THEORY OF THE TIME DEVELOPMENT OF THE STOKES SHIFT IN POLAR MEDIA

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We present a theory for the time evolution of the Stokes shift of a polar molecule in a polar solvent. The time-dependent solute–solvent interaction is calculated in a continuum model by replacing the surrounding solvent by a frequency-dependent dielectric continuum. An expression for the time dependence of the fluorescence maximum is derived. This expression can be considered a direct generalization of the well-known Ooshika–Lippert–Mataga equation to the time domain. We also present an approximate expression for the wavelength dependence of the dynamics of the Stokes shift, and find it to be consistent with recent experimental results. We have investigated the effect of polarizability of the solute molecule and found that for many molecules this effect is not negligible.

1. Introduction

When a molecule is excited to higher electronic states, the values of the permanent dipole moment and the polarizability of the molecule can undergo significant changes from their values in the ground electronic state [1]. If the excited molecule is in solution with a polar solvent, then these changes in the molecular properties of the solute molecule on excitation are manifested through shifts in the maxima of absorption and fluorescence spectra from their values in a non-polar solvent [1–18]. The magnitudes of these shifts depend strongly on the molecule excited as well as on the nature of the solvent and the temperature. For a long time these shifts have been used to estimate the magnitude of the dipole moment of a molecule in its excited state [1–7]. In some cases, these shifts in absorption and fluorescence spectra can be used to study specific solute–solvent interactions, such as the formation of a charge-transfer state [8,9].

Nanosecond spectroscopy has been used to time resolve the fluorescence spectrum at low temperatures [10], and picosecond spectroscopy has enabled direct measurements of the evolution of the Stokes shift in fluid solution, at room temperature [11–15]. The time dependence of the fluorescence spectrum is dependent on solute–solvent interactions and should serve as a good probe of the relaxation of the surrounding molecules. In this paper we develop a description of the evolution of the Stokes shift of a polar molecule in a polar solvent.

If the time dependence of the environmental relaxation can be neglected (which is tantamount to assuming that solvent orientational relaxation is fast compared to the lifetime of the excited molecule), then a reasonable description of the solvent effect on absorption and fluorescence spectra is given by the Ooshika–Lippert–Mataga(OLM) equation [2–5]

\[
\langle \Delta \nu \rangle \equiv \langle \Delta \nu_a \rangle - \langle \Delta \nu_f \rangle = \frac{2(\mu_0 - \mu_s)^2}{h\alpha^3} \left( \frac{\varepsilon_0 - 1}{2\varepsilon_0 + 1} - \frac{n^2 - 1}{2n^2 + 1} \right),
\]

where \( \langle \Delta \nu_a \rangle \) and \( \langle \Delta \nu_f \rangle \) are the average shifts in the frequencies of 0–0 absorption and fluorescence transitions in solution due to polar interactions. The shifts are measured relative to the transition frequency of the solute molecule in a non-polar solvent when both \( \langle \Delta \nu_a \rangle \) and \( \langle \Delta \nu_f \rangle \) are very small.

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or zero. \( \mu_g \) and \( \mu_e \) are the dipole moments of the solute in ground and excited state. \( \varepsilon_0 \) is the static dielectric constant, and \( n \) the refractive index of the solvent.

Eq (1.1) is a simpler form of a more general expression derived from second-order perturbation theory. For most purposes eq. (1.1) is adequate since the higher-order terms are negligible.

In deriving eq. (1.1), the solute molecule is modeled as a spherical cavity of radius \( a \) with a rigid dipole at its center, and the solvent is replaced by a dielectric continuum of dielectric constant \( \varepsilon_0 \). The solute–solvent interaction is given by the interaction of the dipole at the cavity with its own reaction field arising from the polarization of the surrounding dielectric by the dipole. In eq. (1.1) this reaction field is assumed to be given by the expression derived by Onsager [19,20]. Since the process of excitation is much faster than any relaxation involved here, the excited molecule is initially placed in that environment which was in equilibrium with the ground state of the solute molecule. If the subsequent solvent reorganization is much faster than relaxation of the excited molecule, then fluorescence will occur from the excited state in equilibrium with the surrounding solvent to a ground state which is a Franck-Condon state of the excited molecule. The Stokes shift in fluorescence is a direct measure of the change in the dipole moment of the molecule in this transition, as shown by the OLM equation.

There are two reasons that the OLM equation needs to be generalized: first, because of recent interest in direct time-resolved fluorescence studies, and second, because even for steady-state measurements there are many realistic situations in which it may not be correct to assume complete solvent relaxation before any fluorescence decay occurs from the excited state. In particular, if the viscosity of the solvent is high or the temperature is low, the separation of timescales between solvent orientational relaxation and electronic relaxation may no longer hold. In such a situation, the molecule fluoresces from an excited state which is not in equilibrium with the surrounding solvent, and the full stabilization energy due to dipolar interaction is not achieved by the solute molecule at the time of the fluorescence. Since the excited-state energy during this period changes with time, the Stokes shift becomes time dependent. Lippert [7] and also Gonzalo and Escudero [18] have already considered the time dependence of this shift but their treatments are phenomenological. In this paper we derive an expression for the time dependence of the fluorescence shift by assuming a frequency-dependent dielectric continuum [21,22] for the solvent. This naturally gives rise to a time-dependent reaction field and a time-dependent stabilization energy. Our expression can be thought of as a generalization of the OLM equation to the time domain.

