

**MOLECULAR
INTERACTIONS
AND ELECTRONIC
SPECTRA**

by

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MARCEL DEKKER, INC., NEW YORK 1970

Chapter 8

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8-1. INTRODUCTION

It is well known that molecules dissolved in solvent undergo an intermolecular interaction with the solvent. If solutes or solvents have active sites for hydrogen bonding, or if there are possibilities of forming the charge transfer type complexes, the solute-solvent interaction is relatively large. Consequently the electronic absorption spectra of solutes will undergo change more or less with the hydrogen bond formation in such solvents, or new absorption bands will occur, i.e., a charge transfer (CT) band caused by charge transfer complex formation. These kinds of intermolecular interactions will be mainly governed by mass-action-law and will be of a short-range interaction nature. However, even though there is no short-range intermolecular interaction between solutes and solvents, other kinds of molecular interactions such as dispersion force, dipole-dipole interaction, etc., should exist between solutes and solvents. Therefore the

electronic state of molecules in solvents is somewhat different from that of free molecules in the gas phase.

It is now noted that electronic spectra are brought about by electron transition between two electronic states which differ from each other in the nature of the electronic state such as electron distribution, dipole moment, and spatial molecular configuration. So, generally speaking, the solute-solvent interaction ability must vary between the two electronic states pertinent to the electron transition. These circumstances indicate clearly that the band position of electronic spectra, the appearance of vibrational structures, etc., in solution are not the same as those of a free molecule in the gas phase. The band position, band shape, and intensity of electronic spectra vary to some extent according to the change of state from vapor to solvent. In this chapter we discuss the usual solvent effect on the electronic spectra of organic molecules, excluding the short-range intermolecular interaction mentioned above.

8-2. TYPES OF NONHYDROGEN BONDING SOLVENT EFFECT ON ELECTRONIC SPECTRA

Intermolecular interactions in solution may be roughly classified as (1) dispersion forces which are electrostatic in nature and (2) usual electrostatic forces. The former play an important role in the case of nonpolar solutes dissolved in nonpolar solvents, just like diluted benzene or naphthalene solution in *n*-heptane, etc. (saturated hydrocarbon solvents). In these cases the contribution from the usual electrostatic forces is neglected. On the other hand, electrostatic force makes an important contribution to all kinds of mutual interactions between nonpolar molecule and polar molecule or between polar molecule and polar molecule, namely dipole-dipole interaction, dipole-induced dipole interaction, etc.

The physical meaning of dispersion force was first clarified by London (1) by applying the quantum mechanical second-order perturbation method. The interaction energy due to this force between two molecules is approximately given by

$$E = -\frac{3}{2} \frac{\alpha_1 \alpha_2}{r^6} \frac{I_1 I_2}{I_1 + I_2} \quad (8-1)$$

Here I_1 and α_1 are the ionization potential and polarizability of molecule 1, and I_2 and α_2 are the analogous values for molecule 2. We now know that the dispersion force is in intimate correlation with polarizability α which is closely related with dispersion of light. In addition, polarizability of the

molecule is in close relation with the refractive index n of the molecule as, for example, the Lorentz-Lorenz equation shows:

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = \frac{4\pi}{3} N\alpha \quad (8-2)$$

In this respect the spectral shift of a nonpolar solute caused in various nonpolar solvents was examined by Kunst in 1878 in connection with the refractive index of solvents (2, 3). He found that the absorption maximum of a solute shifts to a longer wavelength with the increasing refractive index of solvents. Later the correlation between the red shift phenomenon and the refractive index of solvents was confirmed by many workers (3). After Sheppard (4) had presented a simple theoretical equation for the spectral shift caused by dispersion force, Bayliss (5) gave a more explicit form by combining the quantum theory and the classic theory of electromagnetism, the equation being written as follows:

$$\Delta\nu = \frac{3e^2}{8\pi^2 c^2 m} \frac{f}{va^3} \frac{n^2 - 1}{2n^2 + 1} = 10.71 \times 10^9 \frac{f}{va^3} \frac{n^2 - 1}{2n^2 + 1} \quad (8-3)$$

According to the classical viewpoint, the phenomenon of light absorption brings about enforced vibration of oscillators in a molecule when the molecule is placed in a field of light; the amplitude of the enforced vibration can be correlated with the oscillator strength (f), i.e., band intensity. Consequently the transition dipole induced in the molecule in a field of light is stabilized by the reaction field of solvents which surrounds the solute responsible for light absorption. Thus the absorption spectrum results in a red shift in solvents. As will be mentioned later, this dispersion force effect of solvents on the spectra was extensively discussed in detail by Ooshika (6), McRae (7), Longuet-Higgins and Pople (8), Liptay (9), and others, using the second-order perturbation method. However, that the effect of dispersion force causes the red shift of the absorption band is always true when any theoretical treatment is applied.

The effect of electrostatic force on the band shift of electronic spectra seems to be conveniently divided into the following interaction terms: solute dipole-solvent dipole thereby induced, solute dipole-solvent dipole, and solvent dipole-solute dipole thereby induced. If molecules and solvents are both polar, all effects mentioned above as well as the effect of dispersion force will occur.

Now, before considering these solvent effect terms theoretically the important role of Franck-Condon principle should be stressed. The solutes in solvents may be in the most favorable intermolecular interaction state,

where the solutes would be surrounded by solvent molecules so as to become the energy minimum state, i.e., the most stable configuration between solutes and solvents. Since electrons move with much higher velocity than nuclei (Born-Oppenheimer approximation), absorption spectra are considered to be due to an electron transition from the ground equilibrium state to the Franck-Condon excited state where the molecular configuration of solutes and solvents may be the same as in the ground equilibrium state, although the electronic structure of solutes is surely different from that of the ground state. The conditions applied in discussing the solvent effect on fluorescence spectra naturally should correspond to those necessary for electron transition from an excited equilibrium state to Franck-Condon ground state. It has been reported (10) that relaxation time on the order of $\sim 10^{-11}$ sec at room temperature may be necessary to arrive at the equilibrium excited state from the Franck-Condon excited state. In order to realize the most suitable configuration including solute and solvent molecules, a relaxation time of the order of at least $\sim 10^{-13}$ sec (period of molecular vibration) is necessary when the size of the solute is changed during light absorption. Moreover, when solvent molecules are polar, the relaxation time necessary for the reorientation is about 10^{-10} – 10^{-12} sec at room temperature. It is, however, well known that the lifetime of the excited state (fluorescent state) is of the order of $\sim 10^{-8}$ – 10^{-9} sec when the transition to the excited state is allowed (e, the molecular absorption coefficient, is on the order of $\sim 10^4$; see Chaps. 3 and 4). Therefore the rearrangement of the solvent molecules during the lifetime of the excited state may be possible in general except for some special cases (see Chap. 4). This possibility should be taken into account when considering the molecular structure and molecular interaction in excited states.

8-3. THEORETICAL CONSIDERATION OF SOLVENT EFFECT ON ELECTRONIC SPECTRA

Following the theoretical treatment reported by McRae (7), let us consider a system which consists of a solute molecule surrounded by N identical solvent molecules. Under the zeroth-order approximation, we consider molecules which are free from mutual interactions. In this case the total electronic wave functions are given by the simple product of state functions for the unperturbed component molecules. Because it is assumed that the intermolecular interactions are much smaller compared with the complex formations, the overlap between the wave functions (in other words, the exchange of electrons between the wave functions) would be

ignored. This may allow for lack of antisymmetry of the total wave functions. Some of the total wave functions are written as follows:

$$\Phi_{a(p),0}^0 = \phi_0^{V(1)} \phi_0^{V(2)} \dots \phi_a^{V(p)} \dots \phi_0^{V(N)} \phi_0^U \quad (8-4)$$

$$\Phi_{a(p),j}^0 = \phi_0^{V(1)} \phi_0^{V(2)} \dots \phi_a^{V(p)} \dots \phi_0^{V(N)} \phi_j^U \quad (8-5)$$

$$\Phi_{a(p) \cdot b(q),j}^0 = \phi_0^{V(1)} \phi_0^{V(2)} \dots \phi_a^{V(p)} \phi_b^{V(q)} \dots \phi_0^{V(N)} \phi_j^U \quad (8-6)$$

According to McRae (7) the notation in these equations is as follows: $\Phi_{a(p) \cdot b(q),j}^0$ means that the p th and q th molecules of solvent consisting of total N molecules are in the a th ($\phi_a^{V(p)}$) and b th ($\phi_b^{V(q)}$) excited states, respectively, and that the solute molecule is in j th excited state (ϕ_j^U). The superfix 0 in, for example, $\Phi_{a(p) \cdot b(q),j}^0$ indicates the zeroth-order approximation of the state function. In addition, notations V and U refer to the solvent and solute, respectively. Suffixes i, j, k , etc., are used for solute, and p, q, r , etc., represent solvent molecules. Since the state energy for the zeroth-order electronic state is the sum of the energies of unperturbed component molecules, for example, the energy, $w_{a(p),j}^0$ corresponding to $\Phi_{a(p),j}^0$ is given by

$$w_{a(p),j}^0 = (N-1)w_0^V + w_a^{V(p)} + w_j^U \quad (8-7)$$

Thus energy difference (in cm^{-1}) between the i th and j th states ($j > i$) of a solute can be written as

$$\bar{\nu}_{ji}^U = \frac{(w_j^U - w_i^U)}{hc} = -\bar{\nu}_{ij}^U \quad (8-8)$$

When point dipole approximation is applied to describe the molecular interaction, its Hamiltonian (perturbation term \mathcal{H}') is given by

$$\mathcal{H}' = - \sum_{p=1}^N m^U m^{V(p)} \theta^{U \cdot V(p)} - \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N m^{V(p)} m^{V(q)} \theta^{V(p) \cdot V(q)} \quad (8-9)$$

Here m and θ have, respectively, the nature of the dipole moment and the geometrical factor which depends on the distance and the mutual orientation between two dipoles.

Assuming there is no degenerate state the application of second-order perturbation theory using Eqs. (8-4) through (8-6) and (8-9) produces the following interaction terms:

$$\Phi_i^0 \begin{vmatrix} \Phi_i^0 & \Phi_j^0 & \Phi_{a(p),i}^0 & \Phi_{a(p),j}^0 & \Phi_{a(p)b(q),j}^0 & \text{etc.} \\ H_{ii} & H_{ji} & H_{a(p)i:i} & H_{a(p)j:i} & H_{a(p)b(q)j:i} & \text{etc.} \end{vmatrix} \quad (8-10)$$

The other terms are written in the same manner. Let us now calculate each interaction term shown above. First

$$H_{ji} = \langle \Phi_j^0 | \mathcal{H} + \mathcal{H}' | \Phi_i^0 \rangle = w_i^0 \delta_{ji} + \langle \Phi_j^0 | \mathcal{H}' | \Phi_i^0 \rangle \quad (8-11)$$

This equation is reduced as follows:

$$H_{ji} = w_i^0 \delta_{ji} - \sum_{p=1}^N \theta_{ji:00}^{U,V(p)} M_{ji}^U M_{00}^{V(p)} - \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N \theta_{00:00}^{V(p),V(q)} (M_{00}^{V(p)})^2 \delta_{ji} \quad (8-12)$$

Here

$$M_{ji}^U = \int \phi_j^U m^U \phi_i^U d\tau \quad (8-13)$$

The derivation of Eq. (8-12) is

$$\langle \Phi_j^0 | \mathcal{H}' | \Phi_i^0 \rangle = \left\langle \left(\prod_{p=1}^N \phi_0^{V(p)} \right) \phi_j^U \right| - \sum_{p=1}^N m^U m^{V(p)} \theta^{U,V(p)} - \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N m^{V(p)} m^{V(q)} \theta^{V(p),V(q)} \left| \left(\prod_{p=1}^N \phi_0^{V(p)} \right) \phi_i^U \right\rangle$$

For the first term of \mathcal{H}' ,

$$- \sum_{p=1}^N \theta_{ji:00}^{U,V(p)} \langle \phi_j^U | m^U | \phi_i^U \rangle \left\langle \left(\prod_{q \neq p}^N \phi_0^{V(q)} \right) \phi_0^{V(p)} \right| m^{V(p)} \left| \left(\prod_{q \neq p}^N \phi_0^{V(q)} \right) \phi_0^{V(p)} \right\rangle = - \sum_{p=1}^N \theta_{ji:00}^{U,V(p)} M_{ji}^U M_{00}^{V(p)} \quad (8-14a)$$

For the second term of \mathcal{H}' ,

$$\begin{aligned} & \langle \phi_j^U \phi_i^U | \left\langle \prod_{r \neq q}^N \phi_0^{V(r)} \phi_0^{V(q)} \right| - \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N m^{V(p)} m^{V(q)} \theta^{V(p),V(q)} \left| \prod_{r \neq q}^N \phi_0^{V(r)} \phi_0^{V(q)} \right\rangle \\ & = -\frac{1}{2} \delta_{ji} \sum_{p=1}^N \sum_{q=1}^N \langle \phi_0^{V(p)} \phi_0^{V(q)} | m^{V(p)} m^{V(q)} \theta^{V(p),V(q)} | \phi_0^{V(p)} \phi_0^{V(q)} \rangle \\ & = -\frac{1}{2} \delta_{ji} \sum_{p=1}^N \sum_{q=1}^N \theta_{00:00}^{V(p),V(q)} \langle \phi_0^{V(p)} | m^{V(p)} | \phi_0^{V(p)} \rangle \langle \phi_0^{V(q)} | m^{V(q)} | \phi_0^{V(q)} \rangle \\ & = -\frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N M_{00}^{V(p)} M_{00}^{V(q)} \theta_{00:00}^{V(p),V(q)} \delta_{ji} \\ & = -\frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N \theta_{00:00}^{V(p),V(q)} (M_{00}^{V(q)})^2 \delta_{ji} \quad (8-14b) \end{aligned}$$

