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Theory of the Salt Effect on Solvatochromic Shifts And Its Potential Application to the Determination of Ground-State and Excited-State Dipole Moments

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The theory of solvatochromism based on a dielectric continuum description of the solvent and the classical Onsager cavity model is revisited and extended to include the effect of an added 1:1 salt. An expression is derived for the reaction field inside the solute cavity, which is applicable in the limit of low salt concentrations. Using this result, expressions are obtained for the shifts in the (0−0) absorption and fluorescence maxima on the basis of Marcus' approach to the calculation of the medium reorganization free energy in the ground state and excited (Franck−Condon) state of the solute molecule. The lifetime of the excited state is assumed to exceed the longest relaxation time characteristic of the medium. For the salt-free case, our equations differ markedly from several others reported in the literature dealing with the pure solvent effect, and the origin of the discrepancy is clarified. Finally, it is shown how the new equations can be used, in principle, to obtain estimates for the Onsager radius, polarizability, and dipole moments in the ground state and the lowest excited state of a solute molecule from a simple analysis of absorption and fluorescence data only, except in cases where the dipole moments are noncollinear. Completion of the analysis then requires an independent measurement of the ground-state dipole moment.

1. Introduction

Electric dipole moments may be derived from the application of an electric field to molecules in the gas phase, which is studied using the microwave technique, by observing the normal Stark effect. More commonly, however, experimental dipole moments are obtained in the liquid phase from measurements of dielectric constants. In addition to ground-state dipole moments, excited-state dipole moments are of considerable interest.[1]

Experimental methods for the determination of dipole moments in their electronically excited states are based on the knowledge of the experimental ground-state dipole moment and a change of the position of a band in the electronic spectrum, external (electrochromism) or internal (solvatochromism). Solvatochromic methods, also known as solvent-shift methods, are simpler because they do not require the use of an external field. However, they are less reliable and less accurate because their use involves numerous simplifications and approximations. The various solvatochromic equations make use of ground-state dipole moments and shifts of the absorption and emission (fluorescence, phosphorescence) maxima in solvents of different polarities.[1] The most commonly employed theoretical expressions are those derived by Kawski, Chamma, and Viallet[2−5] and by Bakhshiev[6] for compounds that fluoresce or phosphoresce. The McRae[7] and Suppan[8,9] equations are used for nonemitting compounds.

Several simplifications and shortcomings of these theoretical treatments will be mentioned here. First of all, it is usually assumed that ground- and excited-state dipole moments are collinear, although an effort has been made to introduce a correction for noncollinear dipole moments.[10] Even in the case of collinear ground- and excited-state dipole moments, parallel and antiparallel orientations are possible. Furthermore, specific solute−solvent interactions on absorption and emission profiles are generally not taken into account. The possibility of incomplete solvent relaxation prior to emission is not considered either, although some attempts to improve the theory in this regard can be found in the work of Bakhshiev.[6,11] Also, improvements in the determination of the effective molecular size in terms of the Onsager cavity radius, which is needed in solvatochromic equations, are desirable.[12] Finally, the use of solvatochromic equations may result in negative or imaginary values of excited-state dipole moments for some compounds.

In solution chemistry, one of the important effects upon electronic absorption and emission spectra is exhibited by dissolved salts, resulting in a shift of the maxima to different wavelengths and in changes of the intensity of absorption or emission.

The importance of salt effects is well known, as demonstrated by such diverse phenomena as the dependence of solubility on ionic strength, salting out, et cetera, although organic chemists tend to be more concerned with specific salt effects.[13]

In this contribution, we have set out to explore the theory of solvatochromism on the basis of a dielectric continuum description of the solvent and the Onsager cavity model[14] and in particular to investigate the role of added salt in producing "ionochromic" shifts.

The results can be used to derive expressions for shifts of the 0−0 absorption and emission maxima. It will be shown that

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the equations obtained for solutions without salt are different from most of those reported before and used in the analysis of experimental results but vindicate and generalize the approach taken by Lippert[15] many years ago. It will then be demonstrated how these new equations could be used to estimate the Onsager cavity radius, polarizabilities, and ground- and excited-state dipole moments along with their relative orientation using absorption and fluorescence spectra and an independent measurement of the ground-state dipole moment.

2. Salt Effect on the Reaction Field of a Polar Solute Molecule

Consider a dipole $\mu = q\delta$ (q = charge, δ = distance between $+q$ and $-q$) in a vacuum. In SI units, the potential at distance r and colatitude θ with respect to the direction of $\vec{\mu}$ is given by

$$\varphi(r, \theta) = \frac{\mu \cos\theta}{4\pi\epsilon_0 r^2} \tag{1}$$

in the limit $\delta \rightarrow 0$ (i.e., for a point dipole).