At this stage we should point out that our generalization of the OLM equation neglects the effect of the translational motion of the solvent molecules. As pointed out by van der Zwan and Hynes [23], the polarization surrounding a solute molecule can change either by rotation of solvent molecules or by translational diffusion of the solvent molecules relative to the solute without rotation. The latter effect can be significant in cases where the Debye relaxation of the pure solvent is slow, but the translational diffusion constant of the solvent molecules is large. We do not include this translational effect in the present calculation, although it certainly deserves further study.

In the continuum approximation, the potential energy from polar interactions can be written in the form

\[
\Delta E(t) = -\frac{1}{2} (\varepsilon_c + 2) \mu(t) \cdot R(t),
\]

where \( \varepsilon_c \) is the cavity dielectric constant (discussed later), \( R(t) \) is the time-dependent reaction field and \( \mu(t) \) is the dipole moment of the solute particle at time \( t \), where the magnitude of the dipole moment, \( |\mu(t)| \), is given by the gas-phase value. If the direction of the dipole moment changes by a large amount (more than \( \pi/2 \)), the \( \Delta E(t) \) will be positive at short times and the energy difference between the ground and the excited surface would increase, giving rise to a "blue" shift in fluorescence spectra. This blue shift has already been observed experimentally [11–15]. As the solvent and solute molecules reorient, \( \Delta E(t) \) becomes negative and a red shift in fluorescence is observed [24]. \( \Delta E(t) \) would reach its maximum value at
long times if electronic relaxation does not intervene. In order to calculate the time dependence of the fluorescence shift, we need an expression for the time dependence of the reaction field $R(t)$. This is obtained from a quasi-static boundary value calculation. In order to obtain an explicit form for $R(t)$, we need an analytical form for the frequency-dependent dielectric constant $\varepsilon(\omega)$ of the polar solvent. In this work, we have assumed two different forms for $\varepsilon(\omega)$: (a) a Debye form which corresponds to single exponential decay of orientational polarization, (b) a sum of two Debye forms (known as the Budo formula) [25]. This is appropriate for those polar liquids which show non-Debye behavior at high frequencies. For liquid alcohols like ethanol, propanol or butanol [26-28], the Cole-Cole plot of $\varepsilon(\omega)$ clearly indicates a need for more than one relaxation time to describe the relaxation behavior. However, even the description (b) would break down at very high frequency ($\omega > 10^{13}$ s$^{-1}$), but for the present we are not interested in such high-frequency (or very short-time) behavior of the solvent. When the Budo formula is used for $\varepsilon(\omega)$, then we obtain a bi-exponential time dependence of the Stokes shift, whereas for the simple Debye formula, a single exponential time dependence is obtained. In the limit of long time, our equation reduces exactly to the OLM equation (1.1) if the polarizability of the solute particle is neglected. We have also estimated the effect of polarizability on $\langle \Delta \mu \rangle$ and have found that for typical molecules, use of eq. (1.1) (which neglects polarizability of the solute molecule) would lead to an appreciably larger value of $\mu_e$, the excited-state dipole moment.

For many polar molecules, the polarizability changes significantly on excitation, and this may have an important effect on the Stokes shift. Within the continuum model adopted here, it is not possible to include this effect self-consistently. However, it is possible to estimate the magnitude of the shift in the long time limit. We show that in certain cases, the influence of polarizability may be significant.

One interesting prediction of the present theory is that if the polarizability effect can be neglected, then the normalized time-dependent Stokes shift is independent of the magnitudes of the ground- and excited-state dipole moments. It should be possible to test this prediction by exciting a series of molecules which do not show significant changes in their polarizabilities in the excited state.

The organization of the rest of the paper is as follows. In section 2, we derive the expression for the reaction field $R(t)$ assuming simple Debye form for $\varepsilon(\omega)$; the analogous expression for the Budo formula for $\varepsilon(\omega)$ is rather awkward and is not presented in the paper, though used in numerical calculations. In section 3, we evaluate the time dependence of the fluorescence shift and consider polarizability effects. In section 4, we present some numerical results along with a discussion of their significance. Section 5 concludes with a brief summary.

2. Time-dependent reaction field

We use a simple continuum model to calculate the time dependence of the reaction field. In this model, the polar solvent surrounding the solute molecule is replaced by a uniform dielectric continuum characterized by a frequency-dependent dielectric constant $\varepsilon(\omega)$. The dipolar solute molecule is replaced by a point dipole at the center of a spherical cavity filled with a dielectric material having a dielectric constant $\varepsilon_c$. $\varepsilon_c$ is related to the molecular polarizability $\alpha$ through the Clausius-Mossotti formula [20]

$$\frac{\alpha}{a^3} = \left(\varepsilon_c - 1\right)/\left(\varepsilon_c + 2\right).$$

Many molecules are better represented by a spheroid than by a sphere and the expressions developed below can easily be generalized to include these cases.

