

SOLVATION STRUCTURE IN THE TIME RESOLVED STOKES SHIFT AND ADIABATIC ELECTRON TRANSFER

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Abstract

There is an important connection between the time resolved Stokes shift of a chromophore in a polar solvent and the dynamical contribution to electron transfer reactions. We present a microscopic theory of the time resolved Stokes shift of a chromophore in a polar solvent which incorporates both non-Debye dielectric relaxation and solvation shell structure, then apply it to the Spargaglione-Mukamel theory of electron transfer reactions. We find that molecular effects can dramatically affect the rate of reaction. Moreover, we find that when translational motion is fast compared to rotational motion, dielectric continuum theory gives a good approximation to the reaction rate.

Keywords: Adiabatic electron transfer, time-dependent Stokes shift

I. Introduction

The time and frequency resolved fluorescence spectra of many chromophores show a time dependent red shift which reflects the dynamics of solvent reorganization following the change in the intramolecular charge distribution upon optical excitation. The recent development of ultrafast laser technology and detection systems has allowed the detailed observation of the fluorescence shift in the picosecond to femtosecond regime for a wide range of common solvents. Many theories of adiabatic electron transfer relate the reaction rate to the same solvent reorganization which is responsible for the Stokes shift [1]. In this paper, we apply some recent developments in the theory of the time resolved Stokes shift to adiabatic electron transfer reactions.

Traditionally, theories of solvation dynamics have modeled the solvent as a dielectric continuum [2]. One of the principal predictions of dielectric continuum theory is that for a solvent characterized by a Debye dielectric relation, the energy of solvation relaxes exponentially with a time scale called the longitudinal time τ_L . Experimental results have shown marked deviations from this prediction. Strongly non-exponential relaxation, and even exponential relaxation with a time scale very different from τ_L have been observed [3]. These results underline the need for a theory of solvation that takes into account the microscopic structure of the solvent. There has been previous theoretical work along these lines. Wolynes has proposed the dynamical mean spherical approximation (MSA) [4]. In general, the dynamical MSA provides qualitative agreement with experiment. Fried and Mukamel [5] have proposed a microscopic theory of solvation applicable to non-Debye solvents. This theory includes effects due to translational motion.

Much of the recent work on time dependent solvation can also be applied to electron transfer reactions. This is because the time-dependent polarization correlation function that

is the central quantity in theories of solvation also appears in theories of electron transfer [6]. McManis and Weaver [7] have applied the dynamical MSA model of solvation to adiabatic electron transfer. Sparpaglione and Mukamel [6] have presented a theory of electron transfer that is based on an analogy between reaction rates and nonlinear optical susceptibilities. The Sparpaglione-Mukamel theory depends on an absorption lineshape function, the reaction exothermicity, the nonadiabatic coupling, and the polarization correlation function.

In the present paper, we undertake two tasks. First, we review a theory for the polarization correlation function under which both *solvent structure* and *non-Debye dielectric relaxation* may be taken into account [5]. Secondly, we present some consequences of our theory for adiabatic electron transfer reactions. We find that molecular effects can dramatically shift the reaction rate from continuum predictions. We also emphasize the role of translational diffusion in electron transfer dynamics. We find that in the limit of large translational diffusion, dielectric continuum results hold. This is because rapid translation "smears out" shell structure, making the medium behave effectively as a continuum.

II. Time-dependent Solvation

In this Section we review a new theory for the time-dependent solvation energy $E_S(t)$ that depends on the direct correlation function of the pure solvent and on the dielectric function $\epsilon(\omega)$. We consider a liquid with a single tagged particle (the solute) at thermal equilibrium at $t = 0$. We then change the solute charge distribution, creating a specified time dependent displacement field $\mathbf{D}(\mathbf{r}, t)$ in the medium. This external displacement field in turn induces a polarization field in the medium $\mathbf{P}(\mathbf{r}, t)$. The time-dependent Born solvation energy $E_S(t)$ can be related to the solvent polarization $\mathbf{P}(\mathbf{r}, t)$ by:

$$E_S(t) = - \int_{-\infty}^{\infty} d\mathbf{r} \mathbf{P}(\mathbf{r}, t) \cdot \mathbf{D}(\mathbf{r}, t). \quad (1)$$

It is useful to introduce the dimensionless correlation function of the solvation energy $E_S(t)$:

$$S(t) = \frac{E_S(t) - E_S(\infty)}{E_S(0) - E_S(\infty)}. \quad (2)$$

$S(t)$ is directly measured in a time-dependent Stokes shift experiment.

