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LETTERS

Larger than Expected Free Ion Yields from the Photoexcited *trans*-Stilbene/Fumaronitrile CT Complex in a Variety of Solvents

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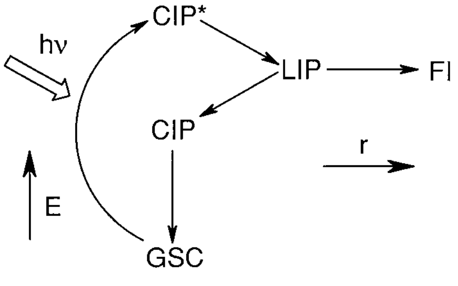
Measurements of the quantum yields of photoinduced charge escape for *trans*-stilbene and fumaronitrile solutions in solvents of different polarity reveal unexpectedly large yields upon direct excitation of the ground-state charge-transfer (CT) complex. Our current explanation, which proposes relaxation of at least a portion of the excited, Franck−Condon, CT pairs into remote ion pairs with thermalized initial separations of up to 10−15 Å, is speculative but emphasizes the need for a substantial revision of the usual picture of ionic charge separation and recombination.

Photoinduced intermolecular electron transfer in solution has been the subject of extensive research. While much is understood, the dynamics involved in the formation of free ions remain subject to intense inquiry.[1−7] Here we report free ion yields resulting from the direct excitation of an intermolecular charge-transfer (CT) complex in a variety of solvents and compare our results with theory. Particularly in less polar solvents, the free ion yields we report are much larger than expected for charge pairs that are initially in contact in a relaxed solvent environment. Our results suggest that shortly after excitation, the "initial" separation of charges is larger than the electron donor−acceptor contact distance. Although other studies of CT complexes have suggested this as well,[1] most recent work ignores this possibility.[3−7]

Our work supports a mechanism of ion separation involving the excitation of a ground-state complex (GSC) into a Franck−Condon excited contact ion pair (CIP*), of which at least a portion relaxes to thermalized, large-radius or loose ion pairs (LIP). These "initial" LIP may then diffusively separate into free ions (FI) or collapse into relaxed LIP or relaxed contact ion pairs (CIP) (see Scheme 1). This mechanism includes a novel speculation concerning the conversion of CIP* to the initial LIP species. We also report the time-resolved photocurrent that results from CT-band excitation of the *trans*-stilbene/fumaronitrile complex in toluene and tetrahydrofuran (THF).

SCHEME 1: Photoinduced Formation of Free Ions by Excitation of a Ground-State Charge-Transfer Complex (GSC) to a Franck−Condon Contact Ion Pair (CIP*)[a]



[a] The scheme emphasizes the role of "initial" loose ion pairs (LIP) in the production of free ions (FI). For simplicity, the scheme omits contact ion pair (CIP) to solvent-separated ion pair (SSIP) interconversion (for example, see ref 3b,c). Gould and Farid have presented evidence that some conversion of CIP* to CIP occurs within the solvent cage.[3c] Sutin (private communication) has suggested that any complete mechanism should also include reverse electron transfer from LIP to reform GSC. Both of these observations increase the importance of a significant yield of large-radius, "initial" LIP as a source of the observed free ions.

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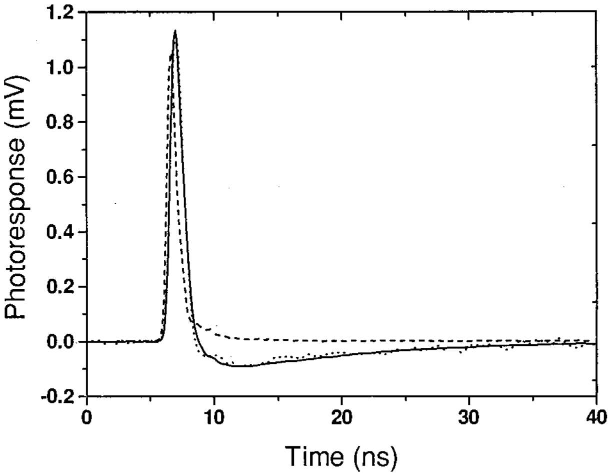

Figure 1. Photoresponse for solution of 0.025 M *trans*-stilbene and 0.125 M fumaronitrile in toluene after absorption of 47 μJ at 355 nm using a time-resolved transient dc photocurrent technique with 50 Ω scope input. The heavy dashed line is the laser pulse, the smaller dashed line is the experimental curve, and the solid line is the best fit produced as described in the text. The best fit yielded a 14.5 D dipole moment and a lifetime of 11 ns.