The energy of interaction of a dipole with its own reaction field is given by eq. (1.2). Effects of polarizability are present only through the reaction field $R(t)$. A quasi-static boundary-value calculation for the reaction field gives

$$R(\omega) = r(\omega)\mu(\omega),$$

where

$$r(\omega) = \left(2/a^3\right)\left[\varepsilon(\omega) - \varepsilon_c\right]/\varepsilon_c \left[2\varepsilon(\omega) + \varepsilon_c\right]$$

$$\times \frac{1}{3}\left(\varepsilon_c + 2\right).$$
This equation can be Fourier inverted to give the time dependence of the reaction field

\[ R(t) = \int_{-\infty}^{t} dt' r(t - t') \mu(t'). \]  

(2.4)

In order to write eq. (2.4), \( r(t) \) must be a stationary function of time. This condition is fulfilled if only the dipole moment of the molecule undergoes a sudden jump at a given time, but it does not hold if the polarizability of the solute molecule changes discontinuously. In the latter case, the quasi-static approach adopted here is not exact. We shall return to this point in the next section.

In order to calculate \( r(t) \), we need an expression for the frequency-dependent dielectric constant \( \epsilon(\omega) \) of the polar solvent. We assume simple Debye relaxation to fit \( \epsilon(\omega) \):

\[ \epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 - i\omega\tau_D}, \]  

(2.5)

where \( \epsilon_\infty \) is the infinite frequency dielectric constant of the solvent and \( \tau_D \) is the Debye relaxation time. In this approximation \( r(t) \) is a single exponential given by

\[ r(t) = \frac{2}{3a^3 \epsilon_\tau_D} \left[ \frac{(\epsilon_c + 2)}{(2\epsilon_\infty + \epsilon_c)} \right] \times \left[ \epsilon_0 - \epsilon_c + \frac{(\epsilon_c - \epsilon_\infty)(\epsilon_c + 2\epsilon_0)}{2\epsilon_\infty} \right] \times \exp \left( -t/\tau_L \right) \equiv \left[ 3/(\epsilon_c + 2) \right] F \exp \left( -t/\tau_L \right), \]  

(2.6)

where

\[ \tau_L = \left[ \frac{(\epsilon_c + 2\epsilon_\infty)}{(\epsilon_c + 2\epsilon_0)} \right] \tau_D \]  

(2.7)

and

\[ F = \frac{2(\epsilon_0 - \epsilon_\infty)/3a^3 \tau_D}{\left[ \frac{(\epsilon_c + 2)}{(\epsilon_c + 2\epsilon_\infty)} \right]^2}. \]

It is worth pointing out that the relaxation time of the reaction field is not \( \tau_D \), but \[ (\epsilon_c + 2\epsilon_\infty)/(\epsilon_c + 2\epsilon_0) \tau_D \] which can be much smaller than \( \tau_D \) for strongly polar solvents. Although this is a well-known fact in the field of dielectric relaxation, recently there have been some attempts to correlate the relaxation time of the Stokes shift with \( \tau_D \) rather than the correct quantity \( \tau_L \).

For many associated polar liquids, like ethanol and propanol, the Debye form (2.5) is inadequate. A multi-exponential form for the orientational correlation function of the dipolar solvent molecules is known to give a better fit to the experimental data [26,27]. In that case, (2.5) may be replaced by [25]

\[ \epsilon(\omega) = \epsilon_\infty + \left( \epsilon_0 - \epsilon_\infty \right) \sum_{k=1}^{N} \frac{g_k}{1 - i\omega\tau_k}, \]  

(2.8)

with

\[ \sum_{k=1}^{N} g_k = 1. \]  

(2.8a)

However, for the solvents which interest us here, a bi-exponential form is adequate and the sum in eq. (2.7) can be truncated at \( N = 2 \). The resulting formula for \( \epsilon(\omega) \) is characterized by two relaxation times \( \tau_1 \) and \( \tau_2 \). These relaxation times and their temperature dependence may be obtained by fitting \( \epsilon(\omega) \) to the experimental data. The expression for \( r(t) \) is then bi-exponential; the derivation is straightforward. The numerical calculations have been carried out mostly with the bi-exponential form.

