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Theory of electronic relaxation in solution in the absence of an activation barrier

Biman Bagchi, Graham R. Fleming,^{a)} and David W. Oxtoby^{a)}

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637
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We present a theory which describes the effects of viscosity on those electronic relaxation processes in solution in which the intramolecular potential surface does *not* present a barrier to the motion leading to the decay of the initially formed excited state. We model the reactive motion as the motion of a solute particle on the excited state potential surface with a *position dependent sink* which gives rise to the decay of the excited state population. Three different types of sinks are considered: (A) a pinhole sink at the minimum of the potential surface; this models the situation when the molecule decays to ground state as soon as it reaches the potential minimum; (B) a Gaussian sink with probability of decay maximum at the potential minimum; (C) a Lorentzian sink with maximum decay at the potential minimum. For case (A) an explicit analytic solution is obtained for the decay rate, but for cases (B) and (C) we obtained the decay rate numerically. Model (A) predicts nonexponential decay at all viscosities except at long times when the decay is single exponential. For cases (B) and (C) the decay is single exponential at *low* viscosities but becomes multiexponential at high viscosities. We show that the experimentally observed fractional viscosity dependence of fluorescence quantum yield arises naturally in this theory due to the position dependence of the sink as well as due to the competition between radiative and nonradiative relaxation. Our model also predicts a crossover from an apparent *negative* (constant viscosity) activation energy at low viscosities to a positive activation energy at high viscosity. The physical significance of these results is discussed in light of the available experimental results on TPM dye relaxation. Some possible generalizations of our theory to more realistic cases are indicated.

I. INTRODUCTION

Electronic relaxation processes involving large amplitude motion can be divided into two categories: those in which an intramolecular potential barrier is present and those in which the intramolecular potential surface does not present a barrier to motion of the initially formed excited state. Solvent friction is clearly important in both classes but in the zero barrier case provides the only "resistance" to motion on the excited state surface. The case with a sizeable internal barrier ($\Delta E > kT$) has been discussed extensively from both experimental¹⁻⁶ and theoretical⁷⁻¹³ viewpoints following the classic work of Kramers.⁷ Recent attention has been directed toward frequency dependent effects in solvent friction when barriers are sharp^{14,15} and to the inertial or energy controlled regime expected at very low values of the solvent friction.^{16,17} The zero barrier case has received much less attention from the theoretical standpoint with the calculations of Förster and Hoffmann¹⁸ and of Cremers¹⁹ being the only discussions of which we are aware.

From the experimental point of view the zero barrier case has attracted considerable interest as a description of the viscosity dependent radiationless decay of the excited singlet state of the triphenyl methane (TPM) dyes.²⁰⁻²⁸ This viscosity dependence has been investigated by a variety of steady state and time resolved spectroscopic techniques and the experimental findings are summarized below.

(i) The fluorescence quantum yield ϕ_f depends on a

fractional power of the solvent viscosity. Following the initial suggestion of Förster and Hoffmann¹⁸ that $\phi_f \propto \eta^{2/3}$ several workers have found adequate fits to this form over large viscosity ranges.^{18,22,27}

(ii) The form of the ground state recovery curve is viscosity dependent. For example, Ippen *et al.*²⁴ found that malachite green exhibits single exponential decay in solvents with viscosity less than 1 P. For solvents with higher viscosity, the decay was fit as a sum of two exponentials,²⁴ but Cremers and Windsor²¹ suggest that a sum of many exponentials is required to fit their ground state recovery and excited state absorption data.

(iii) The form of the fluorescence decay curve has also been described as a double exponential decay but of the time constants obtained by Hirsch and Mahr,²² only their shorter one corresponds to one (the longer) of the time constants observed in the ground state recovery measurements of Ippen *et al.*²⁴ The viscosity dependence of the decay constants of malachite green depended more nearly on $\eta^{1/3}$ ^{22,23} and the discrepancy between this dependence and the $\eta^{2/3}$ dependence of the fluorescence quantum yield was interpreted in terms of viscosity dependent coefficients of the two exponential terms.²² By contrast, Beddard *et al.*²³ fitted the fluorescence decay of crystal violet as the sum of two exponentials (for $\eta > 0.8$ P) and found the decay times to vary as the 0.68 ± 0.1 and 0.58 ± 0.1 powers of the viscosity for the shorter and longer decay times, respectively.

(iv) From a preliminary study Cremers¹⁹ suggested that there was no intrinsic effect of temperature on the radiationless decay of crystal violet. In other words,

^{a)}Camille and Henry Dreyfus Teacher Scholar.

at constant viscosity the activation energy is zero. More recent work on ethyl violet by Gilbro and Sundström²⁹ finds a small (~ 0.8 kcal/mol) but definite *negative* activation energy at constant viscosity.

(v) Ground state recovery experiments carried out at a range of wavelengths have suggested the existence of an unstable intermediate in the relaxation process^{20,30} and may require reinterpretation of some of the earlier studies carried out at a single wavelength. The intermediate is probably a twisted ground state species. The formation time of the intermediate has a roughly $\eta^{2/3}$ dependence but its decay is much more strongly viscosity dependent (decay time $\propto \eta^{1.5}$).

In this paper we present a new theoretical model for radiationless processes involving large amplitude motion in the *absence* of an internal barrier, so that this model is suitable for describing electronic relaxation in TPM dyes. We follow Förster and Hoffmann¹⁸ in assuming that the motion on the excited state surface is effectively one dimensional; the relevant coordinate for the TPM dyes involves the synchronous rotation of the phenyl rings about the bond between each phenyl group and the central carbon atom. Motion of the phenyl rings toward the excited state equilibrium geometry then may lead to a significant enhancement in the rate of internal conversion, presumably through a decrease of the energy gap between the S_0 and S_1 surfaces.

Since there is no high barrier for the reactive motion, there is no natural separation of time scales between the motion in the reactive region and in the rest of the potential surface. We have, therefore, solved for the time-dependent probability of a system remaining on the excited state surface. In this model, the radiationless relaxation is represented by a coordinate dependent sink (which gives rise to decay in excited state population) centered on the excited state potential minimum, and the radiative relaxation by a position independent sink along the potential surface. The motion along the potential surface is governed by the force from the potential (approximated as harmonic) and the viscous drag of the solvent. We model all these competing factors by a modified Smoluchowski equation of the following form

$$\frac{\partial P(x, t)}{\partial t} = A \frac{\partial^2 P(x, t)}{\partial x^2} + B \frac{\partial}{\partial x} xP(x, t) - k_{nr} S(x)P(x, t) - k_r P(x, t), \quad (1.1)$$

where $A = k_B T / \zeta$ and $B = \omega^2 \mu / \zeta$, ω being the frequency of motion on the harmonic surface, ζ the relevant friction coefficient, μ the reduced mass of the reactive motion, and T the temperature. k_{nr} is the magnitude of the radiationless rate at the origin [where $S(x)$ is chosen to be unity] and k_r is the radiative rate constant, independent of position. For the sink function $S(x)$, we have investigated three different functional forms:

(a) The sink is a pinhole at the origin. This models the situation where there is no radiationless transition from anywhere except the origin where the energy gap between the two surfaces may be a minimum and so the decay is very fast. This model is relevant to those situations where there is a "funnel" in some region of

the potential surface.³¹ Mathematically, this model corresponds to the well-known^{8,32,33} problem of diffusion in the presence of an absorption barrier and can be solved exactly to obtain $P(x, t)$.

(b) $S(x)$ is a Gaussian function with a maximum at the origin. This is actually quite realistic because the energy difference between two harmonic surfaces is a quadratic function, and so an exponential energy gap law predicts a shifted Gaussian probability distribution for the transition probability between two surfaces. For this case we have obtained a series solution since analytic solution is not possible. However, some interesting conclusions can be drawn directly from the structure of the equations.

(c) $S(x)$ is a Lorentzian function with the transition probability a maximum at the origin. While the physical basis of this model is not as obvious as for the other two cases, it may be useful in some situations. In addition, this model will serve as a valuable check on the dependence of relaxation on the functional form of $S(x)$.