In the latter medium-polarity solvent and for the first time, a transient "dipole-like" photocurrent is observed at short times, evolving into a steady free ion current at longer times. The THF results are shown to be consistent with expectations (see Scheme 1) on the basis of measurements of FI quantum yields.

trans-Stilbene (TS) and fumaronitrile (FN) were chosen as electron donor and acceptor, respectively. Our initial interest in this system stemmed from a recent disagreement in the literature over the free ion quantum yield in acetonitrile.[4-7] Our measurements were made in a number of solvents including acetonitrile using a transient dc photocurrent technique,[8] which allows FI yield determinations at lower intensities than does measurement via transient absorption.[4-7]

Unless noted otherwise, TS and FN (both from Aldrich) were dissolved at 0.025 and 0.125 M concentrations, respectively. Given the measured equilibrium association constant, $K_{\mathrm{asc}} \sim 0.6\ \mathrm{M}^{-1}$ (values ranged from 0.3 to 1.0 M^{-1} depending on the wavelength and solvent used in the analysis), these concentrations provide a GSC concentration of roughly 10^{-3} M. All solvents (Aldrich reagent and HPLC grades) were used without further purification except for acetonitrile, which was distilled over $\mathrm{CaH_2}$ through a helices-packed column at high reflux ratio. Measurements were made with 355 nm excitation using either an MPB Technologies Orion SE-R (fwhm = 0.4 ns) or a Spectra Physics Quanta Ray GCR-11 (fwhm = 8 ns) Nd:YAG laser. The cells used have been described previously.[8,9] We used two modifications—a continuous-flow cell[8a] (for slow time scale free ion quantum-yield measurements with 8 ns pulses) and a "fast" cell[9] for the "dipole measurements" of Figures 1 and 2. In the latter, the solution was only periodically refreshed. Both cells consisted of two parallel, stainless steel electrodes (1 cm × 1.6 cm) fixed in a dielectric cell body and separated by either 2 mm (slow cell) or 0.9 mm (fast cell). Use of the third harmonic (355 nm) provided excitation of the TS/FN ground-state complex (GSC). Photoinduced currents were measured across a load resistor *R* (varied from 50 Ω to 100 kΩ) by a Tektronix TDS 684A oscilloscope. Model J4-09 Molectron detectors were used to monitor incident and transmitted laser pulse energies.[10]

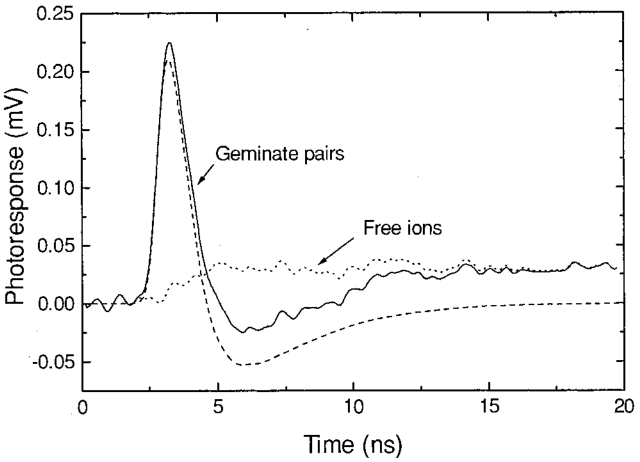

Figure 2. Photoresponse for solution of 0.025 M *trans*-stilbene and 0.125 M fumaronitrile in tetrahydrofuran after absorption of 11 μJ at 355 nm using a time-resolved transient dc photocurrent technique with 50 Ω scope input. As indicated, the experimental signal (solid line) can be deconvoluted into the signal from recombining geminate pairs (dashed line) and the free ion signal (dotted line). The best fit yields an 18.5 D dipole moment and a geminate pair lifetime of 2.5 ns. The rise time of the free ion component of the signal was determined to be 0.8 ns.