Combining Eqs. (8-14a), (8-14b), and the term $w_i^0 \delta_{ji}$, Eq. (8-12) is obtained. A treatment similar to that for the derivation of Eq. (8-12) leads to the following equations for some matrix elements in Eq. (8-10):

$$H_{a(p)j:i} = \langle \Phi_{a(p),j}^0 | \mathcal{H}' | \Phi_i^0 \rangle = -\theta_{ji,a0}^{U,V(p)} M_{ji}^U M_{a0}^{V(p)} - \frac{1}{2} \sum_{q \neq p}^N \theta_{a0:00}^{V(p),V(q)} M_{a0}^{V(p)} M_{00}^{V(q)} \delta_{ji} \quad (8-15)$$

$$H_{a(p)b(q)i:i} = \langle \Phi_{a(p)b(q),i}^0 | \mathcal{H}' | \Phi_i^0 \rangle = -\frac{1}{2} \sum_{q \neq p}^N \theta_{a0,b0}^{V(p),V(q)} M_{a0}^{V(p)} M_{b0}^{V(q)} \quad (8-16)$$

Now the energy for the perturbed system corresponding to the total wave function Φ_i of the i th excited state of the solute is given by Eq. (8-17) which was derived by applying the second-order perturbation method:

$$w_i = H_{ii} + \sum_{j \neq i} \frac{(H_{ji})^2}{w_i^0 - w_j^0} + \sum_{p=1}^N \sum_{a \neq 0} \frac{(H_{a(p)i:i})^2}{w_i^0 - w_{ai}^0} + \sum_{p=1}^N \sum_{j \neq i} \sum_{a \neq 0} \frac{(H_{a(p)j:i})^2}{w_i^0 - w_{aj}^0} + \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N \sum_{b \neq 0} \sum_{a \neq 0} \frac{(H_{a(p)b(q)i:i})^2}{w_i^0 - w_{abi}^0} \quad (8-17)$$

The corresponding energy for ground state can be obtained by replacing the subscript i appearing in Eq. (8-17) with the subscript 0. The shift caused by solvent effect becomes

$$\Delta \bar{\nu} = \frac{1}{hc} [(\overline{w_i - w_0}) - (w_i^0 - w_0^0)] \quad (8-18)$$

Here $\overline{(w_i - w_0)}$ means the time averaged value of $(w_i - w_0)$.

Practically, however, the numerical calculation of Eqs. (8-17) and (8-18) is very difficult because of the lack of data, for example, the excited energy levels of solvents and solutes. Simplification of each term in the equations above is thus necessarily required. First the term which describes only the interaction among solvent molecules would be neglected; for example, Eq. (8-16) and the last term on the right-hand side of Eq. (8-12) may be dropped from the consideration.

Next is the application of Onsager's reaction field model (29) for solute-solvent interaction. This model would describe the interaction of the

solute-solvent system as the function of dielectric constant and refractive index of solvent, and as the function of dipole moment and polarizability of solute molecule. So, undetermined parameters do not appear in the simplified form of Eqs. (8-17) and (8-18). This may be the main reason that most workers have adopted the Onsager model to explain the interaction of the solute-solvent system. In this reaction field model, the solute molecule is reduced to a point dipole at the center of a spherical cavity immersed in a homogeneous solvent dielectric which is acting as an effective electric field on the solute molecule. The electric field is defined as the reaction field R because the field arises from the orientation and inductive polarizations of the solvent dielectric owing to the solute dipole M . The reaction field R for the polarizing molecule is formulated as

$$R = \frac{M + \alpha R}{a^3} \cdot \left[\frac{2(D-1)}{2D+1} \right] \quad (8-19)$$

where M and α are the dipole moment and the mean isotropic polarizability of the solute molecule, respectively, D is the static dielectric constant, and a is the cavity radius mentioned above. Equation (8-19) can be rewritten as

$$R = \frac{M}{a^3} \left[\frac{1}{\left[\frac{2D+1}{2(D-1)} \right] - \frac{\alpha}{a^3}} \right] \quad (8-20)$$

For most organic molecules it is permitted to assume $\alpha \approx a^3/2$ so that the Eq. (8-20) can be simplified to Eq. (8-21) which is frequently used to express the solute-solvent interaction:

$$R = \frac{2M}{a^3} \left(\frac{D-1}{D+2} \right) \quad (8-21)$$

The reaction field (R_{ind}) due to the inductive polarization is also given by equations similar to Eqs. (8-19) through (8-21), in which the term D should be replaced by n_0^2 , which is the optical dielectric constant, i.e., the square of refractive index of the medium. That is,

$$R_{ind} = \frac{2M}{a^3} \left(\frac{n_0^2-1}{n_0^2+2} \right) \quad (8-22)$$

In the usual polar solvents there will occur reaction fields due to both the electrostatic (D) and inductive (n_0^2) polarizations. Thus the reaction field (R_{or}) due to the orientation polarization would be yielded by the subtraction of the term due to the inductive polarization [Eq. (8-22)] from

that of electrostatic polarization [Eq. (8-21)]. Therefore R_{or} can be written as

$$R_{or} = \frac{2M}{a^3} \left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2} \right] \quad (8-23)$$

It is worthwhile to note that the dipole moment M of a free solute molecule becomes M' in solution and that M' is given by $M' = M + \alpha R$; i.e., M' is the function of static polarizability α of the solute and a suitable reaction field R . Note here that αR and MR have the dimension of dipole moment and energy, respectively.

Keeping in mind previous discussions, let us consider the simplified form of each term appearing in Eq. (8-17), using the Onsager reaction field model.

The Term H_{ii} Refer to Eq. (8-12) and drop the term expressing the solvent-solvent interaction; the term H_{ii} is rewritten as

$$\begin{aligned} H_{ii} &= w_i^0 - M_{ii}^U \sum_{p=1}^N \theta_{ii:00}^{U,V(p)} M_{00}^{V(p)} \\ &= w_i^0 - M_{ii}^U \cdot E^V \end{aligned} \quad (8-24)$$

Here E^V denotes the field at the solute dipole having the dipole moment M_{ii}^U due to the permanent dipoles of the surrounding solvent molecules. In the present case E^V may be replaced by the reaction field originating from the orientation polarization R_{or} . Since solvent orientation for solute molecules at the Franck-Condon excited state is considered to be the same as that in the ground equilibrium state for the case of absorption spectra, the reaction field R_{or} should be the same in both the states. Equation (8-24) is thus reduces to

$$H_{ii} = w_i^0 - \frac{2M_{ii}^U \cdot M_{00}^U}{a^3} \left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2} \right] \quad (8-25)$$

A treatment similar to that for Eq. (8-25) gives Eq. (8-26) for the term H_{00} :

$$H_{00} = w_0^0 - \frac{2M_{00}^U \cdot M_{00}^U}{a^3} \left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2} \right] \quad (8-26)$$

From Eq. (8-18) the energy difference between Eqs. (8-25) and (8-26) becomes

$$H_{ii} - H_{00} = \frac{2M_{00}^U (M_{00}^U - M_{ii}^U)}{a^3} \left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2} \right] \quad (8-27)$$

The Second Term of Eq. (8-17). Taking the same approach as that for the simplification of the H_{ii} term, but taking into account the condition $j \neq i$, the second term of Eq. (8-17) is rewritten as

$$\sum_{j \neq i} \frac{(\mathbf{M}_{ji}^U \cdot \mathbf{E}^U)^2}{w_i^0 - w_j^0} = -\frac{1}{hc} \sum_{j \neq i} \frac{(\mathbf{M}_{ji}^U \cdot \mathbf{E}^U)^2}{\bar{v}_{ji}^U} \quad (8-28)$$

For an isotropic molecule, one could easily conjecture that the integration of $\cos^2 \theta$ over the whole surface of a cavity sphere results in $1/3$, which is necessary when the time averaged value of $(\mathbf{M}_{ji}^U \cdot \mathbf{E}^U)^2$ is required.

Thus Eq. (8-28) becomes

$$-\frac{1}{3hc} (E^U)^2 \sum_{j \neq i} \frac{(\mathbf{M}_{ji}^U)^2}{\bar{v}_{ji}^U} = -\frac{1}{2} \alpha_i^U (E^U)^2 \quad (8-29)$$

Here α_i is put as

$$\alpha_i = \frac{2}{3hc} \sum_{j \neq i} \frac{(\mathbf{M}_{ji}^U)^2}{\bar{v}_{ji}^U}$$

which is the usual expression for polarizability. Although the time averaged $(E^U)^2$ value cannot be directly related to macroscopic solvent properties, McRae (7) pointed out that when R_{or} (reaction field due to orientation polarization) is relatively large, $(E^U)^2$ would be on the same order of magnitude as $(R_{or})^2$. We have now arrived at $(E^U)^2 = 3(R_{or})^2$, which will lead to the same expression for solutes having different shapes. Consequently Eq. (8-29) turns out to be

$$-\frac{3}{2} \alpha_i^U (R_{or})^2 = -\frac{6(\mathbf{M}_{00}^U)^2 \alpha_i^U}{a^6} \left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2} \right]^2 \quad (8-30)$$

For ground state we get Eq. (8-31) by changing the subscript i to 0:

$$-\frac{6(\mathbf{M}_{00}^U)^2 \alpha_0^U}{a^6} \left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2} \right]^2 \quad (8-31)$$

The energy difference that contributes to the solvent shift brought about by the second term of Eq. (8-17) becomes

$$\frac{6}{a^6} (\mathbf{M}_{00}^U)^2 (\alpha_0^U - \alpha_i^U) \left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2} \right]^2 \quad (8-32)$$

The Third Term of Eq. (8-17). From Eqs. (8-7) and (8-8) the denominator of the third term becomes

$$\begin{aligned} w_i^0 - w_a^0 &= [Nw_0^V + w_i^U] - [(N-1)w_0^V + w_a^V + w_i^U] \\ &= -(w_a^V - w_0^V) = -hc\bar{v}_{a0}^V \end{aligned} \quad (8-33)$$

Next, the term $(H_{a(p)i:i})^2$ is calculated as follows: Using an equation similar to Eq. (8-15), but neglecting the term

$$\left[\frac{1}{2} \sum_{q \neq p}^N \theta_{a0,00}^{V(p),V(q)} M_{a0}^{V(p)} M_{00}^{V(q)} \right]^2$$

that describes only the solvent-solvent interaction, we write

$$\begin{aligned} (H_{a(p)i:i})^2 &= [\theta_{ii,a0}^{U,V(p)} M_{ii}^U M_{a0}^{V(p)}]^2 \\ &+ [\theta_{ii,a0}^{U,V(p)} M_{ii}^U M_{a0}^{V(p)}] \left[\sum_{q \neq p}^N \theta_{a0,00}^{V(p),V(q)} M_{00}^{V(q)} M_{a0}^{V(p)} \right] \end{aligned} \quad (8-34)$$

If we employ a definition similar to E^U in Eq. (8-24), the term $E^{V(p),V(q)}$ in

$$\sum_{q \neq p}^N \theta_{a0,00}^{V(p),V(q)} M_{00}^{V(q)} M_{a0}^{V(p)} = E^{V(p),V(q)} \cdot \mathbf{M}_{a0}^{V(p)}$$

represents the field at the p th solvent molecule due to the permanent dipoles of the surrounding solvent molecules consisting of the sum of N solvent dipoles, namely, $\sum_{q \neq p}^N M_{00}^{V(q)}$. We shall neglect the contribution from that field to the solvent effect on the solute molecule because the effect is only large when the solvent is highly polar. Equation (8-34) is thus rewritten as

$$(H_{a(p)i:i})^2 = [\theta_{ii,a0}^{U,V(p)} M_{ii}^U M_{a0}^{V(p)}]^2 \equiv [\mathbf{E}_i^{U,V(p)} \cdot \mathbf{M}_{a0}^{V(p)}]^2 \quad (8-35)$$

Combining Eqs. (8-33) and (8-35) the third term of Eq. (8-17) becomes

$$-\frac{1}{hc} \sum_{p=1}^N \sum_{a \neq 0} \frac{1}{\bar{v}_{a0}^V} [\mathbf{E}_i^{U,V(p)} \cdot \mathbf{M}_{a0}^{V(p)}]^2 \quad (8-36)$$

As was done in Eqs. (8-28) and (8-29), the static isotropic polarizability α_0^V of the solvent molecule in its ground state may be written as

$$\alpha_0^V = \frac{2}{3hc} \sum_{a \neq 0} \frac{(\mathbf{M}_{a0}^{V(p)})^2}{\bar{v}_{a0}^V}$$

