensive electron-transfer model, accounting for the solvent dielectric relaxation time and transitions to vibronically excited successor states, is utilized.[12,13,23,24] This is necessary because the fast transients can only be rationalized by fast initial electron-transfer rates, for which both effects become relevant. The same electron-transfer model has also been used in our analysis of the RW experiment; the model is shown in Equation (1) and the Levich–Dogonadze pre-exponential term is given by Equation (2).[22]

\[
w(r) = \sum_{n=0}^{\infty} \frac{U(r)e^{-S_{n}}}{n! + \tau_{5}U(r)e^{-S_{n}}} \exp \left( \frac{-\Delta G_{1}(r) + \lambda(r) + \text{hom}}{4k_{B}T\lambda(r)} \right)
\]

\[
U(r) = \frac{V_{2}(r)}{h} \sqrt{\frac{\pi}{k_{B}T\lambda(r)}}
\]

In Equation (2), \(V(r)\) stands for the diabatic matrix coupling element which is distance dependent and is defined in Equation (3), in which \(\sigma\) is the contact distance and \(L\) the decay of the coupling (equal to \(2/\beta\) in other formulations[25]).

\[
V(r) = V_{c} \exp \left( -\frac{r - \sigma}{L} \right)
\]

For the reorganisation energy, we have either used Matsu- da’s empirical expression [Eq. (4)][23] (in which \(r_{i}\) is a variable parameter accounting for the fact that generally the reorganisation energies at contact are found to be overestimated by the Marcus expression), or alternatively the more common and physically better grounded expression given in Equation (5),[25] valid for reactants of equal size, which constitutes a good approximation in our case.

\[
\lambda(r) = \lambda(\infty) - \frac{r_{i}k_{B}T}{r}
\]

\[
\lambda(r) = \lambda(\infty) \left( 1 - \frac{\sigma}{r} \right)
\]

The Marcus reorganisation energy expressions for infinite, \(\lambda(\infty)\), and close-contact separation, \(\lambda(\sigma)\), obey Equation (6), in which \(n\) stands for the refractive index of the solvent, and \(\varepsilon_{s}\) for its static dielectric constant.

\[
\lambda(\infty) = 2\lambda(\sigma) = \frac{e_{0}^{2}}{2\pi\varepsilon_{0}\varepsilon_{s}} \left( \frac{1}{n^{2}} - \frac{1}{\varepsilon_{s}} \right)
\]

The great advantage of the solvent mixtures used is that the reorganisation energy is kept constant, whereas the viscosity is adjustable over a very wide range by adding increasing amounts of glycerol to dimethylsulfoxide (DMSO). The distance dependence of the Gibbs free energy is expressed by the Weller equation, shown in Equation (7), in which \(E_{\text{red}}\) and \(E_{\text{ox}}\) are the standard potentials of oxidation and reduction for the donor and the acceptor in electron volts, respectively, \(E_{\text{red}}\) is the excited state energy of the fluo-
The model assumes that the dielectric response of the solvent obeys Debye’s law with a single relaxation time, $\tau_D$. The solvent relaxation time in Equation (1) relates to the longitudinal relaxation time ($\tau_L = \tau_D k_B / k_S$) with $\epsilon_\infty$ being the dielectric constant of the medium at infinite electrical field frequency which is also approximated to be constant in the solvent mixtures used, vide infra as shown in Equation (8).

$$\tau_s = 4\tau_L \sqrt{\frac{\pi k_B T}{\epsilon(r)}}$$

(8)

The multichannel parameters are the Huang–Rhys factor $S = \delta / \hbar \omega_0$, which stands for the strength of the coupling between the single reactant mode and the $n^th$ vibronic product mode, and depends on the inner reorganization energy ($\delta_0$) associated with the effective vibrational mode of frequency ($\omega_0$).

Equation (1) represents an interpolation between the perturbative electron-transfer regime, applicable for small coupling matrix elements, and the Zusman expression for solvent-controlled electron transfer in the high friction limit. This interpolation is carried out individually for every vibronic state, obeying Equation (13).

