

of r 's dependence on ν_F and the strong dependence of the N indices on r (through $n = r/2$) imply that ultimately *all of the N indices (except possibly h and g) are related to the size of the polymer chain at the critical point.* This is also an interpretation that says that the deviation of r from its ideal value of $1/2$ is not necessarily related to critical fluctuations.

On the other hand, there are indications that the nonclassical value of r is caused by critical fluctuations. One is the result that when the classical value of n , $n_0 = 1/4$, is rescaled by the intuitive scale factor ν_0/ν , where ν_0 is the classical value of ν , then the rescaled $n = n_0(\nu_0/\nu) = 1/8\nu = 0.198$, which is identical with the value of n obtained from $\Delta\phi$ data. Another similar indication is the observation that the experimental $n/\nu = 0.313 \pm 0.004$ equals $\nu/2$, which implies that $n = \nu^2/2$ and again equals 0.198. Explicit knowledge of r is not required to determine n in these

cases. The de Gennes approximations also suggest that the N indices are completely determined by the ϵ indices. Maybe the most convincing argument is the sum rule $d + g = (\delta - 1)b$. It implies that δ , which is a function of η only, is completely determined by the N indices d , g , and b . This result strongly infers that the N and ϵ indices are interrelated. The corollary is that critical fluctuations shift r to its nonclassical value. Hopefully, future theoretical studies will shed more light on this question.

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Rate Theories, Dephasing Processes, and Nonlinear Optical Line Shapes

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A unified dynamical theory of rate processes such as electron transfer in solution, which interpolates between the nonadiabatic and the adiabatic limits, is presented. The theory is based on expanding the rate perturbatively to fourth order in the nonadiabatic coupling V using the density matrix in Liouville space and performing a partial resummation. The present theory establishes a profound connection between rate theories and nonlinear optical spectroscopies. The rate to order V^2 is related to linear optics and the linear susceptibility $\chi^{(1)}$. The rate to order V^4 is related to the third-order susceptibility $\chi^{(3)}$. This connection arises since the same dephasing mechanisms which affect the optical line shapes also control the dynamics of rate processes. The frequency-dependent reaction rate is calculated and the dielectric continuum model for polar solvation is extended to incorporate the microscopic solvation structure via the wave vector and frequency dependent dielectric function $\epsilon(\mathbf{k}, \omega)$.

I. Introduction

In this article we discuss some recent theoretical developments¹⁻⁴ which establish a general and fundamental connection between rate processes⁵⁻¹⁴ and quantities being probed by nonlinear optical techniques.¹⁵⁻²¹ This connection arises since the same solvation dynamics underlying reaction rates such as electron transfer is also responsible for dephasing processes which affect spectral line shapes (e.g., absorption, fluorescence, pump probe, and four-wave mixing). Information obtained in optical measurements such as femtosecond spectroscopy may therefore be used to predict reaction rates. The present theory is based on the use of projection operator techniques in Liouville space.^{3,22-24} Bob Zwanzig was instrumental in developing these techniques and in pioneering the use of Liouville space (superoperator) methods in condensed-phase molecular dynamics. Our earlier results¹⁻⁴ are extended in this article in two ways. First we present a closed expression for the full frequency-dependent reaction rate (eq (II-12)). This expression allows us to define precisely the transition state even when simple rate equations do not hold and we need to use a generalized master equation instead. It is clearly shown how the transition state then occupies a larger volume in phase space. We further apply our rate theory to electron transfer (ET) in polar solvents and relate the solvent dynamics in ET processes to the complete wave vector and frequency-dependent dielectric function of the solvent $\epsilon(\mathbf{k}, \omega)$ (eq IV-7). This provides a natural extension of the conventional dielectric continuum theories.

II. The Frequency-Dependent Reaction Rate: Liouville Space Dynamics

We consider a reactive molecular system with two electronic levels ($|a\rangle$ and $|b\rangle$) undergoing a rate process such as electron

transfer or isomerization in solution. The total Hamiltonian is

$$H = H_0 + H_{\text{int}} \quad (\text{II-1})$$

where

$$H_0 = |a\rangle H_a \langle a| + |b\rangle H_b \langle b| \quad (\text{II-2a})$$

$$H_{\text{int}} = V(|a\rangle \langle b| + |b\rangle \langle a|) \quad (\text{II-2b})$$

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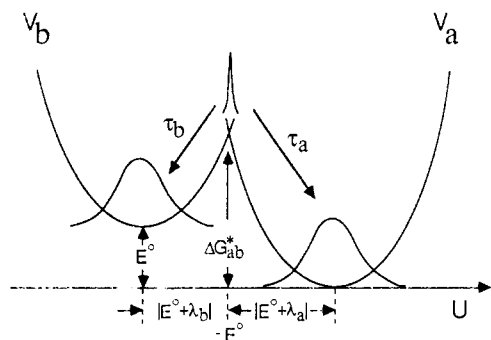


Figure 1. Solvation dynamics during a rate process. U is the solvation coordinate. V_a and V_b denote the adiabatic potential surfaces while λ_a and λ_b are the solvent reorganization energies for reactant and product, respectively. E^0 is the endothermicity, ΔG_{ab}^* is the activation free energy for the forward ($|a\rangle$ to $|b\rangle$) reaction. The solvent time scales τ_a and τ_b characterize the relaxation of a solvent fluctuation at the transition state (curve crossing $U = -E^0$) in the reactant and the product adiabatic surfaces, respectively. In the perturbative limit, the rate depends only on the single Marcus reorganization energy parameter $2\lambda = \lambda_a - \lambda_b > 0$.