3. Fluorescence shift

The dipolar interaction energy, as given by eq. (1.2), can now be written in the form

\[ \Delta E(t) = -\frac{3}{4}(\epsilon_c + 2)\mu(t) \cdot \int_{-\infty}^{t} dt' r(t - t') \mu(t'). \]  

(3.1)

Since the processes of optical excitation and emission are much faster than any relaxation processes involved, we model the change in dipole moment on excitation and fluorescence by Heaviside functions

\[ \mu(t) = \mu(t = 0) \left[ \mu^{(b)}(t = 0) - \mu^{(b)}(t = 0) \right] + H(t - t_1) \left[ \mu^{(b)}(t) - \mu^{(b)}(t) \right], \]  

(3.2)

where \( \mu^{(b)}(t) \) and \( \mu^{(b)}(t) \) are the dipole moments (in the body-fixed frame) of the solute molecule in the ground and excited states, respectively, and \( H(t) \) is a Heaviside function. Eq. (3.2) is simply a
statement of the fact that the molecule is excited from its ground electronic state at time $t = 0$, and it fluoresces back to the ground state at time $t = t_r$. $\mu_g^{(b)}$ and $\mu_e^{(b)}$ will in general differ both in magnitude and in direction. In the discussion which follows, we have neglected the change of polarizability. We shall show later in this section how the effect of this change can be approximately included.

Let $\langle \Delta E \rangle_{eq}^g$ and $\langle \Delta E \rangle_{eq}^e$ denote the average stabilization energies due to dipolar interactions in the ground and excited states of the solute molecule in equilibrium with the polar solvent. $\langle \Delta E \rangle_{eq}^g$ is the interaction energy when the excited solute molecule is in the Franck-Condon state of the ground-state solvent configuration and $\langle \Delta E \rangle_{eq}^e$ denotes the energy in the reverse situation. Let $\langle \Delta E(t) \rangle^e$ denote the time-dependent stabilization energy when the molecule is in the excited state at a time $t$ after the optical excitation; obviously, $\langle \Delta E(t) \rangle^e = \langle \Delta E \rangle_{eq}^e$. The shift in the maximum of the absorption spectrum is then given by

$$hc\langle \Delta \nu_a \rangle = \langle \Delta E \rangle_{eq}^g = F_{\tau_L} (\mu_g - \mu_e) \cdot \mu_g$$

$$= F_{\tau_L} (\mu_g^2 - \mu_e \mu_g \cos \psi). \quad (3.3)$$

where $\psi$ is the angle of rotation of the dipole upon excitation, measured in the body-fixed frame. Depending on the value of $\psi$, $\Delta \nu_a$ can become positive, thus giving rise to a blue shift, relative to the gas phase, in the absorption spectrum.

The unaveraged stabilization energy in the excited state is given by

$$\Delta E(t)^e = -\frac{1}{2} (\epsilon_e + 2) \mu_e(t) \cdot \int_{-\infty}^t dt' r(t-t') \mu(t'), \quad (3.4)$$

so the average energy is

$$\langle \Delta E(t) \rangle^e = -\mu_e \int_{0}^{\infty} d\tau \, e^{-\tau/\tau_c}$$

$$\times \mu(t-\tau) \times \langle \hat{\mu}(t) \cdot \hat{\mu}(t-\tau) \rangle, \quad (3.5)$$

where we have substituted expression (2.6) for $r(t)$, made the transformation $\tau = t - t'$ and separated the magnitude and direction of the dipole moment by $\mu(t) = \mu(t) \hat{\mu}(t)$, $\hat{\mu}(t)$ being the unit vector giving the orientation of the dipole in the space-fixed frame. The time dependence of $F(t)$ is neglected now but will be considered later.

The correlation function $\langle \hat{\mu}(t) \cdot \hat{\mu}(t-\tau) \rangle$ in eq. (3.5) is to be evaluated in a space-fixed frame. By following standard procedures, we obtain the following expression for the correlation function

$$\langle \hat{\mu}(t) \cdot \hat{\mu}(t-\tau) \rangle$$

$$= \frac{4}{3\pi} \sum_{m,m',m''} (-1)^m Y_{lm} \cdot (\theta_B(t), \phi_B(t))$$

$$\times Y_{l'm'}(\theta_B(t-\tau), \phi_B(t-\tau))$$

$$\times \langle D_{m'-m}^{l'}(\Omega(t)) D_{m'-m}^{l'}(\Omega(t-\tau)) \rangle, \quad (3.6)$$

where $\theta_B(t), \phi_B(t)$ are the spherical coordinates of the dipole in the body-fixed frame at time $t$ and $D_{m'-m}^{l'}(\Omega(t))$ is the Wigner matrix of the Euler angles between space-fixed and body-fixed frames. If we assume isotropic rotational diffusion, then [29]

$$\langle D_{m'-m}^{l'}(\Omega(t)) D_{m'-m}^{l'}(\Omega(t-\tau)) \rangle$$

$$= \frac{1}{4} \delta_{m',m} e^{-2D\tau}. \quad (3.7)$$

Eq. (3.6) then gives

$$\langle \hat{\mu}(t) \cdot \hat{\mu}(t-\tau) \rangle = [\cos \gamma(t, t-\tau)] e^{-2D\tau}, \quad (3.8)$$

where $D$ is the rotational diffusion coefficient of the solute molecule, and $\gamma$ is the angle in the body-fixed frame between the dipole moment at time $t$ and that at time $t-\tau$.

