A Review on Effect of Solvents on Fluorescent Spectra

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Article Information

Review Article

ABSTRACT

When absorption spectra are measured in solvents of different polarity, it is found that the positions, intensities, and shapes of the absorption bands are usually modified by these solvents. These changes are a result of physical intermolecular solute–solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.), which above all tend to alter the energy difference between ground and excited state of the absorbing species containing the chromophore. When excited states of a molecule are created in solution by continuous or flash excitation, the excited-state molecule interacts to a varying degree with the surrounding solvent molecules, depending on their polarity, before returning to the ground state. These excited-state solute/solvent interactions found in fluorescent molecules are often reflected in the spectral position and shape of the emission bands as well as in the lifetimes of the excited-state molecules. The solvent-dependence of the position of emission bands in fluorescence spectra is termed as solvatochromism. These review paper presents detail discussion on solvatochromism, Electrochromism, and reaction field theory.

Keywords: Polarity; fluorescent spectra; solvatochromism; electrochromism; reaction field theory.

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1. INTRODUCTION

Electronic absorption and emission spectra of a molecule dissolved in a solvent medium in general are shifted in energy relative to the spectra of the isolated molecule. When absorption spectra are measured in solvents of different polarity, it is found that the positions, intensities, and shapes of the absorption bands are usually modified by these solvents. These changes are a result of physical intermolecular solute solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.), which above all tend to alter the energy difference between ground and excited state of the absorbing species containing the chromophore. Thus, solvent effects on absorption spectra can be used to provide information about solute-solvent interactions [1–5].

A qualitative interpretation of solvent shifts is possible by considering (a) the momentary transition dipole moment present during the optical absorption, (b) the difference in permanent dipole moment between the ground and excited state of the solute, (c) the change in ground-state dipole moment of the solute induced by the solvent, and (d) the Franck–Condon principle [6,7].

Shifts in absorption and emission bands can be induced by a change in solvent nature or composition. The solvent-dependence of the position of emission bands in fluorescence spectra is commonly included in the term solvatochromism [8-10].

A general explanation of solvent effects on fluorescence spectra is based on the differential solvation of the fluorescent molecules (also called fluorophores) in their ground and excited states, mediated by the various non-specific and specific intermolecular forces acting between the solute and solvent [11-13]. When the ground and excited states of a polar fluorophore differ only in their polarizabilities and not in their dipolarities, then only solute/solvent dispersion interactions exist and rather small or no solvent-induced band shifts are observed [14-17].

This review paper presents characteristics of fluorescence, various factors which affects fluorescence spectra with particular emphasis given to the effect of solvents.

2. UV- VISIBLE SPECTROSCOPY

An electronic transition consists of the promotion of an electron from an orbital of a molecule in the ground state to an unoccupied orbital by absorption of a photon. The molecule is then said to be in an excited state. The lowest energy transition is that between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the ground state. The kind of transition that occurs are $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, the energies of transitions is generally in the same order as written.

The efficiency of light absorption at a wavelength λ by an absorbing medium is characterized by the absorbance $A(\lambda)$ is defined as:

$$A(\lambda) = \log \frac{I^o}{I} = -\log T(\lambda) \qquad (1)$$

where T is transmittance, I^o and I are the light intensities of the beams entering and leaving the absorbing medium, respectively.
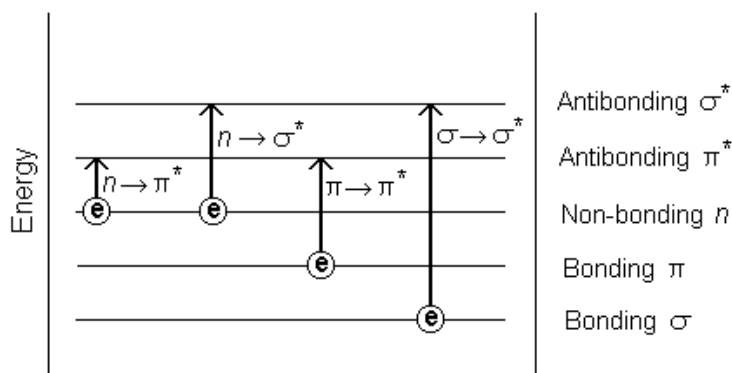

Fig. 1. A diagram showing possible electronic transitions of π, σ, and *n* electrons

The absorbance of a sample follows the Beer–Lambert Law and given by

$$A(\lambda) = \varepsilon(\lambda)cl \qquad (2)$$

where $\varepsilon(\lambda)$ is the molar decadic absorption coefficient (commonly expressed in L mol^{-1} cm^{-1}), c is the concentration (in mol L^{-1}) of absorbing species and l is the absorption path length (thickness of the absorbing medium) (in cm).