We further introduce a macroscopic solvation coordinate U which is the key quantity in describing the solvent effect on the reaction rate

$$U \equiv H_b - H_a - E^0 \quad (\text{II-2c})$$

Here E^0 denotes the endothermicity (standard free energy) of the forward reaction in the absence of the solvent nuclear degrees of freedom. H_a and H_b represent nuclear degrees of freedom (both intramolecular and solvent) and V is the nonadiabatic coupling between the two reacting species (Figure 1). Equation II-2 can represent an electron-transfer process, in which case $|a\rangle$ and $|b\rangle$ denote the state of the system where the electron is on the donor and on the acceptor site and V is the exchange coupling. Alternatively, it can represent an isomerization whereby $|a\rangle$ and $|b\rangle$ represent the reactant and the product and V is the nonadiabatic coupling. The dynamics of the system may be calculated by solving the Liouville equation for its density matrix $\hat{\rho}$

$$d\hat{\rho}/dt = -i[H_0, \hat{\rho}] - i[H_{\text{int}}, \hat{\rho}] \quad (\text{II-3a})$$

and assuming that initially the system is in thermal equilibrium within the $|a\rangle$ state; i.e., $\hat{\rho}(0) = |a\rangle\rho_a\langle a|$, where we define

$$\rho_j \equiv \exp(-H_j/kT) / \text{Tr} \exp(-H_j/kT) \quad j = a, b \quad (\text{II-3b})$$

For brevity we set $\hbar = 1$ in this article, except in the final expressions for the rates. The probability of the system to be in the state $|j\rangle$ at time t , $P_j(t)$, may be obtained by calculating the diagonal density matrix element $\hat{\rho}_{jj}(t)$ and tracing it over all nuclear (intramolecular and solvent) degrees of freedom. This may be accomplished by using projection operator techniques in Liouville

space.^{1,22-24} In general, the system satisfies a generalized rate equation of the form

$$\frac{d}{dt} P_b(t) = \int_0^t d\tau \bar{K}(t-\tau) P_a(\tau) - \int_0^t d\tau \bar{K}'(t-\tau) P_b(\tau) \quad (\text{II-4})$$

$\bar{K}(\tau)$ and $\bar{K}'(\tau)$ are the generalized rates for the forward and for the reverse reactions, respectively. Performing a Laplace transform we introduce the generalized frequency-dependent rate for the forward reaction by

$$K(s) = \int_0^\infty dt \exp(-st) \bar{K}(t) \quad (\text{II-5})$$

The rate $K'(s)$ for the reverse reaction can be defined by a similar expression. Hereafter we shall focus on the forward reaction rate $K(s)$. Using Liouville space projection operators we have derived¹ an exact formal expression for $K(s)$. This expression may then be evaluated perturbatively in the nonadiabatic coupling. We have calculated $K(s)$ to fourth order in V , i.e.,

$$K(s) = C_2(s)(V^2/\hbar) - C_4(s)(V^2/\hbar)^2 + \dots \quad (\text{II-6})$$

and constructed a Padé approximant which provides a partial summation of the series to infinite order, resulting in

$$K(s) = \frac{(V^2/\hbar)C_2(s)}{1 + (V^2/\hbar)C_2(s)[\tau_a(s) + \tau_b(s)]} \quad (\text{II-7a})$$

with

$$C_4(s) = C_4^{(a)}(s) + C_4^{(b)}(s) \quad (\text{II-7b})$$

$$\tau_a(s) \equiv C_4^{(a)}(s)/C_2^2(s) \quad (\text{II-7c})$$

$$\tau_b(s) \equiv C_4^{(b)}(s)/C_2^2(s) \quad (\text{II-7d})$$

$C_4(s)$ has two distinct contributions, which are related to the solvation dynamics described by the H_a and the H_b Hamiltonians, respectively. We have denoted these two contributions by $C_4^{(a)}(s)$ and $C_4^{(b)}(s)$, respectively. Consequently, $\tau_a(s)$ and $\tau_b(s)$ represent characteristic solvent time scales, when the system is in the states $|a\rangle$ and $|b\rangle$, respectively. The precise significance of these quantities will be discussed below. We have derived closed expressions for $C_2(s)$, $C_4^{(a)}(s)$, and $C_4^{(b)}(s)$. The calculation is based on the assumption of a separation of time scales between the diagonal elements of the density matrix, $\hat{\rho}_{aa}$ and $\hat{\rho}_{bb}$, and the off-diagonal elements (coherences), $\hat{\rho}_{ab}$ and $\hat{\rho}_{ba}$. The latter are usually subject to fast *dephasing processes* which allow us to make a short-time approximation for their time evolution. This approximation is usually well justified for solvated molecular systems.⁴ The s scale over which $K(s)$ varies is determined by the solvation time scales and the activation barrier height. The values of s relevant in the generalized master equation are approximately equal to the inverse reaction time scale (the rate). Reactions with large activation barriers are slow and a separation of time scales is expected to hold. We can then neglect the s dependence of $K(s)$ and replace it with $K(s=0)$. In this case the system satisfies an ordinary rate equation with the rate constant $K \equiv K(s=0)$. For barrierless reactions this separation of time scales may not hold. In that case we need to retain the s dependence of $K(s)$. For clarity in the presentation and the subsequent analysis we shall first consider the ordinary rate $K(s=0)$ whose calculation requires the evaluation of $C_2(0)$ and $C_4^{(j)}(0)$, $j = a, b$. These are related to a two-time correlation function and a four-time correlation function of the solvation coordinate, respectively. In this article we shall explore the classical approximation which is based on the separation of solvation time scales. There are two distinct types of solvent dynamical processes which affect electron-transfer reactions. One is the rapid solvent dephasing taking place when the system is in an electronic coherence between the reactant and the product (off-diagonal element of the density matrix). The other is the slower solvent relaxation following the charge rearrangement. The fast dephasing makes the relevant time scale in which the system can be found in a coherence to be very short and allows us to ignore the slower solvent motions during the

