A subpicosecond, subnanosecond and steadystate study of diffusioninfluenced fluorescence quenching
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A subpicosecond, subnanosecond and steady-state study of diffusion-influenced fluorescence quenching

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Subpicosecond and subnanosecond time resolved experiments are combined with steady-state fluorescence measurements to examine the diffusion influenced fluorescence quenching reaction of rhodamine B and ferrocyanide. The classic models of Smoluchowski, and Collins and Kimball are unable to consistently explain both the rapid initial decay and the slower decay seen at long times (> 1 ns) in the experimental data. Neither the short nor the long time data can be reconciled with the steady-state data using these models. Better agreement is found between the data and a simple model incorporating a position dependent intrinsic reaction rate [A. Szabo, J. Chem. Phys. 93, 6929 (1989)] in addition to a diffusional rate. This model suggests a rate of electron transfer for the rhodamine B–ferrocyanide system of (27.5 ± 4 ps)−1. Use of a bare Coulomb potential between reactants is found to be inappropriate in all of the models investigated.

I. INTRODUCTION

The study of reactions whose progress is influenced by the transport of one or both reactants has occupied a central place in physical chemistry for many years.1 If the intrinsic bimolecular reaction rate is sufficiently rapid, mass transport becomes a rate limiting process for reactions in solution. Studies of these reactions have assumed that the transport is described by macroscopic diffusion (i.e., Fick's laws), and the reactions are referred to as diffusion controlled or diffusion influenced. From an experimental point of view fluorescence quenching provides a simple system in which sensitive techniques can be used to study such processes. Until recently, experimental time resolved fluorescence quenching data has been explained satisfactorily with the "classic" models of diffusion-controlled reactions (see below).2,3 In a previous publication we reported an inconsistency between comparisons with the classic models of data covering different time regimes.4 The present paper describes in greater detail data ranging from the subpicosecond time scale to fluorescence intensities under steady-state illumination. Our aim is to test the ability of current models to accurately describe diffusion influenced fluorescence quenching in all of the relevant time regimes.

The two steps determining the kinetics of a diffusion controlled reaction are (1) the mass transport and (2) the intrinsic reaction (chemical transformation). For both processes the influence of the molecular nature of the reactants and the solvent has been extensively discussed but experimental confirmation of the predicted effects is minimal. Theoretical studies in hydrodynamics have shown that the concept of a spatially uniform diffusion coefficient should break down on molecular length scales and should be affected by short-range correlations arising from the interaction potentials of the reactants and solvent.5 A recent molecular dynamics simulation by Andre and co-workers clearly demonstrated the inadequacy of treating the solvent as a continuum within the context of diffusion-controlled reactions, particularly at early times.6 While much progress has recently been made in developing a molecular theory of both equilibrium and dynamic solvation, these ideas have yet to be rigorously incorporated within a hydrodynamic description of diffusion influenced reactions. (For reviews, see Refs. 7 and 8.)

From the chemical perspective, the nature of the quenching reaction is of interest. The classical treatment of diffusion-controlled reactions by Smoluchowski assumed an infinite reaction rate.7 Such a model clearly renders questions regarding the intrinsic reaction rate moot. Collins and Kimball modified the theoretical treatment by introducing a finite reaction rate.8 However, their formalism incorporates a proportionality constant which has "the nature of a specific reaction rate"9 but which should not be interpreted as the intrinsic bimolecular reaction rate. In both the Smoluchowski and the Collins and Kimball descriptions, the reaction is assumed to occur at a single boundary. As noted by Auerbach, et al.,10 any kind of hard boundary condition is likely to be inappropriate for molecular systems. An approach that seems more physically satisfying was proposed by Wilemski and Fixman which incorporates a position-dependent rate coefficient \( k(r) \) into the mathematical description.11 The functional form of \( k(r) \) will depend on the nature of the reaction. For example, the rate of nonadiabatic electron transfer is known to decrease exponentially with increasing distance between donor and acceptor,12 whereas energy transfer by a dipole–dipole mechanism displays a \( 1/r^6 \) dependence.13

Unfortunately the intrinsic reaction rate of diffusion-influenced reactions is so rapid and the effects of varying \( k(r) \) are sufficiently subtle that this aspect of diffusion-influenced reactions is beyond the detection range of standard steady state and time-correlated single photon counting techniques. With the availability of subpicosecond time resolution, the possibility now exists to test both the fundamen-
tional theories of diffusion-controlled reactions and the applicability of microscopically based corrections to these theoretical treatments. Investigating these ideas may lead to new insights into the molecular processes occurring in condensed phase reactions.

The remainder of the paper is organized as follows: Section II summarizes the current theoretical models and the relevant equations for data analysis. Section III describes the experimental methods. In Sec. IV, time-resolved and steady-state data are compared with the theoretical predictions and our conclusions are summarized in Sec. V.

II. THEORETICAL DESCRIPTION

The description of diffusion influenced reactions began with Smoluchowski's work on colloid coagulation and the majority of the theoretical work since that time is based on his approach. As applied to fluorescence quenching, this approach considers the reaction

\[ A^* + B \rightarrow [A^*B] \rightarrow \text{products}, \]

where \( A^* \) is the excited fluorescer and B the quencher. The rate coefficient \( k_1 \) represents the diffusion of reagents to form a "contact pair" \([A^*B]\), and \( k_2 \) is the intrinsic rate of the reaction. Initially we will assume that there is no interaction potential between \( A^* \) and B (or B and B). The concentration of \( A^* \) is assumed to be very low so that an adequate description of the system involves a single \( A^* \) surrounded by many B molecules with a bulk concentration of c. The \( A^* \) is placed motionless at the origin and the B's are allowed to move freely according to Fick's laws of diffusion. In this picture the relative motions of \( A^* \) and B are described by a single diffusion coefficient \( D = D_A + D_B \), the sum of the individual diffusion coefficients of the respective reactants; the accuracy of this approximation has been discussed by Noyes, and Szabo.