Therefore Eq. (8-36) is reduced to the following form:

$$-\frac{1}{2} \sum_{p=1}^N (E_i^{U,V(p)})^2 \alpha_0^V \quad (8-37)$$

Using expressions such as $E_i^{UV(p)} \alpha_0^V = m_i^{V(p)}$ (dipole induced in a solvent molecule by the field $(E_i^{UV(p)})$, $E_i^{UV(p)} = \theta_{ii,a0}^{UV(p)} M_{ii}^U$ [see Eq. (8-35)], and $e_i^V = \sum_{p=1}^N \theta_{ii,a0}^{UV(p)} m_i^{V(p)}$ (the field at the solute dipole M_{ii}^U caused by induced solvent dipoles $m_i^{V(p)}$), Eq. (8-37) may be rewritten as $-\frac{1}{2} M_{ii}^U \cdot e_i^V$. Then e_i^V may be replaced by the reaction field arising from the induced dipoles in the solvent. Then, referring to Eq. (8-19), we write

$$\overline{e_i^V} = R_i^{\text{ind}} = \frac{M_{ii} + \alpha_i R_i}{a^3} \left[\frac{2(n_0^2 - 1)}{2n_0^2 + 1} \right]$$

However, we can neglect term $\alpha_i R_i$ because when R_i is small the contribution from the term $\alpha_i R_i$ becomes quite small, and whenever R_i is large, the contribution from the reaction field R_i^{ind} to the spectral shift becomes relatively small compared with the other terms. Then one may rewrite the equation $-\frac{1}{2} M_{ii}^U \cdot e_i^V$ as

$$-\frac{(M_{ii}^U)^2}{a^3} \left[\frac{n_0^2 - 1}{2n_0^2 + 1} \right] \quad (8-38)$$

The corresponding equation for ground state is

$$-\frac{(M_{00}^U)^2}{a^3} \left[\frac{n_0^2 - 1}{2n_0^2 + 1} \right] \quad (8-39)$$

Then the energy difference between ground and the i th excited states of the solute becomes

$$\frac{(M_{00}^U)^2 - (M_{ii}^U)^2}{a^3} \left[\frac{n_0^2 - 1}{2n_0^2 + 1} \right] \quad (8-40)$$

The Fourth Term of Eq. (8-17). Using the relation of

$$w_i^0 - w_{aj}^0 = N w_0^V + w_i^U - [(N-1)w_0^V + w_a^V + w_j^V] = -hc(\bar{\nu}_{ji}^U + \bar{\nu}_{a0}^V)$$

the denominator is rewritten as

$$-\left(\frac{\bar{\nu}_{a0}^V - \bar{\nu}_{ji}^U}{\bar{\nu}_{a0}^V} \right) \left(\frac{\bar{\nu}_{a0}^V}{(\bar{\nu}_{a0}^V + \bar{\nu}_{ji}^U)(\bar{\nu}_{a0}^V - \bar{\nu}_{ji}^U)} \right) = -\left(1 - \frac{\bar{\nu}_{ji}^U}{\bar{\nu}_{a0}^V} \right) \left(\frac{\bar{\nu}_{a0}^V}{(\bar{\nu}_{a0}^V)^2 - (\bar{\nu}_{ji}^U)^2} \right) \quad (8-41)$$

On the other hand, the numerator is simply reduced to

$$[-\theta_{ji,a0}^{UV(p)} M_{ji}^U M_{a0}^{V(p)}]^2$$

since $\delta_{ji} = 0$ at $j \neq i$. Therefore the fourth term of Eq. (8-17) averaged over all states [see Eqs. (8-28) and (8-29)] is given by

$$-\sum_{p=1}^N \sum_{a \neq 0} \sum_{j \neq i} \left(1 - \frac{\bar{\nu}_{ji}^U}{\bar{\nu}_{a0}^V} \right) \frac{1}{3hc} (E_{ji}^{UV(p)})^2 \left[\frac{\bar{\nu}_{a0}^V (M_{a0}^{V(p)})^2}{(\bar{\nu}_{a0}^V)^2 - (\bar{\nu}_{ji}^U)^2} \right] \quad (8-42)$$

Here

$$E_{ji}^{UV(p)} = \theta_{ji,a0}^{UV(p)} M_{ji}^U$$

Next, McRae (7) introduced a quantity that is a weighted mean wavelength defined by

$$L_{ji} = \frac{\sum_{a \neq 0} \frac{(M_{a0}^V)^2}{(\bar{\nu}_{a0}^V)^2 - (\bar{\nu}_{ji}^U)^2}}{\sum_{a \neq 0} \frac{\bar{\nu}_{a0}^V (M_{a0}^V)^2}{(\bar{\nu}_{a0}^V)^2 - (\bar{\nu}_{ji}^U)^2}} \quad (8-43)$$

It is assumed that one can use the L_{ji} value instead of the value $\sum_{a \neq 0} 1/\bar{\nu}_{a0}^V$ appearing in Eq. (8-42). Then we can derive Eq. (8-44) from Eq. (8-42) as

$$-\frac{1}{2} \sum_{p=1}^N \sum_{j \neq i} (1 - \bar{\nu}_{ji}^U L_{ji}) (E_{ji}^{UV(p)})^2 \alpha_0^V (\bar{\nu}_{ji}^U) \quad (8-44)$$

taking care that the isotropic polarizability $\alpha_0^V(\bar{\nu}_{ji}^U)$ of a solvent molecule in an oscillating field of the frequency $\bar{\nu}_{ji}^U$ is given by

$$\alpha_0^V(\bar{\nu}_{ji}^U) = \frac{2}{3hc} \sum_{a \neq 0} \frac{\bar{\nu}_{a0}^V (M_{a0}^V)^2}{(\bar{\nu}_{a0}^V)^2 - (\bar{\nu}_{ji}^U)^2}$$

A procedure similar to the theoretical treatment applied after Eq. (8-37) is now applied to Eq. (8-44) to derive

$$-\frac{1}{2} \sum_{j \neq i} (1 - \bar{\nu}_{ji}^U L_{ji}) M_{ji}^U \cdot e_{ji}^V \quad (8-45)$$

Here

$$e_{ji}^V = \sum_{p=1}^N \theta_{ji,a0}^{UV(p)} m_{ji}^{V(p)}$$

represents the field at a solute dipole arising from the induced solvent dipole having the moment

$$m_{ji}^{V(p)} = E_{ji}^{UV(p)} \alpha_0^V(\bar{\nu}_{ji}^U)$$

The reaction field corresponding to the field e_{ji}^V is written as

$$\frac{2M_{ji}^U}{a^3} \left[\frac{n_{ji}^2 - 1}{2n_{ji}^2 + 1} \right]$$

By referring to the procedure used for the derivation of Eq. (8-38), Eq. (8-45) can now be reduced to

$$-\sum_{j \neq i} (1 - \bar{\nu}_{ji}^U L_{ji}) \frac{(M_{ji}^U)^2}{a^3} \left[\frac{n_{ji}^2 - 1}{2n_{ji}^2 + 1} \right] \quad (8-46)$$

Since the oscillator strength f_{ji}^U is given [see Chap. 3 and Ref. (11)] by

$$f_{ji}^U = 4.704 \times 10^{29} \bar{\nu}_{ji}^U (M_{ji}^U)^2, \quad M_{ji}^U = 4.803 \times 10^{-18}$$

Eq. (8-46) is rewritten as

$$-2.13 \times 10^{-30} \sum_{j \neq i} \{(\bar{\nu}_{ji}^U)^{-1} - L_{ji}\} \frac{f_{ji}^U}{a^3} \left(\frac{n_{ji}^2 - 1}{2n_{ji}^2 + 1} \right) \quad (8-47)$$

The equation at ground state can be obtained by changing the subscript i to zero; then the energy difference due to the fourth term of Eq. (8-17) is given by

$$2.13 \times 10^{-30} \left[\sum_{j \neq 0} \{(\bar{\nu}_{j0}^U)^{-1} - L_{j0}\} \frac{f_{j0}^U}{a^3} \left(\frac{n_{j0}^2 - 1}{2n_{j0}^2 + 1} \right) - \sum_{j \neq i} \{(\bar{\nu}_{ji}^U)^{-1} - L_{ji}\} \frac{f_{ji}^U}{a^3} \left(\frac{n_{ji}^2 - 1}{2n_{ji}^2 + 1} \right) \right] \quad (8-48)$$

By collecting Eqs. (8-27), (8-32), (8-40), and (8-48), McRae (7) gives the frequency shift caused by the solvent effect on the absorption spectra of an isotropic solute molecule

$$\begin{aligned} \Delta \bar{\nu}_{\text{abs}} = & \frac{2.13 \times 10^{-30}}{hc} \left[\sum_{j \neq 0} \{(\bar{\nu}_{j0}^U)^{-1} - L_{j0}\} \frac{f_{j0}^U}{a^3} \left(\frac{n_{j0}^2 - 1}{2n_{j0}^2 + 1} \right) \right. \\ & - \sum_{j \neq i} \{(\bar{\nu}_{ji}^U)^{-1} - L_{ji}\} \frac{f_{ji}^U}{a^3} \left(\frac{n_{ji}^2 - 1}{2n_{ji}^2 + 1} \right) \\ & + \frac{1}{hc} \frac{(M_{00}^U)^2 - (M_{ii}^U)^2}{a^3} \left(\frac{n_0^2 - 1}{2n_0^2 + 1} \right) \\ & + \frac{2}{hc} \frac{M_{00}^U (M_{00}^U - M_{ii}^U)}{a^3} \left[\frac{D-1}{D+2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right] \\ & \left. + \frac{6}{hc} \frac{(M_{00}^U)^2 (\alpha_0^U - \alpha_i^U)}{a^6} \left[\frac{D-1}{D+2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right]^2 \right] \quad (8-49) \end{aligned}$$

On the other hand, when one considers the solvent effect on the fluorescence spectra of the solute molecule, the application of a theoretical treatment quite similar to the derivation of Eq. (8-49) is possible. If no appreciable dipole reorientation exists during the lifetime of the excited state, Eq. (8-49) is also used for the discussion of the solvent effect on the emission spectra. However, if there is dipole reorientation, direct application of Eq. (8-49) is not satisfactory. McRae (7) gave Eq. (8-50) for this latter case and used a theoretical treatment analogous to the derivation of Eq. (8-49):

$$\begin{aligned} \Delta \bar{\nu}_{\text{fluor}} = & \frac{2.13 \times 10^{-30}}{hc} \left[\sum_{j \neq 0} \left(\frac{1}{\bar{\nu}_{j0}^U} - L_{j0} \right) \frac{f_{j0}^U}{a^3} \left(\frac{n_{j0}^2 - 1}{2n_{j0}^2 + 1} \right) \right. \\ & - \sum_{j \neq i} \left(\frac{1}{\bar{\nu}_{ji}^U} - L_{ji} \right) \frac{f_{ji}^U}{a^3} \left(\frac{n_{ji}^2 - 1}{2n_{ji}^2 + 1} \right) \\ & + \frac{1}{hc} \left[\frac{(M_{00}^U)^2 - (M_{ii}^U)^2}{a^3} \right] \left[\frac{n_0^2 - 1}{2n_0^2 + 1} \right] \\ & + \frac{2}{hc} \left[\frac{M_{ii}^U (M_{00}^U - M_{ii}^U)}{a^3} \right] \left[\frac{D-1}{D+2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right] \\ & \left. + \frac{2}{hc} \left[\frac{M_{ii}^U (5M_{ii}^U - 2M_{00}^U) (\alpha_0^U - \alpha_i^U)}{a^6} \right] \left[\frac{D-1}{D+2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right]^2 \right] \quad (8-50)^\dagger \end{aligned}$$

† As a reference, Ooshika's (6) equation, corresponding to Eqs. (8-49) and (8-50), are given here.

$$\begin{aligned} hc \Delta \bar{\nu}_{\text{abs}} = & \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\mu_g^2 - \mu_g \mu_a}{a^3} - \frac{2(n^2 - 1)}{2n^2 + 1} \frac{(\mu_a - \mu_g)^2}{2a^3} \\ & + \frac{2(\epsilon + 1)(\epsilon - n^2) kT}{3(2\epsilon + n^2)\epsilon} \frac{1}{a^3} \left\{ \sum_{m \neq a} \frac{\mu_{am}^2}{\epsilon_a - \epsilon_m} - \sum_{m \neq g} \frac{\mu_{gm}^2}{\epsilon_g - \epsilon_m} \right\} \\ & + \left(\frac{2(\epsilon - 1)}{2\epsilon + 1} \right)^2 \frac{1}{a^6} \left[3 \sum_{m \neq g} \frac{(\mu_g \mu_{gm})^2}{\epsilon_m - \epsilon_g} - \sum_{m \neq a} \frac{(\mu_g \mu_{am})^2}{\epsilon_m - \epsilon_a} \right. \\ & - 2 \sum_{m \neq g} \frac{(\mu_g \mu_{gm})(\mu_a \mu_{gm})}{\epsilon_m - \epsilon_g} \left. \right] + \frac{1}{2} \frac{2(n^2 - 1)}{2n^2 + 1} \frac{1}{a^3} \left[\sum_{m \neq g} \mu_{gm}^2 \left(1 - \frac{\epsilon_g - \epsilon_m}{E_g - E_n} \right) \right. \\ & \left. - \sum_{m \neq a} \mu_{am}^2 \left(1 - \frac{\epsilon_a - \epsilon_m}{E_g - E_n} \right) \right] \end{aligned}$$

