Photoinduced Electron Transfer, Geminate Recombination, and Diffusion in Liquid Solution

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A theory of photoinduced electron transfer with geminate recombination that includes the effects of spatial diffusion of the donor and the acceptor molecules in liquid solution is developed. The theory is an extension of the recent exact treatment of this problem in solid solution in which the particle positions are fixed. Example calculations are presented that illustrate the electron-transfer dynamics. The method is valid for any diffusion constant and any set of electron-transfer parameters.

Introduction

Photoinduced electron transfer from a donor to an acceptor in an ensemble of randomly distributed donors and acceptors generates a radical cation and a radical anion that are in close proximity. The ions are highly reactive and can go on to do useful chemistry. However, since the thermodynamically stable state of the pair is the neutral parent molecules, there is a strong tendency for electron back transfer to occur prior to ion separation by diffusion. The lifetime of photogenerated ions in solution depends on the forward and back electron-transfer parameters,[1] the concentration of donors and acceptors, and the diffusion[2-6] characteristics of the donor and acceptor (viscosity of the solvent). In this paper, we extend the theory of photoinduced electron transfer and back transfer in solid solutions[7,8] to include diffusion of the particles. This extends the theory to liquids and provides a comprehensive description of the competition between electron back transfer and separation by diffusion.

The effect of diffusion on particle motion has been known for many years.[9-11] More recently, a considerable amount of work has been done on the influence of translational and rotational diffusion on excitation transport among molecules in liquids.[12-20] In these treatments, the assumption of a slow or fast diffusion process relative to the transfer time is assumed to make the mathematics more tractible. The influence of diffusion on electron transfer has also been studied both experimentally[21] and theoretically.[22-25] In these studies various assumptions have limited their applicability. In one study, the low concentration limit of acceptors was used to obtain information only on forward electron transfer.[22] In other studies, transfer is allowed only at contact between the donor and acceptor.[23,24] Steady-state and time-resolved fluorescence was used to measure the effect of diffusion on forward electron transfer between rhodamine B and ferrocyanide.[21]

In this work, we treat the problem for any diffusion constant, any acceptor concentration, and any combination of forward and back electron transfer parameters. In this initial report, we have not included excluded volume effects or the Coulombic attraction of the ions. These can be treated and will be analyzed in a subsequent publication.[26] The ensemble average donor excited-state population function $\langle P_{ex}(t) \rangle$ and donor cation population function $\langle P_{ct}(t) \rangle$ are derived. We also calculate the transient grating observable, which is a measure of ground-state recovery.

Electron Transfer and Back Transfer in Solution

We start by determining the probabilities of finding the donor molecule in its excited state or cation state for a system containing only two molecules, the donor D and the acceptor A in solution. These results are extended to a system that has many acceptors, and the ensemble average is performed over all acceptor positions. For forward transfer our approach leads to results similar to those obtained for excitation transport.[18,19] The back transfer, however, is included in the theory considering forward and back electron transfer rates occurring over all distances (not just at contact)

and valid at all concentrations and diffusion constants.

The donor has only one accessible electronic excited state, and the acceptor has one acceptor state. The concentration of donor molecules is low enough that excitation migration among the donor molecules does not occur. The electron back transfer from anion to cation is geminate. The electron-transfer rates are exponentially decaying functions of the donor-acceptor separation.

System with One Donor and One Acceptor Molecule in Solution. At $t = 0$, the donor is optically excited. In the absence of the acceptor, the probability of finding the donor still excited decays exponentially with the excited-state life time, τ, where $\langle P_{ex}(t) \rangle = \exp(-t/\tau)$. When acceptors are present, the probability decreases more rapidly due to the addition of the electron-transfer pathways to the neutral acceptors.

The three processes, excited-state decay, forward electron transfer, and electron back transfer, are characterized by their respective rates:[1,7]

$$K = 1/\tau \tag{1a}$$

$$K_f(r) = (1/\tau) \exp((R_0 - r)/a_f) \tag{1b}$$

$$K_b(r) = (1/\tau) \exp((R_b - r)/a_b) \tag{1c}$$

where r is the donor-acceptor separation. In solid solution, r is a constant. However, in liquid solution r varies as a function of time. R_0 and R_b are used to parametrize the distance scales of the forward and back transfer. a_f and a_b characterize the falloff of the electronic wave function overlap of the neutral donor and acceptor states and ionic states, respectively.[1,7]