We consider here only the linear part of the solvent response to the solute field \mathbf{D} . Using linear response theory, we introduce the polarizability tensor $\alpha(\mathbf{r}, \mathbf{r}', t)$ such that

$$\mathbf{P}(\mathbf{r}, t) = \int_{-\infty}^{\infty} d\mathbf{r}' \int_0^t dt' \alpha(\mathbf{r}, \mathbf{r}', t - t') \cdot \mathbf{D}(\mathbf{r}', t'). \quad (3)$$

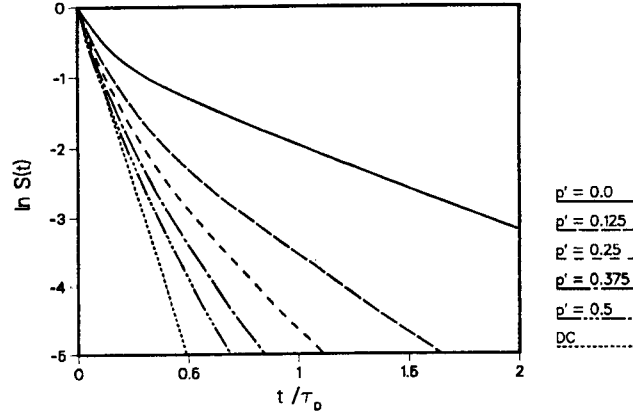
It is convenient to transform the polarizability into wavevector-Laplace (\mathbf{k}, s) space. This gives us

$$\mathbf{P}(\mathbf{k}, s) = \int_{-\infty}^{\infty} d\mathbf{k}' \alpha(\mathbf{k}, \mathbf{k}', s) \cdot \mathbf{D}(\mathbf{k}', s). \quad (4)$$

Let us define the part of the solvent polarizability coming from nuclear degrees of freedom as α' :

$$\alpha(\mathbf{k}, \mathbf{k}', s) = \alpha'(\mathbf{k}, \mathbf{k}', s) + \alpha_{\infty}(\mathbf{k}, \mathbf{k}'), \quad (5)$$

where $\alpha_{\infty}(\mathbf{k}, \mathbf{k}')$ represents the contribution of electronic (high frequency) degrees of freedom to the solvent polarizability. As Madden and Kivelson discuss [8], the nuclear contribution to the macroscopic polarizability may be viewed as coming from an effective permanent

Figure 1: $\ln S(t)$ vs. t for a Debye solvent

dipole moment. Thus, we use a polar but nonpolarizable model of the solvent molecules to find α' .

Since α_∞ leads to an extremely fast relaxation of the polarization \mathbf{P} , we need consider only the nuclear part of the solvent polarizability ($\alpha'(k, s)$.) Our final result for the longitudinal part of the polarizability is:

$$\alpha'_L(k, s) = \frac{1}{4\pi} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right] \left[\frac{1 - \rho_0 c_L(k)}{1 - \rho_0 c_L(0)} - \frac{1}{1 + p'(k\sigma)^2} \frac{\epsilon_\infty(\epsilon(s) - \epsilon_0)}{\epsilon_0(\epsilon(s) - \epsilon_\infty)} \right]^{-1}, \quad (6)$$

where we use the notation $c_L(k) \equiv c(k, l_1 = 1, l_2 = 1, m = 0)$ for the direct correlation function c in the \mathbf{k} frame [9]. $\epsilon_0 \equiv \epsilon(k = 0, s = 0)$, and $\epsilon_\infty \equiv \epsilon(k = 0, s = \infty)$. Also, we call

$$p' = I/2M\sigma^2 \quad (7)$$

the translational diffusion parameter, σ is the solvent diameter, and $\beta = 1/k_B T$. I is the moment of inertia of a solvent molecule, and M is its mass. $\rho_0 = \rho/4\pi$, where ρ is the number density of the solvent.