Förster and Hoffmann¹⁸ studied a model which is similar in spirit to the model presented here. However, they chose a quadratic form for $S(x)$ which is entirely unreasonable since it predicts an increase in rate even when the energy gap between the ground and the excited surfaces increases. There are also some unjustified statistical assumptions in their treatment of relaxation: in particular, they assume that all of the molecules follow the average relaxation pathway, rather than allowing for a random distribution of motions on the excited surface. Their model gives a prediction for the viscosity dependence of the quantum yield ($\phi_f \propto \eta^{2/3}$) which is in accord with the experiment. However, we regard this good agreement as somewhat fortuitous, in view of the fact that the time dependence of the fluorescence decay given by the Förster–Hoffmann model is $\exp(-\alpha t^3)$ which has not been observed experimentally. We shall return to this point later.

An extensive study of the viscosity dependence of electronic relaxation of TPM dyes has been carried out by Cremers¹⁹ who solved a system of coupled Smoluchowski equations for the time dependence of the population in ground and excited states. His treatment differs from our method in that he did not introduce any model for the sink function. Instead, he assumed that the transition probabilities have an exponential dependence on the energy gap between the electronic levels involved and used the numerical values of the potential energies of the two surfaces evaluated by a separate quantum chemical calculation. His work is therefore more specific. Moreover, Cremers' results are unreliable in the low viscosity regime due to problems of convergence. Cremers' also did not consider the temperature dependence of the nonradiative rate. We shall present a more detailed comparison of our theory with that of Cremers in the following sections.

The Smoluchowski equation (1.1) is known to be a limiting form of the phase space Fokker–Planck equation⁸ (sometimes referred to as Kramers' equation) and is strictly valid only when $(\mu/\zeta) \ll \omega^{-1}$. Fortunately,

for many of the TPM dyes, ω is rather small, so Eq. (1.1) may actually be valid over most of the experimentally accessible range of viscosity. However, Eq. (1.1) is definitely not capable of describing relaxation in the short time inertial or energy controlled limit. One must use the full phase space Fokker-Planck equation in this limit. We are presently carrying out such a calculation which will be described in a forthcoming article.

The diverse and interesting viscosity dependences $i-v$ observed in the relaxation of TPM dyes arise from the competition between the steric hindrance within the molecule and the solvent viscosity. The first factor favors the relaxation whereas the second one hinders it. Our model with a coordinate dependent sink in a harmonic potential surface includes these two competing factors in a way which is not only intuitive but also consistent with recent experimental observations. We show by explicit calculation that the fractional values of the exponent α for the viscosity dependence of quantum yield ($\phi_f \propto \eta^\alpha$) naturally arise from this model and that there is *no* theoretical reason for α to be *exactly* equal to $2/3$. In fact, in our model, α is dependent on such natural parameters as ω , k_{nr} , k_r and also on the coordinate dependence of $S(x)$. For a pinhole sink, we find that if k_r is much less than $B(= \omega^2 \mu / \zeta)$, then the exponent α is exactly equal to unity; i. e., the rate of decay is inversely proportional to viscosity. This is reminiscent of the well-known Smoluchowski limit of Kramers' solution for the rate in the presence of a high barrier. But in the present case we have a nonsteady state solution in the absence of an activation barrier, whereas Kramers solution was obtained with the assumption of a steady-state diffusion across a high barrier which would break down when the barrier height is of the order of $k_B T$. Recent experiments on electronic relaxation in DPB (diphenyl butadiene) showed that even though the activation energy in this case is of the order of $k_B T$, the rate is inversely proportional to viscosity.⁶ We believe our calculation with a pinhole sink provides an explanation of this finding. We have also shown that the transition from single exponential to multiexponential decay of excited state population as viscosity is increased can also be explained from this model.

Another very interesting prediction of our model is a cross-over behavior in the temperature dependence of the decay rate. Our model predicts that at low viscosities the rate would decrease as temperature is increased (i. e., an effective "negative" activation energy), but at high viscosities, the rate again increases as temperature is increased (i. e., the effective activation energy is positive). As noted above, this negative activation energy at low viscosities has already been observed.²⁹ We have also considered the dependence of relaxation on the wavelength of excitation.²⁸ In our model this feature enters through the dependence of the probability distribution $P(x, t)$ on the initial condition. Thus, we have shown that all the essential features of electronic relaxation in TPM dyes can be explained in a very simple manner. We believe our model to be the first to provide a systematic account of the features of TPM dye relaxation.

The organization of the rest of the paper is as follows: In Sec. II, we discuss the formal aspects of the theory and in Sec. III we present numerical results along with their interpretation. Section IV concludes with a brief discussion.

II. THEORY

In this section we analyze the form of the equations of motion for the three types of sinks which we are considering. We show that for a pinhole sink the equations may be solved explicitly for the decay rate. For the Gaussian and Lorentzian sinks analytical solution is not possible; we examine the qualitative form of the relaxation for these sinks, but postpone discussion of the full numerical results to Sec. III.

A. Pinhole sink

For this case, once a particle arrives at the origin it decays with unit probability. Mathematically this corresponds to the well-known problem of an absorbing barrier at the origin.^{8,32} For convenience, we write the equation of motion in the following form

$$\frac{\partial \tilde{P}}{\partial t} = \mathcal{L} \tilde{P}, \quad (2.1)$$

where

$$\tilde{P} = \exp(k_r t) P, \quad (2.2)$$

$$\mathcal{L} = B \frac{\partial}{\partial x} \left(\frac{A}{B} \frac{\partial}{\partial x} + x \right). \quad (2.3)$$

\mathcal{L} is an ordinary Fokker-Planck operator in one variable. We solve Eq. (2.1) for the following initial-boundary values for P :

$$P(x, t=0) = \delta(x + x_0), \quad (2.4a)$$

$$P(x = \pm \infty, t) = 0, \quad (2.4b)$$

$$P(x=0, t) = 0. \quad (2.4c)$$

The same conditions also apply for \tilde{P} . Equation (2.4a) is the statement of the fact that the system is placed at $x = -x_0$ at time $t=0$; it is straightforward to generalize this condition to include some simple distribution for x_0 . With the conditions (2.4), the solution of Eq. (2.1) can easily be obtained by the method of images^{8,32,33}

$$\tilde{P}(x, t) = \frac{\sqrt{B/A}}{\sqrt{2\pi(1 - e^{-2Bt})}} \left\{ \exp \left[- \frac{B(x + |x_0| e^{-Bt})^2}{2A(1 - e^{-2Bt})} \right] - \exp \left[- \frac{B(x - |x_0| e^{-Bt})^2}{2A(1 - e^{-2Bt})} \right] \right\}. \quad (2.5)$$

Therefore, the probability distribution $P(x, t)$ for the system to be at position x at time t is obtained from Eqs. (2.2) and (2.5).

Let us define $P_e(t)$ to be the probability of the molecule being in the excited state after time t . Then $P_e(t)$ is given by

$$\begin{aligned} P_e(t) &= \int_{-\infty}^0 dx P(x, t) = \int_0^{\infty} dx P(-x, t) \\ &= \frac{2}{\sqrt{\pi}} \exp(-k_r t) \operatorname{erf}(Z(t)), \end{aligned} \quad (2.6)$$

where $\text{erf}(a)$ is the error function³⁴ defined by

$$\text{erf}(a) = \int_0^a dq e^{-q^2} \quad (2.7)$$

and

$$Z(t) = \frac{|x_0| e^{-Bt}}{\sqrt{2A/B}(1 - e^{-2Bt})}. \quad (2.8)$$

Equation (2.6) gives the relaxation of the excited state population in the presence of an absorbing barrier (pin-hole sink) at the origin. This equation predicts a multi-exponential relaxation, as can easily be appreciated from the following series expansion of the error function³⁴:

$$\text{erf}(Z(t)) = \sum_{n=0}^{\infty} (-1)^n \frac{(Z(t))^{2n+1}}{n!(2n+1)!} \quad (2.9)$$

with $Z(t)$ given by Eq. (2.8). For long times (such that $Bt \gg 1$), $Z(t)$ becomes

$$Z(t) \sim |x_0| \sqrt{\frac{B}{2A}} e^{-Bt}. \quad (2.10)$$

Equation (2.9) then predicts that at sufficiently long times, $P_e(t)$ will become single exponential. Since B is inversely proportional to the viscosity, the decay in this case is governed by t/η .