TABLE 1: Properties of TS/FN Ion Pairs in Different Solvents

solvent	$\phi_{\mathrm{sep}}{}^{a}$	τ (10^{-9} s)[c]	$\epsilon_{\mathrm{r}}{}^{f}$	r_{c} (Å)[g]	r_0 (Å)[h,i]
toluene	$<10^{-6b}$	11.8	2.4	235	
butyl ether	4.8×10^{-6}	7.3	3.1	182	15 (15)
isopropyl ether	3.8×10^{-5}	6.1	3.9	144	14 (14)
o-chlorotoluene	4.7×10^{-5}	6.7	4.7	118	12 (12)
fluorobenzene	4.9×10^{-5}	3.3	5.4	104	10 (10)
THF	1.9×10^{-3}	1.7	7.6	74	12 (12)
$\mathrm{CH_2Cl_2}$	6.7×10^{-3}	1	8.9	63	12 (12)
butyronitrile	9.1×10^{-2}	0.13[d]	24.9	23	8.6 (9.3)
acetonitrile	0.12	0.04[e]	37.5	15	6.1 (7.1)

[a] Measured using 8 ns 355 nm pulses; the error in ϕ_{sep} (based on repeated measurements) is approximately ±10%. Values are corrected to zero applied electric field according to theory.[15] [b] Roughly, 5×10^{-7}. [c] Lifetimes from time-resolved fluorescence experiments except where noted. In all cases, fluorescence decays were fit to a single exponential. [d] Estimated, because lifetime was too short for our experiments and reliable data were unavailable in the literature. [e] Inverse of k_{-et} taken from Thompson et al.[7] [f] Dielectric constants.[24] [g] Calculated as described in the text. [h] Calculated using ϕ_{sep} and Onsager equation (eq 2). [i] Values in parentheses were calculated using eq 2′, $r_{\mathrm{m}} = 3.5$ Å with ϕ_{sep} and τ from Table 1.

Figures 1 and 2 show photocurrent traces obtained with 0.4 ns, 355 nm excitation of the TS/FN GSC in toluene and THF, respectively. The toluene trace exhibits the characteristics of a photoinduced dipole of magnitude 14.2 ± 0.6 D with an excited-state lifetime of 11 ± 1 ns. The agreement of that lifetime with the fluorescence lifetime measured after 355 nm excitation identifies the dipolar species as the relaxed CIP in toluene. Figure 2 shows a similar trace except that the solvent is THF. In contrast with the toluene trace of Figure 1, the current does not return to zero at long times but rises to a steady positive value, which continues (not shown) for milliseconds. The long-lived steady current is from FI and corresponds to a value of $\phi_{\mathrm{sep}} = 1.9 \times 10^{-3}$, in good agreement with the value obtained using the "slow" cell (see Table 1). The dipole signal observed at short times is similar to the CIP signal observed in toluene except that, as described above, the integral of the negative current is no longer equal to that of the positive current. The short-time signal results from geminate ion pairs, some of which dissociate into FI. While a more complex analysis may eventually prove fruitful, we have analyzed Figure 2 as arising from only two contributions to photocurrent. The first comes from the formation followed by reorientation and eventual disappearance of the geminate pairs, which were treated as species with a single radius (dipole moment) and lifetime. The second component is the free ion (FI) current. The FI signal was not constrained in the analysis except that it was assumed to increase monotonically after the laser pulse. This analysis yields a geminate pair dipole moment of 18.5 ± 1.0 D and a lifetime of 2.5 ± 0.4 ns, somewhat longer than the fluorescence decay time of the ion pairs in THF, 1.7 ± 0.2 ns. The rise time of the free ion current is about 0.8 ± 0.1 ns, significantly shorter than the lifetime of the geminate pairs, which indicates that the majority of free ions originate from larger separation distances compared to the geminately recombining ion pairs. The small quantum yield calculated from the FI current provides partial justification for the simple analysis whose results are shown in Figure 2.