Continued on next page

Now some consideration will be taken of the first term of Eq. (8-49), namely, the contribution from the dispersion interaction term. Using the relation of Eq. (8-8) it is obvious that

$$\sum_{j \neq 0} \bar{\nu}_{j0}^U > \sum_{j \neq i} \bar{\nu}_{ji}^U, \quad \text{i.e.,} \quad \sum_{j \neq 0} (\bar{\nu}_{j0}^U)^{-1} < \sum_{j \neq i} (\bar{\nu}_{ji}^U)^{-1}$$

Moreover if the solute absorption band is located at a wavelength region which is quite distant from that of the solvent absorption band, i.e., $\bar{\nu}_{s0}^U \gg \bar{\nu}_{ji}^U$, it can be said [refer to Eq. (8-43)] that the quantity L_{ji} is a constant which is almost independent from one solvent to another solvent. This kind of L_{ji} is now called L_0 ; which is in a quite shorter wavelength than that of the solute absorption band. Thus one can obtain the dispersion term of Eq. (8-49) by writing

$$\Delta \bar{\nu}_{\text{abs}}(\text{dispersion}) = 1.07 \times 10^{-14} \left[\sum_{j \neq 0} \{(\bar{\nu}_{j0}^U)^{-1} - L_0\} \frac{f_{j0}^U}{a^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right) - \sum_{j \neq i} \{(\bar{\nu}_{ji}^U)^{-1} - L_0\} \frac{f_{ji}^U}{a^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right) \right] \quad (8-51)$$

Here it has been assumed that the refraction index for the sodium D line can be employed instead of the n_{j0} , n_{ji} , etc. Now one can deduce from the preceding discussion that the dispersion term usually contributes toward

$$\begin{aligned} hc \Delta \bar{\nu}_{\text{inter}} = & \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\mu_s \mu_s - \mu_s^2}{a^3} + \frac{2(n^2 - 1)}{2n^2 + 1} \frac{(\mu_s - \mu_p)^2}{2a^3} \\ & + \frac{2(\epsilon + 1)(\epsilon - n^2)}{3(2\epsilon + n^2)\epsilon} \frac{kT}{a^3} \left\{ \sum_{m \neq a} \frac{\mu_{am}^2}{\epsilon_a - \epsilon_m} - \sum_{m \neq g} \frac{\mu_{gm}^2}{\epsilon_g - \epsilon_m} \right\} \\ & + \left\{ \frac{2(\epsilon - 1)}{2\epsilon + 1} \right\}^2 \frac{1}{a^6} \left[3 \sum_{m \neq a} \frac{(\mu_s \mu_{am})^2}{\epsilon_a - \epsilon_m} - \sum_{m \neq g} \frac{(\mu_s \mu_{gm})^2}{\epsilon_g - \epsilon_m} \right] \\ & - 2 \sum_{m \neq a} \frac{(\mu_s \mu_{am})(\mu_s \mu_{gm})}{\epsilon_a - \epsilon_m} + \frac{1}{2} \frac{2(n^2 - 1)}{2n^2 + 1} \frac{1}{a^3} \left[\sum_{m \neq g} \mu_{gm}^2 \left(1 - \frac{\epsilon_g - \epsilon_m}{E_g - E_a} \right) \right. \\ & \left. - \sum_{m \neq a} \mu_{am}^2 \left(1 - \frac{\epsilon_s - \epsilon_m}{E_s - E_a} \right) \right] \end{aligned}$$

Here notations are: ϵ = static dielectric constant, n = refractive index of solvent, ϵ_m = m th state energy of solute, E_n = n th state energy of solvent molecule, a = cavity radius, μ_m = solute dipole moment in the m th state, and μ_{im} = solute transition moment between i th and m th states. We can understand there being a considerable similarity between Ooshika's and McRae's equations.

the red shift of the solute absorption band. When the terms pertinent to the $\bar{\nu}_{i0}^U$ and $\bar{\nu}_{0i}^U$ are picked up outside $\sum_{j \neq 0}$ and $\sum_{j \neq i}$, Eq. (8-51) is given by

$$\begin{aligned} \Delta \bar{\nu}_{\text{abs}}(\text{dispersion}) = & 1.07 \times 10^{-14} \left[-\frac{2f_{i0}^U L_0}{a^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right) \right. \\ & + \sum_{j \neq 0} \{(\bar{\nu}_{j0}^U)^{-1} - L_0\} \frac{f_{j0}^U}{a^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right) \\ & \left. - \sum_{j \neq i} \{(\bar{\nu}_{ji}^U)^{-1} - L_0\} \frac{f_{ji}^U}{a^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right) \right] \quad (8-52) \end{aligned}$$

The relation of $\bar{\nu}_{0i}^U = -\bar{\nu}_{i0}^U$ and $f_{0i}^U = -f_{i0}^U$ was adopted here. The first term in brackets of Eq. (8-52) should be compared with Eq. (8-3). We can see that the Bayliss (5) equation [Eq. (8-3)] describes a part of Eq. (8-52). Longuet-Higgins and Pople (8) also derived the following equation for the electronic spectral shift (red shift) of a nonpolar molecule in nonpolar solvents:

$$\frac{1}{6}(\bar{R})^{-6} Z \alpha^V \left[\frac{1}{4} E_i \alpha^U + M_{0 \rightarrow i}^2 \right] \quad (8-53)$$

Here it was assumed that each solute molecule is surrounded by solvent molecules of Z numbers at mean distance \bar{R} . The value in brackets is determined by only the nature of solute: $M_{0 \rightarrow i}$, E_i , and α^U represent the transition moment between ground and i th excited states, transition energy to i th excited state, and solute polarizability at ground state, respectively. The Eq. (8-53) is valid if E_i is much smaller than the mean excitation energy of solvent and solute, and the equation means that the dispersion red shift is parallel to the solvent polarizability α^V . Since α^V can be a function of refractive index [see, for example, Eq. (8-2)], Eq. (8-53) has a meaning similar to Eq. (8-52).

It is noted that Eq. (8-52) can be also rewritten as

$$\Delta \bar{\nu}_{\text{abs}}(\text{dispersion}) = (A + B) \left(\frac{n^2 - 1}{2n^2 + 1} \right) \quad (8-54)$$

where A and B are

$$A = 1.07 \times 10^{-14} \frac{L_0}{a^3} \left[-2f_{i0}^U + \sum_{j \neq 0, i} (f_{j0}^U - f_{j0}^U) \right]$$

$$B = 1.07 \times 10^{-14} \frac{1}{a^3} \left[\sum_{j \neq 0, i} \left(\frac{f_{j0}^U}{\bar{\nu}_{j0}^U} - \frac{f_{ji}^U}{\bar{\nu}_{ji}^U} \right) \right]$$

If we assume L_0 to be almost independent of the solvent to solvent, A and B turn out to be only the function of the solute molecule itself so that Eq. (8-54) shows the spectral red shift due to the dispersion force interaction to be proportional to the refractive index of solvent, as was qualitatively discussed in Sec. 8-2. Using the approximation for deriving Eq. (8-54), Eqs. (8-49) and (8-50), which describe the general solvent effect, can be now simplified as follows: (7)

$$\Delta\tilde{\nu}_{\text{abs}} = (A + B + C) \frac{n^2 - 1}{2n^2 + 1} + E_{\text{abs}} \left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right] + F_{\text{abs}} \left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right]^2 \quad (8-55)$$

$$\Delta\tilde{\nu}_{\text{fluor}} = (A + B + C) \frac{n^2 - 1}{2n^2 + 1} + E_{\text{fluor}} \left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + F_{\text{fluor}} \left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right)^2 \quad (8-56)$$

The meaning of the terms C , E_{abs} , F_{abs} , E_{fluor} , and F_{fluor} , which are functions of the solute itself, is easily understood from the original Eqs. (8-49) and (8-50). When one considers the value of $(\Delta\tilde{\nu}_{\text{abs}} - \Delta\tilde{\nu}_{\text{fluor}})$, it will be expressed as follows:

$$\Delta\tilde{\nu}_{\text{abs}} - \Delta\tilde{\nu}_{\text{fluor}} = (E_{\text{abs}} - E_{\text{fluor}}) \left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + (F_{\text{abs}} - F_{\text{fluor}}) \left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right)^2 \quad (8-57)$$

Here

$$E_{\text{abs}} - E_{\text{fluor}} = \frac{2}{hc} \frac{(M_{00}^U - M_{ii}^U)^2}{a^3}$$

and

$$F_{\text{abs}} - F_{\text{fluor}} = \frac{2}{hc} \frac{(\alpha_0^U - \alpha_i^U)}{a^6} [3(M_{00}^U)^2 - 5(M_{ii}^U)^2 + 2M_{00}^U \cdot M_{ii}^U]$$

It is noted that the quantity of $(\Delta\tilde{\nu}_{\text{abs}} - \Delta\tilde{\nu}_{\text{fluor}})$ was first derived independently by Lippert (12) and by Mataga et al. (13) on the basis of the application of Ooshika's theory (see equations shown in the preceding

footnote), the equation being written as

$$\begin{aligned} & hc(\Delta\tilde{\nu}_{\text{fluor}} - \Delta\tilde{\nu}_{\text{abs}}) \\ &= - \left[\frac{2(\epsilon - 1)}{2\epsilon + 1} - \frac{2(n^2 - 1)}{2n^2 + 1} \right] \frac{(\mu_a - \mu_g)^2}{a^3} + \left[\frac{2(\epsilon - 1)}{2\epsilon + 1} \right] \frac{1}{a^6} \\ & \times \left\{ \sum_{m \neq a} \left[\frac{3(\mu_a \mu_{am})^2 - 2(\mu_a \mu_{am})(\mu_g \mu_{am}) - (\mu_g \mu_{am})^2}{(\mathcal{E}_a - \mathcal{E}_m)} \right] \right. \\ & \left. + \sum_{m \neq g} \left[\frac{3(\mu_g \mu_{gm})^2 - 2(\mu_g \mu_{gm})(\mu_a \mu_{gm}) - (\mu_a \mu_{gm})^2}{(\mathcal{E}_g - \mathcal{E}_m)} \right] \right\} \quad (8-58) \end{aligned}$$

Each notation for the abbreviated terms is the same as that given in the preceding footnote.

8-4. SOLVENT EFFECT ON ELECTRONIC SPECTRA AND ELECTRONIC STATE OF MOLECULES

An examination of Eqs. (8-55), (8-56), and (8-57) will show that the quantitative analyses of the solvent effect on electronic spectra will give reliable information about the electronic state of molecules in the excited or the ground state. When we consider the solvent effect in solvents, whose polarity is not very large, the term having the quantity

$$\left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right]^2$$

would be neglected because of its small contribution to the solvent effect when compared with the other terms (see later discussions of this section). Note here that the preceding quadratic term represents the contribution from the interaction between the solvent permanent dipole and the solute dipole thereby induced, i.e., the solvent Stark effect term. For the case of absorption spectra by referring to Eqs. (8-49) and (8-55) we can write

$$\begin{aligned} \Delta\tilde{\nu}_{\text{abs}} &= \left[A + B + \frac{(M_{00}^U)^2 - (M_{ii}^U)^2}{hca^3} \right] \frac{n^2 - 1}{2n^2 + 1} \\ &+ \left[\frac{2M_{00}^U(M_{00}^U - M_{ii}^U)}{hca^3} \right] \left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (8-59a) \end{aligned}$$

The applicability of this equation was checked by McRae (7), Robertson et al. (14), Kubota and Yamakawa (15), and others.

If absorption spectra are recorded in nonpolar hydrocarbon solvents the quantity

$$\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right)$$

is almost zero so that the second term on the right-hand side of Eq. (8-59a) has negligible value. Therefore Robertson et al. (14) plotted $\Delta\tilde{\nu}_{\text{abs}}$ against the quantity $(n^2-1)/(2n^2+1)$. A good linear relation was thus obtained in their experiments, where the solvent effect on the absorption spectra of azulene, naphthalene, and naphthacene was examined. Next the correlation of $\Delta\tilde{\nu}_{\text{abs}}$ (obtained by recording the spectra in somewhat polar organic solvents) to

$$\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right) \text{ and } \left(\frac{n^2-1}{2n^2+1} \right)$$

was examined, using the value

$$\left[A + B + \left(\frac{(M_{00}^u)^2 - (M_{ii}^u)^2}{hca^3} \right) \right]$$

[see Eq. (8-59a)] evaluated from the slope of the aforementioned plotting against $(n^2-1)/(2n^2+1)$. The value of $E_{\text{abs}} = 2M_{00}^u(M_{00}^u - M_{ii}^u)/hca^3$ was chosen so as to obtain the best fit for the observed $\Delta\tilde{\nu}_{\text{abs}}$. The quantity E_{abs} is the function of the dipole moment in excited and ground states. Since the latter value can be easily measured by the standard method, the M_{ii}^u (excited state dipole moment) may be estimated by using the observed value of E_{abs} and the a which is reasonably estimated as closely as possible. Some of the evaluated values for azulene were $E_{\text{abs}} = +286 \text{ cm}^{-1}$, M_{ii}^u (1L_b state) = -0.81 D at an estimated $a = 4 \text{ \AA}$. When compared with the calculated value -1.36 D by the PPP method (see Chap. 2) the agreement between experimental and theoretical values is reasonable. However, the agreement is not so good at higher excited 1L_a and 1B_u states. One reason for this may be the lower accuracy of the calculated value at the higher excited states. Figure 8-1 gives the correlation (14) between the observed $\Delta\tilde{\nu}_{\text{abs}}^{\text{exp}}$ value and the calculated $\Delta\tilde{\nu}_{\text{abs}}^{\text{calc}}$ value, the latter being obtained using the experimentally determined constants -131 cm^{-1} (1L_b), -2734 (1L_a) and -7154 (1B_u) for $(A+B+C)$ [see Eq. (8-55)], and $+286 \text{ cm}^{-1}$ (1L_b), $+209$ (1L_a), and 0 (1B_u) for E_{abs} .

