

Dielectric relaxation and intramolecular electron transfers

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Intramolecular charge transfer are considered for the case that the motion of the system is on a single potential energy surface. The case where this motion occurred on two surfaces was considered elsewhere. The former is shown to be much preferable for studies of solvent dynamics. Several aspects of the relation between "constant charge" dielectric relaxation time of the polar solvent and the experimental decay time of emission from the polar excited state of the solute are discussed for hydrogen-bonded systems.

I. INTRODUCTION

In the literature of the dielectric relaxation of polar solvents, two types of dielectric relaxation times τ_D and τ_L have been discussed.¹ When there is a constant electric field and a nonequilibrium initial condition, the dielectric displacement changes with a rate constant τ_D^{-1} , where τ_D is typically measured with a pair of electrodes under these conditions. There is a corresponding time dependence of the charge on the electrodes. If, instead, the charge on the surface of an electrode had been held fixed the electric field would have changed with a rate constant τ_L^{-1} . It is the latter relaxation time which has been used in recent work on the dynamical behavior of polar solvents in electron transfer processes.²⁻⁷

In the case of a thermal electron transfer process of the "weak overlap" type,⁸ the system initially moves on some many-dimensional potential energy surface for the reactants and, at the intersection with a potential energy surface for the products, it proceeds abruptly to the second surface as a result of an electron transfer. The charge distribution is spatially fixed, in effect, during the motion on either surface. (More precisely, it would be so in the absence of translational and rotational motion of the reactants.) Fluctuations and relaxation of the dielectric polarization of the solvent thus occur primarily under conditions of constant charge, rather than constant electric field, during the motion on each potential energy surface, and so τ_L is the relevant dielectric relaxation time.

In a photoexcitation process at least two types of intramolecular electron transfer systems have been described. In the first of these the system is excited to some electronic state of the solute, and there is motion on the new potential energy surface, followed by a charge transfer at the intersection with a second surface for which the solute has a different charge distribution (e.g., Ref. 4). A second type of system is one in which the polarity of the electronic state of the solute after photoexcitation is quite different from that beforehand, and the subsequent relaxation of the solvent molecules occurs on a single potential surface, rather than on the pair of surfaces

(e.g., Ref. 5). Previous theoretical work on such systems has been given using a somewhat different (a point-dipole) model⁷ discussed later.

In the present paper we consider the second of these types of systems. Also considered is the value to be used for the constant charge relaxation time τ_L in the case where there exist more than two dielectric dispersions. The appropriate choice depends on the local solvent structure in the vicinity of the solute molecule.

II. DIELECTRIC DISPERSION BEHAVIOR

When the Debye model is adopted for dielectric dispersion, the complex dielectric constant at an angular frequency ω is given by¹

$$\epsilon(\omega) = \frac{\epsilon_s - \epsilon_o}{1 + i\omega/\omega_1} + \epsilon_o, \quad (1)$$

where ω_1 represents the relaxation angular frequency, while ϵ_s and ϵ_o represent, respectively, the static and the optical dielectric constants, the latter of which is given by the square of the refractive index n_o :

$$\epsilon_o = n_o^2. \quad (2)$$

In this case, the relation between the constant field and constant charge relaxation times τ_D and τ_L is given by¹

$$\tau_L = \tau_D \epsilon_o / \epsilon_s \quad \text{with} \quad \tau_D = \omega_1^{-1}. \quad (3)$$

In the case of a point-dipole solute the τ_L is given by a related but somewhat different expression.^{7(c)}

Linear alcohols, which have often been used as solvents in intramolecular electron transfer reactions, have three regions of dielectric dispersion,⁹ centered at angular frequencies ω_1 , ω_2 , and ω_3 , with the lowest frequency dispersion centered at ω_1 having the largest contribution to the dielectric constant. The complex dielectric constant is now given by Eq. (4), assuming a Debye model for each dispersion region:

$$\epsilon(\omega) = \frac{\epsilon_s - \epsilon_{mw}}{1 + i\omega/\omega_1} + \frac{\epsilon_{mw} - \epsilon_{IR}}{1 + i\omega/\omega_2} + \frac{\epsilon_{IR} - \epsilon_o}{1 + i\omega/\omega_3} + \epsilon_o. \quad (4)$$