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period. When this approximation is made we find that the rate may be expressed in terms of two auxiliary quantities. The first is $\sigma_j(x)$, which is the probability distribution of the solvation coordinate U when the system is in state j :

$$\sigma_j(x) \equiv \langle \delta(x-U)\rho_j \rangle \quad j = a, b \quad (\text{II-8})$$

The second quantity is the conditional probability for the solvation coordinate to have the value x at time t , given that it had the value y at $t = 0$, and the system is in the state j , i.e.,

$$W_j(x,t;y) \equiv [\sigma_a(y)]^{-1} \langle \delta[x-U_j(t)]\delta(y-U)\rho_a \rangle \quad j = a, b \quad (\text{II-9})$$

Here U is the solvation coordinate (eq II-2c) and

$$U_j(t) = \exp(iH_j t) U \exp(-iH_j t) \quad j = a, b \quad (\text{II-10})$$

Note that by definition, initially $W_j(x,0;y) = \delta(x-y)$, and at long times $W_j(x,\infty;y) = \sigma_j(x)$. We have derived the following expressions for $C_2(0)$ and $C_4(0)$ in terms of σ_j and W_j :¹

$$C_2(0) = 2\pi\sigma_a(-E^\circ) \quad (\text{II-11a})$$

$$C_4^{(0)}(0) = 4\pi^2\sigma_a(-E^\circ) \int_0^\infty dt [W_j(-E^\circ, t; -E^\circ) - W_j(-E^\circ, \infty; -E^\circ)] \quad (\text{II-11b})$$

The nature of the rate process is determined by the *adiabaticity parameter* $\nu \equiv 2\pi(V^2/\hbar)\sigma_a(-E^\circ)(\tau_a + \tau_b)$ with $\tau_j \equiv \tau_j(0)$. The rate constant $K \equiv K(s=0)$ can now be obtained by substituting eq II-11 into II-7. When $\nu \ll 1$ the reaction is nonadiabatic and we have $K_{NA} = 2\pi V^2\sigma_a(-E^\circ)$. In the opposite limit $\nu \gg 1$ the reaction is adiabatic and the rate is given by $K_{AD} = (\tau_a + \tau_b)^{-1}$. The transition from the nonadiabatic to the adiabatic limit has been discussed previously by many authors.^{8,9,12} The present derivation, which starts with the nonadiabatic representation and is based on the evaluation of the four-time correlation function, provides an unconventional viewpoint for interpreting the expression. Moreover, it establishes the connection with nonlinear optical spectroscopy (see section V). In the semiclassical (static) approximation (eq II-7 and II-11) the nonadiabatic rate constant K_{NA} depends on the value of $\sigma_a(x)$ at one point $x = -E^\circ$. That point is the curve crossing, or the transition state (Figure 1), $U = -E^\circ$ at which the thermal fluctuations of the solvation coordinate make the reaction feasible. K_{NA} could be simply obtained by using the Fermi golden rule. When the adiabaticity parameter is sufficiently large, the reaction becomes adiabatic, and the rate is equal to $(\tau_a + \tau_b)^{-1}$. τ_a and τ_b are the characteristic solvent time scales which control the adiabaticity of the rate process. τ_b is the average time it takes for a solvent fluctuation at the transition state ($U = -E^\circ$) to relax to thermal equilibrium in the $|b\rangle$ state, whereas τ_a is the average time it takes for the same fluctuation to relax to thermal equilibrium in the $|a\rangle$ state. This is represented schematically in Figure 1. If these times are fast, the adiabaticity parameter ν vanishes and the rate process is nonadiabatic. As the solvent time scales become longer, ν increases, and a nonadiabatic rate will eventually turn adiabatic, with a rate equal to the proper inverse solvent time scale.¹

Let us consider now the complete frequency-dependent rate $K(s)$. It can be calculated by using the methodology of ref 1 and 2. We then obtain

$$C_2(s) = 2\pi \int_{-\infty}^{\infty} dx \frac{s/\pi}{(x + E^\circ) + s^2} \sigma_a(x) \quad (\text{II-12a})$$

$$C_4^{(0)}(s) = 4\pi^2 \int_0^\infty dt \exp(-st) \times \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \left(\frac{s/\pi}{(x + E^\circ) + s^2} \right) \left(\frac{s/\pi}{(y + E^\circ) + s^2} \right) \times \sigma_a(y) [W_j(x,t;y) - W_j(x,\infty;y)] \quad j = a, b \quad (\text{II-12b})$$

If we set $s = 0$ in eq II-12, the Lorentzian factors become δ functions and they reduce to eq II-11. Equations II-12 provide an interesting insight on transition-state theory. In the slow

reaction limit, the separation of time scales mentioned above exists, and the rate can be calculated by considering the transition state ($U = -E^\circ$) and using its equilibrium distribution $\sigma_j(-E^\circ)$ and the conditional probability $W_j(-E^\circ, t; -E^\circ)$ for the system to be in the transition state at time t given that it was there at $t = 0$. The configuration with $U = -E^\circ$ is thus the transition state for the rate process. In other words, in this limit the reaction barrier is high and sharp and the transition state can be defined precisely by one point on the free energy surface. When the separation of time scales does not hold, eq II-12 show that we need to average σ_j and W_j over a region of phase space whereby $U \approx -E^\circ \pm s$. *The transition state should now be viewed as the neighborhood of $U \approx -E^\circ \pm s$ rather than the precise regime where $U = -E^\circ$.* The size of this neighborhood is of the order of $s \approx K$, i.e., the inverse of the characteristic time scale of interest.