For molecules such as naphthalene $M_{00}^u \approx M_{ii}^u \approx 0$ because of the molecular symmetry. The term E_{abs} is therefore zero so that the effect

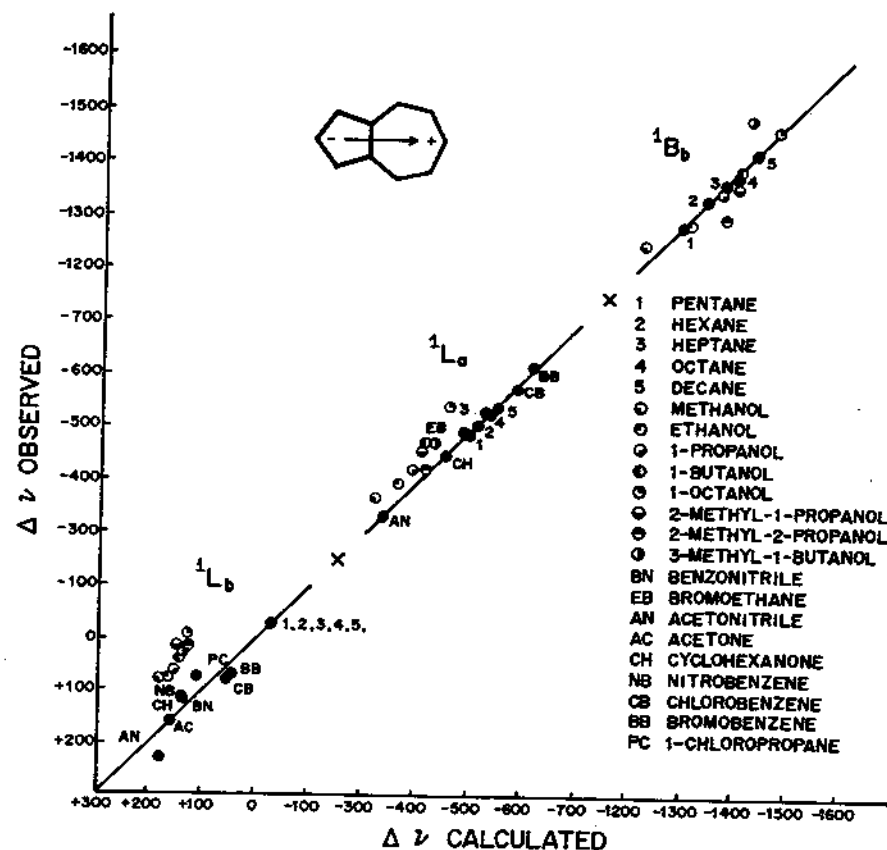


Fig. 8-1. The linear correlation between observed and calculated $\Delta\tilde{\nu}$ of azulene. See text for the calculated values. [Reprinted from W. W. Robertson, A. D. King, and O. E. Weigang, Jr., *J. Chem. Phys.*, 35, 464 (1961), by courtesy of the copyright owner.]

of F_{abs} [see Eq. (8-55)] will be more explicitly distinguishable. For this purpose Robertson et al. (14) also analyzed the effect of solvent on the naphthalene 1L_b and naphthacene 1B_u bands by applying the same treatment as that for azulene. Their conclusion showed that the contribution from the term

$$F_{\text{abs}} \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right]^2$$

to the $\Delta\tilde{\nu}_{\text{abs}}^{\text{exp}}$ seems to be negligible. Recently the contribution from this solvent Stark effect term to the spectral shift of a nonpolar solute in polar

solvents has been also discussed by other workers (16, 17). Their discussions and results are given here briefly.

A suitable method of checking this solvent Stark effect may be the examination of the spectral shift of nonpolar solutes such as alternant hydrocarbons (anthracene, naphthalene, etc.) caused by polar solvents, as Robertson et al. (14) have pointed out. Note, however, that in these cases the contribution from the Stark effect term as well as the dipole-dipole interaction term turns out to be zero when Eqs. (8-49) and (8-55) are applied, because the dipole moment in the ground state, M_{00}^{μ} , is zero. This may not be the actual case, since one could reasonably conjecture that the spectral shift of the nonpolar solute would be also brought about by the polar solvent Stark effect, although the contribution may be small. This contradiction may arise because the derivation of Eq. (8-49) (McRae's equation) as well as the Ooshika equation is made with the approximation of the polar solute chromophore having a dipole moment M_{00}^{μ} so that the conventional cavity model is applicable. In the case of a nonpolar solute dissolved in polar solvent, however, the application of the aforementioned cavity reaction field model does not seem to be strictly suitable. Weigang and Wild (17b, 17c) examined these points and introduced the idea of mol-bond-density of solvent molecules, wherein the change of structure of solvent molecules is taken into consideration to explain this kind of solvent effect.

Later, Baur and Nicol (16) showed that the solvent Stark effect for a nonpolar solute is also formulated by means of solvent macroscopic properties (dielectric constant and refractive index). According to a fluctuation approximation similar to the one reported by Fröhlich (17d), the average mutual interaction energy due to the Stark effect between the nonpolar solute and the polar solvent has been expressed by $\alpha \bar{E}^2$, where α is the polarizability of the solute and \bar{E}^2 is the mean square fluctuation field at the place of solute molecule, brought about by the permanent electric polarization M_s of solvent. Thus the difference ΔE of the interaction energy between the ground and the i th excited states is given by

$$\Delta E_{\text{Stark}} = \left(\frac{\bar{E}^2}{3} \right) (\alpha_i - \alpha_0) \quad (8-59b)$$

The averaging procedure of the distribution function pertinent to the distance and relative orientation between a solute and a solvent molecule leads to 1/3 in Eq. (8-59b), as was seen in the derivation of McRae's equation (see Sec. 8-3). To evaluate the \bar{E}^2 the following model was used:

The solute cavity with a radius d and polarizability α_0 (or α_i) is surrounded by a solvent shell with a radius R that has the same center as that of the solute cavity and is much larger than d . The solvent molecules in this solvent shell have a uniform permanent electric polarization M_s , which may produce a field E_s at the site of the solute molecule and which makes the evaluation of \bar{E}^2 possible. This solvent shell is considered to be embedded in a continuous medium of actual solvent, but the dielectric constant D and the refractive index n in the solvent shell are assumed to be the same as those of the continuous medium, although the values inside and outside the solvent shell are different in the strict sense. Thus the expression of \bar{E}^2 was derived and combined with Eq. (8-59b), the solvent Stark shift for the nonpolar solute being described as

$$\Delta \bar{\nu}_{\text{Stark}} = - \left[\frac{108 \{ \ln(R/d) \}^2 (\alpha_i - \alpha_0) kT}{hcR^3} \right] \left[\frac{(D - n^2)(2D + n^2)}{D(n^2 + 2)^2} \right] \\ \approx K \left[\frac{(D - n^2)(2D + n^2)}{D(n^2 + 2)^2} \right] \quad (8-59c)$$

It is permissible to assume that the value of K is approximately independent of the solvent. The total spectral shift of a nonpolar solute observed in polar solvent may be written as

$$\Delta \bar{\nu} = J \left[\frac{n^2 - 1}{2n^2 + 1} \right] + K \left[\frac{(D - n^2)(2D + n^2)}{D(n^2 + 2)^2} \right] \quad (8-59d)$$

The value J clearly corresponds to the value of $A + B$ (dispersion interaction term) in the first term of Eq. (8-59a), since $M_{00}^{\mu} = M_{ii}^{\mu} = 0$ for the present case. Using many kinds (more than 40) of solvent, Nicol et al. (17a) tested Eq. (8-59d) carefully for the cases of 1L_a bands of anthracene, phenanthrene, tetracene, and chrysene, and 1L_b bands of phenanthrene, naphthalene, chrysene, and picene. The results showed that Eq. (8-59d) clearly explains the polar solvent effect on the electronic spectra of the compounds given above, despite the use of different kinds (hydrocarbons, halogenated hydrocarbons, ethers, ketones, etc.) of solvents. The values of J and K obtained experimentally by the least squares method are in the range of -2670 to -8560 cm^{-1} for J and -5 to -33 cm^{-1} for K , respectively. Note that the effect of the dispersion force (term J) is the most effective, but the solvent Stark effect term (K) makes only a small contribution to the spectral shift and is usually neglected in the discussion of solvent effect on the electronic spectra of solute, especially polar solutes (see also 17b,c). In this work Nicol et al. (17a) also criticized in

detail the treatment of the solvent Stark effect by Abe et al. (17e) from experimental and theoretical viewpoints, and pointed out that the effect of a permanent solvent dipole on the spectral shift and the difference of solute polarizability between ground and excited states are both overestimated. Also it may be noted that the red or blue shift caused by the solvent Stark effect is dependent only upon the conditions $\alpha_i > \alpha_0$ or $\alpha_i < \alpha_0$, respectively.

Let us turn to the application of Eq. (8-59a). Instead of the separate evaluation of $(A + B + C)$ and E_{abs} , as has been already discussed for the case of azulene (14), it is also possible to treat the experimental results yielded in various organic solvents directly by employing the least squares method for Eq. (8-59a). McRae (7) applied this method to analyze the well-known solvent effect (obvious red shift) on the electronic spectra of phenol blue, assuming that the L_0 [see Eq. (8-54)] value for saturated hydrocarbon and bromocyclohexane is 1000 Å but 1250 Å for other solvents. The increase in dipole moment from 5.80 D (ground state) to 7.48 D (excited state) was concluded in the first strong $\pi-\pi^*$ transition.

Kubota et al. (15) also applied the preceding treatment in order to examine the electronic structures in the excited and ground states of aromatic tertiary amine N-oxides and nitril N-oxides. As was discussed in Chap. 7 a common characteristic of the aromatic tertiary amine N-oxides is that they exhibit in near-UV region a strong $\pi-\pi^*$ band that shows a distinct blue shift by the hydrogen bond formation with the oxygen atom of the $N \rightarrow O$ bond. This fact indicates that the net charge on the oxygen atom should be decreased in the excited state because of the intramolecular charge transfer of the oxygen $2p\pi$ electrons to the rest of the conjugated system (for example, the pyridine ring for the case of pyridine N-oxide); then the dipole moment in the $\pi-\pi^*$ excited state would be decreased, as was suggested by the molecular orbital calculation (18). The analyses of the effect of nonhydrogen bonding solvents on the electronic spectra of several kinds of aromatic tertiary amine N-oxides were carried out on the basis of Eq. (8-59a). The results (15) showed that the solvent effect on spectra is satisfactorily explained, using Eq. (8-59a) where the direct least squares method was applied to analyze the experimental results. Some of the correlations between $\tilde{\nu}_{abs}^{obs}$ and $\tilde{\nu}_{abs}^{calc}$ are depicted in Fig. 8-2 for two amine oxides. As a result it has been deduced that the dipole moment at the $\pi-\pi^*$ excited state decreases in magnitude, as the MO calculation suggested.