The (quantum) yield of ion-pair separation is calculated from measurements in the “slow cell” as $\phi_{sep} = N_c/(aN_p)$, where N_p is the number of photons absorbed and a is the fraction of N_p absorbed by the GSC. The number of ion pairs that separate into free ions, N_c, was calculated from the extrapolated[11] signal amplitude, v_{max}, using eq 1:

$$N_c = \frac{d^2 v_{max}}{e(\mu_+ + \mu_-)V_0 R} \tag{1}$$

where d is the distance between electrodes, e is the charge of the electron, μ_+ and μ_- are the positive and negative ion mobilities,[12] and V_0 is the applied voltage. FN does not absorb at 355 nm at all, and TS monomer absorbs only slightly. Under our typical conditions at least 95% of the incident radiation (depending on the solvent) is absorbed solely by the GSC. At zero concentration of FN, no photocurrent was detectable; the signal was at least 100 times less than the nominal TS/FN signal. The TS* lifetime is too short to allow any significant diffusional electron transfer to occur.[6,13] Nevertheless, we checked the dependence of the photocurrent magnitude (normalized by GSC absorption) on the concentration of FN. Within the accuracy of our measurements, we found no apparent variation of ϕ_{sep} in the range of 0.010−0.150 M FN with 0.005 M TS in dichloromethane.

With this method, ϕ_{sep} was determined in the solvents listed in Table 1. The quantum yield of 0.12 in acetonitrile is significantly less than the 0.38 reported by Peters and coworkers,[4] though larger than the yield estimated by Thompson and Simon.[7] Our value of 0.091 for ϕ_{sep} in butyronitrile is smaller than the value of 0.48 reported previously.[4] Our result makes sense because the smaller yield in butyronitrile parallels the reduction in dielectric constant between acetonitrile and butyronitrile. In other solvents, ϕ_{sep} was seen to decrease dramatically with decreasing solvent dielectric constant (see Table 1).

Mauzerall and Ballard reviewed various theories that have been used to analyze ϕ_{sep} data.[14] We have chosen to analyze our data according to treatments by Onsager (O)[15] and by Hong and Noolandi (HN).[16] By solving the diffusion equation for two oppositely charged particles, O and HN derived the following two equations for ϕ_{sep} at zero applied field:

$$\phi^{0}_{sep}(0) = e^{-r_c/r_0} \tag{2}$$

$$\phi^{HN}_{sep}(0) = \frac{e^{-r_c/r_0} + (z-1)e^{-r_c/r_m}}{1 + (z-1)e^{-r_c/r_m}} \tag{2'}$$

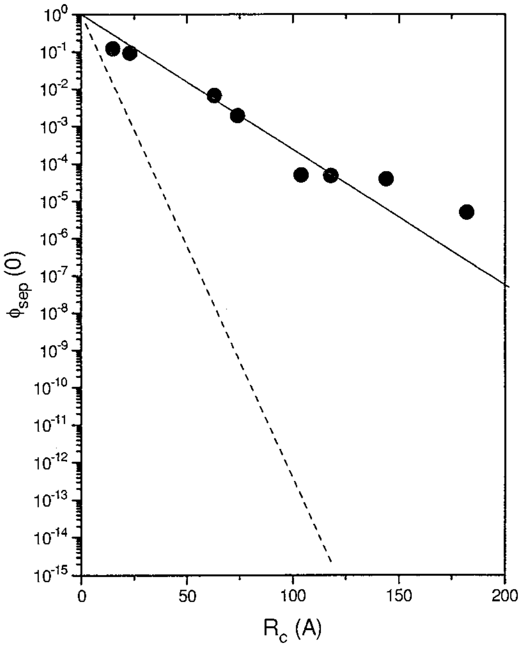

Figure 3. Graph of log $\phi_{sep}(0)$ at zero applied electric field vs r_c. The circles are the experimental data, the solid line was generated by using eq 2 with r_0 = 12 Å, and the dashed line was generated in the same manner except that r_0 was taken to be 3.5 Å.

In both eqs 2 and 2′, r_0 (the thermalization length) is the separation at which the charge pair begins diffusing with $\mu_\pm = eD_\pm/k_BT$, and r_c is the Onsager radius, $r_c = e^2/(4\pi\epsilon_r\epsilon_0 k_BT)$. Both results assume diffusion on a screened Coulomb potential with diffusion constants that are independent of space and time. In eq 2′ of HN, z is a dimensionless constant defined as $z = (D_+ + D_-)r_c/\kappa r_m^2$, where D_+ and D_- are the cation and anion diffusion constants. Recombination of the two charges is governed by the surface rate constant, κ, defined as r_m/τ, where τ (s^{-1}) is the lifetime of recombination at r_m. The two equations for $\phi_{sep}(0)$ differ because of a difference in the boundary conditions used by O and by HN. Onsager assumed that a charge pair disappears forever (recombination) any time that its separation reaches zero while the more flexible boundary conditions of HN allow for an increased separation probability for small-separation charge pairs especially if the dielectric constant is high.