3. FLUORESCENCE SPECTROSCOPY

Absorption of UV radiation by a molecule excites it from a vibrational level in the electronic ground state to one of the many vibrational levels in the electronic excited state. This excited state is usually the first excited singlet state. A molecule in a high vibrational level of the excited state will quickly fall to the lowest vibrational level of this state by losing energy to other molecules through collision. The molecule will also partition the excess energy to other possible modes of vibration and rotation. Fluorescence occurs when the molecule returns to the electronic ground state, from the excited singlet state, by emission of a photon. If a molecule that absorbs UV radiation does not fluoresce it means that it must have lost its energy some other way. These processes are called radiationless transfer of energy.

The emission rates of fluorescence are typically 108s^{-1}, [18] so that a typical fluorescence lifetime is near 10 ns. The lifetime (τ) of a fluorophore is

the average time between its excitation and return to the ground state. An important feature of fluorescence is high sensitivity detection. At room temperature most molecules occupy the lowest vibrational level of the ground electronic state, and on absorption of light they are elevated to produce excited states.

Excitation can result in the molecule reaching any of the vibrational sub-levels associated with each electronic state. Since the energy is absorbed as discrete quanta, this should result in a series of distinct absorption bands. Having absorbed energy and reached one of the higher vibrational levels of an excited state, the molecule rapidly loses its excess of vibrational energy by collision and falls to the lowest vibrational level of the excited state. In addition, almost all molecules occupying an electronic state higher than the second undergo internal conversion and pass from the lowest vibrational level of the upper state to a higher vibrational level of a lower excited state which has the same energy. From there, the molecules again lose energy until the lowest vibrational level of the first excited state is reached. From this level, the molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence. If this process takes place for all the molecules that absorbed light, then the quantum efficiency of the solution will be a maximum, unity. If, however, any other route is followed, the quantum efficiency will be less than one and may even be almost zero.
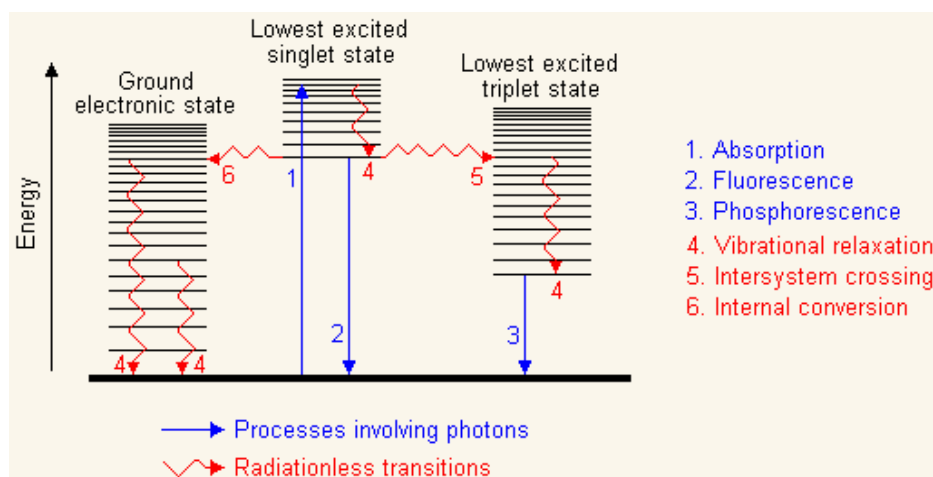

Fig. 2. Possible physical process following absorption of a photon by a molecule

One transition, that from the lowest vibrational level in the ground electronic state to the lowest vibrational level in the first excited state, the 0 - 0 transition, is common to both the absorption and emission phenomena, whereas all other absorption transitions require more energy than any transition in the fluorescence emission. We can therefore expect the emission spectrum to overlap the absorption spectrum at the wavelength corresponding to the $0 - 0$ transition and the rest of the emission spectrum to be of lower energy, or longer wavelength.