Ito et al. (19) used the following technique to investigate the electronic state at the $n \rightarrow \pi^*$ excited state of several types of carbonyl compounds. When the measurement is made using two kinds of solvents, 1 and 2, which

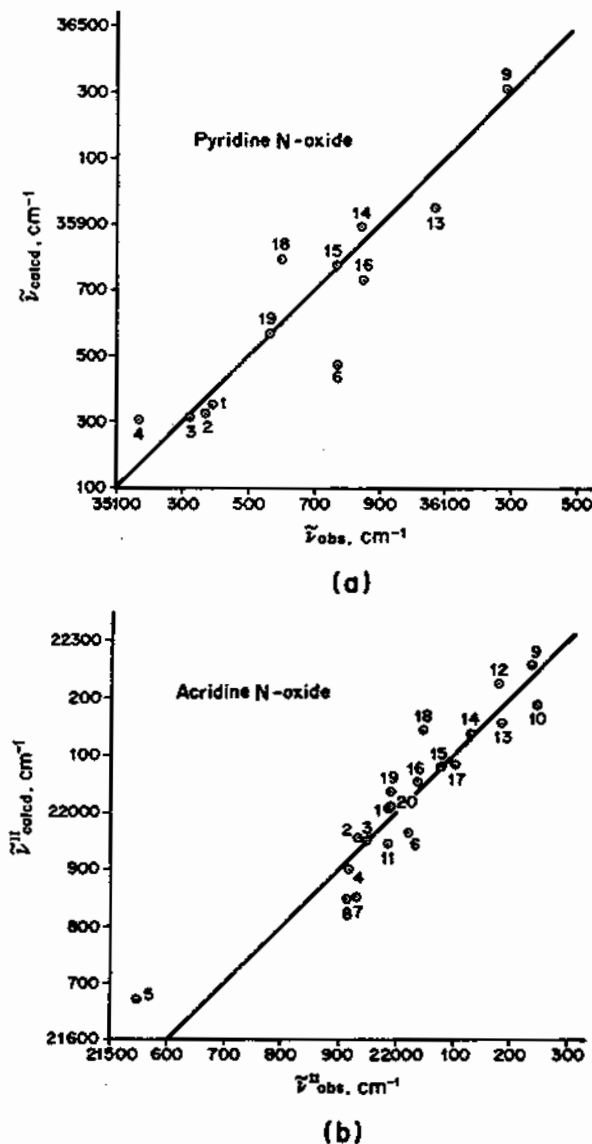


Fig. 8-2. Correlation between $\tilde{\nu}_{abs}$ and $\tilde{\nu}_{calc}$ for pyridine N-oxide (a) and acridine N-oxide (b). Calculated value is due to

$$\tilde{\nu}_{abs} = \tilde{\nu}_{abs}^0 + C_1 \cdot \frac{n^2 - 1}{2n^2 + 1} + C_2 \left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$$

The constants (cm^{-1} unit) for cases (a) and (b) are given below in that order: $\tilde{\nu}_{abs}^0 = 35,980$ and $22,900$; $C_1 = -3260$ and -4660 ; $C_2 = 1280$ and 250 . See original paper for numbering of each solvent, but note that dioxane (No. 6) shows some deviation from linearity as is already known. [Reprinted from T. Kubota and M. Yamakawa, *Bull. Chem. Soc. Japan*, 35, 555 (1962), by courtesy of the copyright owner.]

have the same refractive index but quite different dielectric constant, it follows from Eq. (8-59a) that

$$hc(\Delta\tilde{\nu}_{\text{abs}}^1 - \Delta\tilde{\nu}_{\text{abs}}^2) = \frac{2M_{00}^u(M_{00}^u - M_{ii}^u)}{a^3} \left[\frac{D_1 - 1}{D_1 + 2} - \frac{D_2 - 1}{D_2 + 2} \right] \quad (8-60)$$

We see that the other terms in Eq. (8-59a) except for the dielectric constant of solvent would be canceled out by using the two solvents. For this purpose Ito et al. selected ethyl ether and acetonitrile, whose refractive indexes are 1.356 and 1.344, respectively; however, the dielectric constants are 4.3 for ethyl ether and 37.5 for acetonitrile, a wide difference of values. Moreover, note that since the aforementioned two solvents do not absorb light above 200 $m\mu$, the dispersion term contribution from the solvents seems to be almost the same; that is, the weighted mean wavelength of the two solvents may be almost the same. The frequency shift observed in each of the solvents and in their combination was analyzed according to the Eq. (8-60) in the case of carbonyl $n \rightarrow \pi^*$ band of acetone, methyl oxide, acetophenone, and benzophenone (19). The linear relation expected from Eq. (8-60) remained stable, but the absorption band was found to undergo blue shift with the increase in the dielectric constant of solvent. The slope of the linear plot denotes the $2M_{00}^u(M_{00}^u - M_{ii}^u)/hca^3$. If we assume a^3 to be proportional to the molecular volume, the relative ratio of $M_{00}^u(M_{00}^u - M_{ii}^u)$ for the four ketones is

acetone: methyl oxide: acetophenone: benzophenone = 1:1.8:1.4:28.

This ratio agrees well with the theoretical prediction by means of the simple molecular orbital treatment of the $n \rightarrow \pi^*$ transition. Itô et al. concluded that the dipole moment of ketones decreases sharply in the $n \rightarrow \pi^*$ excited state and that this decrease may be a consequence of more extended π conjugation than that in the lone pair orbital.

Assuming that the dipole moments in ground and excited states are parallel, and taking $a \approx 4 \text{ \AA}$ as a reasonable estimate, we calculate the excited state dipole moment of acetophenone to be 0.5 D. This is comparable to the ground state dipole moment ~ 3 D. However, note that in solvents like alcohols both effects (i.e., electrostatic interaction between solute and solvent molecules, discussed above, and hydrogen bonding interaction) play important roles (especially in hydrogen bonding) in the blue shift phenomena of the $n \rightarrow \pi^*$ band (see Chap. 7). The difference between the dipole moments in the $n \rightarrow \pi^*$ state and the ground state of carbonyl compounds was calculated approximately by Ito et al. (19) based on the following treatment. First M_{00}^u was equated as $M_{00}^u = M_{\sigma}^u + M_{\pi}^u + M_{\pi}^u$, where the first, second, and third terms denote the moment

originating from σ bonding electrons, π bonding electrons, and nonbonding electrons, respectively. Since the spectroscopic orbital for nonbonding electrons of the carbonyl group is thought to have axial symmetry and no hybridization (20), M_{π}^u is taken as zero. Thus $M_{00}^u = M_{\sigma}^u + M_{\pi}^u$. In the excited state we write

$$M_{ii}^u = M_{\sigma}^u + M_{\pi}^u + M_{\pi}^u$$

in which the last term means the π moment due to an electron occupying the π^* orbital after the $n \rightarrow \pi^*$ transition. Accordingly we get $M_{00}^u - M_{ii}^u = -M_{\pi}^u$.

Recently Baba et al. (21) evaluated the dipole moment in the $n \rightarrow \pi^*$ excited state of diazines by treating the frequency shift of absorption and fluorescence spectra with Eqs. (8-60) and (8-61); the latter equation can be easily derived from Eq. (8-56) by employing the assumption that was used to derive Eq. (8-60):

$$hc(\Delta\tilde{\nu}_{\text{fluor}}^1 - \Delta\tilde{\nu}_{\text{fluor}}^2) = \frac{2M_{ii}^u(M_{00}^u - M_{ii}^u)}{a^3} \left[\frac{D_1 - 1}{D_1 + 2} - \frac{D_2 - 1}{D_2 + 2} \right] \quad (8-61)$$

Taking the ratio of Eqs. (8-60) and (8-61), we obtain

$$\frac{(\Delta\tilde{\nu}_{\text{fluor}}^1 - \Delta\tilde{\nu}_{\text{fluor}}^2)}{(\Delta\tilde{\nu}_{\text{abs}}^1 - \Delta\tilde{\nu}_{\text{abs}}^2)} = \frac{M_{ii}^u(M_{00}^u - M_{ii}^u)a^3}{M_{00}^u(M_{00}^u - M_{ii}^u)a^3} \quad (8-62)$$

If one assumes that the difference of the molecular structure as well as the cavity radius between the ground and the excited states is not very large, Eq. (8-62) results in Eq. (8-63):

$$\frac{\Delta\tilde{\nu}_{\text{fluor}}^1 - \Delta\tilde{\nu}_{\text{fluor}}^2}{\Delta\tilde{\nu}_{\text{abs}}^1 - \Delta\tilde{\nu}_{\text{abs}}^2} = \frac{M_{ii}^u}{M_{00}^u} \quad (8-63)$$

This equation was recommended by Baba et al. (21) to evaluate M_{ii}^u because no empirical parameters such as a cavity radius a are required whereas they are needed when only Eq. (8-60) or (8-61) is used to evaluate the excited dipole moment. Referring to Eq. (8-57) but omitting the term

$$(F_{\text{abs}} - F_{\text{fluor}}) \left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right)^2$$

which would make a small contribution to the frequency shift so far discussed, $\Delta\tilde{\nu}_{\text{abs}} - \Delta\tilde{\nu}_{\text{fluor}}$ becomes

$$\Delta\tilde{\nu}_{\text{abs}} - \Delta\tilde{\nu}_{\text{fluor}} = \frac{2}{hc} \frac{(M_{00}^u - M_{ii}^u)^2}{a^3} \left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right) \quad (8-64)$$

Since M_{ii}^* can be determined in a straightforward manner by means of Eq. (8-63), Baba et al. (21) suggested that the cavity radius a could also be estimated experimentally by analyzing the observed spectral shift, using both Eq. (8-63) and Eq. (8-64). For the case of pyridazine and pyrimidine they obtained $a = 3.7 \text{ \AA}$ and 3.9 \AA for the former and the latter, respectively, using the data for ether and acetonitrile recommended by Itô et al. (19). These values appear to be reasonable as cavity radii of diazines. As an example of absorption, fluorescence, and excitation spectra of diazines, the results on pyridazine and pyrimidine are illustrated in Fig. 8-3. We see that the absorption spectra undergo obvious blue shift with an increasing polarity of solvent, but the shift of fluorescence spectra due to solvent

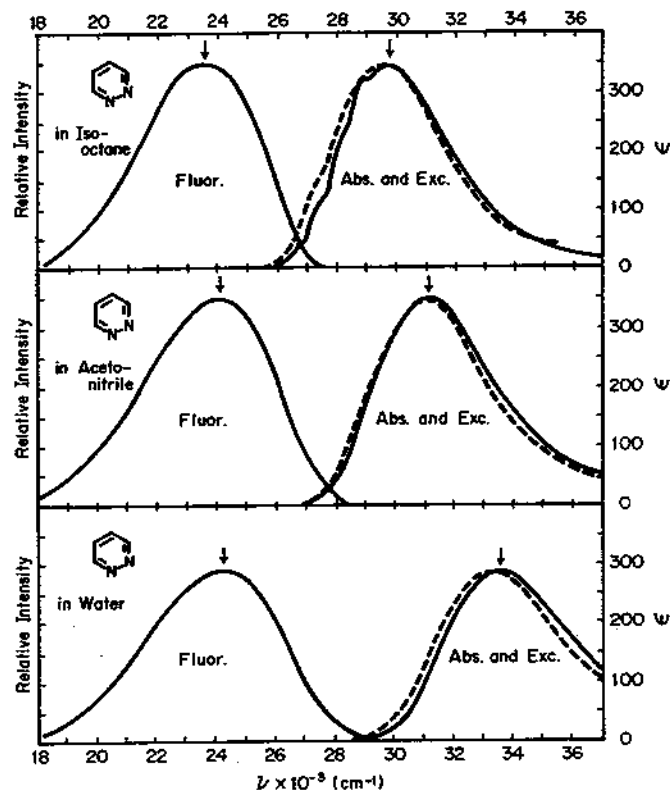


Fig. 8-3. Fluorescence, absorption, and excitation spectra of pyridazine in iso-octane, acetonitrile, and water (broken curves represent the excitation spectra). [Reprinted from H. Baba, L. Goodman, and P. C. Valenti, *J. Am. Chem. Soc.*, **88**, 5410 (1966), by courtesy of the copyright owner.]

polarity is dependent upon the compounds (blue shift for the case of pyridazine and red shift for pyrimidine and pyrazine). It should be noted here that pyrazine has zero dipole moment in both the ground and the $n\pi^*$ excited states because of the molecular symmetry. This means that there is no appreciable frequency shift given by the Eqs. (8-60) and (8-61) in nonhydrogen bonding solvents. Actually, however, this is not the case. A small red shift of the fluorescence spectrum of pyrazine is especially observed in polar solvents (21). This fact may be due to the local solute dipole-solvent dipole interaction, which would make somewhat uncertain the values of the excited state dipole moment determined by application of the equations for the solvent effect as previously presented.

By using the data obtained in ether and acetonitrile and Eq. (8-63), the following dipole moments in the $n\pi^*$ state are yielded: $M_{ii}^*/M_{00}^* = 0.28$, $M_{ii}^* = 1.10 \text{ D}$ ($M_{00}^* = 3.94 \text{ D}$), and $\Delta M^* = -2.84 \text{ D}$ for pyridazine; $M_{ii}^*/M_{00}^* = -0.24$, $M_{ii}^* = -0.52 \text{ D}$ ($M_{00}^* = 2.2 \text{ D}$), and $\Delta M^* = -2.72 \text{ D}$ for pyrimidine. Supposing that the $n\pi^*$ transition brings about the rehybridization of the nitrogen lone pair orbital and that an electron remaining in the original lone pair orbital will enter into a pure $2p$ orbital after the $n\pi^*$ transition due to the rehybridization, the decrease in dipole moment from this origin easily becomes -0.9 D ($-0.37 \times 4.8 \times \cos 60^\circ$, where 0.37 \AA means the distance between the nitrogen nucleus and the centroid of the sp^2 nitrogen lone pair orbital) and -1.6 D for pyrimidine and pyridazine, respectively, when the Slater type atomic orbital for nitrogen atom is employed. These values are much smaller than the observed $\Delta\mu$ values mentioned above. Thus most of the decreasing dipole moment in the $n\pi^*$ state in question should originate in the change of π electron distribution (19, 21). In turn, the red shift of the fluorescence spectrum of pyrimidine, in contrast to the blue shift of the absorption spectrum, was explained as follows: If the relation $M_{ii}^* < 0 < M_{00}^*$ is held between the two dipole moments (this is the case for pyrimidine), it is reasonably acceptable to assume that in the Franck-Condon excited state the solute molecule is still surrounded by the solvent molecules which are in the most stable orientation with the solute in the equilibrium ground state. Since M_{00}^* and M_{ii}^* are in opposite direction to each other, it is safe to say that the dipole-dipole interaction at the Franck-Condon state leads to the destabilization of solute-solvent interaction, as Fig. 8-4 shows.