Next, the same dipole is thought of as having been placed at the center of a spherical cavity of radius a ($\approx$molecular size) in a solvent that is modeled as a continuous dielectric with a relative permittivity of $\epsilon > 1$ (see Figure 1).

In view of the axial symmetry of this system, two coordinates, r and θ, suffice. Two regions will be distinguished: region 1 (the cavity: $0 \leq r \leq a$; $\epsilon = 1$) and the outer region 2 (solvent + salt; $r \geq a$). On the average, the molecule will induce an axially symmetric charge distribution by polarizing the solvent and attracting/repelling ions. This polarized environment generates its own potential distribution in regions 1 and 2 corresponding to the reaction field, $\vec{E}_\mathrm{r}(r, \theta)$.

The total dipole moment $\vec{\mu}$ can now be written as

$$\vec{\mu} = \vec{\mu}_\mathrm{p} + \alpha\vec{E}_\mathrm{r} \tag{2}$$

where $\vec{\mu}_\mathrm{p}$ is the permanent dipole moment and α is the polarizability of the solute molecule.

The potential distribution $\varphi_1(\vec{r})$ inside the cavity is equal to the sum of the dipole potential (eq 1) and the contribution due to the response of the medium, the latter obeying the Laplace equation, so that the potential distribution in region 1 can be written as

$$\varphi_1(r, \theta) = \sum_{n=0}^{\infty} A_n r^n P_n(\cos\theta) + \frac{\mu\cos\theta}{4\pi\epsilon_0 r^2} \qquad (r \leq a, 0 \leq \theta \leq \pi) \tag{3}$$

where $P_n(x)$ is a Legendre polynomial defined as

$$P_n(x) = \frac{1}{2^n n!}\frac{\mathrm{d}^n}{\mathrm{d}x^n}(x^2 - 1)^n \qquad (-1 \leq x \leq 1) \tag{4}$$

These functions satisfy the orthogonality relationship

$$\int_{-1}^{1} P_n(x)\, P_m(x)\, \mathrm{d}x = \frac{2}{2n+1}\delta_{nm} \qquad (\delta_{nn} = 1 \text{ and } \delta_{nm} = 0 \text{ if } n \neq m) \tag{5}$$

The coefficients A_n will be determined later using the boundary conditions at $r = a$.

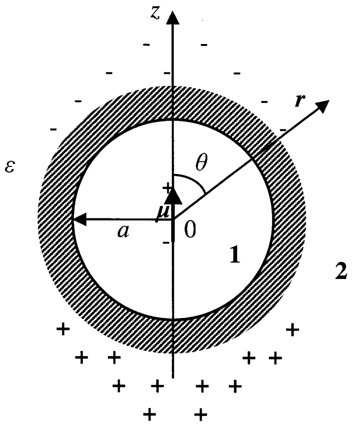

Figure 1. Onsager cavity model and coordinates used in the description of potential distributions.

Next, we turn our attention to the average potential distribution in the exterior region, where a 1:1 salt is assumed to be present at low concentration c_s. Then φ_2 is, to a good approximation, a solution of the linearized Poisson−Boltzmann equation

$$\nabla^2\varphi_2 = \kappa^2\varphi_2 \tag{6}$$

as long as $F\varphi_2 \ll RT$, on average. Here, F is the Faraday constant, and κ is the inverse Debye screening length given as

$$\kappa = \sqrt{\frac{2c_s F^2}{\epsilon\epsilon_0 RT}} \tag{7}$$

It is important to note that eq 6 is of the Helmholtz type. Its general solution for an axially symmetric system is given as[16]

$$\varphi_2(r, \theta) = -\sum_{n=0}^{\infty} B_n \sqrt{\frac{\pi}{2}}\frac{H^{(1)}_{n+(1/2)}(\mathrm{i}\kappa r)}{\sqrt{\mathrm{i}\kappa r}} P_n(\cos\theta) \tag{8}$$

where the B_n's are, as yet, undetermined coefficients, $\mathrm{i} = \sqrt{-1}$, and the $H^{(1)}_{n+(1/2)}(x)$'s are Hankel functions of the first kind, which are linear combinations of Bessel functions, as follows:

$$H^{(1)}_{n+(1/2)}(x) = J_{n+(1/2)}(x) - \mathrm{i}(-1)^n J_{-n-(1/2)}(x) \tag{9}$$