3.1 Characteristics of Fluorescent Emission

The recorded fluorescence intensity as a function of the emission wavelength at a fixed excitation wavelength is termed fluorescence emission spectrum. By contrast, if the wavelength of the exciting light is changed and fluorescence emission is monitored at a constant emission wavelength, the fluorescence excitation spectrum is recorded. If the excitation energy is constant, the fluorescence excitation spectrum corresponds to the absorption spectrum of the substance.

The 0–0 transition is usually the same for absorption and fluorescence. However, the fluorescence spectrum is located at higher wavelengths (lower energy) than the absorption spectrum because of the energy loss in the excited state due to vibrational relaxation. According to the Stokes Rule, the wavelength of a fluorescence emission should always be higher than that of absorption. However in most cases, the absorption spectrum partly overlaps the fluorescence spectrum, i.e. a fraction of light is emitted at shorter wavelengths than the absorbed light. In general, the differences between the vibrational levels are similar in the ground and excited states, so that the fluorescence spectrum often resembles the first absorption band ('mirror image' rule). The gap (expressed in wavenumbers) between the maximum of the first absorption band and the maximum of fluorescence is called the Stokes shift. These Stokes shifts are most dramatic for polar fluorophores in polar solvents due to interactions between the fluorophore and its immediate environment.

Another general property of fluorescence is that the same fluorescence emission spectrum is generally observed irrespective of the excitation wavelength [19]. This is known as Kasha's rule.

Upon excitation into higher electronic and vibrational levels, the excess energy is quickly dissipated, leaving the fluorophore in the lowest vibrational level of S_1. This relaxation occurs in about 10^{-12} s, and is presumably a result of a strong overlap among numerous states of nearly equal energy. Because of this rapid relaxation, emission spectra are usually independent of the excitation wavelength. Exceptions exist, such as fluorophores that exist in two ionization states, each of which displays distinct absorption and emission spectra. Thus presence of two distinct excitation wavelengths indicates presence of two distinct structures in ground state.

It should be noted that emission of a photon is as fast as absorption of a photon ($\approx 10^{-15}$ s). However, excited molecules stay in the S_1 state for a certain time (a few tens of picoseconds to a few hundreds of nanoseconds, depending on the type of molecule and the medium) before emitting a photon or undergoing other de-excitation processes (internal conversion, intersystem crossing). Thus, after excitation of a population of molecules by a very short pulse of light, the fluorescence intensity decreases exponentially with a characteristic time, reflecting the average lifetime of the molecules in the S_1 excited state. Some of de-excitation processes are discussed below:

3.2 Quantum Yield

The quantum yield is defined by the quotient of the number of photons that are emitted and the number of photons that are absorbed. With the transition rates k_f for the fluorescence, k_{ic} and k_{isc} for the internal conversion and for the intersystem crossing, and with the fluorescence quenching by quencher molecules, the quantum yield can be expressed as

$$\Phi = \frac{k_f}{k_f + k_{ic} + k_{isc} + k_q} \tag{3}$$

3.3 Fluorescence Lifetime

The fluorescence lifetime is the time the molecule remains on average in the excited state, before emission takes place. If there are N molecules in the excited state, then the decrease dN of molecules that revert to the ground state in a given time interval dt is expressed by the relation.

$$-dN / dt = k_f \bullet N \qquad (4)$$

The number of excited molecules therefore decreases exponentially with time:

$$N(t) = N_o exp\ (-k_f t) \qquad (5)$$

The time after which the number of excited molecules decreases from N_0 to N_0 / e is called the fluorescence lifetime. Therefore the fluorescence lifetime is given by the reciprocal fluorescence transition rate:

$$\tau_F = 1 / k_f$$

In contrast to this radiation lifetime, the real lifetime of the excited state has to include the non-radiative deactivation processes.

$$\tau = 1/ k_f + k_{ic} + k_{isc} + k_q$$

3.4 Factors Affecting Fluorescence Spectra

3.4.1 Temperature effects

Changes in temperature affect the viscosity of the medium and hence the number of collisions of the molecules of the fluorophore with solvent molecules. Fluorescence intensity is sensitive to such changes and the fluorescence of many certain fluorophores shows temperature dependence. In such cases the use of thermostatted cell holders is to be recommended. Generally, an increase in temperature results in a decrease in the fluorescence quantum yield and the lifetime because the non-radiative processes related to thermal agitation (collisions with solvent molecules, intramolecular vibrations and rotations, etc.) are more efficient at higher temperatures.