It is worthwhile to point out that in writing eq. (3.7), we have neglected the correction to the solute diffusion coefficient from a non-equilibrium distribution of solvent dipoles around the solute particle in the excited state. This correction may be important in the short time regime when the solute dipole will feel a highly unfavorable environment. However, we believe that this correction will not affect the fluorescence decay very much for two reasons. First, the major contribution to the rotational diffusion constant $D$ arises from short range hard core repulsions and corrections from polar effect are small. Second, the solvent relaxation in most of the cases of interest to us is much faster than the rotational diffusion of solute particles and therefore the short time behavior will be little affected.
Substituting eqs. (3.2) and (3.8) in (3.5), we obtain the following expression for the time dependence of the stabilization energy in the excited state

\[ \langle \Delta E(t) \rangle^e = -F \mu_\perp \tau_F \left( 1 - e^{-t/\tau_F} \right) - F \mu_\parallel \tau_F \cos \psi e^{-t/\tau_F}, \]  

(3.9)

where \( \tau_F = \tau_L^{-1} + 2D \). The time dependence of the fluorescence Stokes shift at time \( t_1 \) is

\[ h \Delta \nu_F(t_1) = \langle \Delta E(t_1) \rangle^e - \langle \Delta E(t_1) \rangle^e, \]  

(3.10)

\( \langle \Delta E(t_1) \rangle^e \) is obtained by following a procedure similar to that described for \( \langle \Delta E(t) \rangle^e \) and the result is

\[ \langle \Delta E(t_1) \rangle^e = -F \mu_\perp \tau_F \cos \psi \left( 1 - e^{-t/\tau_F} \right) - F \mu_\parallel \tau_F e^{-t/\tau_F}. \]  

(3.11)

The fluorescence shift at time \( t_1 \) is then

\[ h \langle \Delta \nu_F(t_1) \rangle = F \tau_F (\mu_\parallel - \mu_\perp) \]  

\[ \left[ \mu_\perp + (\mu_\parallel - \mu_\perp) e^{-t/\tau_F} \right] \]  

\[ - F \tau_F \left( \mu_\parallel \mu_\perp \cos \psi - \mu_\perp^2 \right) \left( 1 - e^{-t/\tau_F} \right) \]  

\[ + \tau_F F \left( \mu_\parallel^2 - \mu_\parallel \mu_\perp \cos \psi \right) e^{-t/\tau_F}. \]  

(3.12)

The frequency difference between absorption maximum and fluorescence maximum can easily be obtained from (3.3) and (3.12).

It is interesting to find out that what conditions our expressions reduce to that of Ooshika et al., eq. (1.1). In order to see this, we take the limit \( t_1 \to \infty \), set \( \varepsilon_0 = 1 \) (i.e. neglect the polarizability of the solute molecule), take \( x(<e) \gg 2D \) (which means that solvent orientational relaxation is much faster than that of the solute), and set \( \psi = 0 \); eq. (3.12) then yields

\[ h \langle \Delta \nu_F \rangle = \frac{2}{\hbar a^2} \left( \frac{\varepsilon_0 - 1}{2\varepsilon_0 + 1} - \frac{\varepsilon_\infty - 1}{2\varepsilon_\infty + 1} \right) \left( \mu_\parallel \mu_\perp - \mu_\perp^2 \right), \]  

(3.13)

and for the frequency difference between absorption and fluorescence maxima

\[ \langle \Delta \nu \rangle = \frac{2}{\hbar a^2} \left( \frac{\varepsilon_0 - 1}{2\varepsilon_0 + 1} - \frac{\varepsilon_\infty - 1}{2\varepsilon_\infty + 1} \right) \left( \mu_\parallel - \mu_\perp \right)^2, \]  

(3.14)

which is exactly the same as eq. (1.1).

3.1. Polarizability effects

In many cases, the polarizability of the molecule changes significantly during the process of excitation. We have already mentioned that it is not possible to treat this change exactly within the continuum model. However, it is possible to make a reasonable estimate of the effect of this change on the fluorescence shift.

The OLM equation (1.1) does not consider the polarizability of the solute molecule. Since it is widely used to estimate the magnitude of the excited-state dipole moment we have first investigated the influence of polarizability on the shift of absorption and emission maxima. An expression for \( \langle \Delta \nu \rangle \) can easily be found from eqs. (3.3) and (3.12) if \( D \) is small so \( \tau_F = \tau_L \). The error incurred by using (1.1) instead of the general form with \( \varepsilon_0 \neq 1 \) can easily be found by considering the ratio

\[ \frac{\langle \Delta \nu \rangle_{\varepsilon_0 = 1}}{\langle \Delta \nu \rangle_{\varepsilon_0 = 1}} = \left( \frac{\varepsilon_+ + 2}{3} \right)^2 \frac{(2\varepsilon_0 + 1)(2\varepsilon_\infty + 1)}{(2\varepsilon_0 + \varepsilon_\perp)(2\varepsilon_\infty + \varepsilon_\perp)}. \]  

(3.15)

For molecules with conjugated benzene rings, \( \varepsilon_\perp \) should be typically between 1.5 and 2.0. So, if we consider a polar solvent like ethanol (\( \varepsilon_0 = 21.1, \varepsilon_\infty = 2.0 \)), then the ratio can be significantly larger than unity. For example, if we take \( \varepsilon_\perp = 1.5 \), then the ratio is 1.34. This implies that the OLM equation may overestimate excited-state dipole moments by as much as 15%.