III. Gaussian Approximation for Reaction Rates

A useful approximation for the solvent quantities σ_j and W_j which appear in the semiclassical theory of solvation may be obtained by the cumulant expansion of eq II-8 and II-9 to second order in U . This approximation is equivalent to making the short-time approximation for the fast solvent dephasing time in the relevant response functions.² The distribution of the solvation coordinate assumes, in this case, a Gaussian form

$$\sigma_j(x) = \frac{1}{(2\pi)^{1/2}\Delta_j} \exp\left[-\frac{(x - \lambda_j)^2}{2\Delta_j^2}\right] \quad j = a, b \quad (\text{III-1})$$

and the conditional probabilities of the solvation coordinate are $W_a(x,t;y) =$

$$\{2\pi\Delta_a^2[1 - M_a^2(t)]\}^{-1/2} \exp\left\{-\frac{[x - \lambda_a - M_a(t)(y - \lambda_a)]^2}{2\Delta_a^2[1 - M_a^2(t)]}\right\} \quad (\text{III-2a})$$

$$W_b(x,t;y) = \{2\pi[\Delta^2(t) - \Delta_a^2 M_b^2(t)]\}^{-1/2} \times \exp\left\{-\frac{[x - \lambda(t) - M_b(t)(y - \lambda_a)]^2}{2[\Delta^2(t) - \Delta_a^2 M_b^2(t)]}\right\} \quad (\text{III-2b})$$

Here we have defined²⁵ the static quantities representing the coupling strength of the system to the solvent

$$\lambda_j \equiv \text{Tr} [U\rho_j] \quad (\text{III-3a})$$

$$\Delta_j^2 \equiv \text{Tr} [U^2\rho_j] - \{\text{Tr} [U\rho_j]\}^2 \quad (\text{III-3b})$$

and the dynamical quantities

$$\lambda(t) \equiv \text{Tr} [U_b(t)\rho_a] \quad (\text{III-4a})$$

$$\Delta^2(t) \equiv \text{Tr} [U_b^2(t)\rho_a] - \{\text{Tr} [U_b(t)\rho_a]\}^2 \quad (\text{III-4b})$$

$$M_j(t) \equiv \Delta_a^{-2} \{\text{Tr} [U_j(t)U\rho_a] - \text{Tr} [U_j(t)\rho_a] \text{Tr} [U\rho_a]\} \quad j = a, b \quad (\text{III-4c})$$

$U_j(t)$ is defined by eq II-10. $\lambda(t)$ represents the time-dependent solvent reorganization energy^{9,25} when the system, initially with density matrix ρ_a , undergoes a time evolution governed by H_b . $\Delta(t)$ denotes the variance of the solvation coordinate during this time evolution. λ_a and λ_b denote the coupling strength of the solvent to the system in the states $|a\rangle$ and $|b\rangle$, respectively, and $\lambda(0) = \lambda_a$ and $\lambda(\infty) = \lambda_b$. Similarly $\Delta(0) = \Delta_a$ and $\Delta(\infty) = \Delta_b$. $M_j(t)$ is the normalized correlation function of the solvation coordinate with $M_j(0) = 1$ and $M_j(\infty) = 0$. The calculation of the solvent quantities (eq III-4) for specific model systems can be done using a variety of methods including molecular dynamics and diagrammatic techniques.²⁶ In polar solvents, these quantities may be related approximately to the solvent dielectric function.^{4,27}

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This will be shown in the next section. These quantities may also be evaluated by using a perturbation expansion in the system-solvent interaction strength. To lowest order, we have²⁵

$$\lambda(t) = \lambda' + \lambda[2M(t) - 1] \quad (\text{III-5a})$$

$$\Delta^2(t) = \Delta^2 \quad (\text{III-5b})$$

$$M_j(t) = M(t) \quad (\text{III-5c})$$

Here

$$\lambda' \equiv \frac{1}{2}(\lambda_a + \lambda_b) \quad (\text{III-6a})$$

$$\lambda \equiv \frac{1}{2}(\lambda_a - \lambda_b) \quad (\text{III-6b})$$

$$\Delta^2 \equiv \langle U^2 \rangle - \langle U \rangle^2 \quad (\text{III-6c})$$

$$M(t) \equiv \Delta^{-2}[\langle U(t)U \rangle - \langle U \rangle^2] \quad (\text{III-6d})$$

with

$$U(t) \equiv \exp(iH_B t)U \exp(-iH_B t) \quad (\text{III-7})$$

Here H_B represents the pure solvent (bath) Hamiltonian in the absence of solute molecules. In eq III-6, $\langle \rangle$ denotes the ensemble average over all the solvent configurations. Within this approximation, the only relevant dynamical variable is $M(t)$, the normalized correlation function of the solvation coordinate with $M(0) = 1$ and $M(\infty) = 0$. λ' is the contribution of the solvation coordinate to the reaction free energy, $\Delta G^\circ = E^\circ + \lambda'$, (see eq III-10b) while λ is the solvent reorganization energy.⁹ Upon the substitution of eq III-5 and III-6 in eq III-1 and III-2 we get

$$\sigma_a(x) = (2\pi\Delta^2)^{-1/2} \exp\left[-\frac{(x - \lambda' - \lambda)^2}{2\Delta^2}\right] \quad (\text{III-8a})$$

$$W_a(x,t;y) = \{2\pi\Delta^2[1 - M^2(t)]\}^{-1/2} \times \exp\left\{-\frac{[x - \lambda' - \lambda - M(t)(y - \lambda' - \lambda)]^2}{2\Delta^2[1 - M^2(t)]}\right\} \quad (\text{III-8b})$$