3.4.2 Fluorescence quenching

Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. A variety of molecular interactions can result in quenching. These include excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation, and collisional quenching [20].

3.4.3 Solvent effects on electronic spectra

The electronic spectra of molecules can be substantially influenced by the surrounding condensed medium. The resultant effects arise from a variety of intermolecular interactions between the solute and the solvent molecules in such media. Experimentally, these effects can be observed as the shifts of the spectral maxima (solvatochromic shifts), the change in the intensity of the spectral line or band and the change of the shape and width of the spectral band. Each of those, so-called solvent effects can be described theoretically using different model approaches [21,22].

The solvatochromic spectral shifts are expected to arise from the difference in the solvation of the ground and the excited states of the molecule. As a result of the spectroscopic excitation, the charge distribution of the molecule changes and thus the interaction will be different in the ground state and in the excited state of the molecule. The direction and size of the respective spectral shift depends directly on the difference in the solvation energy of the molecule in those two states. The larger solvation energy of the ground state (S_0), as compared to that of the excited state (S_1), results in the negative solvatochromic shift (blue shift) of the spectral maximum (Fig. 3). Alternatively, the stronger solvation of the excited state, as compared to the solvation of the ground state, leads to the decrease of the excitation energy and is reflected by the positive solvatochromic shift (red shift) in the spectrum of the compound (Fig. 3).

In relation to dipole moment, if the dipole moment of ground state is greater than the dipole moment of the molecule in excited state solvation of the molecule in polar solvents in the ground state is more stable, this results in increase in excitation energy and thus blue shift of the spectrum results. In many cases, because of the substantial charge redistribution in excited excited states, often called charge-transfer (CT) states, the dipole moment increases in the excited state. The larger dipole of the of the molecule in excited state is additionally stabilized by a more polar solvents this leads to the decrease in the excitation energy and to the corresponding solvatochromic red shift of the spectral maximum.
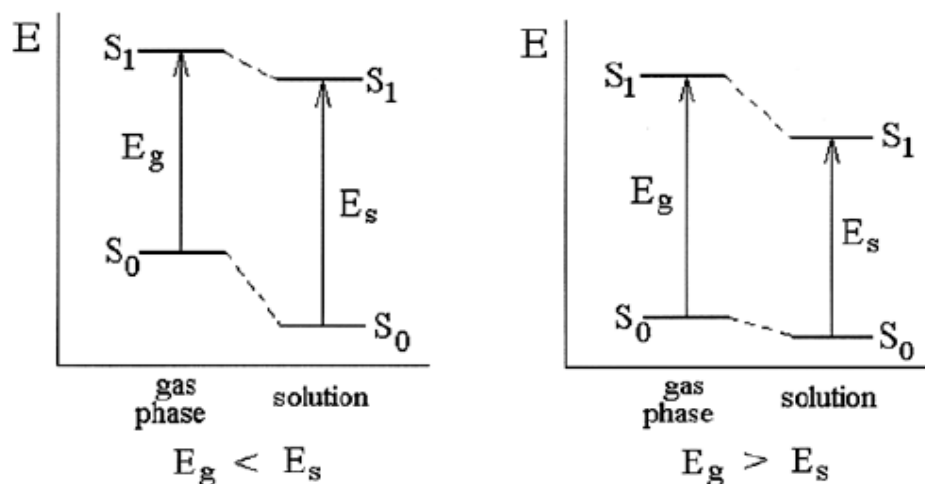
Fig. 3. Solvatochromic shift in compounds based on solvation energy

The solvation energy of a molecule E_{sol} in a given solvent can be divided into the following terms [21,22]

$$E_{sol} = E_{cav} + E_{dis} + E_{elst} + E_{H-bond} \qquad (6)$$

each of which corresponds to a certain type of intermolecular interaction in the condensed media. Thus, E_{cav} denotes the energy of the cavity formation for the solute in the solvent, E_{dis} is the dispersion energy and E_{elst} the electrostatic energy of the interaction of the solute with the surrounding solvent molecules. The term E_{H-bond} accounts for the energy of the hydrogen bond formation between the solute and solvent molecule. Solvent electrostatic polarization and solvent dispersion effects are more on electronic spectra of molecules.