Next, we consider the effect of the change of polarizability on the Stokes shift of the fluorescence in the long time limit. First we note that \( \varepsilon_\perp \) has two related but somewhat different kinds of contributions to stabilization energy. One is a straightforward contribution to the dipole moment of the solute, from the multiplicative factor \( (\varepsilon_\perp + 2)/3 \). The second part is a higher-order effect due to the influence of the increased dipole moment on the reaction field. If the polarizability and the
dipole-moment change instantaneously on excitation (or deexcitation), then the first contribution will also change instantaneously, but the second contribution will be slow to respond, i.e. the reaction field will stay at the value corresponding to the older value of cavity dielectric constant. In this way an estimate of the effect of the change in polarizability may be obtained; significant corrections to the OLM equation result.

4. Numerical results and discussion

In order to study the time dependence of the maximum of the fluorescence spectrum, it is convenient to introduce a correlation function $C(t)$ through

$$C(t) = \frac{\langle \Delta \nu_f(t) \rangle - \langle \Delta \nu_f(\infty) \rangle}{\langle \Delta \nu_f(0) \rangle - \langle \Delta \nu_f(\infty) \rangle}. \quad (4.1)$$

The correlation function $C(t)$ decreases from one to zero as time is increased from zero to infinity. If $\varepsilon(\omega)$ of the solvent is described by a simple Debye formula (2.5), then our theory predicts a single exponential decay for $C(t)$, as discussed in the last section. However, most of the experiments on the time dependence of the Stokes shift of fluorescence have been carried out in liquid monoalcohols for which eq. (2.5) is an inadequate description of $\varepsilon(\omega)$. In these solvents there are additional dispersions at high frequencies and the dielectric relaxation is thus characterized by at least two relaxation constants, $\tau_1$ and $\tau_2$, and an equation of the form (2.7) with $N = 2$ must be used. Then our theory predicts a bi-exponential decay for $C(t)$ with rate constants $\tau_F^{(1)}$ and $\tau_F^{(2)}$ given by

$$\tau_F^{(1)} = (S_+ + 2D)^{-1}, \quad (4.2)$$
$$\tau_F^{(2)} = (S_- + 2D)^{-1}, \quad (4.3)$$

where

$$S_\pm = \frac{1}{2} \left[ A \mp (A^2 - 4B)^{1/2} \right], \quad (4.4)$$
$$A = \left[ (2\epsilon_\infty + \epsilon_c)(\tau_1 + \tau_2) + 2(\epsilon_0 - \epsilon_\infty) \times (g_1\tau_2 + g_2\tau_1) \right] / \tau_1\tau_2(2\epsilon_\infty + \epsilon_c), \quad (4.5)$$
$$B = (2\epsilon_0 + \epsilon_c) / \tau_1\tau_2(2\epsilon_\infty + \epsilon_c). \quad (4.6)$$

Experiments typically give $\tau_2$, the faster component in dielectric relaxation, about an order of magnitude smaller than $\tau_1$ and $\tau_2$ between 0.1 and 0.2. The relative magnitudes of $\tau_F^{(1)}$ and $\tau_F^{(2)}$ will depend on $g_1$ and $g_2$, the relative contribution of the two dispersion terms to $\varepsilon(\omega)$.

The correlation function $C(t)$ has some interesting features which may be tested against experiments, though no experiment has yet measured the time dependence of this function. First we note that $C(t)$ does not depend on the change of dipole moment between ground and excited states. This statement holds only for the simple case where the change in polarizability is neglected. Thus our calculations, at a first level of approximation, should apply to any particular solute provided the experiments are performed in the same solvent system and the molecular polarizability is similar. A note of caution is required, however. In cases where the Stokes shift is very large, the formation of an excited state with significant charge-transfer (CT) character has frequently been suggested. If the formation of the CT excited state involves intramolecular motion of the solute, then the experiments cannot be directly compared with our theory.

Fig. 1 shows the calculated time dependence for $C(t)$ in propanol at three different temperatures. The dielectric relaxation times of propanol were obtained by fitting eq (2.7) (with $N = 2$) to the experimental results of Garg and Smyth [27]. At 20°C, this gives $\tau_1 = 430$ ps, $\tau_2 = 21.9$ ps, $g_1 = 0.91$ and $g_2 = 0.09$. For propanol $\epsilon_0 = 21.1$ and $\epsilon_\infty = 2.08$ at 20°C. We used $D = 5 \times 10^8$ s$^{-1}$, a value obtained for a sphere of 5 Å radius and stick-boundary condition. The results are rather insensitive to the value of $D$ since the $S_\pm$ are significantly larger than $D$. A value of $\epsilon_c = 1.8$ based on a molecular polarizability 26 Å$^3$ was used. For this choice of parameters we obtain at 20°C $\tau_F^{(1)} = 13$ ps and $\tau_F^{(2)} = 92$ ps. The correlation function $C(t)$ has a 1/e time of $\approx 33$ ps.