Note that the dielectric continuum result is recovered in Eq. (6) by setting $k = 0$. Using (1), we obtain an explicit result for the energy of solvation of a suddenly created charge distribution:

$$E_S(s) = \frac{-1}{8\pi^3 s} \int_{-\infty}^{\infty} d\mathbf{k} \alpha'_L(k, s) |D_L(\mathbf{k})|^2, \quad (8)$$

Our theory builds in many important physical features of solvation. The molecular nature of solvation (shell structure, etc.) enters through the direct correlation function c . The solute charge distribution can be built in through the applied field $\mathbf{D}(\mathbf{k})$. Translational effects enter the theory through the translational diffusion parameter p' .

We consider here the behavior of the time dependent Stokes shift $S(t)$ as a function of p' . Figure 1 gives $S(t)$ as predicted by our theory for the solvation of a newly created ionic charge distribution in a Debye solvent. Both the solute and solvent were taken to be spherical, and of the same radius. The mean spherical approximation was used for the direct correlation function $c(k)$, the static dielectric constant ϵ_0 was taken to be 20.0, and ϵ_∞ was taken to be 2.0. These are typical values for a polar molecular fluid.

Figure 1 shows $S(t)$ for several values of the translational diffusion parameter p' . As p' is increased, $S(t)$ approaches the dielectric continuum prediction. This is because rapid

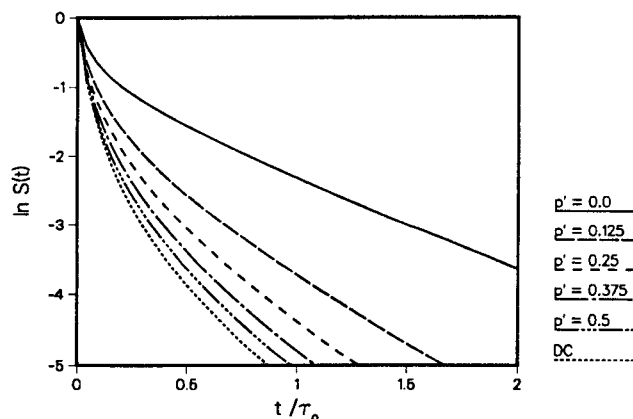


Figure 2: $\ln S(t)$ vs. t for a Cole-Davidson solvent

translation of the solvent “smears out” shell structure, producing a medium that is effectively a continuum on the time scale of the experiment. In Figure 2, we show $S(t)$ for a Cole-Davidson solvent. The Cole-Davidson form of the dielectric dispersion is:

$$\epsilon(s) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{(1 + s\tau_0)^{\beta}}. \quad (9)$$

In Figure 2, we used the same parameters as Figure 1. β was taken to be 0.75. In Figure 2 we see that $S(t)$ once again approaches the dielectric continuum prediction as p' is increased. In this case, however, the dielectric continuum relaxation is non-exponential. This is because the Cole-Davidson form of $\epsilon(\omega)$ contains a distribution of relaxation times.

III. Application to adiabatic electron transfer

We have shown how translational diffusion can lead to dielectric continuum behavior of $S(t)$ in a molecular fluid. We now consider the effect of translational diffusion on electron transfer dynamics. We show here that translational diffusion leads to dielectric continuum results in a molecular fluid.