The quantity to be obtained from the model is the time dependence of the relative concentration of \( A^* \), \( [A^*(t)]/[A^*(0)] \), which is the survival probability \( S(t) \) of the excited state. In the presence of quenchers at concentration \( c \) the survival probability is assumed to satisfy

\[ dS(t)/dt = -\left( (1/\tau_0) + ck(t) \right) S(t), \]

where \( \tau_0 \) is the fluorescence lifetime of \( A^* \), and \( k(t) \) is the time-dependent rate coefficient. Solving Eq. (1) and using the relationship \( I(t)/I(0) = [A^*(t)]/[A^*(0)] \) \( = S(t)/S(0) \) leads to the general fluorescence decay function

\[ I(t) = I(0) \exp \left[ -t/\tau_0 - c \int_0^t k(t')dt' \right]. \]

The time-dependent rate coefficient \( k(t) \) is obtained from the flux of quencher molecules across the surface of contact with \( A^* \). The flux depends on the radial distribution function of quenchers \( p \) which changes according to the diffusion equation

\[ \frac{\partial p(r,t)}{\partial t} = D \nabla^2 p(r,t). \]

This equation is solved subject to the initial and boundary conditions appropriate to the model under consideration.

The Smoluchowski model assumes that the initial distribution of B's is uniform, \( p(r,t=0) = 1 \), and that a reaction occurs with unit probability when a B molecule comes into contact with \( A^* \) \( (r=a) \), so that \( p(a,t) = 0 \). This second assumption, referred to as an absorbing boundary condition, implies that the intrinsic rate of the reaction is infinite. The time-dependent reaction rate is therefore given by the total flux of B molecules across the surface of contact as follows:

\[ k(t) = \int d\sigma \cdot D \left[ \nabla p \right]_{r=a} = 4\pi Da^2 \left[ dp/dr \right]_{r=a}, \]

where \( d\sigma \) is the surface element, which in spherical coordinates is \( r^2 \sin \theta \, d\theta \, d\phi \), and \( h \) is a unit vector normal to the surface. Solving the diffusion equation (3), subject to the Smoluchowski boundary condition gives the following result for the time-dependent rate:

\[ k_1(t) = 4\pi Da \left[ 1 + (a^2/4\pi Dt)^{1/2} \right]. \]

Also of interest is the integral of \( k_1(t) \):

\[ \int_0^t k_1(t')dt' = 4\pi Da \left( t + \frac{2a \sqrt{t}}{\sqrt{D}} \right). \]

To relax the unrealistic assumption of an infinite reaction rate, Collins and Kimball proposed that the probability of reaction is proportional to the probability that a B lies between \( r = a \) and \( r = R = a + \delta R \). In the limit that \( \delta R \to 0 \), the following boundary condition is obtained:

\[ 4\pi DR \left[ dp/dr \right]_{r=a} = k_0(\delta R), \]

The diffusion equation can be solved with this boundary condition to yield

\[ k_{ck}(t) = \frac{4\pi DR k_0}{4\pi DR + k_0} \left[ 1 + \frac{k_0}{4\pi DR} \exp(\alpha^2Dt) \text{erfc}(\alpha\sqrt{D}) \right], \]

where \( \alpha = 4\pi DR + k_0/4\pi DR^2 \).

The integral of Eq. (8) is

\[ \int_0^t k_{ck}(t')dt' = \frac{4\pi DR k_0}{4\pi DR + k_0} \left[ t + \frac{k_0}{4\pi DR^2} \right] \text{erfc}(\alpha\sqrt{D}) + \frac{2\alpha\sqrt{D}}{\pi} - 1 \].

When realistic values are used for the variables one finds that for both the Smoluchowski and the Collins and Kimball models the "time-dependent" rate coefficient becomes rather independent of time (approaches the diffusion-controlled limit) after \( \sim 100 \) ps.

A. Inclusion of a Coulomb potential

The diffusion equation can be expressed so as to incorporate simple interactions between reactants via a potential of mean force \( U(r) \):

\[ \frac{\partial p(r,t)}{\partial t} = \frac{Dd}{r^2 \, dr} \, e^{-U(r)/k_BT} \frac{d}{dr} \, e^{U(r)/k_BT} p(r,t). \]

For ionic reactants \( U(r) \) has been approximated as a bare Coulomb potential giving the well-known Debye–Smolu-
chowski equation (DSE). At distances where the Coulomb interaction is larger than the thermal energy the relative motion of the particles is significantly influenced by the charges. This is quantified via the Onsager length \( r_c \), the distance at which \( U(r) = k_B T \), as follows:

\[
r_c = \frac{q_2 e^2}{4\pi\varepsilon_0 k_B T},
\]

where \( q \) is the particle charge, \( e \) the electron charge, \( \varepsilon_0 \) the permittivity of free space and \( \varepsilon \) the dielectric constant of the solvent.

Although no exact solution of the DSE is known, a number of approximate solutions have been found which utilize a Collins and Kimball type boundary condition.\(^{15,18,19}\) Hong and Noolandi\(^{19}\) were the first to derive an exact result for the Laplace transform of the fluorescence quenching rate. They also gave an expression for the actual rate, valid at long times, which is formally the same as Eq. (5). Delaire \( et\) al.\(^{17}\) have postulated that an analytical solution of the DSE valid over all parameter ranges does not exist. By comparison with a numerical solution of the DSE we find that in our parameter range the solutions of Flannery,\(^{18(a)}\) and of Szabo\(^{15}\) are quite accurate. A discussion of the numerical method is given in the appendix.