Equation (11), $n(r,t)$ is the reactant pair distribution function, which is the solution of the auxiliary diffusion-reaction equation [Eq. (12)], solved with the boundary conditions given in references [21, 22].

$$\frac{\partial n(r,t)}{\partial t} = \frac{L(r)n(r,t) - w(r)n(r,t)}{c}$$

(12)

The diffusion operator, $L(r)$, obeys Equation (13).

$$L(r) = \frac{1}{r^2} \frac{\partial}{\partial r} D(r)r^2 \exp(-v(r)) \frac{\partial}{\partial r} \exp(+v(r))$$

(13)

The diffusion coefficient is either expressed by the Deutsch–Felderhof expression [Eq. (14)] or by the Northrup–Hynes expression [Eq. (15)], and $v(r) = -\ln(r)$ in which $g(r)$ is the solvent structure as obtained from the solution of the Percus–Yevick equation.[33]

$$D(r) = D_\infty \left(1 - \frac{3\sigma}{4r}\right)$$

(14)

$$D(r) = D_\infty \left(1 - \frac{1}{2} \exp\left(-\frac{r - \sigma}{\sigma}\right)\right)$$

(15)

The reader is referred to the Supporting Information accompanying this article for details.

Differential encounter theory (DET) has been employed in the same manner as we have presented it before. We just summarize it here, and the interested reader can find more detailed descriptions in references [1, 21, 22, 30]. The excited-state population decay follows the kinetic expression given in Equation (9).

$$\frac{dN_\varepsilon(t)}{dt} = -(k(t)c + r_c^{-1})N_\varepsilon(t)$$

(9)

Equation (9) has the solution shown in Equation (10), in which the rate constant for the ionization (quenching) reaction is defined as in Equation (11).

$$N_\varepsilon(t) = N_\varepsilon(0)\exp\left(-\frac{t}{L} - c \int_{t=0}^{t} k(t')dt'\right)$$

(10)

$$k(t) = \int w(r)n(r,t)dV$$

(11)

In Equation (11), $n(r,t)$ is the reactant pair distribution function, which is the solution of the auxiliary diffusion-reaction equation [Eq. (12)], solved with the boundary conditions given in references [21, 22].
With the input parameters in Table 1, the parameters compiled in Table 2 yield a satisfactory description of the SV plots, and the diffuse motion of the reactants have been scrutinized in references [21,22] for a detailed discussion. For all combinations (I–VIII) of models for the reorganization energy, the diffusion coefficient, and the solvent structure, DF and NH denote the hydrodynamic friction models accounting for the solvent structure. DF and NH denote the hydrodynamic friction models accounting for the solvent structure. For the ET parameters, the root mean square relative errors for the concentration-dependent SV constant, k(c), all fits of the SV plots are visually indistinguishable. A differentiation of different parameter sets is possible by considering the agreement of the simulations with the long-time quenching rate constant, k(t). Note that McLendon et al. [34] have fitted the reaction-diffusion model described above to the SV plots [Eq. (16)] (for a schematic description of the procedure see Scheme SI.1 in the Supporting Information).

### Results and Discussion

Following the same strategy as in the previous paper, we have fitted the reaction-diffusion model described above to the SV plots [Eq. (16)] (for a schematic description of the procedure see Scheme SI.1 in the Supporting Information). In particular, the coupling matrix element (V_i) and its decay length (L) have been adjusted. For a total of eight solvent mixtures, with viscosities ranging from 2.2 to 62 cP, the diffusion coefficient was modeled as shown in Equation (19), in which the subscript refers to the composition of the solvent, and η(c) denotes the dynamic viscosity of the solution after adding the liquid quencher, MX2N. The d_s have been adjusted freely. Note that a value of d_s=133 or 200 Å^2 ns^{-1} cP is expected for r_p=r_0=α/2=3.25 Å based on the Stokes–Einstein relation with stick or slip boundary conditions, respectively.

\[
D_i(c) = \frac{d_s}{\eta(c)}
\]  

(19)