With $x = \mathrm{i}\kappa r$, this function can also be expressed as

$$H^{(1)}_{n+(1/2)}(\mathrm{i}\kappa r) = -\sqrt{\frac{2}{\pi \mathrm{i}\kappa r}}(g_n(\mathrm{i}\kappa r) + \mathrm{i}f_n(\mathrm{i}\kappa r))e^{-\kappa r} \tag{10}$$

All that we shall need to know about the functions $f_n(x)$ and $g_n(x)$ is that

$$f_0(x) = 1, \qquad g_0(x) = 0, \qquad f_1(x) = x^{-1}, \qquad g_1(x) = 1 \tag{11}$$

Hence,

$$\varphi_2(r, \theta) = \sum_{n=0}^{\infty} B_n(f_n(\mathrm{i}\kappa r) - \mathrm{i}g_n(\mathrm{i}\kappa r))\frac{e^{-\kappa r}}{\kappa r}P_n(\cos\theta) \qquad (r \geq a, 0 \leq \theta \leq \pi) \tag{12}$$

The unknown coefficients A_n (eq 3) and B_n must now be calculated by substituting the general expressions for φ_1 and φ_2 into the boundary conditions at $r = a$ (i.e., the conditions of continuity of the potential and normal components of the dielectric displacement):

$$\varphi_1(a,\theta) = \varphi_2(a,\theta) \tag{13}$$

$$\frac{\partial \varphi_1}{\partial r}(a,\theta) = \epsilon \frac{\partial \varphi_2}{\partial r}(a,\theta) \tag{14}$$

$$(0 \leq \theta \leq \pi)$$

Substitution of the series expansions and use the orthogonality property of the P_n's, eq 5, then lead to the two sets of linear equations:

$$A_0 = B_0 \frac{e^{-\kappa a}}{\kappa a} \tag{15a}$$

$$A_1 a + \frac{\mu}{4\pi\epsilon_0 a^2} = -\mathrm{i}B_1\left(1 + \frac{1}{\kappa a}\right)\frac{e^{-\kappa a}}{\kappa a} \tag{15b}$$

$$A_n = B_n(f_n(\mathrm{i}\kappa a) - \mathrm{i}g_n(\mathrm{i}\kappa a))\frac{e^{-\kappa a}}{\kappa a} \qquad n \geq 2 \tag{15c}$$

and

$$B_0 = 0 \tag{16a}$$

$$A_1 - \frac{2\mu}{4\pi\epsilon_0 a^3} = \mathrm{i}B_1\epsilon\kappa\left(1 + \frac{2}{\kappa a} + \frac{2}{(\kappa a)^2}\right)\frac{e^{-\kappa a}}{\kappa a} \tag{16b}$$

$$nA_n a^{n-1} = B_n\epsilon\kappa\left[\mathrm{i}f_n{}'(\mathrm{i}\kappa a) + g_n{}'(\mathrm{i}\kappa a) - (f_n(\mathrm{i}\kappa a) - \mathrm{i}g_n(\mathrm{i}\kappa a))\left(1 + \frac{1}{\kappa a}\right)\right]\frac{e^{-\kappa a}}{\kappa a} \qquad n \geq 2 \tag{16c}$$

from which it is immediately obvious that $A_n = B_n = 0$ if $n \neq 1$, and as a consequence, the potential of the reaction field inside the cavity, $\varphi_r(r, \theta)$, takes the simple form

$$\varphi_r(r,\theta) = A_1 r \cos\theta \tag{17}$$

which implies that the reaction field is uniform inside the cavity and equal to $\vec{E}_r = -A_1\vec{\mu}/\mu$. Solving eqs 15b and 16b for A_1 finally yields

$$\vec{E}_r = \frac{2\vec{\mu}}{4\pi\epsilon_0 a^3}\frac{\epsilon'-1}{2\epsilon'+1} \tag{18}$$

where ϵ' denotes an "effective" relative permittivity:

$$\epsilon' = \epsilon\left(1 + \frac{\frac{1}{2}(\kappa a)^2}{1 + \kappa a}\right) \tag{19}$$

Equation 18 is recognized as a modified version of the familiar Onsager formula for the reaction field acting on a dipole immersed in a continuous dielectric, which is retrieved upon setting $c_s = 0$.