$\sigma_b(x)$ and $W_b(x,t;y)$ can be obtained from eq III-8a and III-8b, respectively, by changing $-\lambda$ to λ . At high temperatures, the fluctuation dissipation theorem implies that

$$\Delta^2 = 2\lambda k_B T \quad (\text{III-9})$$

When eq III-8-III-9 are substituted in eq II-7 and II-11, the rate constant $K \equiv K(s=0)$ assumes the activated form

$$K = A \exp(-\Delta G^*_{ab}/k_B T) \quad (\text{III-10a})$$

where the activation free energy is

$$\Delta G^*_{ab} = \frac{(E^\circ + \lambda' + \lambda)^2}{4\lambda} \equiv \frac{(\Delta G^\circ + \lambda)^2}{4\lambda} \quad (\text{III-10b})$$

and the preexponential factor is

$$A = \frac{[\pi/(\lambda k_B T)]^{1/2}(V^2/\hbar)}{1 + [\pi/(\lambda k_B T)]^{1/2}(V^2/\hbar) \exp(-\Delta G^*_{ab}/k_B T)(\tau_a + \tau_b)} \quad (\text{III-10c})$$

The reverse reaction rate K' can be expressed in the similar way:

$$K' = A \exp(-\Delta G^*_{ba}/k_B T) \quad (\text{III-11})$$

Here the activation free energy ΔG^*_{ba} is given by the right-hand side of eq III-10b with replacing $\Delta G^\circ + \lambda$ by $\Delta G^\circ - \lambda$. The forward and reverse rates thus satisfy the detailed balance condition, which assures that the system relaxes to the correct thermal equilibrium at long times:

$$K/K' = \exp(-\Delta G^\circ/k_B T) \quad (\text{III-12})$$

IV. Electron Transfer and Dielectric Fluctuations in Polar Solvents

We shall now apply our rate theory to electron transfer in polar solvents. In this case the charge-transfer system couples to the dielectric fluctuations of the medium and we can derive simple expressions for the parameters λ , λ' , Δ , and $M(t)$. Let us denote the nuclear polarization of the solvent at point \mathbf{r} by $P(\mathbf{r})$. The system charge distribution when it is in the state $|j\rangle$ creates an electric field $D_j(\mathbf{r})$. The solvent-system interaction in the state $|a\rangle$ is then given by $-\int d\mathbf{r} D_a(\mathbf{r}) P(\mathbf{r})$ whereas in the state $|b\rangle$ it is $-\int d\mathbf{r} D_b(\mathbf{r}) P(\mathbf{r})$. The solvation coordinate (eq II-2c) is now given by

$$U = \int d\mathbf{r} D_{ab}(\mathbf{r}) P(\mathbf{r}) \quad (\text{IV-1})$$

where

$$D_{ab}(\mathbf{r}) \equiv D_a(\mathbf{r}) - D_b(\mathbf{r}) \quad (\text{IV-2})$$

Since the solvation coordinate is related to the solvent polarization, its dynamics may be related to the dielectric fluctuations of the solvent which are described by its polarization correlation function,²⁷

$$C_{pp}(\mathbf{k},t) = \int \langle P(\mathbf{r},t) P(\mathbf{0},0) \rangle \exp(i\mathbf{k}\cdot\mathbf{r}) d\mathbf{r} \quad (\text{IV-3})$$

We further introduce the static polarization structure factor $S(\mathbf{k}) \equiv C_{pp}(\mathbf{k},0)$. Equation III-6 then results in

$$\lambda' = \frac{1}{2} \int_0^{1/k_B T} d\eta \int d\mathbf{k} [|D_a(\mathbf{k})|^2 - |D_b(\mathbf{k})|^2] C_{pp}(\mathbf{k},-i\eta) \quad (\text{IV-4a})$$

$$\lambda = \frac{1}{2} \int_0^{1/k_B T} d\eta \int d\mathbf{k} |D_{ab}(\mathbf{k})|^2 C_{pp}(\mathbf{k},-i\eta) \quad (\text{IV-4b})$$

$$\Delta^2 = \int d\mathbf{k} |D_{ab}(\mathbf{k})|^2 S(\mathbf{k}) \quad (\text{IV-4c})$$

$$M(t) = \frac{1}{\Delta^2} \int d\mathbf{k} |D_{ab}(\mathbf{k})|^2 C_{pp}(\mathbf{k},t) \quad (\text{IV-4d})$$

Here

$$D_j(\mathbf{k}) \equiv (2\pi)^{-3/2} \int d\mathbf{r} \exp(i\mathbf{k}\mathbf{r}) D_j(\mathbf{r}) \quad j = a, b, \text{ and } ab \quad (\text{IV-5})$$