Its real part is schematically shown in Fig. 1, where the dielectric constants of the dispersion free regions are written as ϵ_s , ϵ_{mw} , ϵ_{IR} , and ϵ_o in the order of decreasing magnitude (denoting static, microwave, infrared, and optical spectral

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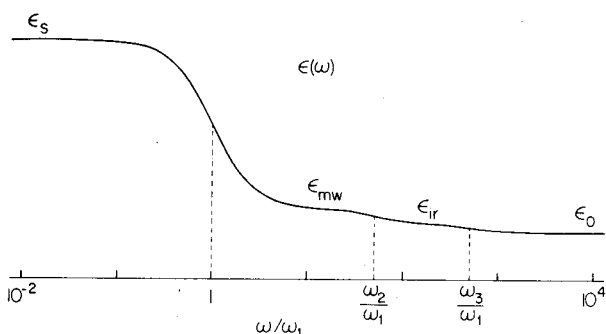


FIG. 1. Schematic dispersion plot of $\epsilon(\omega)$ vs ω/ω_1 for alcohols.

regions). Under a certain condition the relaxation time at constant charge should be given by $\tau_D \epsilon_{mw}/\epsilon_s$, with $\tau_D = \omega_1^{-1}$, instead of by Eq. (3). This condition occurs when $\tau_D \epsilon_{mw}/\epsilon_s \gg \omega_2^{-1}$, since in a time interval of the order of $\tau_D \epsilon_{mw}/\epsilon_s$ the time evolution of the polarization associated with the middle (ω_2^{-1}) and highest (ω_3^{-1}) frequency dispersion regions is complete when this inequality is fulfilled.

III. DIELECTRIC RELAXATION AND FLUORESCENCE SPECTRA

Before considering the solvent dynamics for the case of motion on a single excited-state potential energy surface, we first recall how the two types of systems differ in their fluorescence. Examples of the two-state systems include a dimethylaminobenzonitrile (DMABN)^{4,11,12} and an aminonaphthalene sulphonic acid (TNSDMA).⁴ An example of the one-state system in the literature is 4-aminophthalimide.^{5,7} In examples of the former there has also been assumed to be an internal twist about a bond (a C-N bond in the cited examples) which disrupts the conjugation and permits the formation of a charge-transfer state.¹³

In the two-state type of system, two fluorescence bands have been reported, the shorter wavelength one being formed first (and instantaneously). Its subsequent decay time has agreed with the rise time of the second emission band.^{11,12} The short wavelength emission, which is observed also in nonpolar solvents, has been attributed to a nonpolar state of the solute, and the longer wavelength emission band to a polar excited state. Normally plotted for this type of system is the emission intensity of each band vs time.^{11,12} A detailed discussion of this type of system, including both vibrational and solvent orientational contributions, is given elsewhere.³ The instantaneous fluorescence spectrum plot shows, as a function of time, an isobestic point.¹⁴

In the one-state type of system, on the other hand, there is only one emission band. As the solvent reorganization proceeds in this single excited-state system, the peak energy, $E_p(t)$, of the emission band shifts to the red. The time dependence of $E_p(t) - E_p(\infty)$ has been determined in Ref. 5 and found, for the system studied, 4-aminophthalimide in 1-propanol, to decay with a single exponential time constant.¹⁵ In Ref. 5 the decay for the $\ln[E_p(t) - E_p(\infty)]$ plot was 40 ± 5 ps, as compared to the value of 45 ps for $\tau_D \epsilon_o/\epsilon_s$ and 90 ps for $\tau_D \epsilon_{mw}/\epsilon_s$ at 20 °C.¹⁰ In this type of system the fluorescence spectrum shows no isobestic point, only a red shift.¹⁴

In the present treatment we will assume, as in the previous two-state case,³ that the vibrational motion within the solute molecule adjusts itself so rapidly to the instantaneous orientations of the surrounding solvent molecules that an equilibrium for the intramolecular vibrational modes is always maintained during the process. In the two-state type of system the intramolecular vibrational motions can trigger electron transfer.³ Partly for this reason, the one-state type of system is more suitable for singling out the dynamics of the orientational reorganization process of the solvent molecules than the two-state system.