The analytical approximation of Szabo gives the following expression for the time-dependent rate coefficient:

\[
k_m(t) = \frac{4\pi D R_E k_0 \exp[-U(R)/k_B T]}{4\pi D R_E + k_0 \exp[-U(R)/k_B T]} \times \left[ 1 + \frac{k_0 \exp[-U(R)/k_B T]}{4\pi D R_E} \times \exp(g^2Dt) \text{erfc}(g\sqrt{D}t) \right],
\]

where

\[
g = \frac{4\pi D R_E + k_0 \exp[-U(R)/k_B T]}{4\pi D R_E}.
\]

If one ignores all interactions except the Coulomb potential then \( U(r)/k_B T = r_c / r \) and the expression for \( R_E \), the effective reaction distance, is

\[
R_E = \frac{1}{\int_0^{r_c} r^{-2} \exp[U(r)/k_B T] dr} = \frac{r_c}{\exp(r_c/R) - 1}.
\]

(Recall that the variable \( R \) is the distance at which the radiation boundary is placed, and is generally referred to as the reaction distance.) The integral of Eq. (12) is

\[
\int_0^{r_c} k_m(t') dt' = \frac{4\pi D R_E k_0 \exp[-U(R)/k_B T]}{4\pi D R_E + k_0 \exp[-U(R)/k_B T]} \times \left[ 1 + \frac{k_0 \exp[-U(R)/k_B T]}{4\pi D R_E} \times \exp(g^2Dt) \text{erfc}(g\sqrt{D}t) \right.
\]

\[
+ \left. \frac{2g(Dt)}{\sqrt{\pi}} - 1 \right].
\]

A point to note is that Eqs. (12) and (14) have the same functional forms as the Collins and Kimball solution, Eqs. (8) and (9). In the limit that the Onsager distance \( r_c \) goes to zero, \( R_E \) converges to the reaction distance.

In addition to the Flannery and Szabo solutions, which are indistinguishable from the numerical solution for parameter values typical for our data, we also examined the solution given by Hong and Noolandi.\(^{19}\) This solution gives an integrated time-dependent rate coefficient, \( \int k(t) dt \), which is characterized at early times by a rapid transient not present in the numerical solution of the DSE. Accordingly, we do not present fits of our data to the Hong and Noolandi solution.

### B. Position-dependent rate

As already mentioned, using a boundary condition as a means of incorporating reaction into the picture of diffusion neglects much of the molecular nature of the system. Wilemski and Fixman\(^{12}\) proposed that a more physically clear approach is to add a sink term \(-k(r)p\) to the diffusion equation as follows:

\[
\frac{\partial p}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial p}{\partial r} - k(r)p.
\]

As before, \( p = p(r,t) \) is the time-dependent radial distribution function for the quenching species. The term \( k(r) \) is a unimolecular rate coefficient which depends on the reactants' separation and corresponds to the inverse of the nonradiative lifetime of the fluorescer \((A^*)\) in the presence of a single quencher \((B)\) at distance \( r \) from \( A^* \).\(^{20}\) In this formalism, the time-dependent rate coefficient is obtained as follows:

\[
k(t) = \int k(r)p(r,t) dv,
\]

where \( dv \) is a volume element.

One consequence of a position-dependent rate is the possibility for fluorescer—quencher pairs to be separated by sufficiently small distances that upon excitation these pairs will react with a rate dominated by the intrinsic reaction rate. This phenomenon is generally referred to as static quenching.

A very simple position dependent rate is one in which the lifetime of \([A*B]\) is \( \tau \), where \( k(r) = \tau^{-1} \), for separations \( r \) in the range \( a < r < R \), and is infinite \( [k(r) = 0]\) for \( r > R \). We again refer to \( R \) as the reaction distance to distinguish it from the contact distance \( a \). Szabo has analytically solved the diffusion equation with this sink function and a reflecting boundary at contact \( (r = a)\).\(^{15,21}\) Following Szabo's method the Laplace transform of the time-dependent rate coefficient \( \hat{k}(t) \) is as follows:

\[
\hat{k}(z) = \nu(1 + \tau z)^{-1} - (1 + \tau z)^{-2} \frac{K(z)\hat{K}_s(z,R)}{K(z) + \hat{K}_s(z,R)}.
\]

The variable \( \nu = 4\pi (R^3 - a^3)/3 \) is the volume surrounding \( A^* \) in which the quenching reaction can occur; \( \hat{K}_s(z,R) \) is the Laplace transform of the Smoluchowski rate coefficient, Eq. (5), with \( a \) replaced by \( R \); and \( K(z) \) is a function of the diffusion coefficient, the intrinsic lifetime \( \tau \), the Laplace variable \( z \), and the contact and reaction distances. The in-
verse Laplace transform of Eq. (17) will give an expression for $k(t)$ which is valid for all time. Obtaining the inverse Laplace transform is difficult for such a complicated function. We can, however, obtain approximate analytical expressions for $k(t)$ which are valid within specific time limits.

We first consider the very short time behavior and set the diffusion coefficient to zero. (For reference, in 25 ps the root-mean-square displacement of a particle with diffusion coefficient $1.25 \times 10^{-5} \text{cm}^2\text{s}^{-1}$ is $\approx 4.3 \text{Å}$. For $t < 50$ ps the Laplace variable $z$ is large and the first term in Eq. (17) dominates. The inverse Laplace transform of $\nu(1+\tau z)^{-1}$ gives the short time approximation for the time-dependent rate coefficient

$$k(t) = (\nu/\tau) \exp(-t/\tau),$$  
(18)

where $\nu$ and $\tau$ are as given above. By using Eq. (18) and Eq. (2), the expression for the fluorescence decay at early time is found to be as follows:

$$I(t)_{D=0} = I_0 \exp[-\nu c(1-e^{-t/\tau}) - t/\tau_0].$$  
(19)

Equation (19) corresponds to the "static quenching" contribution to the decay and can be used with high time resolution data to obtain an estimate of the intrinsic lifetime $\tau$.

To obtain an expression which describes the entire time range of fluorescence quenching we make an ad hoc combination of Eq. (19) with a diffusional term to give an approximate function for the fluorescence decay:

$$I(t) = I_0 \exp\left[-\nu c(1-e^{-t/\tau}) - t/\tau_0 - \int k_D(t')dt'\right],$$  
(20)

where $k_D(t)$ is an expression for the rate of diffusive quenching such as the Collins and Kimball result, Eq. (8).