Another physical quantity relevant to the discussion of relaxation in the presence of an absorbing barrier is the first passage time distribution $Q(t, x_0)$.³³ $Q(t, x_0)$ is the probability that the particle, starting at position x_0 at time $t=0$, reaches the barrier for the first time at time t . In other words, it gives the probability of being absorbed in the time interval between t and $t+dt$. For a barrier at the origin, this is given by³³

$$Q(t, x_0) = -\frac{d}{dt} \int_{-\infty}^0 dx P(x, t) = -\frac{d}{dt} P_e(t) \quad (2.11)$$

which is equal to

$$Q(t, x_0) = \frac{2B}{\sqrt{\pi}} \left[1 + \frac{e^{-2Bt}}{1 - e^{-2Bt}} \right] Z(t) \exp[-(Z(t))^2], \quad (2.12)$$

where we have neglected k_r for this discussion. The average first passage time $\langle t \rangle_{\text{av}}$ is defined by

$$\langle t \rangle_{\text{av}} = \int_0^{\infty} t Q(t, x_0) dt = \int_0^{\infty} dt P_e(t) \quad (2.13)$$

which is the inverse of the "average" rate k of relaxation, of excited state population. Thus, expression (2.12) for $Q(t, x_0)$ has some interesting detailed information on relaxation of the excited state population.

The complete expression for the relaxation rate from the excited surface is given by

$$k^{-1} = \frac{1}{B\sqrt{\pi}} \sum_{n=0}^{\infty} (-1)^n \frac{|x_0|^{2n+1} (B/2A)^{n+(1/2)}}{n!(2n+1)!} \frac{\Gamma(k_r/2B + n + \frac{1}{2})}{\Gamma(k_r/2B + 2n + 2)}. \quad (2.14)$$

Since A and B have the same viscosity dependence, Eq. (2.14) predicts an inverse viscosity dependence of rate at small viscosity. This is due to the fact that B is inversely proportional to the friction coefficient ($B = \omega^2 \mu / \zeta$) and so it becomes larger than k_r at small viscosities ($\eta \sim 1$ CP) for reasonable values of k_r and ω . Often ω is

large enough that $k_r \ll \omega^2 \mu / \zeta$ over a large range of viscosity; in that case, inverse dependence of rate on viscosity should be detectable experimentally. We shall come back to this point in the next section.

Due to the simple expression for the rate constant, it is possible to study its temperature dependence analytically. To do this, we write

$$\begin{aligned} \frac{\partial}{\partial T}(k^{-1}) &= \frac{2}{\sqrt{\pi}} \int_0^{\infty} dt \frac{\partial}{\partial T} \int_0^{Z(t, T)} dq e^{-q^2} \\ &= -\frac{1}{T\sqrt{\pi}} \int_0^{\infty} dt Z(t, T) \exp[-(Z(t, T))^2] \end{aligned} \quad (2.15)$$

at constant viscosity, so that $\partial k / \partial T$ is positive (i.e., the rate increases with increase of temperature). This implies an effective positive activation energy. The physical significance of this result will be discussed later.

B. Gaussian sink

The general Gaussian sink is represented by a Gaussian function centered at a point x_m

$$S(x) = \exp[-(x - x_m)^2 / a^2]. \quad (2.16)$$

This can model the situation where the minima of ground and excited state surfaces are shifted by certain amount in coordinate space so that the energy gap between the two surfaces can be fitted to a quadratic form. When $x = x_m$, $S(x) = 1$, but as $x \rightarrow \infty$, $S(x) \rightarrow 0$, so that k_r takes its full value at $x = x_m$. $x_m = 0$ implies that $S(x)$ is peaked at the minimum of the excited surface.

In the Gaussian case, due to the complicated structure of Eq. (1.1), it has not been possible to solve this equation exactly for $P(x, t)$. Instead, we have solved it by a series expansion. However, some conclusions regarding the viscosity and temperature dependences can be drawn immediately from the analytic structure of the series solution.

A convenient way to solve Eq. (1.1) is to expand it in the eigenfunctions of the Fokker-Planck operator \mathcal{L} defined by Eq. (2.3). The expansion solution is

$$P(x, t) = \sum_{n=0}^{\infty} \sigma_n(t) b_n(x), \quad (2.17)$$

where $b_n(x)$ is the n th eigenfunction of \mathcal{L} ³⁵

$$\mathcal{L} b_n = -nB b_n, \quad (2.18a)$$

$$b_n(x) = A_n^{1/2} \exp(-x^2/2V^2) H_n\left(\frac{x}{\sqrt{2}V}\right), \quad (2.18b)$$

where H_n is the Hermite polynomial of order n , $V = (A/B)^{1/2}$ and the normalization constant A_n is given as

$$A_n = (Vn! 2^n \sqrt{2\pi})^{-1}. \quad (2.19)$$

The conjugate eigenfunction b_n^* is defined through³⁵

$$b_n^* \mathcal{L} = -nB b_n^*, \quad (2.20a)$$

$$b_n^* = A_n^{1/2} H_n\left(\frac{x}{\sqrt{2}V}\right). \quad (2.20b)$$

It can easily be checked that b_n and b_n^* are orthonormal

$$\int dx b_n^*(x) b_m(x) = \delta_{n,m} . \tag{2.21}$$

Following the usual procedure, we obtain the following system of equations for $\sigma_n(t)$:

$$\begin{aligned} \dot{\sigma}_m(t) = & -mB\sigma_m(t) \\ & -k_{nr} \sum_{n=0}^{\infty} A_n^{1/2} A_m^{1/2} I_{m,n} \sigma_n(t) - k_r \sigma_m(t) . \end{aligned} \tag{2.22}$$

For $S(x)$ given by Eq. (2.16), $I_{m,n}$ is

$$\begin{aligned} I_{m,n} = & a\sqrt{\pi} \sum_{k=0}^{\min(m,n)} 2^k k! \binom{m}{k} \binom{n}{k} \left(\frac{2V^2 - a^2}{2V^2} \right)^{(m+n/2)-k} \\ & \otimes H_{m+n-2k} \left(\frac{x_m}{(2V^2 - a^2)^{1/2}} \right) . \end{aligned} \tag{2.23}$$

For $x_m = 0$ (i. e., a Gaussian centered at the origin) $I_{m,n}$ simplifies to

$$\begin{aligned} I_{m,n} = & (-1)^{m+n/2} 2^{m+n+(1/2)} V \left(1 + \frac{a^2}{2V^2} \right)^{-(m+n/2)} \left(\frac{a^2}{a^2 + 2V^2} \right)^{1/2} \\ & \otimes \Gamma \left(\frac{m+n+1}{2} \right) {}_2F_1 \left(-m, -n; \frac{1-m-n}{2}; \frac{a^2 + 2V^2}{4V^2} \right); \\ & (m+n) \text{ even} , \end{aligned} \tag{2.24}$$

where ${}_2F_1$ is an ordinary hypergeometric function³⁴ defined as

$${}_2F_1(a, b; c; z) = \sum_{l=0}^{\infty} \frac{(a)_l (b)_l}{(c)_l l!} z^l . \tag{2.25}$$

$(Y)_l$ is Pochhammer's symbol.³⁴ In this case both a and b are either negative integers or zero, so ${}_2F_1$ is a polynomial with the upper limit of the sum (2.25) at $\min(m, n)$.