We consider first the theoretical behavior of the peak energy of the emission band for a simple case. The process of orientational relaxation of the polar solvent occurring after photoexcitation of the solute molecule can be regarded as diffusion of the polarization vector under the influence of a potential. This potential surface for the excited state is different from that for the ground state of the solute molecule. Within the Debye model, in which the free energy for polarization fluctuations is quadratic in polarization components, we can select, for notational brevity, a scalar variable X proportional to a certain component of the polarization vector which passes through the two minimum energy points associated with the two free energy surfaces (the ground state and the excited state) in the polarization coordinate space. Only this component X is relevant to the process while along the other two ones perpendicular to X the two free energy surfaces are "parallel" only with a vertical shift. We have introduced the variable X as in Ref. 3, and in the final expression any energy term for this X polarization can be replaced by the appropriate free energy term available from an earlier analysis.⁸

The diffusion equation for the distribution function $P(X;t)$ present at coordinate X at time t is given by

$$\frac{\partial P}{\partial t} + D \frac{\partial^2 P}{\partial X^2} + \frac{D}{k_B T} \frac{\partial}{\partial X} \left[P \frac{dV_e(X)}{dX} \right], \quad (5)$$

where D and T represent, respectively, the diffusion constant and temperature, while $V_e(X)$ represents the excited-state free energy potential for polarization fluctuations. The corresponding free energy function for the ground state is written as $V_g(X)$. Within the Debye model, both $V_g(X)$ and $V_e(X)$ are quadratic functions of X :

$$\begin{aligned} V_g(X) &= \frac{1}{2} X^2, \\ V_e(X) &= \frac{1}{2} (X - X_e)^2 + \Delta G^0, \end{aligned} \quad (6)$$

where X_e represents the relaxed value of the polarization component X appropriate for the excited state of the solute molecule, and ΔG^0 is the free energy shift.¹⁶ The emission spectrum $K(E;t)$ from the excited state at time t is given by

$$K(E;t) = \int P(X;t) \delta[E - V_e(X) + V_g(X)] dX, \quad (7)$$

upon using the Franck-Condon principle.

When the emission spectrum does not have a large asymmetry, its peak energy can be approximated by its average energy as

$$E_p(t) = \int E K(E;t) dE. \quad (8)$$

Then, introducing Eqs. (6) and (7), interchanging the order of integration, and using the normalization $\int P(X;t)dX = 1$, one obtains

$$E_p(t) = E_p(\infty) - X_e \bar{X}(t) \quad (9)$$

with

$$\bar{X}(t) = \int (X - X_e) P(X;t) dX, \quad (10)$$

where $E_p(\infty)$ is given by $\Delta G^0 - \frac{1}{2} X_e^2$. Upon multiplying both sides of Eq. (5) by X , and integrating over X by parts, it can be shown from Eqs. (5) and (6) that $\bar{X}(t)$ satisfies