Using the input parameters in Table 1, the parameters compiled in Table 2 yield a satisfactory description of the SV plots and the diffuse motion of the reactants have been scrutinized in references [21,22] for all eight combinations (I–VIII) of models for the reorganization energy, the diffusion coefficient, and the solvent structure. Concerning the multichannel ET parameters, we have used the same values as for the analysis of the Rehm–Weller plot (see reference [22] for a detailed discussion). For all combinations in which the solvent structure and the hydrodynamic effect have been simultaneously accounted, a decay length of L ≈ 2 Å has been found. This value is of similar size to those found previously for the reactions between perylene and N,N-dimethylaniline or rubrene and duroquinone, for example.\[32,33\] Note that McLendon et al.\[34\] have determined a coupling decay constant of 1.4 Å for glassy glycerol matrices. This is not in disagreement with this work, as one might
be tempted to assume at first glance: the value predicted for the coupling decay depends on the overall distance dependence of the electron-transfer model, and not just on the intrinsic dependence of coupling on distance. In the Marcus normal region, the distance dependence of the reaction probability can indeed be well approximated by the exponential model. However, in doing so, a smaller effective value of $L$ is to be expected compared to that resulting from the full-fledged Marcus ET model. Since McLendon’s value is based on the exponential model, it is not in conflict with our data. Indeed, a value close to or larger than $L = 2$ Å was obtained when a more comprehensive ET model was employed (the exact value again depends on the overall $r$ dependence).

The Marcus expression for the reorganization energy [Eq. (5)] gives rise to a larger $V_o$ than Matsuda’s proposal [Eq. (4)], which has been utilized here with $r_s k_B T = 8.7$ ÅeV. This is not surprising in view of the fact that for the latter the reorganization energy at contact amounts to only 62% of the Marcus value ($\lambda(0) = 0.60$ vs. 0.97 eV). In fact, combination II results in the best agreement for the quenching radii, $R_Q$. However, due to its empirical nature, we did not pursue this reorganization energy model any further. Therefore, only combination I, which is superior to combinations III–VIII in explaining the changes of quenching radii with viscosity, will be discussed in the following sections. This combination yields $L = 2.0$ Å and $V_o = 50$ meV. These parameter values agree strikingly with those obtained previously in our study on the RW experiment[22] (although with a larger $\lambda(0)$). Figure 1 allows a comparison of simulated and experimental quenching rate constants, $\kappa(c)$.

A multitude of parameter sets yield quasi-identical fits for the SV plot. A differentiation of these sets is, however, possible by considering the long-time limit of the diffusion-influenced quenching rate constant [Eqs. (17) and (18)], which we express in terms of the quenching radius, $R_Q$, in Equation (20), in which $D(\eta)$ is the bulk diffusion coefficient (see the Supporting Information for more details about $k_\infty(\eta)$).

$$R_Q = \frac{k_\infty(\eta)}{4\pi D(\eta)}$$

(20)

Based on the parameter set I given above, the dependence of $R_Q$ on $D$ given in Figure 2 is obtained. Except for the point corresponding to the second highest viscosity, all experimental quenching radii exceed the simulated results, the deviation being typically smaller than 10%. Nonetheless, the trend followed by the experimental points clearly obeys that given by the simulations. In fact, the deviation of $R_Q$ as given in Figure 2 is systematic, and discerning its cause is not difficult: In determining the $R_Q$ values from the single-photon-counting traces, we made use of the long-time Smoluchowski asymptote [Eq. (21)], together with Equation (20) and the diffusion coefficients obtained from the analysis of the SV plots.

$$k_{\text{Smol}}(t) = k_\infty \left(1 + \frac{k_\infty}{4\pi D(\sqrt{\piDt})} \right)$$

(21)

Equation (21) is expected to hold for times significantly exceeding $R_Q^2/D \geq r_{\text{bar}} = \sigma^2/D$. However, given the finite number of sampled decay events in combination with a non-zero number of dark counts, the single-photon-counting curves contain kinetic information only up to a certain time; the faster the quenching and the smaller the excited-state lifetime of the fluorophore, the shorter the time. In order to have a significant portion of the decay curve avail-