4. ELECTROCHROMISM, REACTION FIELD THEORY AND SOLVATOCH-ROMISM

The position and intensity of an electronic band can be influenced by an electric field and the phenomenon is called electrochromism. In any solution, molecules having a permanent dipole moment are located in an electric field, which is the reaction field of the molecule. The reaction field acts on the dissolved molecules in the same way as an electric field, capable of causing a band shift and a change in the transition moment and hence in the intensity of the band. The

solvent dependence of the position and intensity of an electronic band is known as solvatochromism. The fundamental cause of strong solvatochromism, such as is observed in polar dye molecules, is the same as that of electrochromism [23-25].

4.1 Band Shift in an External Electric Field

The electronic excitation of a molecule may be associated with a change in the dipole moment μ_a - μ_g (μ_g and μ_a = dipole moment in the ground and excited state). The energy of a molecule in the ground state in an electric field is given by [23].

$$E_g^F = E_g^{Sol} - \mu_g F_e \cos\vartheta \qquad (7)$$

where E_g^{Sol} is the energy of the dissolved molecule in the ground state with no external field, F_e is the effective field strength at the position of the molecule, ϑ is the angle between the vector μ_g and F_e. Similarly, the energy of the molecule in the ground state in the electric field is given by

$$E_a^F = E_a^{Sol} - \mu_a F_e \cos\vartheta \qquad (8)$$

where E_a^{Sol} is the energy of the dissolved molecule in the excited state with no external

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field. For simplicity the dipole moment μ_a in the excited state is assumed to be parallel to μ_g in the ground state. For a given transition having the absorption wave number $\tilde{v}_a^{sol}$ in solution with no electric field ($hc\tilde{v}_a^{sol} = E_a^{Sol} - E_g^{Sol}$), the absorption wave number $\tilde{v}_a^F$ in an electric field is given by

$$\tilde{v}_a^F = \frac{E_a^F - E_a^{Sol}}{hc} = \tilde{v}_a^{sol} - \left[\frac{(\mu_a - \mu_g)F_e \cos \vartheta}{hc} \right] \quad (9)$$

The change in the dipole moment $(\mu_a - \mu_g)$ thus leads to a field-dependent shift of the band, which also depends on the angle ϑ between the dipole moment and the field direction. From equation (9) taking $\mu_a > \mu_g$, dependence of the absorption wave number on the orientation of the dipole moment with respect to the field direction can be considered as, if F_e = 0, $\tilde{v}_a^F$ is proportional to $\tilde{v}_a^{sol}$. If $\mu_{g\uparrow\uparrow} F_e$ (parallel to), $\cos\vartheta$ =1, so that the energy in the ground state is reduced by $\mu_g F_e$ and that in the excited state by $\mu_e F_e$, since $\mu_a > \mu_g$ is considered, the absorption wave number $\tilde{v}_{\uparrow\uparrow} < \tilde{v}_a^{sol}$. Similarly, if $\mu_{g\uparrow\downarrow} F_e$, $\tilde{v}_{\uparrow\uparrow} > \tilde{v}_a^{sol}$, and the dipole moment is perpendicular to the field, $\cos\vartheta$ = 0, and $\tilde{v}_{per}$ (perpendicular orientation = $\tilde{v}_a^{sol}$). The above results in unsymmetrical broadening of an absorption band due to the band shift, Fig. 4.