Experimental results for ϕ_{sep} and r_0 values, calculated using eqs 2 and 2′, are listed in Table 1. In most cases, eqs 2 and 2′ give indistinguishable results.[17] For the ϕ_{sep} values we observe and for solvent dielectric constants below about 10, the difference between the O and HN boundary conditions is inconsequential. The log of ϕ_{sep} is plotted versus r_c in Figure 3, and for comparison, curves are given using eq 2 with r_0 = 12 Å and with the typical “contact” ion-pair radius of r_0 = 3.5 Å. The results in Figure 3 clearly favor the larger initial separation distance as characteristic of those “just thermalized” geminate ion pairs that contribute to the FI yield.

How might these large initial separations be achieved, and what does r_0 mean? In eqs 2 and 2′, r_0 represents the distance between ions in their *initial thermalized configuration.* The origin of the large r_0 required to explain our experiments is not clear and, especially for small ion separations, could result from inaccuracies associated with the semicontinuum approximation used in both the O and HN models. However, there are a number of reasons why the initial thermalized separations may exceed distances close to contact, r_m = 3.5 Å. Even though the Franck−Condon excited state (CIP*) is (most likely) formed at contact upon excitation, CIP* has excess energy stored in the interaction between its dipole moment and the solvent. Some studies[18] have suggested that the free ion yield resulting from the photoexcitation of various CT complexes is dependent on the amount of this excess energy. With 355 nm excitation, this energy is roughly 0.5 eV above the zero-point level of CIP depending on the solvent used. Since at distances close to contact the volumes of the solvent molecules cannot be ignored, the relaxation of CIP* must be viewed as a process involving an ensemble of solvent molecules together with the two ions of CIP*. The solvent reorganization and the relaxation of interionic vibration could produce extended thermalization lengths in some cases. Although the contributions to this increase in initial distance are most likely entropic in nature, there are energetic contributions to this process as well. The dipole moment of CIP* polarizes the surrounding solvent and creates a reaction field on itself,[19] which tends to pull the CIP* ions apart to form ion pairs with large separation (LIP), or in other words, the solvation energy of CIP* is less than that of a separated ion pair. Thus we view r_0 as an initial LIP separation distance.

In solvents of low dielectric constant, Coulombic forces are expected to cause most of the extended pairs (initial LIP's) to collapse to CIP's, probably within a nanosecond. Solvent-separated ion pairs (SSIP) should be important intermediates in this equilibration,[3] but our experiments offer no insights into SSIP−CIP interconversion. However, they do show that some extended initial LIP separation distances are required in order to allow formation of FI with a larger probability than would be expected for the CIP.

Additionally, in most of the solvents studied and for the large r_0 values that are found, the inaccuracy of the semicontinuum approach is not likely to be important. To see this, consider r_0 in greater detail. It certainly represents an average over some distribution of initial separations. Longer distances are weighted more heavily in our FI yield measurements especially in solvents of low dielectric constant.[20] If a distribution of "initial" geminate pair radii is considered, the mean radius required for agreement with the measured values of ϕ_{sep} is smaller than the "δ function" values of r_0 in Table 1. For example, if one assumes that the distribution of separations in "initial" LIP's is a spherical Gaussian function,[8b] the mean ion-pair separation required to agree with the measured yield in THF is 9.0 Å. This is still a much larger separation than that for contact ion pairs. Moreover, 90% of the FI yield arises from initial pairs separated by 11.3 Å or more. The clear implication is that *if the interionic potential energy at, say, 1 nm is screened Coulombic*, most of the FI formed in solvents with dielectric constants less than about 10 do not arise from the dissociation of equilibrated CIP's.