Figure 1. Anamorphosis of the conventional SV plot, allowing for a better appreciation of the dependence of $\kappa(c)$ on concentration and viscosity. All available datasets are shown. The solid lines reproduce the fits for combination I, which is based on Marcus’ multi-channel electron-transfer model [Eq. (1)], Deutch–Felderhof hydrodynamic hindrance [Eq. (14)], and solvent structures obtained from Monte Carlo simulations (for a quencher concentration of 0–0.5 M).[21] The fit parameters are available in Table 2.
able for analysis, we were thus forced to commence the fitting by Equation (21) at \( t = \tau_{\text{diag}} \). At this instance of time, however, the (true) time-dependent rate constant evaluated by DET, \( k(t) \), exceeds its approximation given by Equation (21) with \( R_Q \) evaluated from Eq. (17) significantly. As a consequence, the experimental \( R_Q \) values systematically exceed the true ones. It has to be noted that the stationary limit is not actually attained here within the time window of the SPC experiments. This holds true even though a fluorophore with a long excited-state lifetime has been employed. The discrepancy is expected to be even more stringent for studies using fluorophores with fluorescence lifetimes of several nanoseconds only. The latter are in fact not rare in the scientific literature.\(^{[37]}\) A proof of this claim is available in Figure 3, which reproduces the ratio of \( k(t)/k_{\text{num,n}}(t) \) as a function of time for several diffusion coefficients. Note that for the experimentally accessible part of the decay curve, \( k(t) > k_{\text{num,n}}(t) \) by approximately 10%. Furthermore, the deviation from the Smoluchowski limit is expected to increase with increasing quencher concentration, because the experimentally accessible time window is shortened by the quenching process. We have tested whether this gives rise to an additional concentration dependence of \( k_{\text{c,n}}(\eta) \). It turns out that for the measurements conducted here, the effect is negligible; that is, for decays spanning at least 50 ns, the additional variation of \( R_Q \) due to different concentrations within a series amounts to less than 1%. All \( k_{\text{c,n}}(\eta) \) and thus all \( R_Q \) values of the entire series are, however, systematically shifted to larger values, with the effect being more pronounced in viscous solvents. Moreover, the stationary rate constants extracted from the long-time asymptotes are weakly correlated with the diffusion coefficient assumed for its determination by Equation (21). In Figure 2 we utilize the \( k_{\text{c,n}}(\eta) \) that are appropriate for the diffusion coefficient as determined from the SV plots through Equation (19). Empirically, a linear dependence of \( k_{\text{c,n}}(\eta) \) on the \( D \) used for its determination has been found (not shown).

The virtue of our novel approach is that the short-time quenching, which was not compliant with the electron-transfer model used in reference \([22]\), can now be accounted for. We have two sets of FU measurements available that reveal the early events closely related to the static quenching. For one set, a fixed concentration of MX2N (0.34 m) has been used, and the fluorescence decay has been recorded at five different viscosities with a sampling interval of 3 ps. The second set pertains to the quenching in DMSO, which has been comprehensively discerned at four different concentrations, ranging from 0.2 to 0.5 m, with points every 0.1 ps.

With the very same set of parameters as used above (combination I) the initial fluorescence decays at the different viscosities can be simulated (set I). Only the shift of the first point with respect to the delta excitation response function and its relative amplitude have to be introduced as adjustable parameters. The time-shift has been uniformly set to 4 ps, a value suggested by comparing the kinetic term \([\text{Eq. (22)}]\) with that of the experiments from the second set, which exhibit a higher point density at short times.

\[
\int_{0}^{t} k(t') dt' = -(\ln(I/I_0) + t/\tau_F)/c
\]  

\[ (22) \]

Indeed, within the time frame available for the different experiments, we found matching kinetic terms. This suggests that the assumption of one dielectric relaxation time independent of solvent composition is in fact appropriate. Figure 4 gives the analysis of the initial fluorescence decay, with the relative amplitude of the first point being the only free parameter. For all curves, a value of 0.8 for the latter gave the best agreement. The diffusion coefficient of the mixtures was determined by interpolating the \( d_i \) values from the SV fit with respect to the mole fraction of glycerol. Given that the electron-transfer parameters have, in essence, been determined from the SV plots and not further re-adjusted, this is a good agreement of theory and experiment. Note, also, that no second decay channel, which has been frequently invoked for similar studies, is necessary to account for the data. In addition, no increase in the coupling matrix element \( (V_{\text{c,n}}) \) is required.