Rather than introducing a second independent rate parameter into Eq. (20) (i.e., $k_0$), it is desirable to express $k_0$ in terms of the variables of our simple sink function model. Szabo has shown that such a relationship can be found by considering the long time limit ($t \to \infty$, or $x \to 0$) of Eq. (17) and the resulting description of steady-state fluorescence quenching.\(^{15,21}\) For $\tau/\tau_0 \ll 1$, and $c \ll 1$, the Stern–Volmer relation is given by

$$\frac{I}{I_0} = 1 + \nu c + \frac{4\pi DR (1 + R/\sqrt{D\tau_0}) K(0)\tau_0\epsilon}{K(0) + 4\pi DR (1 + R/\sqrt{D\tau_0})} + \cdots,$$  
(21)

where $I_0$ and $I$ are the measured steady-state fluorescence intensities in the absence and presence of quencher at concentration $c$, respectively. $K(0)$ is given by

$$K(0) = 4\pi DR \left[ \frac{\epsilon \lambda \cosh \lambda - (\epsilon - \lambda^2 a R/\epsilon) \sinh \lambda}{a \lambda \cosh \lambda + \epsilon \sinh \lambda} \right]$$  
(22)

with $\lambda = \epsilon/\sqrt{D}$ and $\epsilon = R - a$. The term "$\nu c$" in Eq. (21) arises from static quenching and the third term is identical to the Collins and Kimball prediction if $k_0 = K(0)$ and the partially absorbing boundary is at $R$. In fact, a deceptively simple Stern–Volmer expression which is true for all quenching concentrations relates the "real" steady state ratio $I_0/I$ directly to the Collins and Kimball prediction as follows:

$$\frac{I_0}{I} = \exp(\nu c) \left(\frac{I_0}{I}\right)_{CK}.$$

(23)

The Collins and Kimball intensities are obtained from the integrals $I = \int f(c,t)dt$, and $I_0 = \int f(c=0,t)dt$, using $k_0 = K(0)$ as above. The factor $\exp(\nu c)$ readily accounts for the positive curvature observed in many steady-state Stern–Volmer experiments that is attributed to static quenching.\(^{22}\) Thus, for the case of $U(r) = 0$, Eqs. (20) and (23) enable us to fit the full range of time-resolved data and the steady-state data to a model with a single rate parameter $\tau$, a diffusion coefficient $D$, and contact and reaction distances $a$ and $R$.

Figure 1 compares the fluorescence decay curves which are predicted by the Collins and Kimball model, Eq. (2) with Eq. (9), and by the simple sink function model, Eq. (20) with Eq. (9). A single exponential fluorescence decay curve, corresponding to the case in which no quencher is present, is included for reference. The values of the variables are realistic for the rhodamine B–ferrocyanide system, and $k_0 = K(0)$.

A simple model such as the one just described can be useful for gaining a qualitative understanding of the complexity of fluorescence quenching. While the simple position-dependent rate is expected to be a better description than a hard boundary condition formalism, one expects that a more realistic functional form for the position-dependent rate should lead to an even greater improvement in the model.

The system examined in this study is one in which electron transfer is the mechanism of fluorescence quenching. The position dependence of nonadiabatic electron transfer has been shown to have the following functional form:\(^{13}\)

$$k(r) = k(0) \exp[-\beta(r-a)]$$  
(24)

where $k(0)$ is the intrinsic nonadiabatic electron transfer rate of the reactant pair at separation $r = a$ and $\beta$ is a factor determining the distance dependence of the rate. For cova-
lently linked donor-acceptor pairs, electron transfer has been shown to be dominated by through-bond interactions with a typical value of $\beta = 1 \AA^{-1}$. Beratan et al. have predicted a $\beta$ value approximately twice as large for through-space electron transfer.\(^\text{23}\)

The functional form for the rate of nonadiabatic electron transfer given by Eq. (24) can be used in the Wilemski-Fixman form of the diffusion equation, Eq. (15). We have numerically solved the diffusion equation with this sink term and used the result to fit our data.

### III. EXPERIMENTAL DETAILS

Rhodamine B (rhodamine 610 chloride), was used as received from Exciton and ferrocyanide [potassium ferrocyanide, $K_4Fe(CN)_6\] was used as received from Fischer. All solutions were prepared from stock solutions of the reactants (0.5 M ferrocyanide and $2 \times 10^{-4}$ M rhodamine B) and the pH was adjusted to 1.5 immediately prior to use (by addition of concentrated HCl). This assures that the rhodamine B is a monocation.

Steady-state fluorescence intensities were measured with a Perkin-Elmer MPF-66 spectrometer. The excitation wavelength was 580 nm and the emission intensity was recorded at both 620 and 635 nm. The concentration of rhodamine B was $5 \times 10^{-5}$ M and the concentration of ferrocyanide was varied from 0.1 to 0.4 M.

The two techniques used to acquire fluorescence decay data were time-correlated single photon counting\(^\text{24}\) (which we will refer to as simply photon counting) and fluorescence upconversion.\(^\text{25}\) The photon counting data were recorded at 4.6 ps/channel with an instrument response function having a full width at half-maximum (FWHM) of 1-2 ps. The fluorescence upconversion data was recorded at 0.2 ps/channel with an instrument response function FWHM of 1-2 ps. The decay curves obtain in both types of experiment displayed no emission wavelength dependence in the range 620-635 nm.

The data were fit to the various theoretical models by a direct nonlinear least squares method using iterative reconvolution with the appropriate instrument function.\(^\text{26}\) The algorithm used in the numerical solutions of the diffusion equations was developed by Agmon, Kosloff and co-workers.\(^\text{21,27}\)

### IV. RESULTS

In discussing the results it is important to be aware of the time resolution involved in the different sets of data. The upconversion data were recorded at 0.2 ps/channel with an instrument response function having a FWHM of 1-2 ps. Figure 2 shows typical upconversion data. Notice the initial component in the decay at higher quencher concentrations. We will refer to upconversion data as a demonstration of short (0-25 ps) and intermediate (0-200 ps) time behavior.

In contrast, the photon counting data typically collected with an instrument function of 70 ps FWHM and 200 ps full width at 10th maximum probes the \"long\" time behavior (~100 ps-4 ns). Note that the rapid component observed in the upconversion data carries a very small weight in the photon counting data, and the fitting procedure will therefore emphasize different aspects of the two data sets. Figure 3 dramatizes this point by showing upconversion and photon counting data on the same time scale. For reference, the photon counting instrument function is also shown. The rapid component evident in the upconversion data is very difficult to detect in photon counting experiments due to the relatively large instrument function width of the single photon counting apparatus.