A general relationship exists between the polarization correlation function $C_{pp}(\mathbf{k},t)$ and the wave vector and frequency-dependent dielectric function of the solvent, $\epsilon(\mathbf{k},\omega)$. This relationship is based on the fluctuation dissipation theorem. The relevant frequency scale of $\epsilon(\mathbf{k},\omega)$ is typically less than 1 cm^{-1} , while at room temperature $k_B T \approx 200 \text{ cm}^{-1}$. In this case the high-temperature limit is valid and we obtain^{1,27}

$$C_{pp}(\mathbf{k},t) \cong \frac{k_B T}{i8\pi^2} \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \exp(i\omega t) \left[\frac{1}{\epsilon(\mathbf{k},\omega)} - \frac{1}{\epsilon(\mathbf{k},0)} \right] \quad (\text{IV-6a})$$

so that

$$S(\mathbf{k}) \cong \frac{k_B T}{i8\pi^2} \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \left[\frac{1}{\epsilon(\mathbf{k},\omega)} - \frac{1}{\epsilon(\mathbf{k},0)} \right] \\ = \frac{k_B T}{4\pi} \left[\frac{1}{\epsilon(\mathbf{k},\infty)} - \frac{1}{\epsilon(\mathbf{k},0)} \right] \quad (\text{IV-6b})$$

We then get

$$\lambda' = \frac{1}{8\pi} \int d\mathbf{k} [|D_a(\mathbf{k})|^2 - |D_b(\mathbf{k})|^2] \left[\frac{1}{\epsilon(\mathbf{k},\infty)} - \frac{1}{\epsilon(\mathbf{k},0)} \right] \quad (\text{IV-7a})$$

$$\lambda = \frac{1}{8\pi} \int d\mathbf{k} |D_{ab}(\mathbf{k})|^2 \left[\frac{1}{\epsilon(\mathbf{k},\infty)} - \frac{1}{\epsilon(\mathbf{k},0)} \right] \quad (\text{IV-7b})$$

$$M(t) = \frac{1}{2\pi i} \frac{\int dk |D_{ab}(\mathbf{k})|^2 \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \exp(i\omega t) \left[\frac{1}{\epsilon(\mathbf{k},\omega)} - \frac{1}{\epsilon(\mathbf{k},0)} \right]}{\int dk |D_{ab}(\mathbf{k})|^2 \left[\frac{1}{\epsilon(\mathbf{k},\infty)} - \frac{1}{\epsilon(\mathbf{k},0)} \right]} \quad (\text{IV-7c})$$

Usually the full wave vector and frequency-dependent dielectric function is not known. In most cases we readily have only its long-wavelength limit $\epsilon(\mathbf{k}=0,\omega) \equiv \epsilon(\omega)$. If we assume that $\epsilon(\mathbf{k},\omega)$ is independent of \mathbf{k} which amounts to neglecting the local solvent structure, eq IV-7 reduce to the results of the dielectric continuum approximation:

$$\lambda' = \frac{1}{8\pi} \int dk [|D_a(\mathbf{k})|^2 - |D_b(\mathbf{k})|^2] [1/\epsilon_{\infty} - 1/\epsilon_0] \quad (\text{IV-8a})$$

$$\lambda = \frac{1}{8\pi} \int dk |D_{ab}(\mathbf{k})|^2 [1/\epsilon_{\infty} - 1/\epsilon_0] \quad (\text{IV-8b})$$

$$M(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \exp(i\omega t) \frac{1/\epsilon(\omega) - 1/\epsilon_0}{1/\epsilon_{\infty} - 1/\epsilon_0} \quad (\text{IV-8c})$$

Here ϵ_0 is the static ($\omega = 0$), and ϵ_{∞} is the high-frequency (optical) value of $\epsilon(\omega)$. Equations IV-7 or IV-8 provide closed expressions for the response functions (eq III-6) and relate them to the solvent dielectric function. This relation, together with eq III-8 and the formulation in section II, constitute a theoretical basis for the study of the effect of solvent dielectric fluctuations on the electron-transfer rate. If we approximate the electric charge distribution of the charge-transfer system by an electric dipole in a hard-sphere cavity, eq IV-8b yields

$$\lambda = R^{-3} |\mu_b - \mu_a|^2 (1/\epsilon_{\infty} - 1/\epsilon_0) \quad (\text{IV-9})$$

Here μ_a and μ_b are the permanent dipole moments of the system in its $|a\rangle$ and $|b\rangle$ electronic states, respectively. R is the effective hard-sphere radius. The solvent dynamics are contained in $M(t)$, which is the normalized correlation function of the solvation coordinate. Equations IV-8c and IV-9 are the basis for the Marcus theory of electron transfer⁵ and generalize it to a solvent with an arbitrary dielectric function $\epsilon(\mathbf{k},\omega)$. It has been argued recently by Kakitani and Mataga²⁸ that when gross changes occur in charge type or cavity type in the course of reaction, the solvation coordinate may have a very different interaction with the system in the two states $|a\rangle$ and $|b\rangle$. In particular, Δ_a and Δ_b (eq III-3b), which are related to the line width of the absorption and the fluorescence line shapes, respectively, in the semiclassical theory (cf. section V), and which give the harmonic frequencies of the solvation coordinate in the two states, may be very different. In such cases we cannot use eq III-5 and III-6, which are based on the lowest perturbative expansion (eq III-5) of the solvent-solute interaction; we need to use the more general results of section III (eq III-1-III-4). In concluding this section, we shall consider the solvation dynamics in a Debye solvent in the dielectric continuum limit with a single relaxation time τ_D :

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau_D} \quad (\text{IV-10})$$