Finally, the short-time quenching in DMSO at different concentrations shall be addressed. Figure 5 reproduces the experimental decays together with the simulations. No adjustable parameter has been used at all. The diffusion coefficient was determined from the appropriate \( d_i \). The agreement is apparently good, but abates with increasing quencher concentration. Note, however, that the larger effective concentrations even exceed those utilized in the SV plot. Our attempts to improve the fits have thus far always resulted in suboptimal SV simulations. The contribution of a second (contact) reaction channel, contributing mainly to the static quenching process at the highest quencher concentrations used here, is possible, although clearly not overwhelming.
Conclusion

We have successfully explained the fluorescence deactivation of DMBCN by MX2N in a variety of solvent systems exhibiting moderate to high viscosities. Our approach builds on a remote electron-transfer model, which accounts for the solvent dielectric relaxation time and the transfer to vibronically excited successor states. By accounting fully for the solvent structure and the hydrodynamic effect, a coherent description of time-resolved and steady-state experiments has been achieved. On the other hand, no consistent description of all the data is possible without including all these features simultaneously. Once the appropriate model has been chosen, the analysis of the steady state deactivation for at least ten concentrations in the bending region of the SV plot is sufficient to determine the pertinent electron-transfer parameters.

However, discerning the suitability of different electron-transfer models is ultimately only possible by detecting the initial static and non-stationary decay. The appropriate choice of contact distance is critical, that is, by choosing larger smaller ones the steady-state quenching data as well as the long-time asymptotes may often be described in terms of a diabatic or an adiabatic electron-transfer model. It is important to note that in the present case, the chosen contact distance leads to values for the coupling matrix element and its corresponding decay length, which are within the applicability and physical meaningful limits of the electron-transfer model used. This would not be the case for other radii.

Here, the entire quenching process, comprising the fast, static initial decay, the beginning non-stationary transients, the long-time asymptote, and the integral fluorescence, has been comprehensively described without requiring the inclusion of a second fast contact or remote (decay to excited ions) deactivation channel, which are frequently postulated in similar studies. It is quite likely that the inclusion of many of these additional reaction channels could be avoided by taking the discrete nature of the solvent (the solvent structure) into account. The latter is unquestionably present for any solvent (unlike a second decay channel), and failure to take it into account may lead one to unnecessarily postulate artificial reaction channels. It is our conviction that many previous publications ought to be revisited by properly accounting for the details of diffusive motion, the solvent structure, and hydrodynamic hindrance.

The fast initial fluorescence deactivation is often attributed to so-called tight ion pairs (TIP). Although its direct spectroscopic observation has not been realized until recently, the TIP has always been regarded as a transient contact species, which is distinguished from the solvent-separated ion pair (SIP) by an exceptionally large electronic coupling and, thus, a fast intrinsic ET reaction rate, irrespective
of the free energy difference. Arguably, the notion of the TIP hence belongs to the realm of exciplex formation rather than that of outer-sphere ET. The data presented here do not indicate a significant contribution attributable to the TIP up to a quencher concentration of at least 0.3 m. In particular, the fluorescence deactivation can be fully explained in terms of a single ET process with distance-dependent reactivity, which in the TIP/SIP model would rather be attributed to the SIP.[39] Some caution might be appropriate here.

The model used here is based on the use of the Marcus expression for reorganization energy, which is fine for large distances and large reactants, but probably not at close distances. The reactants are also supposed to be spheres with an exponential dependence of V with distance. In this case the nature of a SIP is quite clear, because distance is the only parameter that controls V and l. However, real systems are not like this. SIP is clearly a pair where the ions are less coupled, but there are other degrees of freedom than just distance. Thus, the transformation of the distance obtained from the model into a molecular parameter is perhaps not so evident.

To the knowledge of the authors this is the first time that such a comprehensive set of data (comprising ultrafast to nanosecond time-resolved decays, steady-state fluorescence quenching, viscosity change, and concentration change) has been quantitatively described by means of a physically grounded bimolecular electron-transfer model. Moreover, the final set of parameters found for the electron-transfer elementary reaction are compatible with the driving-force dependence of the quenching rate constant for the same fluorophore.

Experimental Section

Chemicals: The synthesis and properties, mainly photophysical, of the fluorophore, 2,5-bis(dimethylamino)-1,3-benzenedicarbonitrile (DMBCN), have been described elsewhere.[40] The sources of the quencher, 1,3-dimethyl-2-nitrobenzene (MX2N), and of the solvents and their handling, were the same as in references [21,22]. Table 1 details the relevant properties of the system.