It is also helpful to bear in mind the range of values which are physically realistic for the experimental parameters (in this case the diffusion coefficient $D$, the reaction
and contact distances $R$ and $a$, and the intrinsic reaction rate $k)$. The diffusion coefficient for Fe(CN)$_6^{4-}$ in water has been reported to be $0.75 \times 10^{-5}$ cm$^2$s$^{-1}$. Using the Stokes–Einstein relation and comparisons with similarly shaped molecules, we estimate $D_\text{a} = 0.5 \times 10^{-5}$ cm$^2$s$^{-1}$ for rhodamine B in water. Consequently, we expect the relative diffusion coefficient to be $1.25 \times 10^{-5}$ cm$^2$s$^{-1}$. From crystallographic measurements$^{29}$ and space filling models, we estimate the van der Waals radius of Fe(CN)$_6^{4-}$ to be 5-6 Å. Rhodamine B, a highly asymmetric molecule, presents a more difficult problem for estimating an appropriate radius. The distance from the center of the molecule to the van der Waals surface lies in the range 5-11 Å depending on orientation. Thus, the contact distance, which is the sum of the reactants’ radii, is expected to lie between 10 and 20 Å. When fitting our data we typically fix the value of $D$ at $1.25 \times 10^{-5}$ cm$^2$s$^{-1}$ and constrain the contact and/or reaction distance to be between 10 and 20 Å.

A. Short and Intermediate time regimes

Considering first the upconversion data we begin our analysis by examining the rapid initial decay of the fluorescence intensity which appears to be at least partially nondiffusional (Fig. 2). Assuming for the moment that there is no diffusion, the first 25 ps of upconversion data can be fit to the simple sink function model described by Eq. (19). The solid lines in Fig. 2 are the corresponding fits, which give a value of the intrinsic lifetime $\tau = 20 \pm 6$ ps independent of the concentration over the range 0.1 to 0.4 M.

In order to fit the data beyond 25 ps the model must include diffusion. To do this we use Eq. (20) with $k_D(t)$ represented by the Collins and Kimball result Eq. (8). Equation (22) is used to express the Collins and Kimball proportionality constant $k_0$ in terms of the intrinsic lifetime $\tau$, the reaction and contact distances $R$ and $a$, and the diffusion coefficient $D$.

Figure 4 shows fits to Eq. (20) with the Collins and Kimball form of $k_D(t)$ for 0.1 and 0.4 M quencher. Reasonably good ($\chi^2 < 2.0$) fits can be obtained over the 0–200 ps time range with $D = 1.25 \times 10^{-5}$ cm$^2$s$^{-1}$, $a = 1.0$ nm and $R = 1.1-1.2$ nm. With these parameters $k_0$ shows no systematic concentration dependence and corresponds to a value of $\tau = 27.7 \pm 5$ ps. Table I summarizes the parameters obtained from fits of the upconversion data.

The upconversion data was also fit with the simple Collins and Kimball model Eq. (2) and Eq. (9). See Table II. For low concentrations of quencher ($c < 0.2$ M) there is little difference between the quality of fits to the Collins and Kimball model and fits to the simple sink function model discussed above. However, at higher concentrations ($c > 0.2$ M) the quality of the fits becomes increasingly poor. This can be attributed to the emergence of a significant static quenching component in the decay which cannot be accounted for by a simple Collins and Kimball boundary condition description. In addition, the value of $k_0$ ($\sim 2 \times 10^{-1}$ nm$^3$s$^{-1}$) obtained from fits of the upconversion data to the Collins and Kimball model is about ten times larger than that used to fit the longer time photon counting data [see Fig. 5(a)]. As Fig. 5(b) shows, attempts to transfer the upconversion parameters to the photon counting data leads to very poor fits.

Before comparing the upconversion and single photon
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TABLE I. Parameter values from fitting the data to the simple sink function model, Eq. (20), with \( k_a(t) \) given by Eq. (8) and \( k_o \) by Eq. (22).*

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Reaction distance ( R ) (nm)</th>
<th>Intrinsic lifetime ( \tau ) (ps)</th>
<th>( k_o ) (nm(^4) ps(^{-1}))</th>
<th>Contact distance ( a ) (nm)</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upconversion data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>1.23</td>
<td>36.5</td>
<td>( 7.66 \times 10^{-2} )</td>
<td>1.0</td>
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<td>87.05</td>
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</table>

*The diffusion coefficient, \( D = 1.25 \times 10^{-5} \) cm\(^2\)/s, is fixed.

counting data further we digress briefly to discuss the steady-state quenching experiments.

B. Steady-state quenching

A Stern–Volmer plot of the steady state data is shown in Fig. 6. The ratio of the steady-state fluorescence intensity in the absence and presence of quencher is plotted as a function of the concentration of quencher. The data clearly deviates significantly from linearity—the classic symptom of static quenching. The upper curve through the data is calculated using Eq. (23) with \( \tau = 25 \) ps, \( a = 1.0 \) nm, \( R = 1.13 \) nm, \( D = 1.25 \times 10^{-5} \) cm\(^2\)/s and \( \tau_0 = 1.3 \) ns. The lower curve is the result predicted by the Collins and Kimball model for the given parameter values. Figure 7 illustrates the sensitivity of the Stern–Volmer relation Eq. (23) to the value of the intrinsic lifetime \( \tau \). Clearly, the steady-state fluorescence yield is very sensitive to \( \tau \). When values for \( a, R, \) and \( D \) are known this provides a sensitive method for determining \( \tau \). Stated alternatively, it is remarkable that, given values for \( a \) and \( D \), time-resolved data over only 180 ps suffices to quantitatively predict the Stern–Volmer plot.

C. Long time regime

1. Smoluchowski model

Examining the longer time dynamic behavior (0–4 ns) as seen in the photon counting data, we expect this time regime to be more strongly “diffusion controlled.” The classic Smoluchowski diffusion-controlled reaction model given by Eq. (2) with Eq. (5) for \( k(t) \), does not fit our data (\( \chi^2 > 100 \)) unless the contact distance or diffusion coefficient are allowed to be significantly smaller than that which seems physically realistic (e.g., with \( D = 1.25 \times 10^{-5} \) cm\(^2\)/s, values of \( a \) in the range 0.6–0.7 nm fit the data with \( \chi^2 = 1.4 \)).