$$d\bar{X}(t)/dt = -\bar{X}(t)/\tau_L \quad (11)$$

with

$$\tau_L = k_B T / D,$$

and hence that

$$\bar{X}(t) = \bar{X}(0) \exp(-t/\tau_L), \quad (12)$$

where $\bar{X}(0)$ represents the initial value of $\bar{X}(t)$. X is a component of the polarization vector and Eq. (11) shows that the average value of X relaxes with a rate constant τ_L^{-1} . This τ_L corresponds to the constant charge dielectric relaxation time. According to Eq. (9), the peak energy of the emission spectrum decays with the same rate constant τ_L^{-1} as that for the polarization vector. We note here that this result does not depend on the initial distribution $P(X;0)$ of X obtained just after photoexcitation. Therefore, the data in Ref. 5, in which the decay time agreed with $\epsilon_0 \tau_D / \epsilon_s$ for the system studied, show that τ_L was given by Eq. (3) in spite of the fact that linear alcohols have three regions of dielectric dispersion. Since the observed decay time is much larger than both ω_2^{-1} and ω_3^{-1} ,¹⁰ one expects that the ϵ_0 in Eq. (3) should be replaced by ϵ_{mw} , as already noted. It is noteworthy, therefore, that the agreement for the 1-propanol system with $\tau_D \epsilon_0 / \epsilon_s$ was better than that with $\tau_D \epsilon_{mw} / \epsilon_s$. To be sure these ratios differ¹⁰ only by a factor of about 2 for 1-propanol. For 1-octanol,⁹ the difference between $\tau_D \epsilon_0 / \epsilon_s$ and $\tau_D \epsilon_{mw} / \epsilon_s$ is only a factor of 1.35. The lifetime data for DMABN and TNSDMA in a series of alcohols⁴ were also reported to agree well with $\tau_D \epsilon_0 / \epsilon_s$.¹⁷

Specific interactions have often been invoked in discussions of solute-solvent interactions,¹⁸ instead of using a dielectric continuum model. In the former case one still needs to explain, nevertheless, the type of agreement reported in Refs. 4 and 5 between rate constants for the fluorescence emission and the bulk dielectric relaxation rates. One explanation is to assume that the rupture or formation of any specific interaction is rapid, followed by a rate-controlling dielectric relaxation step. For example, in DMABN in an alcohol the formation of the charge-transfer state from the relatively nonpolar one involves, presumably, the rupture of a hydrogen bond between the alcohol and the amine nitrogen, after the latter has acquired its positive charge. If this process is very rapid, the slow step might be the ensuing dielectric relaxation.

Given the reported correspondence between dielectric relaxation times and fluorescence emission times^{4,5} in alcohols there are several models which might be considered for

a solute-solvent dielectric continuum interaction after the occurrence of the specific effects. In one of these the bulk dielectric properties are used, leading to a relaxation time of $\tau_D \epsilon_{mw} / \epsilon_s$.^{7f} In another the solute molecule acts as a "seed" for the clustering of solvent molecules, leading (Sec. IV) to a relaxation time of $\tau_D \epsilon_0 / \epsilon_s$. We consider this latter case in the next section.

IV. RELAXATION MODEL IN BULK AND NEAR SOLUTE

In the bulk liquid, most alcohol molecules are believed to be in a state of hydrogen-bonded polymeric clusters^{9,19} and the dielectric dispersion at ω_1 has been postulated to be associated with breaking of a hydrogen bond in the cluster followed by the rotation of the now liberated molecule.⁹ The dielectric dispersions at ω_2 and ω_3 have been postulated⁹ to be associated with a small fraction of alcohol molecules occurring in a monomeric state. The dispersion at ω_2 was attributed to the rotation of a free monomer as a whole, while that at ω_3 to the rotation of the hydroxyl group of a free monomer.⁹

In a model leading to $\tau_D \epsilon_0 / \epsilon_s$ it will be supposed that almost all of the alcohol molecules surrounding the solute are in the polymeric cluster form. The relevant relaxation property in the vicinity of the solute can then be obtained as follows.

The dielectric constant $\epsilon(\omega)$ of the bulk liquid alcohol has contributions from the polymeric and the monomeric parts.⁹ The optical dielectric constants of these two parts can be assumed to be the same as ϵ_0 , since they are each associated with electronic excitation of a single molecule. The complex dielectric constant of the polymeric part will be written as

$$\epsilon_p(\omega) = \frac{\epsilon_p - \epsilon_0}{1 + i\omega/\omega_1} + \epsilon_0, \quad (13)$$

where ϵ_p represents the static dielectric constant of the polymeric part and $\epsilon_p - \epsilon_0$ is proportional to the mean square of the dipole moment associated with the rotation of a molecule in a polymeric cluster.²⁰ The dielectric constant of the monomeric part will be written as