By expanding eq 18 up to terms of second order in the small parameter κa and introducing, for future reference, the dimensionless quantity

$$u \equiv \frac{3F\mu}{4\pi\epsilon_0(2\epsilon + 1)a^2RT} \tag{20}$$

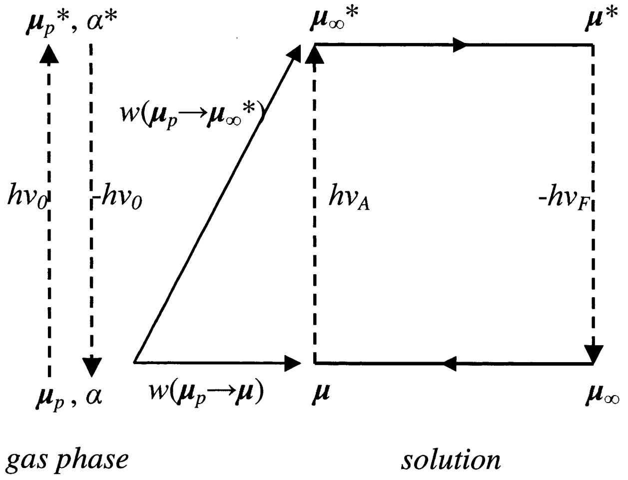

Figure 2. Schematic representation of the sequence of absorption, emission, and relaxation processes for transitions between the lowest vibrational levels corresponding to the electronic ground state and the first excited (singlet) state of a solute molecule (0−0 transition). Also indicated are the dipole moments at the various stages.

one arrives at the approximate expression

$$\vec{E}_r \cong \frac{RTu}{3Fa}\left(2(\epsilon - 1) + \frac{3\epsilon}{2\epsilon + 1}(\kappa a)^2\right)\frac{\vec{\mu}}{\mu} \qquad (\kappa a \ll 1) \tag{21}$$

3. Solvatochromic Shifts in the Presence of a 1:1 Salt

When a polar molecule in its ground state with permanent dipole moment $\vec{\mu}_p$, polarizability α, and total dipole moment $\vec{\mu}$ is promoted to the lowest vibrational level of the first excited (singlet) state (characterized by $\vec{\mu}_p^*$, α^*, and $\vec{\mu}^*$), it absorbs energy $h\nu_0$ when present in the gas phase and emits the same energy in the fluorescence step (0−0 transition), as illustrated in Figure 2.

In solution, we need to distinguish between four total dipole moments:

$\vec{\mu}$: Ground state, in equilibrium with medium (solvent + ions).

$\vec{\mu}_\infty^*$: After absorption of a photon with energy $h\nu_A$, the lowest excited state is reached with the permanent dipole moments of solvent molecules and averaged ionic distribution remaining "frozen". Only the electronic part of the medium polarization responds ("optical", infinite-frequency response).

$\vec{\mu}^*$: Provided the excited state is sufficiently long-lived, the medium adapts to the excited dipole, and a new equilibrium is established.

$\vec{\mu}_\infty$: During the emission of a photon of energy $h\nu_F$, there is only an electronic response by the medium, so no equilibrium and therefore no true ground state is attained at first. Then, the dipole−medium system relaxes back to its ground state with dipole moment $\vec{\mu}$.

Throughout the subsequent discussion we shall assume that the cavity radius is constant (i.e., $a^* = a$). The angle between ground-state and excited-state dipole moments equals ζ.

The energy $h\nu_A$ will be calculated next as the difference between the amounts of work involved in forming dipoles $\vec{\mu}_\infty^*$ and $\vec{\mu}$ from a ground-state dipole $\vec{\mu}_p$ in a vacuum:

$$h\nu_A = w(\vec{\mu}_p \rightarrow \vec{\mu}_\infty^*) - w(\vec{\mu}_p \rightarrow \vec{\mu}) \tag{22}$$

The second contribution is simply the stabilization energy of the ground-state dipole moment $\vec{\mu}$:

$$w(\vec{\mu}_{\mathrm{p}} \rightarrow \vec{\mu}) = \frac{1}{2}\alpha E_0^{\,2}(\vec{\mu}) - \int_0^{\vec{\mu}} \vec{E}_0(\vec{\mu}')\cdot \mathrm{d}\vec{\mu}' \tag{23}$$

where we denote by $\vec{E}_0(\vec{\mu}')$ the *equilibrium* reaction field due to the dipole $\vec{\mu}'$.

The first term is equal to the work of polarizing the molecule in a vacuum, whereas the second represents the reversible work performed in an imaginary process in which the positive and negative charges on the dipole are merged in a vacuum and subsequently separated again in solution.