The initial condition $P(x, t=0) = \delta(x + x_0)$ gives

$$\sigma_m(0) = b_m^*(-x_0) . \tag{2.26}$$

The expression for $P_e(t)$, in this case, is given by

$$P_e(t) = \int_{-\infty}^{\infty} dx P(x, t) = \sqrt{2\pi A_0} V \sigma_0(t) . \tag{2.27}$$

Equation (2.27) has the consequence that we have to consider only the even eigenstates, i. e., $\sigma_0, \sigma_2, \sigma_4, \dots$, etc., in Eq. (2.24). The expression for the rate constant is also very simple and is given by

$$k^{-1} = \int_0^{\infty} dt P_e(t) = (\sqrt{2\pi} V)^{1/2} \hat{\sigma}_0(s=0) , \tag{2.28}$$

where $\hat{\sigma}_0(s)$ is the Laplace transform of $\sigma_0(t)$

$$\hat{\sigma}_0(s) = \int_0^{\infty} dt e^{-st} \sigma_0(t) .$$

Both Eqs. (2.23) and (2.24) are easy to solve numerically because the matrix \mathbf{M} defined as

$$\dot{\sigma}(t) = \mathbf{M} \sigma(t) \tag{2.29}$$

is a real symmetric matrix. This is the advantage of expanding $P(x, t)$ in the eigenfunctions of the Fokker-Planck operator \mathcal{L} .

C. Lorentzian sink

In this case, we assume the following form for $S(x)$:

$$S(x) = \frac{a^2}{x^2 + a^2} . \tag{2.30}$$

For this choice of $S(x)$, the series expansion of $P(x, t)$ in eigenfunctions of \mathcal{L} leads to the following system of equations:

$$\begin{aligned} \dot{\sigma}_m(t) = & -mB\sigma_m(t) \\ & -k_{nr} \sum_{n=0}^{\infty} A_n^{1/2} A_m^{1/2} I_{m,n} \sigma_n(t) - k_r \sigma_m(t) , \\ & \{n+m \text{ even}\} , \end{aligned} \tag{2.31}$$

where

$$\begin{aligned} I_{m,n} = & \pi a \exp(a^2/2V^2) \\ & \times (-1)^{n+m/2} \mathcal{J}_n \left(\frac{a}{\sqrt{2}V} \right) \mathcal{J}_m \left(\frac{a}{\sqrt{2}V} \right) . \end{aligned} \tag{2.32}$$

$\mathcal{J}_n(Y)$ are polynomials somewhat different from Hermite polynomials. They are defined through the following generating function:

$$G(Y, t) = \exp(2Yt + t^2) = \sum_{l=0}^{\infty} \frac{\mathcal{J}_l(Y)}{l!} t^l \tag{2.33}$$

and have the following recursion relation:

$$\mathcal{J}_{l+1}(Y) = 2Y \mathcal{J}_l + 2l \mathcal{J}_{l-1} . \tag{2.34}$$

Equation (2.31) is of the same form as Eqs. (2.23) or (2.24). We expect models B and C to give similar results for small x_0 . The expressions for $P_e(t)$ and $(k)^{-1}$ are still given by Eqs. (2.27) and (2.28), respectively. Though the final solutions for cases B and C have to be obtained numerically, there are some interesting features which can be deduced merely from the structure of Eqs. (2.22) and (2.31). We write these equations in the following form:

$$\dot{\sigma}_m(t) = -mB\sigma_m(t) - k_r \sigma_m(t) - k_{nr} \sum_{n=0}^{\infty} J_{nm} \sigma_n(t) , \tag{2.35}$$

where J_{nm} now symbolize the rest of the factor in those three equations. First, consider the case of extremely small viscosity, so that $B (= \omega^2 \mu / \zeta)$ is very large. In this limit, σ_0 dominates because higher coefficients decay rapidly, so we have

$$\sigma_0(t) = \sigma_0(0) \exp[-(k_r + k_{nr} J_{00})t] . \tag{2.36}$$

For the Gaussian sink peaked at the origin, J_{00} is given by

$$J_{00} = \left(\frac{a^2}{a^2 + 2V^2} \right)^{1/2} . \tag{2.36a}$$

Thus, in this low viscosity limit, the excited state population relaxation, as given by Eq. (2.27), is single exponential. Another interesting point is that the rate constant of this decay is independent of viscosity. This is due to the fact that viscosity dependence in Eq. (2.35) enters only through B .

As viscosity is increased, B decreases and other bath states enter into the picture. There may be a region in viscosity where σ_0 and σ_2 dominate. Then Eq. (2.35)

predicts a biexponential decay, for the Gaussian sink ($x_m = 0$), of the following form:

$$\sigma_0(t) = \frac{m_+ \sigma_0(0) + u}{m_+ - m_-} e^{m_+ t} + \frac{m_- \sigma_0(0) + u}{m_- - m_+} e^{m_- t}, \quad (2.37)$$

where

$$m_{\pm} = \frac{1}{2}[-Q \pm \sqrt{Q^2 + 4R}], \quad (2.37a)$$

$$Q = (J_{00} + J_{22})k_{nr} + 2B + 2k_r, \quad (2.37b)$$

$$R = k_{nr}^2 J_{20} - (2B + k_r + k_{nr} J_{22})(k_{nr} J_{00} + k_r), \quad (2.37c)$$

and

$$u = (k_r + k_{nr} J_{00})\sigma_0(0) + k_{nr} J_{02}\sigma_2(0). \quad (2.37d)$$

In the limit of small viscosity

$$B \gg k_{nr}(J_{00} + J_{22}), \quad Q^2 \gg 4R,$$

so we have

$$m_+ \approx R/Q; \quad R < 0, \quad (2.38a)$$

$$m_- \approx -Q - R/Q; \quad Q > 0. \quad (2.38b)$$

In this limit, Eq. (2.37) gives a biexponential decay with rate constants given by Eq. (2.38). One of the rate constant (m_-) is large, predicting a sharp initial decay if the prefactor for this decay term is larger than the prefactor of the $\exp(m_+ t)$ term.

As viscosity is further increased, Eq. (2.35) predicts multiexponential decay. The transition from single exponential decay at very low viscosity to multiexponential decay at high viscosities with a biexponential decay at intermediate values of viscosity has already been observed in the experiments of Cremers and Windsor²¹ and of Ippen *et al.*²⁴

Next we examine the temperature dependence of the rate constant given by Eq. (2.28). The derivative of the rate constant with respect to the temperature can be written in the form

$$\frac{\partial k}{\partial T} = -\frac{k}{2T} - k^2 (V\sqrt{2\pi})^{1/2} \int_0^\infty dt \frac{d\sigma_0}{dT}. \quad (2.39)$$

For the low viscosity case, the rate constant k is approximately given by

$$k \approx (V\sqrt{2\pi})^{-1} (k_r + k_{nr} J_{00}). \quad (2.40)$$

It is easy to see that both $\partial/\partial T(V^{-1})$ and $\partial J_{00}/\partial T$ are negative for both Gaussian and Lorentzian sinks. This implies that $\partial k/\partial T$ in Eq. (2.40) is also negative which means that we have an effective *negative* activation energy for this case of very small viscosity. However, as viscosity is increased, higher eigenstates of \mathcal{L} become important and $\partial k/\partial T$ can become positive. We shall show in the next section that numerical calculation indeed predicts such a cross-over behavior of $\partial k/\partial T$ as viscosity is increased from small values. As mentioned in the Introduction, negative activation has already been observed in relaxation of some TPM dyes at low viscosities.²⁹

III. NUMERICAL RESULTS AND DISCUSSION

In this section we describe and discuss the results obtained by numerical solution of the equations described

in the previous section.

In order to obtain the time dependent probability function $P_e(t)$ for the position dependent sinks (cases B and C), we need to solve systems of Eqs. (2.22) and (2.31). For practical purposes we must truncate the expansion (2.17) at some finite value n_{\max} of the summation index n . This is physically very reasonable for small values of viscosity η because in this case the first term dominates and we need to include only a small number of eigenstates $b_n(x)$ in order to obtain good convergence. For high values of η , the higher eigenstates become important. Then the expansion becomes increasingly awkward because a large number of eigenstates are needed for good convergence. We have limited our study to a maximum value of 50 P for viscosity η . At this value of η , we get good convergence by truncating the series at $n_{\max} = 48$ for the Gaussian sink, but for a Lorentzian sink we had to include as many as 84 eigenstates in order to obtain reliable convergence. Above the value of 50 P of η , it becomes extremely difficult to obtain satisfactory convergence.