Substituting eq IV-10 into (IV-8c), we obtain^{1,4}

$$M(t) = \exp(-t/\tau_L) \quad (\text{IV-11})$$

with τ_L being the longitudinal solvent time scale

$$\tau_L = \tau_D(\epsilon_{\infty}/\epsilon_0) \quad (\text{IV-12})$$

V. Relation to Ultrafast Pump-Probe and Fluorescence Spectroscopy

We shall consider now the analogous model system for linear and nonlinear optical spectroscopy. Consider a molecule with a

ground electronic state $|a\rangle$ and a single excited electronic state $|b\rangle$, interacting with the electromagnetic field. The Hamiltonian is given by eq II-1, but H_{int} represents the interaction with a classical electromagnetic field $E(\mathbf{r},t)$:

$$H_{\text{int}} = -\mu E(\mathbf{r},t)(|a\rangle\langle b| + |b\rangle\langle a|) \quad (\text{V-1})$$

Here H_a and H_b represent the Hamiltonians for the intramolecular (vibration, rotation) and for the solvent degrees of freedom, when the system is in the electronic states $|a\rangle$ and $|b\rangle$, respectively, and μ is the electronic transition dipole matrix element. The optical properties of the system may be related to the time-dependent polarization $P(\mathbf{r},t)$. The polarization is usually expanded in a Taylor series in E

$$P(\mathbf{r},t) = P^{(1)}(\mathbf{r},t) + P^{(2)}(\mathbf{r},t) + P^{(3)}(\mathbf{r},t) + \dots \quad (\text{V-2})$$

$P^{(1)}$ is related to the linear optical properties, whereas $P^{(2)}$, $P^{(3)}$, etc., constitute nonlinear contributions.³ In an isotropic medium $P^{(2)} = 0$; we shall therefore focus on $P^{(1)}$ and $P^{(3)}$. The polarization is calculated by taking the expectation value of the dipole operator $\hat{\mu} \equiv \mu(|a\rangle\langle b| + |b\rangle\langle a|)$, after $\hat{\rho}$ is calculated to the desired order (first order for $P^{(1)}$, third order for $P^{(3)}$). In a steady-state experiment we take $E(\mathbf{r},t)$ to be the sum of a few monochromatic fields. $P^{(1)}$ and $P^{(3)}$ are then related to the optical susceptibilities $\chi^{(1)}$ and $\chi^{(3)}$, respectively. We have shown² that the same terms which contribute to $C_2(s)$ enter in the calculation of $P^{(1)}$ and the terms contributing to $C_4(s)$ enter in the calculation of $P^{(3)}$. These results establish a fundamental connection between the calculation of rate processes and the optical polarization. The reaction rates and the optical polarization are related to the same dynamical quantities. The development of appropriate microscopic solvation models and approximation schemes results in a unified picture for reaction rates and optical line shapes.²

We shall now illustrate our results by applying them to two specific $\chi^{(3)}$ techniques:^{4,25} ultrafast pump-probe (hole-burning) and fluorescence spectroscopy. Both techniques start with the application of a short laser pulse. Prior to the absorption of a photon, the solvent molecules are in equilibrium with the ground-state solute. Upon excitation, the solute-solvent system undergoes a Franck-Condon transition to a state in which the solute dipole has its excited-state value, but the solvent molecules still occupy their previous configuration. The solvent molecules then relax to a configuration of lower energy, which is in equilibrium with the electronically excited solute. The solvation dynamics is probed by sending a second short pulse, with a variable delay t with respect to the first pulse, and probing its frequency-resolved absorption (pump-probe measurement) or by collecting a spontaneously emitted photon (fluorescence measurement).

For our model system, the steady-state absorption spectrum is given by $\sigma_a(\omega_1 - \omega_{ba})$ while the stationary fluorescence spectrum is given by $\sigma_b(\omega_2 - \omega_{ba})$. Here σ_a and σ_b are given by eq II-8, III-1, or III-8a. $\omega_{ba} = E^0/\hbar$ represents the 0-0 transition frequency of the solute (cf. eq II-2c). λ_a and λ_b are the corrections due to the nuclear degrees of freedom of solvent (eq III-3a). The absorption spectrum $\sigma_a(\omega_1 - \omega_{ba})$ is centered at $\omega_1 = \omega_{ba} + \lambda_a$ with width Δ_a (cf. eq III-1), while the fluorescence $\sigma_b(\omega_2 - \omega_{ba})$ is centered at $\omega_2 = \omega_{ba} + \lambda_b$ with width Δ_b . The Stokes shift, defined by the frequency difference between the peaks of fluorescence and absorption, is then given by $\lambda_a - \lambda_b \equiv 2\lambda > 0$. The time-resolved hole-burning spectrum is given by

$$S_{\text{HB}}(\omega_2, t; \omega_1) = \omega_2 \sigma_a(\omega_1 - \omega_{ba}) [W_a(\omega_2 - \omega_{ba}, t; \omega_1 - \omega_{ba}) + W_b(\omega_2 - \omega_{ba}, t; \omega_1 - \omega_{ba})] \quad (\text{V-3})$$

The time resolved fluorescence is

$$S_{\text{FL}}(\omega_2, t; \omega_1) = \omega_1 \omega_2^3 \sigma_a(\omega_1 - \omega_{ba}) W_b(\omega_2 - \omega_{ba}, t; \omega_1 - \omega_{ba}) \quad (\text{V-4})$$

Here ω_1 is the frequency of the pump field, while ω_2 is the frequency of the probe field (pump-probe) or of the spontaneously emitted photon (fluorescence). W_j , $j = a$ or b , is the conditional probability of the solvation coordinate given by eq II-9 or III-2 or III-8b. According to eq III-2b, the peak of the fluorescence (eq V-4) at the delay time t is given by $\omega_2 = \omega_{ba} + \lambda(t) + M_b(t)(\omega_1$

(28) Kakitani, T.; Mataga, N. *Chem. Phys.* **1985**, *93*, 381; *J. Phys. Chem.* **1987**, *91*, 6277.