The nonequilibrium excited dipole $\vec{\mu}_\infty{}^*$ can be formed from $\vec{\mu}_{\mathrm{p}}$ following the sequence of steps shown below, with $w(\vec{\mu}_{\mathrm{p}} \rightarrow \vec{\mu}_\infty{}^*)$ being equal to the sum of the corresponding energy contributions:

$$\text{Excite the molecule in vacuum: } h\nu_0 \tag{i}$$

$$\text{Polarize the excited molecule: } \frac{1}{2}\alpha^* E^2(\vec{\mu}_\infty{}^*) \tag{ii}$$

Here, $\vec{E}(\vec{\mu}_\infty{}^*)$ is the reaction field produced by the medium in the nonequilibrium state described earlier. It can be written as the sum of $\vec{E}(\vec{\mu})$ and the response to the "excess" dipole moment $(\vec{\mu}_\infty{}^* - \vec{\mu})$ by a uniform medium with relative permittivity n^2 (using Onsager's equation; see also eq 18):

$$\vec{E}(\vec{\mu}_\infty{}^*) = \vec{E}_0(\vec{\mu}) + 2\frac{\vec{\mu}_\infty{}^* - \vec{\mu}}{4\pi\epsilon_0 a^3}\,\frac{n^2 - 1}{2n^2 + 1} \tag{24}$$

Collapse the dipole $\vec{\mu}_\infty{}^*$ in vacuum and rebuild it in solution. During the second stage, the work is done with the dipole exposed to the field $\vec{E}_0(\vec{\mu}')$ from $\vec{\mu}' = 0$ to $\vec{\mu}' = \vec{\mu}$:

$$-\int_0^{\vec{\mu}} \vec{E}_0(\vec{\mu}')\cdot \mathrm{d}\,\vec{\mu}' \tag{iii}$$

From then onward, $\vec{E}_0(\vec{\mu})$ remains a fixed component of the reaction field while only the electronic response varies as $\vec{\mu}'$ increases further from $\vec{\mu}$ to $\vec{\mu}_\infty{}^*$:

$$-\vec{E}_0(\vec{\mu})\cdot(\vec{\mu}_\infty{}^* - \vec{\mu}) - \frac{(\vec{\mu}_\infty{}^* - \vec{\mu})^2}{4\pi\epsilon_0 a^3}\,\frac{n^2 - 1}{2n^2 + 1} \tag{iv}$$

Adding up the contributions (i–iv), subtracting eq 23, and defining the solvatochromic shift for the 0–0 absorption as $\Delta\tilde{\nu}_{\mathrm{A}} = (\nu_{\mathrm{A}} - \nu_0)/c$ gives

$$hc\Delta\tilde{\nu}_{\mathrm{A}} = \frac{1}{2}\alpha^* E^2(\vec{\mu}_\infty{}^*) - \frac{1}{2}\alpha E_0^{\,2}(\vec{\mu}) - \vec{E}_0(\vec{\mu})\cdot(\vec{\mu}_\infty{}^* - \vec{\mu}) - \frac{(\vec{\mu}_\infty{}^* - \vec{\mu})^2}{4\pi\epsilon_0 a^3}\,\frac{n^2 - 1}{2n^2 + 1} \tag{25}$$

For reasons of symmetry, the corresponding expression for the shift in the fluorescence wavenumber is found by simply interchanging "starred" and "unstarred" α's and $\vec{\mu}$'s in this equation:

$$-hc\Delta\tilde{\nu}_{\mathrm{F}} = \frac{1}{2}\alpha E^2(\vec{\mu}_\infty) - \frac{1}{2}\alpha^* E_0^{\,2}(\vec{\mu}^*) - \vec{E}_0(\vec{\mu}^*)\cdot(\vec{\mu}_\infty - \vec{\mu}^*) - \frac{(\vec{\mu}_\infty - \vec{\mu}^*)^2}{4\pi\epsilon_0 a^3}\,\frac{n^2 - 1}{2n^2 + 1} \tag{26}$$

In terms of the quantity u (eq 20) and using the solution for the reaction field, eq 21, the expression for the magnitude of the total dipole moment of the solute molecule in its ground state, $\mu = \mu_{\mathrm{p}} + \alpha E_0$, is transformed into

$$u = u_{\mathrm{p}} + \frac{\alpha'}{2\epsilon + 1}\left\{2(\epsilon - 1)u + \frac{3\epsilon}{2\epsilon + 1}u_0(\kappa a)^2\right\} \tag{27}$$

defining the scaled polarizability $\alpha' = \alpha/4\pi\epsilon_0 a^3$. Here, only terms up to order $(\kappa a)^2$ have been retained, which requires the introduction of the zeroth-order solution u_0 of this equation, corresponding to $\kappa = 0$:

$$u_0 = \frac{(2\epsilon + 1)u_{\mathrm{p}}}{2\epsilon + 1 - 2\alpha'(\epsilon - 1)} \tag{28}$$