We have already pointed out that the matrix M of Eq. (2.29) is a real symmetric matrix, and therefore it is straightforward to obtain the solution of $P_e(t)$ which is given by Eq. (2.27). Similarly, the rate k , given by Eq. (2.28), can also be obtained without difficulty.

It is interesting to note the difference between our method of series solution and Cremers' finite-difference numerical quadrature.¹⁹ Cremers' method becomes inefficient at small values of viscosity where very small time steps are needed in order to obtain reliable results. This difficulty in Cremers' method originates from the fact that at small values of viscosity, the motion of the solute particle in the potential well is highly oscillatory (or undamped) and it is very difficult to follow the time evolution of $P_e(x, t)$ numerically. In contrast, the series solution (2.17) is exceedingly simple for small viscosity, but becomes awkward at very large viscosity. This is due to the fact that at large viscosity we need a large number of Hermite polynomials which are not appropriate for describing a positive definite function such as our probability distribution function $P_e(x, t)$. This is a well-known difficulty in the numerical solution of reaction rates.⁹

In order to carry out explicit calculations, we need numerical values for a number of quantities: the friction coefficient ζ , the reduced mass μ , the initial position x_0 on the excited surface, the parameter "a" of the sink function $S(x)$ (for cases B and C), the radiative rate constant k_r and the nonradiative rate constant k_{nr} . In the numerical calculations presented here, we have assumed stick boundary conditions for the rotational friction. For synchronous rotation of three phenyl groups, the total friction is given by

$$\zeta = 3\zeta_r, \quad (3.1)$$

and

$$\zeta_r = 8\pi\eta R^3, \quad (3.2)$$

where η is the zero frequency shear viscosity and R is the hydrodynamic radius of the rotating group. In writ-

ing Eq. (3.2), we have assumed a spherical shape for the rotating phenyl groups. For more accurate results, one should consider a spheroid instead of a sphere but for qualitative purposes, this does not make any difference since the crucial factor is the proportionality between ζ and η . We have chosen R equal to 5 Å which approximately corresponds to the volume of a phenyl group (assumed spherical) of crystal violet. For the reduced mass μ , we take it equal to three times the moment of inertia of each phenyl group about its axis of rotation. These choices of ζ and μ imply that the assumed reactive motion is an average of the synchronous rotation of the three phenyl groups and that the stochastic forces on the three rings are independent of each other at all times. For ω , we have rather arbitrarily chosen values between 5.0×10^{11} and 5.0×10^{12} s⁻¹ in order to simulate relaxation both on shallow and on steep potential surfaces. In the absence of more precise experimental and theoretical data for ω , we do not have a way to estimate it. For the initial position x_0 on the excited surface, we have mostly worked with the value 0.1 which corresponds to six degrees, a value which seems reasonable. We have, of course, varied x_0 to study its effect on relaxation. For the sink parameter a , we have chosen a value of 0.01 and varied it to study its effect. For k_{nr} and k_r we have chosen values equal to 1.0×10^{12} and 1.0×10^9 s⁻¹, respectively. These values are consistent with the experiments on TPM dye relaxation at very low viscosities (when k_{nr} dominates) and at very large viscosities (when k_r dominates).

A. Viscosity dependence of fluorescence quantum yield

As noted after Eq. (2.14), the pinhole sink model predicts an inverse dependence of nonradiative rate on viscosity. This is an expected result because all that is needed for nonradiative relaxation is the arrival of the solute particle at the origin. In our model, the solute particle is basically undergoing a random walk type of diffusive motion on a potential surface and so the rate of diffusion is inversely proportional to viscosity. Therefore, at low viscosities, this model predicts an approximate linear viscosity dependence of the fluorescence quantum yield. However, at high viscosities when

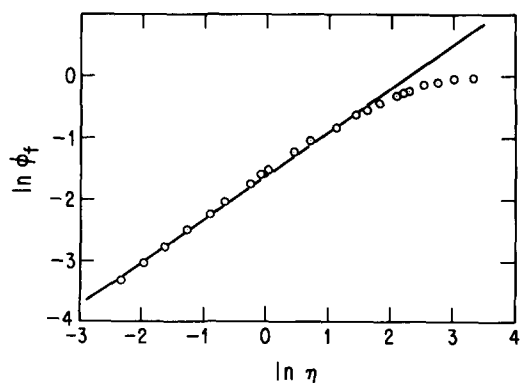


FIG. 1. Dependence of fluorescence quantum yield (ϕ_f) on viscosity (η) predicted by this theory for Gaussian sink. $a=0.01$, $x_0=0.1$, $k_{nr}=1.0 \times 10^{12}$, $k_r=1.0 \times 10^9$, $\omega=1 \times 10^{12}$. Viscosity (η) is in poise.

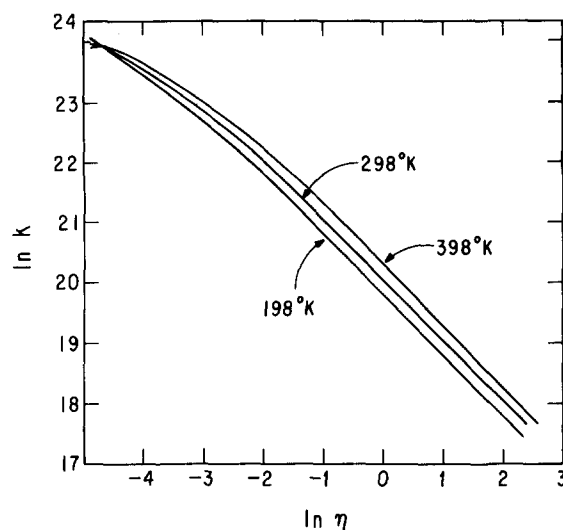


FIG. 2. Dependence of nonradiative rate (k) on viscosity (η) at three different temperatures. $a=0.01$, $x_0=0.1$, $k_{nr}=1.0 \times 10^{12}$, $k_r=0.0$, and $\omega=1 \times 10^{12}$. Viscosity (η) is in poise.

radiative relaxation competes with nonradiative relaxation, the fluorescence quantum yield is no longer proportional to viscosity, although the pure nonradiative part always retains the inverse viscosity dependence.

For Gaussian and Lorentzian sinks, a fractional viscosity dependence of fluorescence quantum yield is obtained. Figure 1 illustrates a representative calculation for a Gaussian sink. The slope of the plot of $\ln \phi_f$ vs $\ln \eta$ in the lower viscosity region is ~ 0.64 for the parameters chosen. The graph becomes flatter in the high viscosity region. Similar behavior is also obtained for the Lorentzian sink. In fact, a careful analysis of the data shows that the slope of the plot $\ln \phi_f$ vs $\ln \eta$ always changes with viscosity except at low viscosities, and it may not be meaningful to consider this slope as a constant independent of viscosity. In order to study the effect of viscosity on the nonradiative relaxation, we have carried out a calculation with $k_r=0$. Figure 2 shows the result of this calculation at three different temperatures. After a slow start at small viscosities, the nonradiative rate falls rapidly with viscosity and at large viscosities ($\eta \gtrsim 1$ P), the slope is approximately equal to -1 ; i. e., inverse viscosity dependence.