4.2 Band Shift in a Reaction Field

Reaction field of dissolved molecule have similar effect on electronic spectra as external electric field [23-25]. This can be illustrated by the following example for p- nitroaniline and similar donor acceptor compounds like DMABA, Fig. 5. In the figure, a molecule in the gas state with a dipole moment, μ, causes an electric dipole field in its environment, the field line shown in broken lines. In b, in solution these dipole moments act on the surrounding solvent molecules. Solvents having permanent dipole moment orient themselves as nearly as possible parallel to the field lines. In case were the solvent have no dipole moment, a dipole moment is induced in the dipole field of the molecule. In c, if the electronic and nuclear configurations of all the solvent molecules are imagined to be frozen and the dissolved molecule then removed, a cavity surrounded by solvent molecules remains. Each of the solvent molecules has a dipole moment, made up of the permanent and the induced moment and each of which produces a dipole field its environment. In the cavity, at the position of the dissolved molecule, the dipole fields of the solvent molecules superimpose and produce a field having the same direction as the dipole moment of the original dissolved molecule; this field if known as the reaction field, F_R. If the dissolved molecule is now imagined to be back in to the cavity, it is clearly in an electric field.
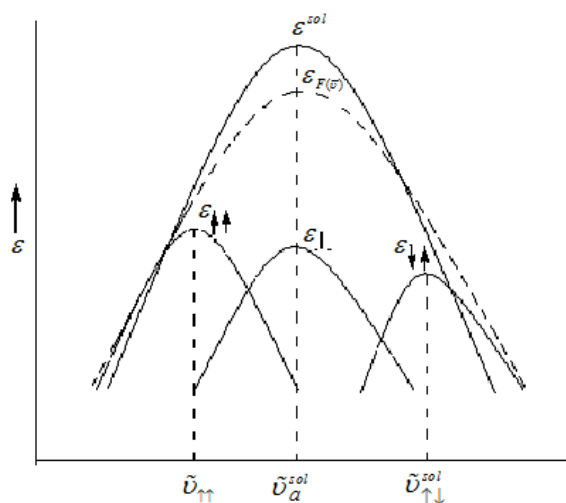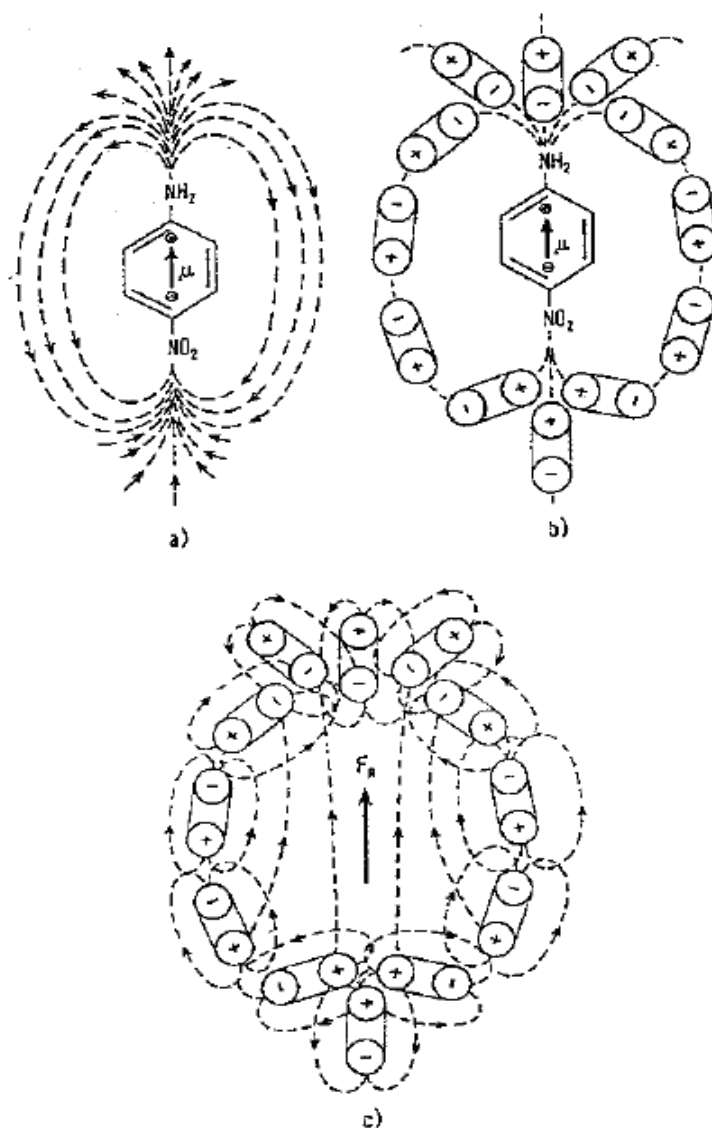

Fig. 4. Unsymmetrical broadening of an absorption band as a result of the band shift

Fig. 5. Reaction field of a dissolved molecule

According to the above approximation the solvent is regarded as a homogeneous isotropic dielectric continuum having a dielectric constant ε. The dissolved molecules are assumed to be accommodated in spherical cavities having a radius a. The dipole moment is represented by a point dipole located in the center of the spherical cavity.