$$\epsilon_m(\omega) = \frac{\epsilon_m - \epsilon_n}{1 + i\omega/\omega_2} + \frac{\epsilon_n - \epsilon_0}{1 + i\omega/\omega_3} + \epsilon_0, \quad (14)$$

where ϵ_m represents the static dielectric constant of the monomeric part and $\epsilon_m - \epsilon_n$ and $\epsilon_n - \epsilon_0$ are, respectively, proportional to the mean square of the dipole moments associated with the rotation of a free monomer and its hydroxyl group.²⁰ Then, the dielectric constant of the alcohol is assumed to be given by

$$\epsilon(\omega) = C_p \epsilon_p(\omega) + C_m \epsilon_m(\omega) \quad \text{with } C_p + C_m = 1, \quad (15)$$

where C_p and C_m represent, respectively, the volume fraction of the polymeric and the monomeric parts in the liquid.²¹ From a fitting of this model to the dielectric constants of the solvent in the dispersion free regions, the various constants can be evaluated as follows.

Adjusting the real part of the dielectric constants given by Eq. (15) in the dispersion-free regions to those shown in Fig. 1, we arrive at

$$\begin{aligned}\epsilon_s - \epsilon_{mw} &= C_p(\epsilon_p - \epsilon_o), \quad \epsilon_{mw} - \epsilon_{IR} = C_m(\epsilon_m - \epsilon_n), \\ \epsilon_{IR} - \epsilon_o &= C_m(\epsilon_n - \epsilon_o).\end{aligned}\quad (16)$$

From the first relation we obtain

$$\begin{aligned}\epsilon_p &= \frac{\epsilon_s - \epsilon_{mw}}{C_p} + \epsilon_o = \epsilon_s + \frac{C_m}{C_p}(\epsilon_s - \epsilon_{mw}) \\ &\quad - (\epsilon_{mw} - \epsilon_o).\end{aligned}\quad (17)$$

From the last two relations in Eq. (16) combined with $\epsilon_{mw} - \epsilon_{IR} \ll \epsilon_s - \epsilon_{mw}$ and $\epsilon_{IR} - \epsilon_o \ll \epsilon_s - \epsilon_{mw}$,¹⁰ one can confirm that $C_m \ll 1$, if the three dipole moments mentioned above are assumed to have magnitudes not so different from each other. (Both $\epsilon_m - \epsilon_n$ and $\epsilon_n - \epsilon_o$ should then be of the same order of magnitude as $\epsilon_s - \epsilon_{mw}$.)

In the solute-solvent cluster model it will be supposed that each neighboring solvent molecule near the solute molecule is in a polymeric cluster. Even in this case, the dielectric constant describing these molecules is, in general, not the same as $\epsilon_p(\omega)$ given by Eq. (13). In general, both $\epsilon_p - \epsilon_o$ and ω_1 appearing in Eq. (13) contain frictional effects²⁰ of free monomers which are uniformly mixed with polymeric clusters in the pure liquid. However, the volume fraction C_m of the free monomers is small in the alcohol. Therefore, their effect on the dielectric constant $\epsilon_p(\omega)$ of the polymeric part can be neglected, and the dielectric property of the solvent molecules surrounding the solute molecule can be approximated by $\epsilon_p(\omega)$. Then, the relaxation time τ_L of the orientational fluctuation of these solvent molecules can be given by $\tau_D \epsilon_o / \epsilon_p$ with $\tau_D = \omega_1^{-1}$, where ϵ_p is given by Eq. (17). Thereby, ϵ_p / ϵ_s equals

$$1 + \frac{C_m}{C_p} \frac{\epsilon_s - \epsilon_{mw}}{\epsilon_s} \left[1 - \frac{\epsilon_{mw} - \epsilon_{IR}}{\epsilon_s - \epsilon_{mw}} \left(1 + \frac{\epsilon_{IR} - \epsilon_o}{\epsilon_{mw} - \epsilon_o} \right) \right].$$