The fractional power viscosity dependence of fluorescence quantum yield can arise from two different sources: either from the influence of the position dependent sink on the nonradiative relaxation, or from the competition between the radiative and the nonradiative relaxations. At very low viscosities, the contribution of the radiative relaxation to the overall decay is negligible and the influence of the position dependence of the sink becomes important. For the pinhole sink case, we have $\phi_f \propto \eta^{-1}$ whereas for a position independent sink (i. e., pure radiative decay), $\phi_f \propto \eta^0$. Therefore, it is obvious that for Gaussian or Lorentzian sinks, we will have a fractional dependence of ϕ_f on viscosity. This is further confirmed by our finding that the fractional power depends on the width of the sink function. If the sink function is made narrower, then the fractional

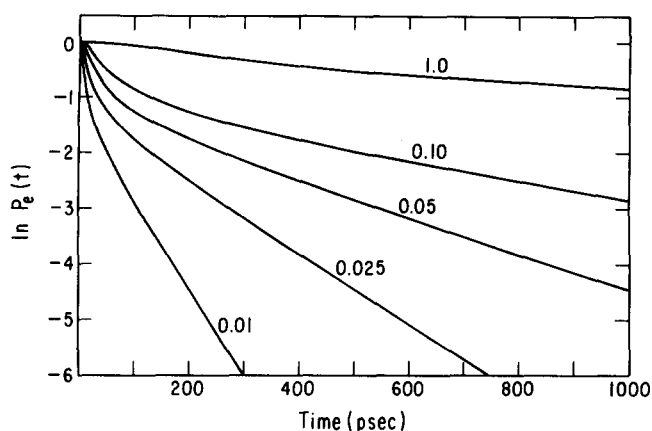


FIG. 3. The decay of excited state population for pinhole sink case at different viscosities. Viscosities (in poise) are indicated on the graph. $x_0 = 0.1$, $k_{nr} = 1.0 \times 10^{12}$, $k_r = 0.0$, and $\omega = 1.0 \times 10^{12}$.

power increases at low viscosities. As the viscosity of the solvent is increased, the contribution from the radiative part increases. At high viscosity, although the nonradiative rate itself becomes inversely proportional to viscosity, the radiative part makes the dependence of ϕ_f on η weaker, giving rise to a fractional power less than unity. However, in the intermediate viscosity regime where both damping of solute motion and radiative decay are significant, both these factors influence the dependence of fluorescence quantum yield on viscosity. In order to separate these effects, it might be useful to analyze the viscosity dependence of only the nonradiative decay from experimental data rather than the quantum yield.

It is interesting to contrast the fractional viscosity dependence obtained in the present zero barrier case with that obtained in our earlier studies of photochemical isomerization in the presence of a significant internal barrier.^{4,5} In the latter case, a fractional viscosity dependence is obtained only as a result of the breakdown of the ordinary hydrodynamic approximation for the friction, and generalized hydrodynamics has to be used for the explanation of the viscosity dependence of the rate.¹⁵ In the present zero barrier case, the fractional viscosity dependence arises quite naturally within the ordinary hydrodynamic model for the friction. Our study seems to indicate that this dependence arises from two factors: competition between radiative and nonradiative relaxation and from the position dependence of the sink function $S(x)$.

The fractional power α depends on the parameters ω , a , and x_0 which enter naturally into this theory. The value of α depends strongly on ω , the frequency of the (assumed) harmonic surface. If ω is decreased, then α also decreases which is obviously due to the greater importance of k_r . The same effect is seen if x_0 is increased or a is decreased.

Thus, our study indicates that the fractional power α depends on several physical quantities which are determined by the particular molecule and experiment under study. Further theoretical and experimental investiga-

tions with an aim to characterize the influence of these parameters are required to give a better understanding of the viscosity dependence of fluorescence quantum yield in systems where the barrier height is low or negligible.

B. Time dependence of the excited state population decay

In general the decay behavior of $P_e(t)$, for all cases studied, is rather strongly dependent on the viscosity range. For the pinhole sink case, the decay behavior is governed by the ratio t/η and the decay is, in general, nonexponential. For the cases of coordinate dependent sinks, the decay is single exponential at low viscosities, but becomes nonexponential at large viscosities.

Figure 3 shows $\ln P_e(t)$ vs time for several different viscosities in the pinhole sink case. At low viscosities ($\eta \sim 0.01$ P), there is a rapid initial decay which is followed by a slower exponential decay at longer times. At intermediate viscosities ($\eta \gtrsim 0.1$ P), the decay curve has three regions; at very short time ($t \lesssim 20$ ps for this particular calculation), the decay is rather slow which is then followed by a fast decay in the intermediate time region. The decay becomes exponential at long times. At large viscosities ($\eta \gtrsim 1$ P), the nonradiative decay is very slow though it still retains the three regions of different slopes.

The form of the curves in Fig. 3 can be interpreted with the use of Fig. 4, where the distribution function $P(x, t)$ is shown at three different times, for the case of the pinhole sink at the origin and $\eta = 0.1$ P. The area under each $P(x, t)$ curve represents the total population remaining on the excited surface after time t and the position of the base line of each curve represents the average potential energy at that particular time. In the pinhole sink case there can be no population decay until the distribution has broadened sufficiently to reach the position of the sink (i. e., the origin). Thus, in the calculation shown in Fig. 4, at 5 ps the distribution has broadened considerably, but all the molecules are still present on the excited state surface, and there has been no decay. Once the distribution has traveled down the potential surface and broadened enough to reach the

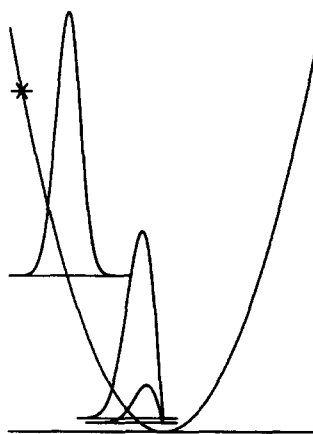


FIG. 4. Distribution function $P(x, t)$ at three different times for pinhole sink and for $\eta = 0.1$ P. The * marks the initial excitation at x_0 .

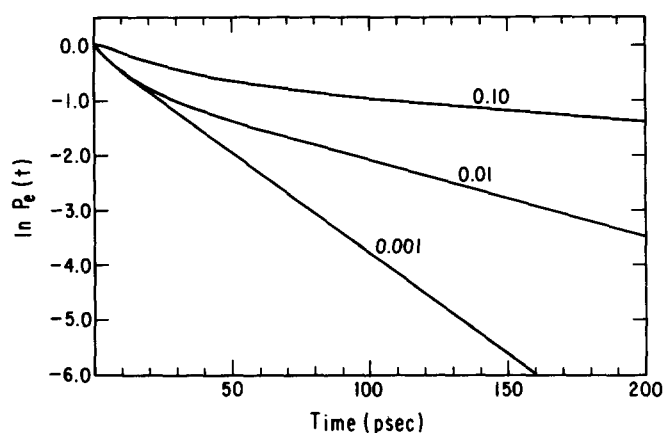


FIG. 5. The decay of excited state population for a Gaussian sink. Parameters are the same as in Fig. 2. Viscosities (in poise) are indicated on the graph.

position of the sink, very rapid decay takes place and the distribution becomes asymmetric. The decay at this stage is rapid because the distribution is still centered around a rather high position on the potential surface so the rate of fall is rapid and there are rapidly increasing numbers of molecules lying above the sink. At longer times, the distribution moves at a slower speed toward the origin and a steady state is reached. This gives rise to the long time exponential decay observed in Fig. 3. Figures 5 and 6 show the decay curve $P_e(t)$ for the Gaussian sink function for several different viscosities. The behavior for the Lorentzian sink is quite similar and is not plotted separately. For low viscosities, the decay becomes exponential after an initial sharp decay (Fig. 5). As viscosity is progressively increased, the decay becomes nonexponential and at large viscosity ($\eta \approx 1$ P), the decay is nonexponential except at very long times when it becomes roughly exponential (Fig. 6).

We interpret the above results in the following way: in the low viscosity regime, the initial delta function distribution broadens slowly and retains a sharply peaked Gaussian form for a rather long time (of the order of several hundred ω^{-1}). During this time, the distribution oscillates back and forth on the potential surface and it decays by a certain amount each time it passes through the origin where the sink function is peaked. The probability of decay is therefore proportional to the height of the distribution function and also to the amount of time it spends near the origin. At low viscosities, the latter factor is weakly time dependent and therefore the former factor dominates. This implies that the rate of change of $P_e(t)$ is proportional to $P_e(t)$, giving rise to an exponential decay.