2. Collins and Kimball model

The Collins and Kimball model, Eq. (9) used in Eq. (2), is a reasonable description of the low \( c = 0.1 \) M concentration photon counting data (see table II). Recall that this model also fit the 0.1 M upconversion data reasonably well. However, the \( k_o \) value obtained by fitting the photon counting data is a factor of 10 smaller than the value obtained from the corresponding upconversion data fit (see Fig. 5). Additionally, the Collins and Kimball model becomes an increasingly inadequate description at higher quencher concentrations \( c > 0.2 \) M, a trend also seen in the upconversion data.

3. Debye–Smoluchowski equation with Collins and Kimball boundary condition

Considering the ionic nature of the reactants in the system under study, a more accurate description may be found using the Debye–Smoluchowski equation. As we have noted in Sec. II the analytical solutions of the DSE have the same form as the Collins and Kimball solution. The solution of
Szabo, Eqs. (12) and (14), is convenient since one can fit to a parameter $k_E = k_0 \exp[-U(r)k_BT]$ and $R_E$ rather than $k_0$ and $R$. This is a valid approach for a spherically symmetric, continuous potential of mean force $U(r)$ which contains no local maxima or minima between $r = a$ and $r = \infty$. In this case Eq. (12) reduces to Eq. (8) with the rate and distance parameters having the interpretation just noted. The entries in Table II now correspond to $R_E$ and $k_E$. $R_E$ can be related to $R$ via Eq. (13). (Note that for attractive charges $r_c$ is negative.) However, the small values of $R_E$ obtained from fitting the data lead to undefined contact distances since Eq. (14) is not valid for $R_E < r_c$. If we restrict $R_E$ to be greater than $r_c$, the quality of the fits is quite poor.

Figure 8(a) shows a typical fit to Szabo’s approximate solution of the DSE with $R_E > r_c$. It was thought that a more exact solution to the DSE might lead to better agreement between our data and the theory. Using the method of Agmon and Kosloff27 and assuming $BU(r) = r_c/r$ we have numerically solved the DSE and fit the data to this solution.

The result is shown in Fig. 8(b). Both the qualitative deviations and the values of the parameters are very similar for the fits to the numerical and approximate solutions. Based on these results and numerical comparisons, we find that Szabo’s approximate solution is accurate in this parameter range. However, the quality of these fits suggests that the simple unscreened Coulomb potential is inappropriate.

**4. Simple sink function**

On the basis of the reasonable fits to low concentration ($c < 0.2$ M) photon counting data, it seems likely that the Collins and Kimball model is a reasonable description for diffusion dominated time regimes ($t > 200$ ps). The obvious inadequacy of the model in the first 100 ps and the discrepancy between fits to intermediate and long time data suggest that this model fails to describe the time regime in which the intrinsic reaction kinetics dominate and/or contribute substantially to the overall kinetics. We now return to the Wilkenski and Fixman formalism with the simple sink function used in our initial discussion of the upconversion data, and use Eq. (20) with the Collins and Kimball form of $k_D(t)$, Eq. (8), to analyze the photon counting data.

Recall that the deviation between the experimental data and the simple Collins and Kimball theoretical curves results from more rapid fluorescence quenching occurring at early times (0–300 ps) than is consistent with the theoretical predictions for the 1–4 ns behavior. Figure 9 shows a fit of 0.1 M photon counting data using Eq. (20) and the Collins and Kimball form for $k_D(t)$. The solid line is a fit with the contact distance $a$ fixed at 1 nm and the diffusion coefficient, $D$ at $1.25 \times 10^{-5}$ cm$^2$ s$^{-1}$. The fit is excellent ($\chi^2_R = 1.15$) and gives a value for the intrinsic lifetime $\tau$ of 87.7 ps ($k_0 = 2.31 \times 10^{-2}$ nm$^3$ ps$^{-1}$) and a value for the reaction distance $R$ of 1.15 nm. The dashed line in Fig. 9 is a fit using Eq. (20) and the parameters that described the upconversion data in Fig. 4(a). The fit is obviously poor but the discrepancy between the values for $\tau$ (or $k_0$) (upconversion data vs photon counting data) is reduced to about a factor of 3 compared to the factor of 10 seen for the simple Collins and Kimball model.

Before discussing the final model used to analyze our data, a number of problems should be addressed. One curiosity is the finding that the short time behavior predicts the steady-state behavior (i.e., the Stern–Volmer plot) very well but does a poor job of predicting the long time, time-resolved data. Recall that the steady-state fluorescence Stern–Volmer behavior could be predicted by only 180 ps of high resolution time resolved data. When static quenching occurs there will be a rapid initial drop in $I(t)$, as seen in our upconversion data, and thus a substantial decrease in the total fluorescence intensity. For example, in our 0.25 M upconversion data the fluorescence intensity at 25 ps after the excitation pulse is one half of the intensity at $t = 0$. Since the intrinsic lifetime $\tau$ determines how rapidly $I(t)$ decreases, it significantly affects the total area under the decay curve and thus the steady-state intensity. The behavior of the diffusional part of the decay curve is relatively unimportant in determining the shape of the Stern–Volmer plot in this system.

Another apparent anomaly is that, although our reac-

**Table II. Parameter values from fitting the data to the Collins and Kimball Model, Eq. (2) and Eq. (9).**

<table>
<thead>
<tr>
<th>Conc. of quencher (M)</th>
<th>Reaction distance ($R$) (nm)</th>
<th>$k_o$ (nm$^{-3}$ ps$^{-1}$)</th>
<th>$\chi^2$</th>
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<td>Upconversion data with parameter values from photon counting fits</td>
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*The diffusion coefficient, $D = 1.25 \times 10^{-5}$ cm$^2$/s, is fixed.*
FIG. 5. Fits of the short, intermediate and long time data to the Collins and Kimball model Eqs. (2) and (9), 0.1 M ferrocyanide. (a) Up-conversion data (0.2 ps/channel). The solid line through the data and the lower residuals are from a fit where $R = 1.19$ nm, $k_0 = 3.0 \times 10^{-1}$ nm$^3$/ps and $D = 1.25 \times 10^{-5}$ cm$^2$/s; the upper residuals and the dashed line are for a fit with the parameters of a best fit of the long time data, panel b. (b) Photon counting data (4.6 ps/channel). The solid line through the data is a fit where $R = 1.00$ nm, $k_0 = 2.89 \times 10^{-2}$ nm$^3$/ps and $D = 1.25 \times 10^{-5}$ cm$^2$/s; the upper residuals and the dashed line are for a fit with the parameters of a best fit of the intermediate time data, panel (a).