Solving u from eq 27 and reverting to $\vec{\mu}$ yields the following explicit form of the latter up to first order in $(\kappa a)^2$:

$$\vec{\mu} = \frac{2\epsilon + 1 + 4\pi\epsilon\epsilon_0 a^2\alpha'\frac{RT}{F}u_0(\kappa a)^2/\mu_{\mathrm{p}}}{2\epsilon + 1 - 2\alpha'(\epsilon - 1)}\vec{\mu}_{\mathrm{p}} \tag{29}$$

Substituting this into the equation for the equilibrium reaction field $\vec{E}_0(\vec{\mu})$ yields

$$\vec{E}_0(\vec{\mu}) = \frac{2(\epsilon - 1)/4\pi\epsilon_0 a^3 + \frac{RT}{Fa}\epsilon u_0(\kappa a)^2/\mu_{\mathrm{p}}}{2\epsilon + 1 - 2\alpha'(\epsilon - 1)}\vec{\mu}_{\mathrm{p}} \tag{30}$$

If eqs 29 and 30 are then substituted into eq 24, then the result is a relationship between $\vec{E}(\vec{\mu}_\infty{}^*)$ and $\vec{\mu}_\infty{}^*$. These quantities are of course also related according to

$$\vec{\mu}_\infty{}^* = \vec{\mu}_{\mathrm{p}}{}^* + \alpha^*\,\vec{E}(\vec{\mu}_\infty{}^*) \tag{31}$$

which allows $\vec{E}(\vec{\mu}_\infty{}^*)$ and $\vec{\mu}_\infty{}^*$ (and hence $\Delta\tilde{\nu}_{\mathrm{A}}$) to be expressed directly in terms of $\vec{\mu}_{\mathrm{p}}$, $\vec{\mu}_{\mathrm{p}}{}^*$, α, α*, a, ϵ, n^2, and c_{s}. Introducing the approximation $\alpha^* = \alpha$ (as is usually done in the literature), one obtains, after some lengthy algebra,

$$\Delta\tilde{\nu}_{\mathrm{A}} = -\frac{\vec{\mu}_{\mathrm{p}}{}^* - \vec{\mu}_{\mathrm{p}}}{4\pi\epsilon_0 a^3 hc}\cdot\left\{\frac{2(\epsilon - 1) + 8\pi F a^4 u_0 c_{\mathrm{s}}/\mu_{\mathrm{p}}}{2\epsilon + 1 - 2\alpha'(\epsilon - 1)}\vec{\mu}_{\mathrm{p}} + \frac{(n^2 - 1)(\vec{\mu}_{\mathrm{p}}{}^* - \vec{\mu}_{\mathrm{p}})}{2n^2 + 1 - 2\alpha'(n^2 - 1)}\right\} \tag{32}$$

(up to first order in the salt concentration c_{s}) and, in an entirely analogous manner,

$$\Delta\tilde{\nu}_{\mathrm{F}} = -\frac{\vec{\mu}_{\mathrm{p}}{}^* - \vec{\mu}_{\mathrm{p}}}{4\pi\epsilon_0 a^3 hc}\cdot\left\{\frac{2(\epsilon - 1) + 8\pi F a^4 u_0{}^* c_{\mathrm{s}}/\mu_{\mathrm{p}}{}^*}{2\epsilon + 1 - 2\alpha'(\epsilon - 1)}\vec{\mu}_{\mathrm{p}}{}^* - \frac{(n^2 - 1)(\vec{\mu}_{\mathrm{p}}{}^* - \vec{\mu}_{\mathrm{p}})}{2n^2 + 1 - 2\alpha'(n^2 - 1)}\right\} \tag{33}$$

It is well known that other factors also contribute to the wavenumber shifts; for example, a dynamic effect, which can be interpreted within the context of classical dispersion theory as being a consequence of the high-frequency reaction field induced by vibrating electrons, needs to be taken into consideration. This field counteracts the "restoring force" on each electron and hence gives rise to a red shift in the case of absorption, which is separate from and independent of the spectral shifts discussed so far. Both the classical model and a detailed quantum mechanical analysis of the problem lead to the following expression for these dynamic shifts:[17]

$$\Delta\tilde{\nu}^{\mathrm{dyn}}_{\mathrm{A,F}} = -\mathrm{const} \times \frac{f_{\mathrm{A,F}}}{\tilde{\nu}_0\alpha}\,\frac{n^2-1}{2n^2+1} \tag{34}$$

where f is the oscillator strength (positive for absorption, negative for emission).

For polar molecules, this correction is usually relatively small and is therefore not taken into account, as is an additional shift associated with dispersion interactions between the solute and solvent.