But as the viscosity is increased, the motion on the potential surface becomes damped within a short time (within a few ω^{-1}) and the distribution $P(x, t)$ also quickly becomes broad. The rate determining step in the decay of $P_e(t)$ is then the time of travel of the distribution from its initial position to the origin. Since different parts of the broad distribution travel at different speeds, they arrive near the origin at different times and this

gives rise to a nonexponential decay. In other words, the rate of decay of $P_e(t)$ is never proportional to $P_e(t)$ except, perhaps, at very long times when the distribution is localized near the origin and decays at a rate determined solely by the sink function and k_{nr} .

C. Temperature dependence of the decay rate at constant viscosity

For the pinhole sink, the temperature dependence of the decay rate at constant viscosity is straightforward. Decay can only occur from the minimum of the potential surface and the rate limiting step is thus the time taken to reach the minimum from the initial configuration. As the temperature is increased the kinetic energy of the particle is increased and thus the minimum is reached more rapidly. This is true at all viscosities and so the constant viscosity activation energy will be positive in all cases.

For the position dependent sink, the situation is more subtle. In this case the particle oscillates in the potential well for sometime before decaying. At low viscosities this oscillation persists for many passages through the potential minimum. (Of course there is some probability of decay on each passage.) Now the overall decay rate is determined by the length of time the particle spends on the region of the surface where the decay probability is significant. At higher temperatures, the amplitude of the oscillation will be larger and the particle will have a lower probability of decay. Put in another language, in the low viscosity case, at higher temperatures the population of levels with longer lifetimes is increased and thus the average rate of decay is decreased. Thus, for small viscosities, the overall decay rate decreases with increasing temperature and the activation energy at constant viscosity will appear to be negative.

At high viscosities, i. e., when $(\mu/\xi) < \omega^{-1}$, the picture changes. In this case, the rate determining step is the time taken to reach the region of rapid decay. The particle is so heavily damped that it will not oscillate as in the low viscosity range. Now as the temperature is in-

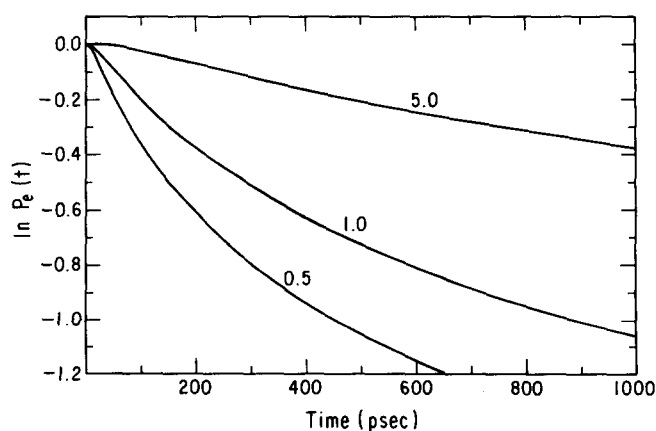


FIG. 6. The decay of excited state population for Gaussian sink. Viscosities (in poise) are indicated on the graph. Other parameters are the same as in Fig. 2.

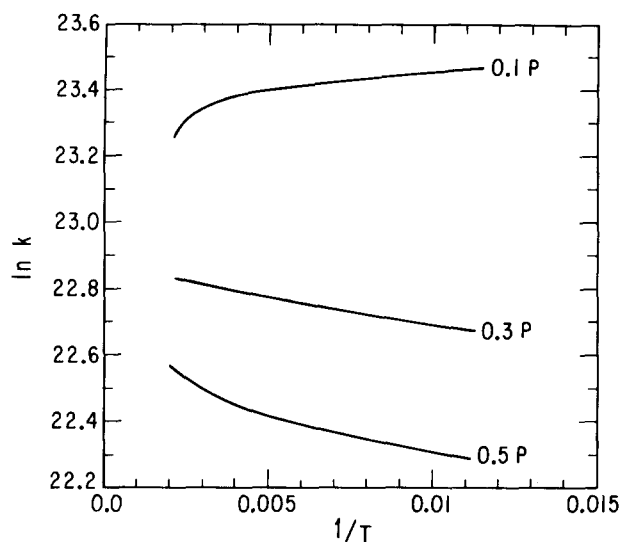


FIG. 7. The temperature dependence of the nonradiative rate showing the crossover from negative to positive activation energy as viscosity is increased from very low values. $\alpha=0.001$, $x_0=0.1$, $\omega=3 \times 10^{12}$, $k_{nr}=10^{12}$, $k_r=0.0$. Viscosities (in poise) are indicated on the graph.

creased the kinetic energy of the particle is increased and the region of rapid decay is reached more rapidly. In the alternative language, increasing temperature broadens the distribution about the critical configuration and leads to progressively greater population of the rapidly decaying levels. Thus, in the large viscosity case, as in the pinhole sink case, the overall rate of decay increases with increasing temperature. Now the constant viscosity activation energy will be positive.

The intuitive considerations presented above are confirmed by the numerical calculations. Figure 7 shows Arrhenius plots for a Lorentzian sink at 10, 30, and 50 cp. The crossover from negative to positive activation energy between 10 and 30 cp is clearly shown by the calculation. Similar results are found for the Gaussian sink case and for a wide range of values of ω and the sink half-width, although, of course, the precise viscosity at which the switch over occurs depends on these parameters. As noted in the Introduction, recent data of Gillbro and Sundström for ethyl violet at 5 and 10 cp indicate a small but definite ($E_0 = -0.8$ kcal/mol) decrease in rate with increasing temperature.²⁹ It will be fascinating to see if the switch over to positive E_0 can be observed in the TPM dyes.

D. Influence of excitation wavelength

The decay of the excited state population function $P_e(t)$ depends²⁸ on the wavelength of excitation due to the obvious fact that light of different wavelengths will excite the molecule to different positions on the excited state potential surface. In our model this fact enters through x_0 , the initial position of the solute particle. For long wavelength excitation, x_0 will tend to be smaller than at short wavelengths. We have studied this dependence of $P_e(t)$ on x_0 , and find that the decay at constant viscosity becomes slower when x_0 is increased, as expected. The change in decay is, however, not uni-

form as x_0 is increased, being smaller at large values of x_0 .

IV. CONCLUSION

Let us first summarize the main results of this paper. We have developed a new theory to explain the viscosity dependence of the relaxation behavior of TPM dyes in solution. Since the electronic relaxation in these dyes involves an insignificant activation barrier, we have modeled the relaxation as the motion of a solute particle on a potential surface without any barrier. In our model, the decay of the excited state population arises from a position dependent sink in the potential surface. Although the idea of a sink as the source of the excited state population decay is not new, we believe that ours is the first theoretical study which treats the Brownian dynamics in a consistent way. We have shown that many of the features of the TPM dye relaxation are consistent with our model. We believe our model represents an improved description of the photophysics of these molecules over that provided by the models of Förster and Hoffmann¹⁸ and of Cremers.¹⁹ In particular, we mention the fractional viscosity dependence of the fluorescence quantum yield, the change in form of the excited state decay from single through double to multiple exponential, and the apparent negative activation energy at constant viscosity. The model offers predictions of a crossover to positive activation energy at higher viscosity, of subtle effects resulting from changes in excitation wavelength, and of the detailed form of the time dependence of the population decay. Our model should be applicable to a wide range of systems which show coordinate dependent relaxation processes, but lack an internal barrier to the reactive motion. Since the well-known Kramers theory of chemical reactions is valid only for a high activation barrier, the present theory of reaction in the absence of any barrier may be regarded as complementary to Kramers' theory.