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The donor and acceptor molecules undergo Brownian motion characterized by their corresponding diffusion constants D_D and D_A. It is convenient to describe the position of the acceptor molecule in a reference frame whose origin coincides at any given instant of time with the center of mass of the donor. In this reference frame the acceptor molecule undergoes Brownian motion relative to the donor characterized by the diffusion coefficient D = D_D + D_A.[6,16] We define the function $P_{ex}(r,t;r^0)$. It is the probability of finding the donor molecule still in its excited state at time t with the acceptor on a spherical shell of radius r (about the donor) when the acceptor is initially located at a distance r^0 (from the donor). This does not include donor decay to the ground state (fluorescence lifetime). Similarly, we also define $P_{ct}(r,t;\rho^0)$ so that it is the probability of finding an ion pair with separation r at time t when initially the ions are separated by ρ^0. The functions $P_{ex}(r,t;r^0)$ and $P_{ct}(r,t;\rho^0)$ change their values due to molecular motion and electron transfer and satisfy the following diffusion equations:

$$\partial P_{ex}(r,t;r^0)/\partial t = D\nabla^2 P_{ex}(r,t;r^0) - K_f(r) \, P_{ex}(r,t;r^0) \quad (2)$$

$$\partial P_{ct}(r,t;\rho^0)/\partial t =$$
$$D\nabla^2 P_{ct}(r,t;\rho^0) - K_b(r) \, P_{ct}(r,t;\rho^0) + K_f(r) \, \exp(-t/\tau)P_{ex}(r,t;r^0) \quad (3)$$

where ∇^2 for the the spherically symmetric case considered here is

$$\nabla^2 = \frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}$$

These equations are Fick diffusion equations with a sink term that accounts for the electron transfer. In eq 2 only decay because of electron transfer has been included. Decay from the excited-state lifetime of the donor is independent of the electron transfer and diffusion and is incorporated in the final results by multiplying by $\exp(-t/\tau)$.

An absorption boundary condition is used. Because excluded volume is not included in this treatment, the forward and back transfer rates are infinite at $r = 0$. As will be shown in detail elsewhere,[26] this boundary condition, for point particles, gives the same results as a reflecting boundary condition for point particles. This is because the volume element at the origin is zero ($4\pi r^2 \, dr$ = 0 for $r = 0$). With the inclusion of excluded volume the reflecting boundary condition is used[26] because contact absorption with finite particles can artificially reduce the population. Equations 2 and 3 are solved numerically.

System of One Donor and Many Surrounding Acceptors. In a system of a single donor and many acceptors with each acceptor position $r_i(t)$ (i = 1, 2, ..., N) time dependent, the problem becomes more complex. The motions of the molecules in the solvent are taken to be uncorrelated, i.e., the diffusion coefficients are independent of their concentration. For the forward transfer, the donors and acceptors are neutrals and exert no long-range forces on each other. It is possible that at very high concentrations they may tend to aggregate. Here we treat the case of no aggregate formation. The probability of finding the donor molecule still in its excited state at time t (without lifetime decay) can be written as the product of the single particle results found in the previous subsection:

$$P_{ex}(r_1, ..., r_N,t;r_1^0, ..., r_n^0) = \prod_{i=1}^{N} P_{ex}(r_i,t;r_i^0) \quad (4)$$

where $P_{ex}(r_i,t;r_i^0)$ is the solution of eq 2.

In the forward-transfer process the donor molecule can transfer an electron to any acceptor with the transfer rate determined by the D–A separation. The back transfer is different. The anion will transfer the electron back to the cation (original donor molecule). Transfer from the anion to a neutral acceptor is not included since there is no net driving force for the transfer, and barriers for electron tunneling are generally large.[27] Transfer

from an anion to a cation that was not the original source of the electron is not included because the concentration of donors is low and the concentration of donor cations is even lower. Therefore the back-transfer process involves only two particles. Coulombic attraction of the cation and anion will be treated subsequently.[26] Here their motions are taken to be diffusive. The dependence of the cation probability on the distribution of the other acceptors is contained in the details of the forward transfer. Equation 3 can be generalized to the case of many acceptors as follows:

$$\partial P_{ct}^i(r_1, ..., r_N,t;\rho_N^0)/\partial t = D\nabla_i^2 P_{ct}^i(r_1, ..., r_N,t;\rho_1^0, ..., \rho_N^0) -$$
$$K_b(r_i) \, P_{ct}^i(r_1, ..., r_N,t;\rho_1^0, ..., \rho_N^0) +$$
$$K_f(r_i) \, \exp(-t/\tau)P_{ex}(r_1, ..., r_N,t;r_1^0, ..., r_N^0) \quad (5)$$

where the function $P_{ct}^i(r_1, ..., r_N,t;\rho_1^0, ..., \rho_N^0)$ is the probability of finding a donor molecule being a cation with the ith acceptor at location r_i at time t being n anion. At t = 0, we have the initial condition $P_{ct}^i(r_1, ..., rN,0;\rho_1^0, ..., \rho_N^0)$ = 0.