Procedures and apparatuses: The fluorescence up-conversion (FU) measurements were performed by means of a home-built setup. The laser source was a Kerr lens mode-locked Ti:Saphire oscillator (KMLabs) delivering about 30 fs pulses around 800 nm at a repetition rate of 40 MHz and a power of about 400 mW, pumped by 5.2 W at 527 nm of a Nd:YVO4 laser (Millenia VIs Spectra Physics). The output pulses were delivered into the rotating cell containing the sample (of typically 0.4 mm thickness), whereas the remaining 800 nm pulses were deferred by a motorized delay line. The fluorescence was then mixed with the 800 nm gating pulses in another BIBO crystal for up-conversion. The resulting UV output was focused into a Cornerstone 260 1/4 m monochromator equipped with a photomultiplier tube (R654P Hamamatsu) operating in the photon-counting mode. Instead of transmissive elements (except for a 400 nm dielectric mirror to separate the 800 and 400 nm beams, a half-wave plate to control the 400 nm polarization, a 2 A Kodak Wratten Gelatin filter of 0.1 mm to remove the 400 nm remaining excitation beam after the sample, and a dichroic mirror to bring the gating pulses to the second nonlinear crystal at an angle of 10° with the fluorescence), off-axis parabolic mirrors were used to focus and to collimate both the gating and the pump beams as well as the fluorescence. Under these conditions, a Gaussian instrument response function of 70 fs FWHM could be obtained. The experiment was computer-controlled using a Labview-based program.

DMBCN fluorescence was monitored at 520 nm, a wavelength at which the measured time profiles are not affected by the solvation-induced dynamic Stokes shift in DMSO. All measurements were performed under magic angle conditions to avoid anisotropy effects. The quencher concentration was adjusted to approximately 0.3 m for the viscosity-dependence measurements, and between 0.2 and 0.5 m for the concentration dependence in DMSO. See the Supporting Information for the fine determination of these concentrations.

The other experiments mentioned in this paper were as described in references [21,22].

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[20] A multitude of approaches addressing the diffusion influence of distance electron-transfer phenomena has been suggested. We employ the DET framework here, as it has proven valuable in a variety of related studies. However, we do not imply that DET is the only model able to comprehensively account for the experimental data. The inclined reader should realize that DET and the approach paved by Tachiya and Fayer are equivalent, with one resulting from
the other by adjoining the differential operator of the diffusion equation. The mathematical tools necessary to prove the equivalence of these and related Sturm–Liouville problems are, for example, summarized in Mathematics for Physicists (Eds.: P. Dennery, A. Krzywicki), Dover, New York.


[36] Due to the formal correspondence with Smoluchowski’s influential expression for the probability of coagulation (with \( R_s \) substituting \( o \)) we will henceforth refer to Equation (21) as the Smoluchowski asymptote. Note, however, that Equation (21) is generally valid, whereas Smoluchowski has assumed a black sphere. Note furthermore that the \( k_s \) values extracted from the time traces are only marginally dependent on the particular choice of \( D \), when chosen in the range preset by the stick and slip boundary condition. Thus, \( k_s \) needs to be extracted only once. Confer to ref. [21] for details on the data handling protocol. In general, the Smoluchowski asymptote is expected to hold for times significantly exceeding \( R_s D / \tau_{	ext{diff}} = \alpha / D \).”


[39] Note, however, that a priori differential encounter theory does not require a strict distinction of the SIP or TIP, the transition being (possibly) smooth. Indeed, the TIP could, in the DET picture, be introduced either as an “efficiently coupled” ion pair or as an additional contact species. Literature suggests the second proposition, which is also assumed here. It is crucial to note that a TIP-free model is sufficient for modeling the diffusive ET deactivation at low to moderate concentrations in most cases. This statement also applies to the interpretation of the Rehm-Weller experiment given in ref. [22]. Apparently, the effective reaction volume associated with the TIP is too small to contribute significantly, except possibly at exceptionally large concentrations. It is expected that the recent advancement in spectroscopic techniques will stimulate research on the bending questions of the TIP. Our study makes it clear that no correct interpretation of these experiments will be possible without due consideration of the solvent structure.


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