In the present work, we have not attempted a quantitative interpretation of the TPM data, but rather concentrated on interpreting the striking qualitative features of the photophysics of these interesting molecules. Quantitative calculation will require reliable values for the frequency ω of the potential surface and for the width and shape of the sink function. In some particular cases, it may also be necessary to consider specific solvent effects^{4,6} and the possible involvement of different tautomeric species.²⁸

The formalism presented in this paper is based on the Smoluchowski equation which may not be valid at very short times. However, our formalism can easily be extended to more general cases. One obvious generalization is to consider the phase space Fokker-Planck equation.⁸ For this case our equation of motion with the coordinate dependent sink takes the form

$$\frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} + \frac{F(x)}{\mu} \frac{\partial P}{\partial v} = \frac{\zeta}{\mu} \frac{\partial}{\partial v} \left(v + \frac{k_B T}{\mu} \frac{\partial}{\partial v} \right) P - k_{nr} S(x) P - k_r P, \quad (4.1)$$

where v is the velocity of the solute particle and $F(x)$ is

the force equal to $-\omega^2 x$ for a harmonic surface. This equation can in general be solved by expanding $P(x, v, t)$ in the eigenfunctions of the operator

$$\mathcal{L}_v = \frac{\zeta}{\mu} \frac{\partial}{\partial v} \left(v + \frac{k_B T}{\mu} \frac{\partial}{\partial v} \right) \quad (4.2)$$

which are again Hermite polynomials, but this time functions of velocity instead of coordinate. The rest of the calculation will be carried out numerically by the finite difference method.⁸

Another possible generalization is to consider a kinetic equation for the phase space distribution function $P(x, v, t)$ of the form

$$\frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} + \frac{F(x)}{\mu} \frac{\partial P}{\partial v} = -\mathcal{L}_c P(x, v, t) - k_{nr} S(x)P - k_r P, \quad (4.3)$$

where \mathcal{L}_c is a collision operator defined by the equation

$$\mathcal{L}_c P(x, v, t) = \int_{-\infty}^{\infty} dv' \{K(v, v')P(x, v, t) - K(v', v)P(x, v', t)\}. \quad (4.4)$$

Several simple forms are available in the literature for the kernel $K(v, v')$ to simulate the collisions of the solute particle with solvent molecules. One general form used by Skinner and Wolynes¹² is

$$K(v, v') = g \frac{\gamma + 1}{2\sqrt{\gamma}} \left(\frac{\beta\mu}{2\pi} \right)^{1/2} \times \exp \left\{ -\frac{\mu\beta}{8\gamma} [(\gamma - 1)v + (\gamma + 1)v']^2 \right\}, \quad (4.5)$$

where g is the average collision frequency defined by

$$g = \int_{-\infty}^{\infty} dv f_{eq}(v) \int_{-\infty}^{\infty} dv' K(v, v') \quad (4.6)$$

with

$$f_{eq}(v) = \left(\frac{\beta\mu}{2\pi} \right)^{1/2} \exp \left[-\frac{\beta\mu}{2} v^2 \right]$$

and γ is the solvent to solute mass ratio. The eigenvalues and eigenfunctions of this operator \mathcal{L}_c are given by Skinner and Wolynes who also pointed out that the Fokker-Planck operator (4.2) is a limiting form of \mathcal{L}_c in the limit $\gamma \rightarrow 0$. Equation (4.3) can thus be solved by expanding in the eigenfunctions of \mathcal{L}_c .

Thus, the formalism developed here can be generalized to consider a broader class of problems. We hope to consider some of these generalizations in a future publication.

ACKNOWLEDGMENTS

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- ¹F. E. Doany, B. I. Greene, Y. Liang, D. K. Negus, and R. M. Hochstrasser, in *Picosecond Phenomena II*, edited by R. M. Hochstrasser, W. Kaiser, and C. V. Shank (Springer, New York, 1980), p. 259.
- ²C. J. Tredwell and A. D. Osborne, *J. Chem. Soc. Faraday Trans. 2* **76**, 1627 (1980).
- ³S. P. Velsko and G. R. Fleming, *Chem. Phys.* **65**, 59 (1982).
- ⁴S. P. Velsko and G. R. Fleming, *J. Chem. Phys.* **76**, 3553 (1982).
- ⁵S. P. Velsko, D. H. Waldeck, and G. R. Fleming, *J. Chem. Phys.* **78**, 249 (1983).
- ⁶K. M. Keery and G. R. Fleming, *Chem. Phys. Lett.* **93**, 322 (1982).
- ⁷H. A. Kramers, *Physica* **7**, 284 (1940).
- ⁸S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).
- ⁹P. B. Visscher, *Phys. Rev. B* **13**, 3272 (1976); **14**, 347 (1976).
- ¹⁰D. Chandler, *J. Chem. Phys.* **68**, 2959 (1978).
- ¹¹J. Montgomery, D. Chandler, and B. Berne, *J. Chem. Phys.* **70**, 4056 (1979); J. Montgomery, S. Holmgren, and D. Chandler, *ibid.* **73**, 3688 (1980).
- ¹²J. L. Skinner and P. G. Wolynes, *J. Chem. Phys.* **69**, 2143 (1978); **72**, 4913 (1980).
- ¹³S. H. Northrup and J. T. Hynes, *J. Chem. Phys.* **69**, 5246 (1978); **68**, 3203 (1978); *Chem. Phys. Lett.* **54**, 244, 248 (1978).
- ¹⁴R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **73**, 2715 (1980); **74**, 4465 (1981).
- ¹⁵B. Bagchi and D. W. Oxtoby, *J. Chem. Phys.* **78**, 2735 (1983).
- ¹⁶R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **77**, 3736 (1982).
- ¹⁷B. Carmeli and A. Nitzan, *Phys. Rev. Lett.* **49**, 423 (1982); *J. Chem. Phys.* **76**, 5321 (1982).
- ¹⁸Th. Förster and G. Hoffmann, *Z. Phys.* **75**, 63 (1971).
- ¹⁹D. A. Cremers, Thesis, Washington State University, 1980.
- ²⁰V. Sundström, T. Gillbro, and H. Bergström, *Chem. Phys.* **73**, 439 (1982).
- ²¹D. A. Cremers and M. W. Windsor, *Chem. Phys. Lett.* **71**, 27 (1980).
- ²²M. D. Hirsch and H. Mahr, *Chem. Phys. Lett.* **60**, 299 (1979).
- ²³G. S. Beddard, T. Doust, and M. W. Windsor, in *Picosecond Phenomena II*, edited by R. M. Hochstrasser, W. Kaiser, and C. V. Shank (Springer, New York, 1980), p. 167.
- ²⁴E. P. Ippen, C. V. Shank, and A. Bergman, *Chem. Phys. Lett.* **38**, 611 (1976).
- ²⁵W. Yu, F. Pellegrino, M. Grant, and R. R. Alfano, *J. Chem. Phys.* **67**, 1766 (1977).
- ²⁶C. J. Mastrangelo and H. W. Offen, *Chem. Phys. Lett.* **46**, 588 (1977).
- ²⁷L. A. Brey, G. B. Schuster, and H. G. Drickamer, *J. Chem. Phys.* **67**, 2648 (1977).
- ²⁸J. M. Grzybowski, S. E. Sugamori, D. F. Williams, and R. W. Yip, *Chem. Phys. Lett.* **65**, 456 (1979).
- ²⁹T. Gillbro (private communication).
- ³⁰V. Sundström, T. Gillbro, and H. Bergström, in *Picosecond Phenomena III*, edited by K. B. Eisenthal, R. M. Hochstrasser, W. Kaiser, and A. Laubereau (Springer, New York, 1982), p. 242.
- ³¹J. Michl, *Topics in Current Chemistry* (Springer, Berlin, 1974), Vol. 46.
- ³²W. Feller, *An Introduction to the Probability Theory* (Wiley, New York, 1966).
- ³³E. W. Montroll and B. J. West, in *Fluctuation Phenomena*, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1979).
- ³⁴M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
- ³⁵B. Bagchi and D. W. Oxtoby, *J. Phys. Chem.* **86**, 2197 (1982).