It is of interest to consider the dynamics of $c(t)$ in liquid water which has a very high static dielectric constant and is highly polar. Another notable characteristic of water is that the dielectric relaxation can be described very well by a simple Debye form over a rather large range of temperature.
Fig. 1 Time dependence of the correlation function $C(t)$ at three different temperatures, $T = 20^\circ C$, $T = 40^\circ C$, $T = 60^\circ C$.

For example, at $20^\circ C$, the parameters are: $\tau_D = 9 \times 10^{-12}$ s, $\varepsilon_0 = 81.0$ and $\varepsilon_\infty = 5.0$. If we consider a typical value of $\varepsilon_c = 1.8$ for the cavity dielectric constant, then our theory predicts a value of $\tau_F = 0.64$ ps for the decay time; subpicosecond laser pulses will be required to study the dynamics of the Stokes shift in water.

The calculation depicted in Fig. 1 cannot be compared directly with experiments since it plots the time dependence of the spectral maximum, whereas the experiments usually study the time dependence of the fluorescence intensity at a particular wavelength. For example, Halliday and Topp [11,12] studied 2-amino-7-nitrofluorene (ANF) in isopropanol at various wavelengths and temperatures and found that the relaxation time depends strongly on the wavelength monitored. The decay was distinctly slower in the red tail of the spectrum than in the blue edge. Okamura et al. [13] recently reported measurements of the time evolution of the Stokes shift in $\alpha$-naphthylamine, also in isopropanol. They studied the time dependence at two wavelengths, one in the blue edge and the other in the red tail, and found, in contrast to Halliday and Topp, the same decay rate at the two wavelengths. In what follows, we offer some explanations for the above results.

In order to carry out a full comparison of theoretical predictions with the wavelength-dependent dynamics of the Stokes shift, a detailed calculation of the lineshape is necessary. In this paper, however, we adopt a simpler approach. We assume that the shape of the fluorescence spectrum remains unchanged in time and is approximately gaussian. We can then write the following simple expression for the fluorescence intensity

$$I(\nu, t) = \exp\left[-(\nu - \langle \nu(t) \rangle)^2/\sigma^2\right]$$

$$= \exp\left[-(\Delta \nu - \langle \Delta \nu(t) \rangle)^2/\sigma^2\right],$$

(4.7)

where $\Delta \nu = \nu - \nu_0$ and $\Delta \nu(t) = \nu(t) - \nu_0$ are the shifts from the unperturbed transition frequency. $\sigma$ is related to the full width at the half height of the fluorescence spectrum. Eq. (4.7) is no more than the statement that the spectrum moves in time without any change in its assumed gaussian shape; i.e. every part of the spectrum moves at the same speed as that of the maximum. Of course, eq. (4.7) is a rather crude representation of a very complicated process occurring in real systems, but we believe that it will reproduce the essential qualitative features.

Fig. 2 shows the time dependence of the fluorescence shift calculated with eq. (4.7) at two different frequencies, one at the blue edge, the other at the red tail of the spectrum. For these calculations, $\sigma$ is obtained from Fig. 1b of Okamura et al. for $\alpha$-naphthylamine, and we have used $\mu_\pm = 1.53$ D, $\mu_c = 5.93$ D which are taken from Mataga [5]. As before, all calculations are performed for propanol.

Fig. 2. Time dependence of the correlation function $C_f(\nu, t)$. $\cdots$ fluorescence decay in the blue edge, $\cdots$ fluorescence rise in the red tail. The values of the parameters are discussed in the text.
Fig. 2 reproduces the essential features of the time dependence of the fluorescence shift. The intensity decays in the blue edge of the spectrum and rises in the red tail and the curves look exponential. In order to make a more quantitative analysis of the rate of decay it is convenient to introduce the following time-correlation function

\[ C_I(\nu, t) = \frac{I(\nu, t) - I(\nu, t = \infty)}{I(\nu, t = 0) - I(\nu, t = \infty)}. \]  (4.8)

\( C_I(\nu, t) \) thus defined decays from unity to zero for all frequencies \( \nu \) as time goes from zero to infinity.