The quantities $(\epsilon_{mw} - \epsilon_{IR}) / (\epsilon_s - \epsilon_{mw})$ and $(\epsilon_{IR} - \epsilon_o) / (\epsilon_s - \epsilon_{mw})$ are both about 0.1 at about room temperature, while $(\epsilon_s - \epsilon_{mw}) / \epsilon_s \approx 0.8$.¹⁰ Since $C_m / C_p \ll 1$, it is seen that ϵ_p / ϵ_s has a value very close to unity. Thus, the relation (3) for τ_L has been obtained, provided the relevant alcohol molecules exist as a polymeric cluster when they are in the vicinity of the solute molecule.

It should be noted that the present discussion assumes throughout a Debye-type model for the relaxation. Other effects, in particular solvent inertial effects and resonance effects, can also occur and affect the expressions. The influence of inertial effects on the lowest frequency dispersion region is estimated to be relatively minor.^{7(d),22} Again, attention is focused in the present paper on the slowest relaxation. At very short times there will be smaller spectral shifts in the luminescence, with other time constants, due to the other relaxation times.

V. DISCUSSION

We would first like to comment on some early theoretical studies⁷ of dielectric relaxation for motion on a single potential energy surface. In these studies a point dipole model was assumed for the solute, and the solvent dielectric relaxation, even multiple relaxation,^{7(b)} was considered. This model yields a τ_L which is moderately close to that in Eq. (3).^{7(e),7(f)} Thereby, the discussion in the previous section

remains substantially unaffected. A separate question is the appropriateness of a solute point dipole model itself, for molecules which have, instead, separated charge distributions.²³

A comparison of the treatment in Sec. III with that in Ref. 3 makes it clear that the solvent dynamics for one-state systems are much simpler to treat than that for two-state systems, particularly when the role of rapid vibrational motion which can trigger the reaction is taken into account in the "curve crossing" occurring in the two-state system.

Thus, while two-state systems are interesting in their own right, and have been almost exclusively the systems studied, one-state systems such as 4-aminophthalimide are much better suited for studying the solvent dynamics. Solvents such as the nitriles, which unlike the alcohols have single relaxation time,²⁰ might be even simpler in the interpretation (contrast the discussion in Sec. IV). It is clear that in spite of the good agreement^{4,5} apparently found for the emission fluorescence times and $\tau_D \epsilon_o / \epsilon_s$, there are a number of questions. There is the one raised earlier as to whether the comparison should be with $\tau_D \epsilon_o / \epsilon_s$ (model in Sec. IV) or with $\tau_D \epsilon_{mw} / \epsilon_s$ (bulk dielectric model). There is also the question of the significance of agreement or disagreement of factors of 2 in the rate constant when continuum models are used. Further experimental studies, preferably with one-state systems in single-relaxation time solvents, may help clarify such questions. Again, it would be useful with the several-relaxation-time solvents to see if the earlier reported multiexponential decay at low temperatures^{7(b)} is confirmed with the more recent picosecond pulse type of excitation.

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- ²³In the various solute molecules studied experimentally (Refs. 4 and 5) there is typically in the excited electronic state a charge transfer between an aromatic ring and a substituent, giving rise thereby to a distributed charge distribution, which is sometimes approximated by a point dipole. The error in using a point dipole model for a pair of separated charges can be estimated from expressions in the literature given, for example, in R. A. Marcus, *J. Chem. Phys.* **43**, 1261 (1965), and in references cited therein. The τ_L obtained in a point dipole model differs somewhat from that in Eq. (3) because of dielectric image effects (reaction field effects). A model in which such effects are minimal is that of two separated spheres in contact, each containing a charge. Its image effects are given in the literature, for example, R. A. Marcus, *J. Chem. Phys.* **43**, 58 (1965), and references cited therein. One might expect, therefore, that a separated-charge model of the solute will yield a τ_L somewhat intermediate between that given by Eq. (3) and that given by point dipole models, and hence close to the value given by Eq. (3).