Consequently a red shift of fluorescence spectra will be caused in contrast with a large blue shift of absorption spectra. It is noted that in the $n \rightarrow \pi^*$ excited state the hydrogen bonding power of solutes is greatly decreased because of the removal of one of the lone pair electrons to the π^* orbital,

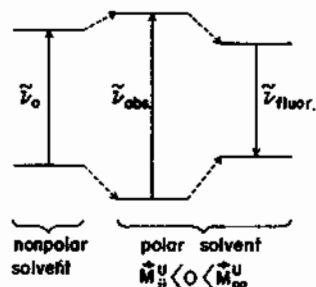
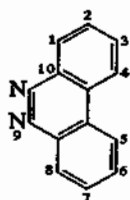


Fig. 8-4. Schematic representation of the interaction of polar solvent with the solute dipole moment which is in the relation $\vec{M}_{00}^u < 0 < \vec{M}_{00}^u$ in ground and excited states.

which expands over all atoms comprising the π system (see Chap. 7). Later, Mugiya and Baba (22) applied a treatment similar to that mentioned above to the analyses of the nonhydrogen bonding solvent effect on the $n-\pi^*$ band of 9,10-diazaphenanthrene; Lippert et al. had reported previously that its $n-\pi^*$ band is quite fluorescent. The analyses showed that the dipole



moment (M_{00}^u) in the fluorescent $n-\pi^*$ state is 1.15 D, compared with ground state dipole moment $M_{00}^u = 3.93$ D, and that the cavity radius is $a = 4.8$ Å, which was determined experimentally by referring to the solvent effect on absorption and fluorescence spectra. The foregoing values seem to be reasonable magnitudes and are comparable with the corresponding values ($M_{00}^u = 1.10$ D and $a = 3.7$ Å) at the $n-\pi^*$ state of pyridazine.

After Ooshika's (6) equation [see footnote, pp. 385 and 386] of the solvent effect on electronic spectra had been presented, Lippert (12) and Mataga et al. (13) also independently derived Eq. (8-65) by applying the Ooshika theory to the difference of solvent effect on fluorescence and absorption spectra [see Eq. (8-58)]:

$$(\Delta\tilde{\nu}_{abs} - \Delta\tilde{\nu}_{fluor}) = \frac{2}{hc} \frac{(M_{00}^u - M_{00}^u)^2}{a^3} \left[\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \right] + (\text{additional term with small quantity}) \quad (8-65)$$

Equation (8-65) has a form quite similar to that of Eq. (8-64), if the additional term with small quantity is neglected. Here it is assumed that the wave number difference between the 0—0 band and band maximum is constant for solvent change. Thus the linear relation of $(\tilde{\nu}_{abs} - \tilde{\nu}_{fluor})$ to

$$F(D, n) \equiv \left[\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \right]$$

would be held.

In Fig. 8-5 are shown the effects of nonhydrogen bonding solvents on the $\pi-\pi^*$ band of α - and β -naphthylamines (23) for illustrating the relation of Eq. (8-65). Both fluorescence and absorption spectra show red shift, the

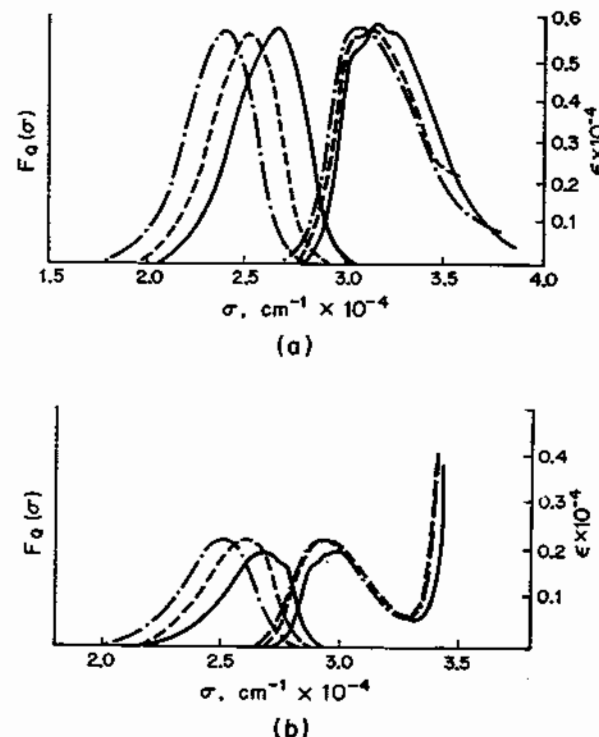


Fig. 8-5. Absorption and fluorescence spectra of α -naphthylamine (a) and β -naphthylamine (b). Solvent: — (n-hexane), --- (monochlorobenzene), - · - · - (acetonitrile). Concentration: $\sim 0.8 \times 10^{-4}$ and $\sim 2.0 \times 10^{-4}$ mole/liter for the former and the latter, respectively. [Reprinted from N. Mataga, *Bull. Chem. Soc. Japan*, 36, 654 (1963), by courtesy of the copyright owner.]

shift of the former being much larger than that of the latter. These facts indicate that $M_{ii}^* > M_{00}^*$ and the stabilization energy in the equilibrium excited state would be larger than in the ground state. The mutual relation of $(\bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{fluor}})$ to $F(D, n)$ is depicted in Fig. 8-6 for the systems (23)

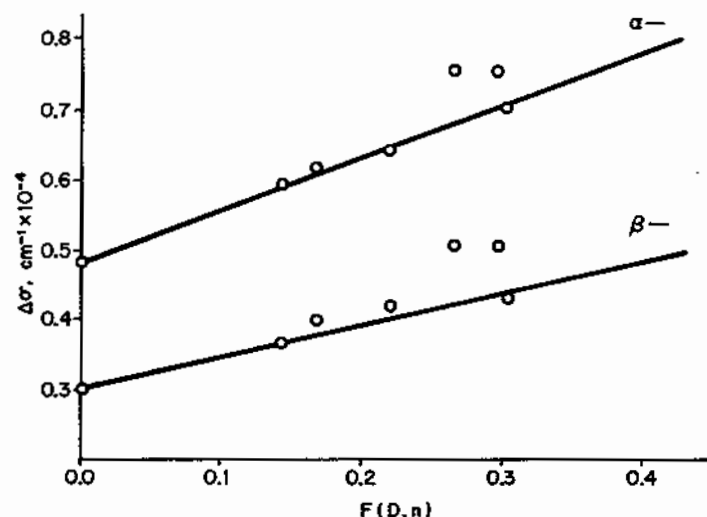
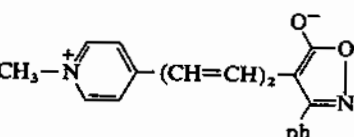


Fig. 8-6. $\Delta\sigma (= \bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{fluor}})$ versus $F(D, n)$ (see text) relation for naphthylamines. Deviation points are for alcoholic solvents. [Reprinted from N. Mataga, *Bull. Chem. Soc. Japan*, 36, 654 (1963), by courtesy of the copyright owner.]

discussed above. Generally speaking, when a substituent such as NH_2 or OH is introduced into aromatic hydrocarbons such as benzene and naphthalene, it is well known from theoretical and experimental studies that the π dipole moment due to the electron transfer of a lone pair type π electron on a substituent to the aromatic ring is much larger in the excited state than in the ground state. So, M_{ii}^* turns out to be larger than M_{00}^* . Assuming a suitable a value appearing in Eq. (8-65) the $(M_{ii}^* - M_{00}^*)$ value is evaluated from the slope of straight lines shown, for example, in Fig. 8-6. Many data have been thus collected in Table 8-1. In Table 8-1 it is noted that the magnitude M_{ii}^* of compound 13 is much less than that in the ground state. This is due to the large blue shift of absorption spectra and the small blue shift or almost no shift of fluorescence spectra.

To derive Eqs. (8-64), (8-65), etc., which make the determination of the excited state dipole moment possible, it was assumed that the molecule in the Franck-Condon excited state relaxed to an equilibrium fluorescence

TABLE 8-1
Experimental Value of $(M_{ii}^* - M_{00}^*)$ and a (Å) Evaluated Using Equation (8-65)

No.	Compound ^a	$(M_{ii}^* - M_{00}^*)$	a (Å)
1	β -Methoxynaphthalene ^a	0.5	3
2	β -Naphthol		
3	α -Naphthylamine	4.4	3
4	β -Naphthylamine	3.5	3
5	α -Dimethylaminonaphthalene ^b	4.4	3
6	Aniline ^c	2-2.5	2-2.5
7	Indole ^d	5	3
8	Carbazole ^d	1.2	4
9	Acridone ^e	2.4	3
10	4-Amino-4'-nitrobiphenyl ^f	12	7
11	4-Dimethylamino-4'-nitrostilbene ^f	24	8
12	4-Dimethylamino-4'-cyanostilbene ^f	23	8
13		$\sim(-8)$	6

^a N. Mataga et al., *Bull. Chem. Soc. Japan*, 28, 690 (1955); 29, 465 (1956).

^b N. Mataga, *Bull. Chem. Soc. Japan*, 36, 620 (1963).

^c N. Mataga, *Bull. Chem. Soc. Japan*, 36, 1607 (1963).

^d N. Mataga, Y. Torihashi, and K. Ezumi, *Theoret. Chim. Acta*, 2, 158 (1964).

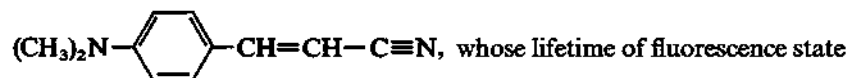
^e H. Kokubun, *Naturwiss.*, 44, 233 (1957); *Z. Elektrochem.*, 62, 599 (1958).

^f E. Lippert, *Z. Naturforsch.*, 10a, 541 (1955); *Z. Elektrochem.*, 61, 962 (1957).

state with the solvent orientation suitable to the excited state solute dipole moment. However, if the lifetime of the fluorescence excited state is very short, there is a possibility that fluorescence will be emitted before the molecule in Franck-Condon excited state has relaxed to the equilibrium excited state. In these cases the linearity expected from the aforementioned equations may not be very good and the M_{ii}^* thus yielded will not be sufficiently accurate. Examples that can be attributed to this factor are known (23, 24).

Let us consider the π - π^* excited state of *o*-, *m*-, and *p*-aminobenzoic acids, which have two substituents: One is a strong electron donor (NH_2) and the other is a strong electron acceptor ($-\text{COOH}$). The intramolecular charge transfer interaction between these two substituents should be larger

in the excited π - π^* state than in the ground state, and also the interaction should be largest for the parasubstituent among the three isomers. Thus one may reasonably predict the $(M_{ii}^u - M_{00}^u)$ for the parasubstituent to be much larger than for the ortho- or metasubstituent. Experimental results plotted linearly from Eq. (8-65), however, show that the slope [coefficient of $F(D, n)$] of the plotting is parasubstituent < metasubstituent, in contradiction to the theoretical expectation. The absorption intensities of the π - π^* band of the three isomers appearing in the longest wavelength region are $p \gg o > m$, so that the emission probability for the parasubstituent may be overwhelmingly large and could be $\tau_0 \approx 10^{-9}$ sec. In addition, there is fluorescence quenching caused by various radiationless processes. Therefore the mean lifetime of fluorescence may be much shorter than $\sim 10^{-9}$ sec and perhaps would be on the order of $\sim 10^{-10}$ sec. So, fluorescence does not seem to be emitted from the equilibrium state, but the system may be only partly relaxed. This fact seems to be the main reason for the aforementioned contradictory observation about the amino substituted benzoic acids (23). An observation similar to that described above was also made by Lippert et al. (24) for N,N-dimethylaminocinnamic acid nitrile,



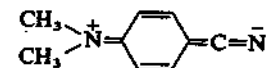
was experimentally determined to be less than 6×10^{-10} sec. In general the orientation relaxation time τ_a depends upon temperature and becomes larger with decreasing temperature so that the relaxation does not occur during the lifetime of fluorescence at a temperature below a critical one. From this viewpoint, Lippert et al. (24) examined the temperature dependence of absorption and fluorescence spectra of stilben derivatives ($M_{ii}^u > M_{00}^u$, see Table 8-1), and found that in spite of a monotonous red shift of absorption spectra with a decreasing temperature, fluorescence spectra first undergo red shift and then blue shift, as was expected. This inversion temperature of red-to-blue shift is, of course, dependent upon the solvents used. On the other hand, when temperature is raised thermal motion becomes vigorous. Strong orientation between solute and solvent molecules will be inhibited so that it is possible that the shift of fluorescence spectra again becomes smaller with increasing temperature.

8-5. REVERSAL OF EXCITED ENERGY LEVELS DUE TO SOLVENT EFFECT

If two different excited energy states S_1 and S_2 , which have quite different electronic structure, lie in close proximity, there is a possibility that the

solvent effect will bring about the inversion of two different energy states because the solvent effect on these two excited states seems to be considerably different. When this kind of inversion occurs in some solvents, the considerable change of fluorescence spectra and intensity is invariably observed, although absorption spectra will remain almost unchanged. An example was first pointed out by Lippert et al. (24, 25) for the fluorescence spectra of *p*-cyano-N,N-dimethylaniline (also refer to the Fig. 8-8 and later discussions on this figure).