4.3 The Reaction Field of a Non-polarized Point Dipole

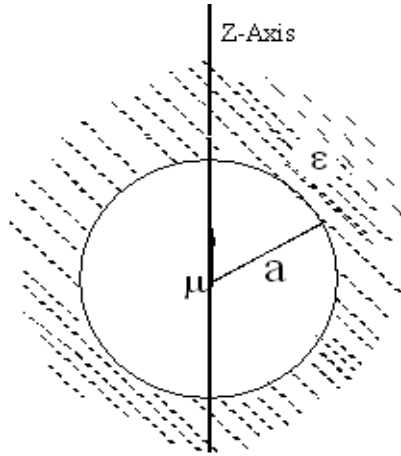When a molecule, having a permanent dipole moment μ, is surrounded by other particles, the inhomogeneous field of this dipole polarizes these particles, since they have a polarisability even when they possess no permanent dipole moment. This inhomogeneous polarization of the environment will give rise to a field at the dipole. As a result of the molecular movements the field strength will fluctuate in the course of the time, but for reasons of symmetry its average value F_R will have the same direction as the dipole vector μ and again F_R is proportional to μ [26,27], thus

$$F_R = f\mu$$

The field F_R is called the reaction field of the dipole and f the factor of the reaction field. An

accurate calculation of the average value F_R may be made using the methods of statistical mechanics.

Fig. 6. A spherical cavity with radius *a* in a continuous dielectric of dielectric constant ε

The better model introduced for calculation is Bell's model. Bell's model consist of a spherical cavity with radius *a* in a continuous dielectric of dielectric constant ε. In the centre of the cavity is placed a non-polarizable point dipole with moment μ. In this simplified picture of the interaction between a permanent dipole and its surroundings, the value chosen for a is of important. Bell took a about equal to the radius of the molecule. Onsager, however, who adopted Bell's calculations, used for the evaluation of his general of his general equations for the case when only one sort of molecule is present, the relation:

$$4/3\pi Na^3 = 1,$$

where N is the number of particles per cm³.

To calculate the reaction field the potential in the cavity must be known, due both to the dipole itself and to the interaction of the dipole with the surrounding dielectric. When the centre of the dipole is taken as the origin of a coordinate system and direction of the z-axis along the dipole vector is chosen, symmetry about the z – axis will exist. The general equation of LAPLACE'S in such case is given by

$$\phi = \sum_{l=0}^{\infty} (a_1 + b^l / r^{l+1}) P_l(\cos\theta) \quad (10)$$

Taking the potential outside the sphere ϕ_1 and the inside the sphere ϕ_2. The boundary conditions are in this case:

1. $(\phi_1)_{r\to\infty} = 0$

2. $(\phi_1)_{r=a} = (\phi_2)_{r=a}$,

3. $\varepsilon\left(\dfrac{\delta\phi_1}{\delta r}\right)_{r=a} = \left(\dfrac{\delta\phi_2}{\delta r}\right)_{r=a}$,

4. $(\phi_2)_{a=\infty} = \dfrac{\mu}{r^2}\cos\theta$, for if the dielectric is omitted the field of a dipole is obtained in vacuum.

Applying the boundary conditions and making use of LEGENDRE functions that they are mutually linearly independent, ϕ_1 and ϕ_2 can be obtained as

$$\phi_1 = \frac{3}{2\varepsilon+1}\frac{\mu}{r^2}\cos\theta \quad (11)$$

$$\phi_2 = \frac{\mu}{r^2}\cos\theta - \frac{2\varepsilon-2}{2\varepsilon+1}\frac{\mu}{a^3}\cos\theta \quad (12)$$

The potentials ϕ_1' and ϕ_2', due to the apparent surface charge on the surface of the cavity are, according 11 and 12, given by

$$\phi_1' = -\frac{2\varepsilon-2}{2\varepsilon+1}\frac{\mu}{r^2}\cos\theta,$$

$$\phi_2' = -\frac{2\varepsilon-2}{2\varepsilon+1}\frac{\mu}{a^3}r\cos\theta.$$

Comparing this two equations with LAPLACE'S equation (eq 10), it can be seen that ϕ_1' and ϕ_2' are due to an apparent surface charge distribution, with a dipole moment

$$m = -\frac{2\varepsilon-2}{2\varepsilon+1}\mu.$$

According to 12, the field in the cavity is a superposition of the dipole field in vacuo and a uniform field F_R, is given

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$$F_R = \frac{1}{a^3} \cdot \frac{2\varepsilon - 2}{2\varepsilon + 1} \mu \qquad (13)$$

Therefore the reaction field F_{Rg} of a dissolved molecules in the electronic ground state is given as

$$F_{Rg} = \frac{1}{a^3} \cdot \frac{2\varepsilon - 2}{2\varepsilon + 1} \mu_g{}' \qquad (14)$$

$\mu_g{}'$ is the total dipole moment (Permanent plus induced moment) of the dissolved molecule.