FIG. 6. Steady-state fluorescence intensity ratio as a function of quencher concentration $c$ (Stern–Volmer plot). Experimental data ($\times$). Theoretical curves given by (a) Eq. (23) and (b) the Collins and Kimball prediction. Parameter values for both theoretical curves are: $a = 1.0$ nm, $R = 1.13$ nm, $D = 1.25 \times 10^{-5}$ cm$^2$/s, $\tau_0 = 1.3$ ns, $\tau = 25$ ps.

FIG. 7. Stern–Volmer plot illustrating the sensitivity of Eq. (22) to the intrinsic lifetime $\tau$. Values of $\tau$ are (a) 10 ps, (b) 20 ps, (c) 40 ps, (d) 100 ps, (e) 200 ps.

...tants are ionic, assuming that the potential interaction between reactants is zero describes the data better than the use of a Coulomb potential. Although we obtain better fits for a potential of mean force of zero [$U(r) = 0$] than for a Coulomb potential, the quality of fits decreases as the concentration of quencher increases regardless of the model. This concentration effect is also likely to be related to the interaction potential between reactants. Simple Debye–Huckel screening for ions of finite size shows that even at the lowest ionic strength used in our experiments [at 0.1 M $K_4Fe(CN)_6$] the Coulomb interaction between the rhodamine B and the ferrocyanide ions is significantly reduced (20% of bare Coulomb) at center-of-mass separations of 10 Å and is negligible (2%) at 15 Å. The measured rotational diffusion time of rhodamine B in water and alcohol solvents provides further evidence for the weakness of this molecule's Coulomb attraction. Unlike the diionic fluorescein derivatives, the rotation time for rhodamine B corresponds to a bare molecular volume (i.e., no attached solvent).30 Similar effects have...
been found in the solvent reorganization energy associated with electron transfer between two large aromatic species. Thus neglecting the Coulomb potential appears reasonable.

However, even a simple hard-sphere liquid displays a definite structure in the radial distribution of molecules surrounding a given molecule. This structure occurs over several molecular diameters, the region of space expected to determine the fast initial dynamics observed in the upconversion data. The higher the quencher concentration is, the greater their contribution will be to this structure. Unfortunately, obtaining a realistic potential of mean force and radial distribution function is a difficult task. This lack of an appropriate potential may well be the cause of the discrepancy between the short and long time data fits.

5. Sink function for nonadiabatic electron transfer

The final model used to fit our data is the numerical solution of the diffusion equation in the Wilmeski and Fixman form, Eq. (15), with the position dependent rate given by Eq. (24) for nonadiabatic electron transfer. Although only fits of the lower concentration data can be categorized as "good" fits, it is instructive to observe the trends seen in the experimental variables for the different time regimes. We first discuss solutions where the potential of mean force is zero and end with a brief description of the low quality of fits obtained when a Coulomb potential is included. See Table III for a full comparison of typical fits to this model.

When fitting either upconversion or photon counting data, the quality of the fits decreases dramatically ($\chi^2$ increases and the deviations in the residuals become more structured) as the quencher concentration increases. The
of electron transfer appears to be stronger in this bimolecular system than in the bridged donor acceptor systems studied by Closs, Miller and co-workers\textsuperscript{13} (our $\beta \approx 2 \text{ Å}^{-1}$ rather than $\beta \approx 1.1 \text{ Å}^{-1}$). Beratan \textit{et al.}\textsuperscript{23} suggested a similar change in $\beta$ when comparing “through-bond” vs “through-space” electron transfer.

The discrepancy between the values of the intrinsic lifetime for the photon counting data and the upconversion data is consistent with the discrepancies observed when fitting to the other models to the data. None of the models tested here gave consistent or good fits to the full complement of experimental data. A number of physical details are likely to contribute to the inadequacy of existing models. Among these is the lack of an accurate potential of mean force experienced by the reactants. Another involves the probable angular dependence of the intrinsic reaction rate.

Rhodamine B is a highly asymmetric molecule with two large, relatively flat sides and approximately four comparatively thin edges. The faces are expected to allow a more highly electron dense region than the edges. The rotational relaxation time for rhodamine B in water is $163 \pm 10 \text{ ps}$\textsuperscript{30}. This slow rotation is expected to lead to a nonuniform radial distribution of quenchers, violating a basic assumption of all the theoretical models.

### V. CONCLUDING REMARKS

Analysis of our data leads us to conclude that the simple Collins and Kimball model is inadequate. Our system cannot be described with this model for quencher concentrations greater than 0.17 M. This can be attributed in part to the neglect in the model of static quenching or a distance dependence in the intrinsic reaction rate.

The inclusion of a simple model in which the reaction rate ($\tau^{-1}$) is constant over a finite distance reduces the discrepancy between the time dependence of our short time and long time data noted earlier.\textsuperscript{4} There still remains about a factor of 3 difference in the elementary rate found when fitting the two time regions with the potential of mean force equal to zero. It seems likely that the origin of this discrepancy lies in our ignorance of the true potential of mean force in this complex system. Attempts to include a Coulomb interaction between the reactants did not lead to satisfactory fits and it seems likely that for such a large molecule as rhodamine B a simple point charge model is quite inappropriate. A more satisfactory test of the model would involve a neutral system in which the fluorescing molecule had a much faster rotational relaxation time than rhodamine B, thus reducing the sensitivity of the experiment to the orientational aspects of the reaction. The short/intermediate time and steady-state fluorescence quenching data can be analyzed self-consistently with the simple sink function model. The combination of short time and steady-state data allow, within the context of the model, a consistent concentration independent estimate of the elementary rate of electron transfer between rhodamine B and ferrocyanide, $k(0) = (28 \text{ ps})^{-1}$ at $24^\circ \text{ C}$. Of interest are the temperature and free energy dependences of this rate, particularly in the context of the recent work of Kakiati and Mataga\textsuperscript{31} in which the Marcus “in-

### TABLE III. Parameter values from fitting the data to a numerical solution of Eq. (15) with $k(r)$ given by Eq. (24) for electron transfer.\textsuperscript{a}

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<table>
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<th>$\chi^2$</th>
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<th>Concentration (M)</th>
<th>$k(0)$ (ps)</th>
<th>$\beta$ (Å$^{-1}$)</th>
<th>Reaction distance ($R_{\text{nm}}$)</th>
<th>$\chi^2$</th>
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\textsuperscript{a} The diffusion coefficient, $D = 1.25 \times 10^{-5}$ cm$^2$/s, is fixed.
verted region” is not observed in photoinduced charge separation reactions in polar solvents.