Assuming the latter types of shifts to be comparatively insignificant and specific interactions such as hydrogen bonding to be absent, eqs 32 and 33 suggest the following procedure for analyzing absorption and fluorescence data.

First of all, in the absence of salt ($c_{\mathrm{s}} = 0$), $\tilde{\nu}_{\mathrm{A}}$ and $\tilde{\nu}_{\mathrm{F}}$ are measured for the 0−0 transition in two different solvents. The difference[6,15]

$$\tilde{\nu}_{\mathrm{A}} - \tilde{\nu}_{\mathrm{F}} = \frac{2(\vec{\mu}_{\mathrm{p}}{}^{*} - \vec{\mu}_{\mathrm{p}})^2}{4\pi\epsilon_0 a^3 hc}\left(\frac{\epsilon-1}{2\epsilon+1-2\alpha'(\epsilon-1)} - \frac{n^2-1}{2n^2+1-2\alpha'(n^2-1)}\right) \tag{35}$$

is evaluated for each. Dividing one by the other, an equation results from which α' can be solved. Subsequently, $(\vec{\mu}_{\mathrm{p}}{}^{*} - \vec{\mu}_{\mathrm{p}})^2/a^3 = (\mu_{\mathrm{p}}{}^2 + \mu_{\mathrm{p}}{}^{*2} - 2\mu_{\mathrm{p}}\mu_{\mathrm{p}}{}^{*}\cos\zeta)/a^3$ is obtained.

Next, for each solvent,

$$\frac{\tilde{\nu}_{\mathrm{A}} + \tilde{\nu}_{\mathrm{F}}}{2} = \tilde{\nu}_0 - \frac{\mu_{\mathrm{p}}{}^{*2} - \mu_{\mathrm{p}}{}^2}{4\pi\epsilon_0 a^3 hc}\,\frac{\epsilon-1}{2\epsilon+1-2\alpha'(\epsilon-1)} \tag{36}$$

is calculated,[5] which yields values for $\tilde{\nu}_0$ and $(\mu_{\mathrm{p}}{}^{*2} - \mu_{\mathrm{p}}{}^2)/a^3$.

In particular, the above relationships can be used to calculate $(\vec{\mu}_{\mathrm{p}}{}^{*} - \vec{\mu}_{\mathrm{p}})\cdot\vec{\mu}_{\mathrm{p}}/a^3$. For one solvent, the salt effect on $\tilde{\nu}_{\mathrm{A}}$ is then measured. The limiting slope of the $\tilde{\nu}_{\mathrm{A}}$ versus c_{s} relationship, along with the value obtained for $(\vec{\mu}_{\mathrm{p}}{}^{*} - \vec{\mu}_{\mathrm{p}})\cdot\vec{\mu}_{\mathrm{p}}/a^3$, is now used to obtain the Onsager cavity radius a and, from the known value of α', the polarizability α as well.

From the values of a, $(\mu_{\mathrm{p}}{}^{*2} - \mu_{\mathrm{p}}{}^2)/a^3$, and $(\vec{\mu}_{\mathrm{p}}{}^{*} - \vec{\mu}_{\mathrm{p}})^2/a^3$ found earlier, the magnitudes of the dipole moments in the ground and excited states can be calculated only in the case that these are collinear. Otherwise, the angle ζ would appear as an extra unknown, and insufficient information is contained in the spectral shifts to determine μ_{p}, $\mu_{\mathrm{p}}{}^{*}$, and ζ separately. In those situations, a separate measurement of μ_{p} (or some combination of μ_{p} and a) is necessary. However, it is entirely possible that an improved approximation beyond the linearized Poisson−Boltzmann level (eq 6) will render the solvatochromic data sufficient again to determine all individual parameters, including ζ, without the need for additional experiments.

4. Discussion

The present treatment of the influence of the medium on absorption and fluorescence spectra through local ordering follows the Onsager model in that it assumes that spectral shifts are due mainly to nonspecific, electrostatic interactions. In accordance with this model, the solvent is described as a continuum, characterized in terms of a refractive index n and a bulk permittivity ϵ. Since it was first proposed, the model has been extended to account for dielectric saturation in the vicinity of the solute dipole by allowing ϵ to approach the bulk value more gradually.[18,19] Although this modification is reasonable enough, different forms of the distance dependence of ϵ have been suggested, and there seems to be some difficulty in assessing their relative merits quantitatively.