Ensemble Averages. The donor excited-state and cation-state probability functions obtained in the previous subsection depend on the configuration of acceptors. Observables can be obtained by averaging over all possible configurations and then taking the thermodynamic limit. For the excited-state population the averaging procedure is described in refs 12–16. The results is

$$\langle P_{ex}(t)\rangle = \exp(-t/\tau) \exp\left(-4\pi C\int_{r_m}^{\infty}[1 - P_{ex}(r,t)]r^2 \, dr\right) \quad (6)$$

Since excluded volume in not included in this treatment, r_m = 0. $P_{ex}(r,t)$ is the solution to the following differential equation (eq 2 averaged over r^0):

$$\partial P_{ex}(r,t)/\partial t = D\nabla^2 P_{ex}(r,t) - K_f(r) \, P_{ex}(r,t) \quad (7)$$

For the cation probability we have the following equation, which is the average over the final coordinate (the ith acceptor that has received the electron):

$$\langle P_{ct}(t)\rangle = 4\pi C\int_{r_m}^{\infty}\langle P_{ct}^i(r,t)\rangle_{r^0,N-1,\rho^0}r^2 \, dr \quad (8)$$

where $\langle\ \rangle_{r^0,N-1,\rho^0}$ is an average over the initial positions (r^0) of the acceptors, the $N - 1$ positions (ith acceptor excluded) at time t, and the initial position (ρ^0) of the anion. The averaging procedure used above is described in ref 7. The novel averaging procedure that was developed provided an exact solution to the problem in the absence of diffusion (solid solution). Here it provides a method that makes an accurate treatment of this problem tractible. $\langle P_{ct}^i(r,t)\rangle_{r^0,N-1,\rho^0}$ is the solution to the following equation:

$$\partial\langle P_{ct}^i(r,t)\rangle_{r^0,N-1,\rho^0}/\partial t = D\nabla^2\langle P_{ct}^i(r,t)\rangle_{r^0,N-1,\rho^0} -$$
$$K_b(r)\langle P_{ct}^i(r,t)\rangle_{r^0,N-1,\rho^0} + K_f(r) \, \exp(-t/\tau)P_{ex}(r,t)\langle P_{ex}(t)\rangle \quad (9)$$

The differential equations were solved by using the Crank–Nicholson[6] method, and the integrals were solved by using Gaussian quadrature.[28] In both cases, great care was exercised to ensure the accuracy of the numerical procedures. It was necessary to choose small enough distance and time steps to get stable and accurate solutions to the partial differential equations. The choice depends on the parameters used in the calculations. Distance steps as small as 0.1 Å and time steps as small as 0.0001 ns were used. All computations were performed on a DEC station 3100, and the code was written in the C language.

Results and Discussion

Figure 1 shows the solution to eq 6. It is the probability the donor is in its excited state for various diffusion constants. The parameters are given in the figure caption. They are one set of parameters used in the calculations in solid solutions reported previously.[7] A more detailed account of this work will be presented with a survey of parameters.[26] As can be seen, increasing the diffusion constant from 0 to 100 × 10^{-7} cm^2/s makes the excit-

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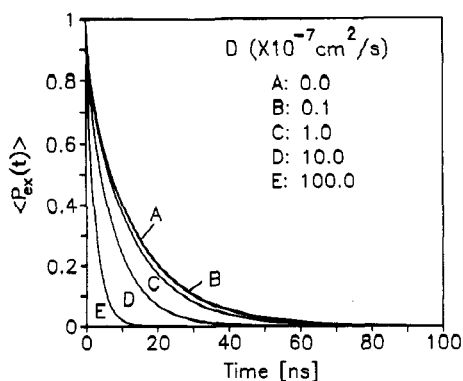
Figure 1. Excited-state population. The electron-transfer parameters used are $a_f = a_b = 1.0$ Å, and $R_0 = R_b = 10.0$ Å. The fluorescence lifetime $\tau = 16$ ns. The concentration of acceptors $C = 0.1$ M. As can be seen, increasing the diffusion constant makes the excited-state population decay faster.
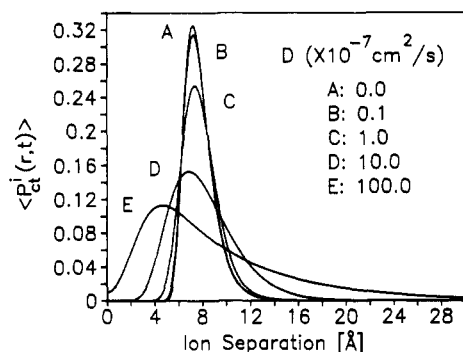

Figure 2. Probability that the ith acceptor is an anion as a function of distance at $t = 1$ ns for different diffusion constants. The parameters are the same as those used in Figure 1. As the diffusion constant increases, the peak of the ion probability decreases and the width increases.

ed-state population decay faster. Diffusion allows acceptors to move toward and away from the excited donor. Since the rate of transfer decreases exponentially with distance, acceptors moving toward the donor cause an increase in the transfer rate that is greater than the decrease created by acceptors moving away from the donor.