The change in position and intensity of the electronic band depend not only on the reaction field in the ground state, shown above, but also on the reaction field in the excited electronic state. When the Franck Condon, the primary state after excitation process, is taken in to account, the expression for the reaction field in the excited state contains other additional terms that depend on the refractive index *n* of solution. The effect of the field on the position and intensity of electronic bands is therefore determined by the dielectric constant and the refractive index of the solution in this approximation. The effect of the reaction field is the main cause of strong solvatochromism, which is observed in particular with molecules having large dipole moments, and hence strong reaction fields. For two reasons the effect of the reaction field on the electronic bands is much greater than that of the external electric field, the first is the much greater strength of the reaction and the second is the reaction field on average is always parallel to the dipole moment of the dissolved molecule. In the external field on the other hand, the molecules are distributed over all possible orientations with respect to the field thus largely cancel one another out in the average, so that the observed effects are small.

For a molecule having a permanent dipole moment μ_g in the electronic ground state and a moment μ_a parallel to it in the ground state, the solvent dependence of the wave-number $\tilde{v}_a^{sol}$ of the absorption maximum is given to a good approximation by the following equation [23]

$$\tilde{v}_a^{sol} \cong \tilde{v}_a^o - \frac{(\bar{\mu}_a - \bar{\mu}_g)(F_{RM})}{hc} - \frac{2(n^2 - 1)}{a^3(2n^2 + 1)} D \qquad (15)$$

$\tilde{v}_a^O$ is the wave number of the absorption maximum in the free molecule (gas state). This equation corresponds to the previous equation in the case of electric field, eq 15, except that it contains a term that depends on a quantity D. This term describes the solvent dependence of the position of the absorption band due to the dispersion interaction between dissolved molecules and the surrounding solvent molecules. The effective electric field F_{RM} is the mean of the reaction fields of the dissolved molecule in the ground state and in the Franck-Condon excited state. It relates dielectric constant of the solution, refractive index and the polarizability tensor of the molecule.

Assuming a point dipole situated in the center of the spherical cavity and neglecting the mean solute polarizability α in the states involved in the transition ($\alpha = \alpha_a = \alpha_g = 0$), the solvatochromic effects on the spectral position of the absorption maxima can be given by [28,29]

$$hc\tilde{v}_{abs}^{sol} = \tilde{v}_{abs}^o - \frac{2\bar{\mu}_g(\bar{\mu}_a - \bar{\mu}_g)}{a_o{}^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\frac{n^2 - 1}{2n^2 + 1}\right] \qquad (16)$$

$hc\tilde{v}_{abs}^{sol}$ and $\tilde{v}_{abs}^o$ are the energy related to spectral position of charge transfer absorption maxima in solutions and to the value extrapolated to the gas-phase, respectively; $\bar{\mu}_g$ and $\bar{\mu}_a$ are the dipole moments of the solute in the ground and excited state, a_o is the effective radius of Onsager's cavity [30], ε is the dielectric constant, and *n* is the refractive index of the solvent.

Under the same assumption Lippert and Mataga have obtained the following expression for the fluorescence solvatochromic shit [28,29]

$$h\tilde{v}_{flu}^{sol} \cong \tilde{v}_{flu}^o - \frac{2\bar{\mu}_a(\bar{\mu}_a - \bar{\mu}_g)}{a^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\frac{n^2 - 1}{2n^2 + 1}\right] \qquad (17)$$

Where, $\tilde{v}_{flu}^{sol}$ and $\tilde{v}_{flu}^O$ are the spectral positions of the fluorescence maxima in solution and the value extrapolated to the gas-phase, respectively.

5. CONCLUSION

The absorption and fluorescence emission spectra of many fluorophores are sensitive to the polarity of their surrounding environment. Therefore, study of the effect of solvents on the electronic absorption and fluorescence spectra of a variety of molecules forms an important subject for research because this plays a significant role in the photophysics of the excited states. Thus, having detail knowledge of the effect of solvent is a very important area of study. And these review paper presented in detail electrochromism, reaction field theory and solvatochromism.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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