The primary objective of this investigation, however, is to establish the influence of added salt on the reaction field (inside the cavity) and, by extension, on the position of absorption and fluorescence peaks, in particular those corresponding to the 0−0 transition (which coincide for molecules in the gas phase). This study was motivated by the desire to introduce a controllable length gauge, in the form of the Debye screening length, which could be used to “measure” the Onsager cavity radius indirectly. In the absence of salt, this radius is the only characteristic length in the model system, which is the reason that solvent studies allow only certain combinations of parameters, such as $\mu_{\mathrm{p}}{}^2/a^3$ or α/a^3, to be determined from spectroscopic data.

It should be stressed that our result for the reaction field, eq 21, is exact only in the limit of low salt concentrations, as the use of the Poisson−Boltzmann equation implies. At the same time, this restriction serves to suppress complications that would otherwise have arisen as a result of ion association,[20] which can be expected to be quite extensive, especially in solvents of low relative permittivity such as the ones that are commonly used in investigations of this kind.

Our analysis of the reorganizational free-energy changes accompanying absorption or emission of radiation leads to eqs 32 and 33, where the applicability of the second is obviously limited to those cases where the excited singlet state survives long enough for the medium to adapt to its corresponding dipole moment, $\vec{\mu}_{\mathrm{p}}{}^{*}$. The slowest process is most likely the rearrangement of ions, with a characteristic time on the order of the double-layer relaxation time of the salt solution. Of course, it needs to be decided in each individual case how reasonable the assumption of medium equilibration is. Corrections for solvent relaxation in the case of short-lived excited states typically involve the use of the Debye model. No attempt to include corrections for medium relaxation has been made in the present study.

From numerical estimates, it can be inferred that the magnitude of the salt-induced shifts in wavelength, $|\Delta\lambda_{\mathrm{s}}| \cong \lambda_0^2|\Delta\tilde{\nu}_{\mathrm{s}}|$, in many cases can be expected to be very (even prohibitively) small in the limit of small $(\kappa a)^2$. High accuracy in determining the variation of spectral shifts with salt concentration (which even in favorable cases may amount to no more than a few nanometers) will then be required. The application of this method will therefore probably be limited to molecules that are not too large (since u_0 is proportional to a^{-2}, the salt-induced shift varies according to a^{-1}; see eqs 32 and 33) with large dipole moments exhibiting strong charge transfer at long wavelengths (as in certain dyes). For example, a preliminary experiment shows that a maximum at 275 nm ($\log \epsilon_{\mathrm{A}} = 3.57$) for a 1×10^{-4} M solution of methyl red in methanol is shifted to 271 nm ($\log \epsilon_{\mathrm{A}} = 2.61$) for 1×10^{-3} M methyl red in 0.1 M methanolic lithium perchlorate.

A comparison of our results for the purely solvent-induced shifts with expressions that have been published in the past by several workers in the field (and which are still widely applied) reveals a surprising disagreement, considering that all treatments are essentially based on the same simple electrostatic picture. One therefore should not expect to find any ambiguity in the implications of such a model.

First of all, authors usually choose a value for α' a priori, typically $\alpha' = 0$[15] or $^1/_2$,[6,7,21,22] whereas we prefer to leave it unspecified, as an adjustable parameter. The choice of solvent then manifests itself in the form of “solvent functions” that depend solely on ϵ and n^2. Our eqs 32 and 33 are equivalent to expressions derived by Lippert,[15] who assumed that $\alpha = 0$ (and, of course, $c_s = 0$) and the ground-state and excited-state dipole moments are collinear, but differ substantially from those arrived at in later papers by other authors.[2,6]

The source of the discrepancy can be traced to an erroneous notion about the orientational contribution of permanent solvent dipole moments to the reaction field. In both earlier and current theories[23] of solvatochromism, this contribution is isolated from the net cavity field by simply subtracting an electronic contribution that is postulated to possess the same form as Onsager's equation, with ϵ replaced by the square of a zero-frequency refractive index, n_0. Usually, n_0 is conveniently taken to be equal to n. The problem with this argument is that it implicitly assumes that the continuity conditions on potential and dielectric displacement at the cavity boundary are imposed *separately* on each one of the components (i.e., dipolar and electronic) of the polarization field. Clearly, there is no good physical reason that this should be so, and indeed it would be highly fortuitous if it were.

Our method of calculation avoids this flaw by exploiting the close analogy between the nonequilibrium solvent configuration that occurs in response to a sudden change of the solute dipole moment (consequent upon absorption or emission of a photon) and that due to a rapid loss or gain of an electron by an ion. The solvent reorganization free energies in the latter case are calculated using the well-established method first employed by Marcus in his general theory of fast electron-transfer processes (for a concise and enlightening recent overview, see ref 24), and it is essentially this approach that has been adopted in this paper.

Experimental tests of the new equations are currently under way, and we expect to present the results in a future publication.

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