The Sparpaglione-Mukamel theory of electron transfer predicts that in the adiabatic limit the rate is given by:

$$K = \frac{1}{\tau(\Delta G_{ab}) + \tau(\Delta G_{ba})} \exp(-\Delta G_{ab}/k_B T), \quad (10)$$

where $\tau(\Delta G_{ab})$ and $\tau(\Delta G_{ba})$ is the relevant solvent time scale controlling the forward and backward reactions, respectively. ΔG_{ab} and ΔG_{ba} are the activation free energies for the forward and backward reactions, respectively. The solvent time scale function is given by:

$$\tau(\Delta G) = \exp(-\Delta G/k_B T) \int_0^{\infty} dt \left\{ \frac{1}{\sqrt{1 - M^2(t)}} \exp \left[\frac{2\Delta G M(t)}{k_B T(1 + M(t))} \right] - 1 \right\}. \quad (11)$$

$M(t)$ is the same as the Stokes shift function $S(t)$, with the modification that the D fields in the expressions for $S(t)$ (Eq. (8)) are replaced by the difference between the electric displacements between the a and b electronic states: $D(k) \rightarrow D_a(k) - D_b(k)$.

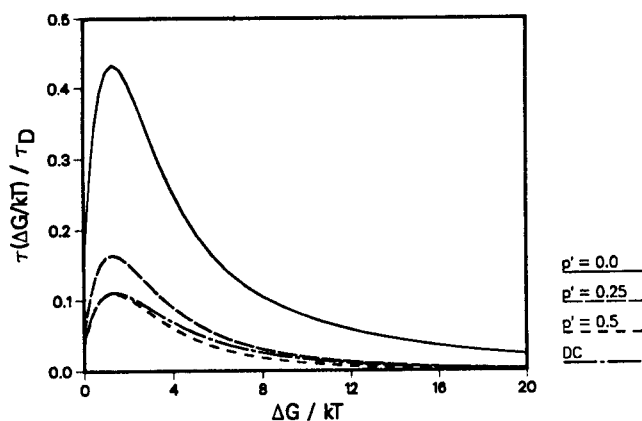


Figure 3: The solvent timescale τ is displayed vs. ΔG for the Debye solvent of Figure 1.

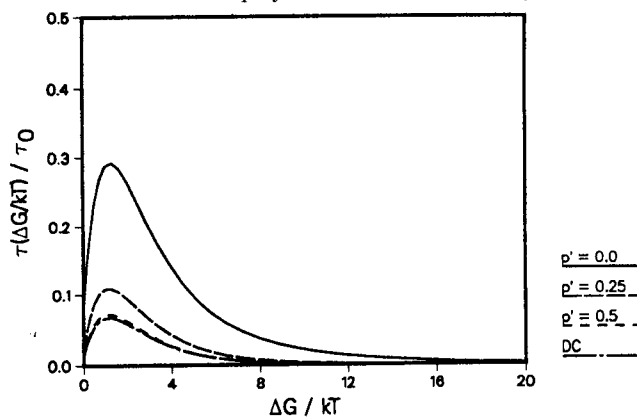


Figure 4: The solvent timescale function τ vs. ΔG for the Cole-Davidson solvent of Figure 2.

We consider here the case where $M(t)$ is equal to $S(t)$. As discussed by McManis and Weaver [7], this corresponds to an electrochemical oxidation-reduction reaction sufficiently far from an electrode. In Figure 3 we show the solvent time scale function τ as a function of the activation free energy ΔG for the same Debye solvent considered in Figure 1. It is apparent that translational diffusion can have a dramatic effect on the solvent time scale, and hence on the electron transfer rate. In particular, we note that the solvent time scale can be substantially slower than what is predicted on the basis of dielectric continuum theory. The sensitivity of the rate to solvent molecularity, however, also depends on the activation free energy. The solvent time scale is most sensitive to molecular effects when in the neighborhood of its maximum as a function of ΔG . Figure 4 shows the solvent time scale for the Cole-Davidson solvent studied in Figure 2. Once again, molecular effects lead to a pronounced increase in the solvent time scale. Large values of the translational diffusion lead to near-continuum results.

Acknowledgements

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