In order to compare our results with the experiments of Okamura et al., we calculated \( C_I(\nu, t) \) at the two values of the wavelength studied by them. They correspond, approximately to \( \Delta \nu = 1.3 \times 10^3 \text{ cm}^{-1} \) for the wavelength at the blue edge and \( \Delta \nu = -3 \times 10^3 \text{ cm}^{-1} \) for the wavelength at the red tail. We find that \( C_I(\nu, t) \) decays at an almost identical rate for both these frequencies and the decay (or rise) time is approximately equal to 33 ps. Okamura et al. also found identical decay times at the above two wavelengths. Their reported decay time is 52 ps which is somewhat larger than our value. However, in view of the crude approximations that we made in writing eq. (4.8) and in finding \( \sigma \) and \( \Delta \nu \) the disagreement is not unexpected. The important thing to note is that our results seem to reproduce the interesting observation of Okamura et al. [13] on the equality of decay constants in two different regions of the fluorescence spectrum. In fact, we find that the rate of decay of \( C_I(\nu, t) \) is rather insensitive to \( \Delta \nu \) within a limited range of frequencies in both the red and the blue region of the fluorescence spectrum. This result and also that of Okamura et al. indicates that the rate at which fluorescence disappears in the blue edge is the same with which it reappears in the red tail of the spectrum.

When the excited-state electronic relaxation is of comparable rate to the time dependence of the Stokes shift it is necessary to consider the quantity \( I(\nu, t) \exp(-t/\tau_n) \), where \( \tau_n \) is the fluorescence lifetime. In the case of \( \alpha \)-naphthylamine the Stokes shift occurs on a much faster timescale than the electronic relaxation and we may safely neglect the latter. It is more difficult to compare the results of Halliday and Topp on ANF [11] with the theory for two reasons. First, the timescale separation between Stokes shift and electronic relaxation cannot be made: at higher temperatures a simple rise to a constant value of the red-shifted emission is not observed. Second in the case of ANF it is unlikely that the shape of the emission spectrum is unaltered during the relaxation process. Thus quantitative interpretation of the wavelength-dependent relaxation observed by Halliday and Topp is not warranted. Qualitatively, however, their observation of an increase in relaxation rate as the fluorescence is probed further toward the blue (i.e. as \( \Delta \nu \) is increased) is in accord with the time dependence of \( C_I(\nu, t) \). The faster decay in the blue edge region arises from two effects. The first is simply the influence of the spectral shape. If observations are made at a point in the spectrum where the intensity is decreasing rapidly toward shorter wavelength, then a small red shift in the spectrum will produce a large decrease in emission at the observation wavelength. In addition the bi-exponential nature of the dielectric relaxation will also cause the decay of emission on the blue edge of the spectrum to appear more rapid than for longer wavelengths. This is because the fluorescence from the blue edge occurs only at early times, and the decay is dominated by the faster component of the dielectric relaxation.

5. Conclusion

Let us first summarize the main results of this paper. We have derived an expression for the time dependence of the maximum of the fluorescence spectra of a polar molecule in a polar solvent. This expression is derived by replacing the solvent by a frequency-dependent dielectric continuum and the solute molecule by a spherical cavity of dielectric constant \( \epsilon_c \). Our expression for \( C(t) \), as given by eq. (4.1), is to be considered as a direct generalization of the well-known OLM equation to the time domain. We have predicted that if polarizability effects can be neglected, then \( C(t) \) is a universal function depending only on solvent time constants and dielectric properties. This prediction may be tested in future experiments. We have considered
the effects of polarizability on fluorescence shift and found that for many molecules these effects are non-negligible. Since recent experiments measured the dynamics of the Stokes shift at specific wavelengths, we noted that $C(t)$ cannot be compared directly with these experiments. In order to explain the wavelength-dependent dynamics of the fluorescence shift, we have constructed, albeit crudely, a correlation function $C_\nu(v, t)$ by assuming the time invariance of the shape of the spectrum which we take to be gaussian. The correlation function, given by eq. (4.8), correctly reproduces the essential features of the wavelength dependence of the dynamics of the Stokes shift. The calculated values of the rate constants are in semi-quantitative agreement with the experiments of Okamura et al [13] and of Hallidy and Topp [11,12].

Although our calculations have been carried out by assuming a spherical shape for the molecular cavity, it is straightforward (but tedious) to generalize to such non-spherical shapes as spheroids by following the standard procedure [25].

One objection that can be raised against the theory presented here is the use of the continuum model for the solute–solvent interaction. As we have already mentioned, the theory is not suitable for cases where the excited state molecule is a charge-transfer complex with intramolecular motion or has some specific interaction with the surrounding molecules. The theory can also break down if the solute dipole moment increases by a very large amount on excitation. However, we believe that in many other cases, our theory is semi-quantitatively valid and is reliable to the same extent that the theories of dielectric relaxation based on frequency-dependent continuum theories are. The theory can, in principle, be extended to cases where the solvent is a mixture of two or more polar molecules. A new feature of this system will, however, need to be taken into account. If the dipole moments of the different solvent molecules have widely differing magnitudes, then the more polar solvent molecules will tend to aggregate around the solute molecule. This non-random distribution is not included in the continuum picture. If the solute becomes much more polar on excitation it is possible that the equilibrium composition of solvent molecules around the solute may differ in ground and excited states and an additional process – solvent exchange – enters the problem [32].

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