Figure 2 shows the probability that the donor is a cation with the ith acceptor an anion as a function of the ion pair separation (eq 9). The plot is for $t = 1$ ns. The curves show the distribution of ion-pair separations for various diffusion constants. Curve A is for $D = 0$. There are no pairs with separations ≤ 4 Å. A pair with separation of 3 Å will have been created at early time and by 1 ns will have recombined. There are also no ion pairs with separations ≥ 14 Å. Given the forward-transfer rate, none have been created. As D increases from 0, the curves spread to both large and small distances. Ion pairs created with separations of ≤ 14 Å can diffuse out before recombining. Ion pairs can also diffuse in. When the diffusion constant is large, $D = 100 \times 10^{-7}$ cm^2/s, the distribution has broadened considerably in both directions as compared to the case of $D = 0$ (solid solution). (Note that the values as a function of separation are not multiplied by $4\pi r^2 dr$. See ref 7 for a detailed discussion of this type of plot.)

Figure 3 shows the total cation probability as a function of time and diffusion constant. Because of the exponential decrease in the transfer rate with distance, ion pairs tend to be formed with small separations. For $D = 0$ only electron-transfer events to relatively distant acceptors produce ions that are long lived. As D increases, there is an increasing probability of the cation and anion moving apart, which increases the ion lifetime and the probability of ions existing. The details of the curves in Figures 1–3 depend on the choices of the forward and back parameters. For example, if the forward transfer is very short ranged and the
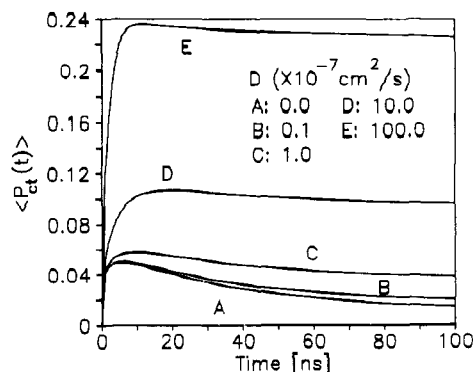

Figure 3. Ensembled averaged ion probability as a function of time. The parameters are the same as those used in Figure 1. Increasing the diffusion constant increases the number of ions found at long time.
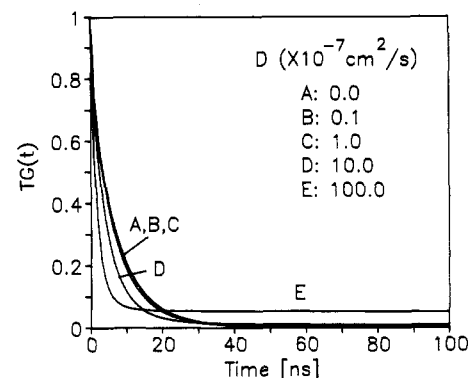

Figure 4. Transient grating observable. The parameters are the same as those used in Figure 1. Increasing the diffusion constant makes the observable decay faster at early time and leaves an offset at long time.

back transfer has a substantially longer range, D will have to become much larger before there is a substantial change from the $D = 0$ case.

Figure 4 shows calculations of the transient grating experimental observable.[7,8,29] This is a ground-state recovery experiment that is proportional to the squares of the sum of the excited state (eq 6) and cation state (eq 8) populations.[7] It is essentially the square of the result that would be obtained in a pump–probe experiment. With time-resolved fluorescence measurements, the time dependence of the excited-state population (forward electron transfer) can be determined. Combining the fluorescence results with transient grating measurements gives the back-transfer dynamics. This has been done for solid solutions ($D = 0$).[8] As D increases, the decay becomes faster and a constant signal develops at long time. The size of the constant signal is a measure of the ions that are long lived because they have escaped geminate recombination through diffusion.

The formal theory will always cause an eventual decay to zero signal, i.e., total geminate recombination, because given an infinite time and no other quenchers, geminate recombination will always occur. In a detailed account of this work[26] we calculate a well-defined quantity, $C1\%$, which is the concentration of a fictitious ion quencher that quenches 1% of the ions by a hypothetical collision controlled chemical reaction. $C1\%$ permits a quantitative discussion of the competition between geminate recombination and escape by diffusion.

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