$-\omega_{ba} - \lambda_a$). The time-dependent Stokes shift is defined²⁶ by the frequency difference between the peak of absorption and the peak of the fluorescence with the resonance excitation $\omega_1 = \omega_{ba} + \lambda_a$. Therefore, the time-dependent Stokes shift is given by $\lambda_g - \lambda(t)$. The solvation dynamics is usually measured by the normalized time-dependent Stokes shift function defined by

$$\frac{\lambda(t) - \lambda(\infty)}{\lambda(0) - \lambda(\infty)} = \frac{\lambda(t) - \lambda_e}{\lambda_g - \lambda_e} \quad (\text{V-5})$$

In the linear perturbation theory for the solute-solvent interaction (eq III-5a) this quantity is equal to $M(t)$, the normalized correlation function of the solvation coordinate.

A major goal of spectroscopic studies in condensed phases is to provide information which could allow the prediction of reaction rates in the same solvent. If we consider our simplest level of approximation (eq III-5-III-9), the solvation effect is characterized by a single static parameter λ and a dynamical quantity $M(t)$. The solvent reorganization energy λ in the optical spectra may be very different from that in the chemical rate system, due to the different nature of the solvation coordinates and the system charge rearrangement in these two physical situations. However, the dynamical quantity, $M(t)$, which describes the solvent fluctuations, is approximately the same in these two physical situations (cf. eq IV-8c). The spectroscopic measurements (e.g., the Stokes shift) of a chromophore in a solvent provide a direct probe of $M(t)$ which can then be used to calculate τ_a and τ_b (eq II-7) and correspondingly the adiabatic electron-transfer rate in the same solvent.

Recent time-dependent Stokes shift measurements²⁶ provide a direct probe for $M(t)$. The analysis of these measurements using the continuum model (eq IV-8c) showed that it cannot always reproduce the experimental results. In particular it was found that, even in a solvent, for which the continuum Debye model was conventionally considered to be valid, $M(t)$ showed a multiex-

ponential behavior. This result is in contrast with eq IV-11 which predicts a single relaxation time scale, namely the solvent longitudinal dielectric relaxation time, τ_L . Molecular dynamics simulations performed by Maroncelli and Fleming in liquid water showed that these multiple time scales result from the solvation structure; i.e., the solvent relaxation depends on its distance from the solute. The mean spherical approximation (MSA) was proposed as a means to account partially for solvation structure by taking into account the hard-sphere radii of the solvent and the solute.²⁹ The procedure modifies the frequency dependence of $\epsilon(\omega)$ and gives a multiple time scale behavior even for Debye solvents. This is in qualitative agreement with the Stokes shift measurements.^{26,30} There are two problems, however, with that procedure. First the MSA was originally developed for the static dielectric function $\epsilon(\mathbf{0},0)$. Its extension to $\epsilon(\mathbf{0},\omega)$ by an analytical continuation clearly does not incorporate the complete solvation dynamics. Moreover, the analysis presented in the previous section shows that the more systematic way to introduce solvent structure is through the wave vector (\mathbf{k}) dependence of $\epsilon(\mathbf{k},\omega)$, i.e., using eq IV-7c instead of eq IV-8c. Any procedure based on the $\mathbf{k} = \mathbf{0}$ alone is not sufficient to take full account of the solvation structure. Theoretical effort should therefore be directed toward developing microscopic models for $\epsilon(\mathbf{k},\omega)$ and exploring its effect on nonlinear optical measurements as well as on electron-transfer processes.^{27,31}

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Molecular Theory of Solvation and Solvation Dynamics of a Classical Ion In a Dipolar Liquid[†]

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A microscopic theory of equilibrium solvation and solvation dynamics of a classical, polar, solute molecule in dipolar solvent is presented. Density functional theory is used to explicitly calculate the polarization structure around a solvated ion. The calculated solvent polarization structure is different from the continuum model prediction in several respects. The value of the polarization at the surface of the ion is less than the continuum value. The solvent polarization also exhibits small oscillations in space near the ion. We show that, under certain approximations, our linear equilibrium theory reduces to the nonlocal electrostatic theory, with the dielectric function ($\epsilon(\mathbf{k})$) of the liquid now wave vector (\mathbf{k}) dependent. It is further shown that the nonlocal electrostatic estimate of solvation energy, with a microscopic $\epsilon(\mathbf{k})$, is close to the estimate of linearized equilibrium theories of polar liquids. The study of solvation dynamics is based on a generalized Smoluchowski equation with a mean-field force term to take into account the effects of intermolecular interactions. This study incorporates the local distortion of the solvent structure near the ion and also the effects of the translational modes of the solvent molecules. The latter contribution, if significant, can considerably accelerate the relaxation of solvent polarization and can even give rise to a long time decay that agrees with the continuum model prediction. The significance of these results is discussed.

I. Introduction

An understanding of time-dependent response of a dipolar solvent to a changing charge distribution in a polar solute molecule is essential to understand solvent effects on many important chemical reactions, such as electron- and proton-transfer reactions.

[†] Dedicated to Professor Robert W. Zwanzig who has been an inspiring teacher of one of us (B. Bagchi) for many years.

This is currently an active area of research, both experimentally¹⁻⁹ and theoretically.¹⁰⁻²⁵

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