Others have shown earlier that long-range electron transfer can take place between diffusing photoexcited acceptor and donor molecules in polar solvents[14,21] provided that the driving force for CIP formation is very large and corresponds to the so-called inverted Marcus region. In contrast, photoexcitation in the charge transfer band should create only the ion pair formed from the electron donor and acceptor associated in the GSC. However, one could envision long-range electron transfer between CIP* and one of the electron donors or acceptors that are in close proximity. We do not expect this to occur in the case of CT complexes because of the fast relaxation of CIP* in polar solvents[22] and of the lack of driving force in nonpolar solvents. In addition, ternary effects should be concentration-dependent, but ϕ_{sep} proved to be independent of donor and acceptor concentrations in our experiments as described earlier. Therefore we rule out the above-mentioned diffusional route for long-range electron transfer as the source of the large initial LIP separation.

In summary, we have reported free ion quantum yields resulting from the direct excitation of the TS/FN charge-transfer complex in a variety of solvents. A comparison of our data with theories developed by Onsager and by Hong and Noolandi supports the mechanism presented in Scheme 1, in which at least a portion of the CIP*'s formed relaxes to extended or loose ion pair. These "initial" LIP's can dissociate to free ions or relax to CIP's. The existence of thermalized initial LIP's with separations in the 10−15 Å range[23] (see Table 1) is required to explain the large FI yields, provided that the interionic potential is simple screened Coulombic (at least for distances equal to or greater than the r_0 values of Table 1).

In addition, for the first time, fast photocurrent measurements for the TS/FN system in THF allow the observation of a two-component signal in which formation and reorientation of geminate ion pairs give rise to a "dipole-like" component at early times and ion-pair dissociation produces a constant free ion current at longer times. The rise time of the free ion current appears to be shorter than the lifetime of the ion-pair dipoles, while the latter is longer than the observed fluorescence lifetime. These observations are in accord with the mechanism presented in Scheme 1.

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(10) Laser intensities used never exceeded 300 μJ per 8 ns pulse for a 0.1 cm^2 spot size; a linear dependence of the photoconductivity signal was always observed. Thompson and Simon[7] showed that the linear dependence of their transient absorption signal for this system is retained with laser intensities 3 orders of magnitude greater than those used in our experiments.

(11) Because, with a large input resistor, the slow rise of the signal is limited by the circuit RC time (<5 μs), $\upsilon_{\max}$ was obtained by extrapolating to the time of excitation. The corrected values are typically within 5% of

the experimental voltage maxima. Decays were first order in solvents of high conductivity such as acetonitrile and butyronitrile. In less conductive solvents, the decay was either a mixture of first and second order or completely second order, depending on the solvent and the laser intensity.

(12) (a) The diffusion constants of TS and FN in acetonitrile (1.6×10^{-9} and 1.2×10^{-9} m^2/s, respectively)[6] were used to calculate ion mobilities by $\mu_{\pm} = eD_{\pm}/k_BT$. Although reported values are for neutral molecules, the diffusion constants for the ions D_+ and D_- should not be much different.[12b] Mobilities in other solvents were scaled according to solvent viscosities. (b) Lombardi, J. R.; Raymonda, J. W.; Albrecht, A. C. *J. Chem. Phys.* **1964**, *40*, 1148.

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(17) The second term in both the numerator and denominator of eq 2′ is negligible in all but the most polar of the solvents.

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(20) Therefore, the δ function values of r_0 that are given in Table 1 are expected to get larger in less polar solvents, and some evidence for this may be seen.

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(22) As an example, the lifetime of the CIP in acetonitrile from transient absorption spectroscopy is 40 ps.[7] We expect the lifetime of CIP* to be significantly shorter. The 3.48 eV provided by photoexcitation is 0.62 eV above the energy of the solvated free ions. According to Niwa et al.[21a] for a similar difference in free energy, the rate constant for electron transfer by diffusional encounter is 2.0×10^{10} M^{-1} s^{-1}, which corresponds to aquenching radius of 5.6 Å. With an acceptor concentration of 0.125 M, the quenching time is 400 ps, which is too slow to allow any significant diffusional electron transfer to occur.

(23) Naturally our conclusions also depend on the applicability of the diffusion equations solved by O and by HN to our results. These equations involve some approximations as discussed in the text. It is possible that improvements of the approximations could suggest a modified interpretation.

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