Numerical fits of our data to a model in which the electron transfer rate is assumed to depend exponentially on separation were also made. In general the quality of the fits was less good than when a constant reaction rate over a finite distance was assumed. However, the best quality fits to the exponential model suggest a distance parameter, \( \beta \), of 2–3 Å\(^{-1} \) which is significantly larger than the values of \( \beta \) found in intramolecular electron transfer [typically \( \beta = 1 \) Å\(^{-1} \) (Ref. 13)]. Although the reduced quality of the fits (compared to the constant \( \tau \) model) do not encourage firm conclusions, it seems that our data imply a stronger distance dependence than in the intramolecular cases. It will be interesting to see if further work substantiates this.

As a final point it should be noted again that the model for the distance-dependent rate of electron transfer is valid for the nonadiabatic case. If the electron transfer is adiabatic over a distance greater than 0.5 Å in the rhodamine B–ferrocyanide system this may explain why the simpler model assuming a constant rate describes the data better than the model with an exponentially decaying rate. It is possible that a model including both adiabatic and nonadiabatic electron transfer would give better results.

Studies of geminate electron–cation recombination in solution have a number of parallels with the work described in this paper. Braun and Scott13 have successfully used the Hong and Nooolandi solution of the DSE19 to model the recombination dynamics. However, recent femtosecond studies of Eisenthal and co-workers33 have revealed that the geminate recombination dynamics of electrons with simple ions agrees poorly with a continuum diffusion model.

ACKNOWLEDGMENTS

We thank Attila Szabo and Gerhard Closs for many enlightening discussions and suggestions, Norah Shemtoulkis for assistance in collecting data, and Scott Northrup for a numerical solution of the DSE. We also extend special thanks to Noam Agmon for use of his numerical algorithm for solving the diffusion equation and for many helpful discussions. This work was supported by a grant from the NSF. B.G.D. is supported by an NSF predoctoral fellowship and a University of Chicago McCormick fellowship.

APPENDIX

Numerical solution of the Debye Smoluchowski equation (DSE)

The algorithm we use to numerically solve the DSE and also the diffusion equation containing a sink term was developed by Agmon, Kosloff and co-workers.27 Here we briefly outline their method and note the modifications used for the distance-dependent trapping rate. We formulate the problem as that of a spherically symmetric potential surrounding the trap such that the DSE is

\[
\frac{\partial q(r,t)}{\partial t} = \frac{1}{4\pi r^2} \left[ D \frac{\partial}{\partial r} \left[ r^2 \exp(-V) \frac{\partial}{\partial r} \exp(V) q \right] \right], \tag{A1}
\]

where \( \rho \) is the probability density function, \( J \) is the diffusional flux, and \( V \) is the potential energy in units of \( k_B T \). The symmetrical three-dimensional problem is reduced to a one-dimensional problem by a coordinate transformation and making the substitutions \( q(r,t) = 4\pi r^2 \rho(r,t) \) and \( U(r) = dr V(r) - 2 \ln(r) \). Equation (A1) is now written as

\[
\frac{\partial \rho(r,t)}{\partial t} = \frac{1}{\rho} \left[ D \frac{\partial}{\partial r} \left[ \rho \frac{\partial}{\partial r} \exp(U) \right] \right] = \rho q, \tag{A2}
\]

where \( L \) is the diffusion operator. The radial coordinate is constructed such that the second element of the array is the reaction–contact distance and the maximum value of \( r \) is chosen such that there is a minimal depletion of the outer boundary over the course of the time propagation. The first element of the array is defined as the trap and is located at \( R = \Delta r/2 \). The initial population density is simply the Boltzmann concentration or

\[
\rho(i) = (c_0/4\pi) \exp[-V(r)/k_B T/r^2] dr, \tag{A3}
\]

where \( c_0 \) is the bulk concentration of the quencher and \( dr \propto d\rho \). The diffusion operator \( L \) is discretized into vectors of nearest neighbor transition probabilities and a quenching vector for reacting with the trap. In this form the diffusion operator becomes a master equation that satisfies detailed balance (total probability is conserved during the time propagation). There are then four transition probability vectors which determine the diffusional flux consisting of the probability of going from radial coordinate site \( i \) to \( i + 1 \), \( i \) to \( i - 1 \), \( i \) to \( i \), and \( i \) to the trap. The values of the elements of the first three vectors are simply the transform normalized potential-diffusion constants while the fourth vector, which determines the trapping rate, satisfies the appropriate boundary/sink condition. For example, if a solution for a distance-dependent electron transfer type of trapping rate is to be tested the vector would be evaluated according to the functional form of the distance dependence. The propagation scheme is described in Ref. 27 and consists of the formal solution of Eq. (A2) to yield

\[
q(r,t+\Delta t) = \exp(-\Delta t L)q(r,t) \tag{A4}
\]

which is solved numerically by expanding the exponent in a Chebyshev series.
Eads, Dismer, and Fleming: Diffusion-influenced fluorescence quenching

5M. Smoluchowski, Phys. Z. 17, 55 (1916).
21As noted by Szabo (Ref. 11), the Collins and Kimball boundary condition corresponds to the special case where 

\[ k(r) = \frac{k_0\delta(r-a)}{A(a)} \]

where \( a \) is the sum of the radii of the fluoroscer and the quencher, \( A(a) \) is the area of a hypersphere of radius \( a \), and \( \delta \) is the dirac delta function.
22Personal communication with Attila Szabo.
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31Personal communication with Attila Szabo.