The absorption band of this compound shows apparently only one peak at $\tilde{\nu}_{\text{abs}} = 35 \times 10^3 \text{ cm}^{-1}$, but fluorescence spectra have two peaks at $\tilde{\nu}_{\text{fluor}}^1 \approx 28 \times 10^3 \text{ cm}^{-1}$ and $\tilde{\nu}_{\text{fluor}}^2 = 24 \sim 20 \times 10^3 \text{ cm}^{-1}$. This latter fluorescence peak, $\tilde{\nu}_{\text{fluor}}^2$, is sensitive for solvent change; in nonpolar solvents like cyclohexane there appears only one peak, $\tilde{\nu}_{\text{fluor}}^1$, but with an increasing polarity of solvent $\tilde{\nu}_{\text{fluor}}^2$ appears and shifts to a longer wavelength as the solvent polarity increases. From the results of many theoretical calculations it can be reasonably expected that the absorption band $\tilde{\nu}_{\text{abs}}$ consists of a strong band 1L_a with large intramolecular CT configuration and a weak 1L_b band localized mainly in the benzene ring. As has been stated above, the 1L_a band would be contributed largely from the intramolecular CT structure, the structure of which is formally written as



That is, its dipole moment is very large so that the M_{ii}^u value of *p*-dimethylaminobenzonitrile would be very large in the 1L_a state, but is not so large in the 1L_b state because of a quite localized transition in the benzene ring. Keeping in mind these considerations the aforementioned abnormal fluorescence spectra of the compound can now be explained as follows: In nonpolar solvent the 1L_b state is the lowest π - π^* excited state and the 1L_a state is the next higher state, as is shown in Fig. 8-7. Therefore the fluorescence $\tilde{\nu}_{\text{fluor}}^1$ (see Fig. 8-8) emitting from the 1L_b state is observed.

In polar solvent the 1L_a state is strongly stabilized in the excited equilibrium state because of the large dipole-dipole interaction and turns out to be the lowest excited state whose position is, however, adjacent to the 1L_b state (see Fig. 8-7). Therefore we can now observe two fluorescence maxima corresponding to 1L_a (longer wavelength peak) and 1L_b states. Increasing the solvent polarity, then, stabilizes the 1L_a state more than in the 1L_b state, resulting in a red shift and an intensification of the longer wavelength fluorescence peak $\tilde{\nu}_{\text{fluor}}^2$. Actually the evaluation of $(M_{ii}^u - M_{00}^u)$ which used Eq. (8-65) at the 1L_a band gave a large value of $\sim 17 \text{ D}$; thus

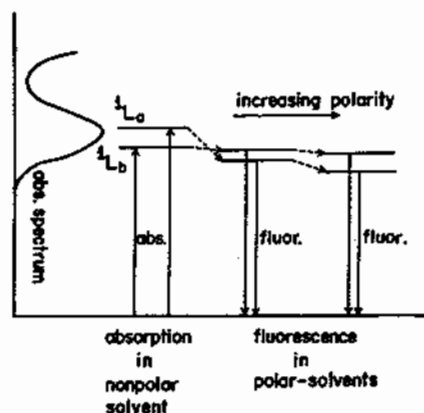


Fig. 8-7. Excited state energy level inversion caused by mutual interaction between solute in excited state and polar solvent.

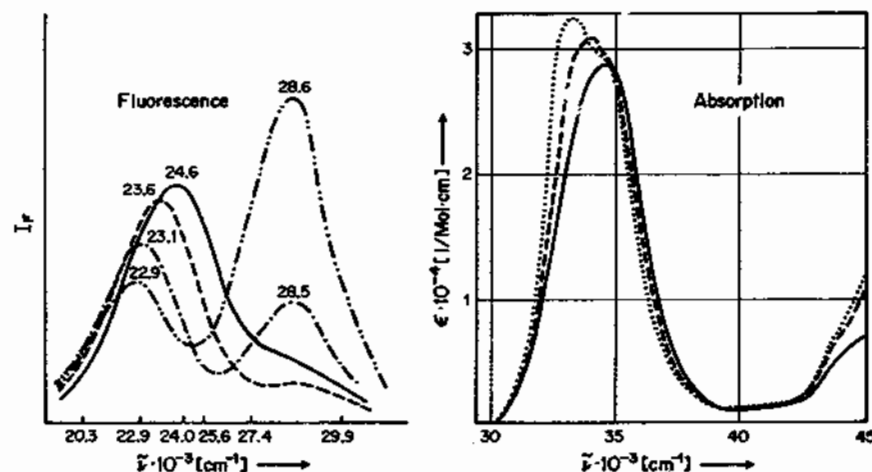


Fig. 8-8. Fluorescence and absorption spectra of *p*-cyanodiethylaniline in buthyl-chloride-methylcyclohexane-isopentane mixture (12:3:1 in volume). Fluorescence: 5×10^{-5} mole at — 293°K, - - - 234°K, — · — · 173°K, — · — · — 148°K. Absorption: 1.6×10^{-5} mole at — 293°K, - - - 193°K, · · · · · 113°K. [Reprinted from E. Lippert et al., (24a), *Angew. Chem.*, 73, 695 (1961), by courtesy of the copyright owner.]

$M_{ii}^U \approx 23$ D, since $M_{00}^U \approx 6$ D. If the experiment is performed below a certain temperature, the effect of orientation relaxation time τ_s would become effective, as was discussed before. Thus the intensity of $\bar{\nu}_{\text{fluor}}^2$ seems

to be decreased. This was also found by Lippert et al. (refer to the last part of (Sec. 8-4) (24, 25). Some examples are shown in Fig. 8-8. As can be understood from this figure the decreasing intensity of the $\bar{\nu}_{\text{fluor}}^2$ fluorescence peak was found below $\sim 200^\circ\text{K}$. Excited state energy level inversion, as was discussed above, was also suggested by Mataga (26a) and Mataga et al. (26b) for α -naphthylamine, the fluorescence spectra of which is shown in Fig. 8-5(a), and for indole. For the fluorescence behavior of indole in connection with the exciplex formation (which seems to affect the fluorescence of indole markedly), see Chap. 9. The plotting of Eq. (8-65) led to the conclusion that the quantity $(M_{ii}^U - M_{00}^U)$ of α -naphthylamine is larger (4.4 D) than that (3.5 D) of β -naphthylamine in spite of the reverse relation for naphthols on the $(M_{ii}^U - M_{00}^U)$; that is, β -naphthol $>$ α -naphthol. Using the 1L_b state wave function, written (27) as $\Psi(^1L_b) = a \cdot ^1\chi_{i \rightarrow k} + b \cdot ^1\chi_{j \rightarrow l}$, dipole moment difference between ground and 1L_b states is given by

$$M(^1L_b) - M_{00}^U = a^2(M_{kk} - M_{ii}) + b^2(M_{ll} - M_{jj})$$

Here, for instance, M_{kk} means the orbital π dipole moment corresponding to the MO $\psi_k = \sum c_{kv} \phi_v$. M_{kk} is easily given by

$$M_{kk} = e \sum c_{kv}^2 R_v$$

where R_v is the position vector to atom v from the origin (pseudo-orthogonality between the $2p\pi$ AOs was assumed). From actual calculation, however, Mataga (23) concluded that α -naphthylamine has a smaller dipole moment difference $(M(^1L_b) - M_{00}^U)$ (0.92 D) than that of β -naphthylamine (1.16 D), just as in the case of α - and β -naphthols, as was stated above. Moreover, that the 1L_a state of α -naphthylamine has a larger dipole moment than in the 1L_b state was also theoretically indicated. Based on the aforementioned experimental and theoretical studies Mataga concluded the fluorescence emitting state in the equilibrium excited state of α -naphthylamine to be the 1L_a state and not the 1L_b state expected from absorption spectra. It is well known that the electron donating substituent effect on the 1L_b and 1L_a bands of naphthalene (whose 1L_b band with weak intensity appears in a longer wavelength region than in the 1L_a band) is quite large for the 1L_a band in the case of an α substituent and in the 1L_b band in the case of a β substituent. The amino group is a quite strong electron donating substituent and therefore the large red shift of the 1L_a band is caused by an α -NH₂ substituent despite the small red shift of the 1L_b band. It then follows that the 1L_a state will be very close to the 1L_b state, although the latter would be the lowest singlet excited state. Because

the aforementioned dipole moment at the 1L_a state of α -naphthylamine is larger than in the 1L_b state, it is very probable that the energy level reversal between the 1L_a and 1L_b bands is caused by solute-solvent interaction, especially in a polar solvent. To support this theory the state energy of α -naphthylamine has been calculated (23) by the method of composite system under conditions suitable to the fluorescence state. That is, the nitrogen atom of the NH_2 group was taken to be in sp^2 hybridization in the excited state but not in the geometrical configuration such as that of NH_3 in ground state, since the intramolecular CT effect from the NH_2 group to the aromatic ring is much larger in excited state than in ground state. Calculation showed that in the excited state the lowest $\pi-\pi^*$ state becomes the 1L_a state and then the 1L_b state in α -naphthylamine. Obviously there is an energy level reversal.

In connection with the energy level reversal discussed here it should be noted that strong hydrogen bonding interaction in the excited state also causes energy level reversal. In Chap. 7 we discussed the hydrogen bonding ability of naphthols in ground state and in excited fluorescence state. It was verified that strong proton acceptors such as triethylamine bring about an ion pair formation, owing to proton transfer from naphthol to the amine in the fluorescence state, in contrast to the usual hydrogen bonding complex formation at ground state. Suzuki and Baba (28) carried out a polarization study at the fluorescent state of hydrogen bonded α -naphthol. The polarization degree (p) of fluorescence excitation spectra was measured by the method of photoselection at liquid nitrogen temperature, with mixed solvent consisting of isopentane (4 parts) and methylcyclohexane (1 part) being employed as a glass forming solvent. Their experimental results are shown in Fig. 8-9, where we see that the polarization spectrum with ether as a proton acceptor has positive vibrational peaks which correspond to those of the 1L_b absorption band; it also exhibits the positive p value in the wavelength region of the 1B_2 absorption band, with almost the same magnitude as that of the 1L_b band.

These facts lead to the conclusion that fluorescence stems from the 1L_b state when the proton acceptor is ether. On the other hand, when triethylamine is the proton acceptor, the pattern of polarization spectrum is just the reverse of that obtained in the case of ether as a proton acceptor (see Fig. 8-9). That is, the peaks corresponding to the vibrational structure of the 1L_b absorption band become minimum and lie on the strong positive polarization curve which is clearly due to the 1L_a state, since the 1L_a and 1L_b bands have different transition moments. The former is almost parallel with the short axis of naphthalene but the latter band almost parallels the

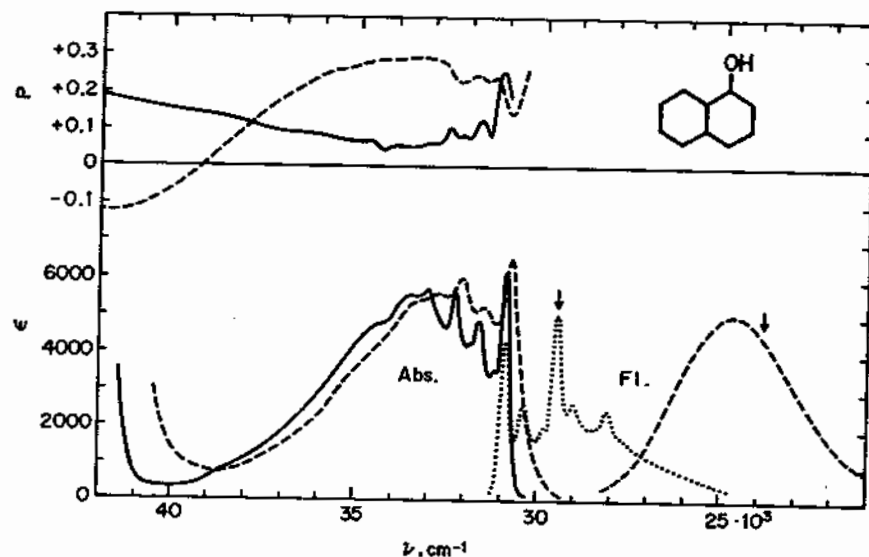


Fig. 8-9. Upper: polarization of fluorescence excitation spectra of α -naphthol. Lower: absorption and fluorescence spectra of α -naphthol. Solid and dotted curves: spectra in 4:1 isopentane and methylcyclohexane mixture (PM) (glass-forming solvent) with 1.0 mole ether. Dashed curves: spectra in 4:1 PM with 0.2 mole triethylamine. Arrows indicate the frequency at which the observation of the fluorescence was made. [Reprinted from S. Suzuki and H. Baba, *Bull. Chem. Soc. Japan*, 40, 2199 (1967), by courtesy of the copyright owner.]

long axis. In addition, the polarization in the 1B_2 band becomes negative, which is just the reverse of the case where ether is used as a proton acceptor. These observations can be explained by considering that the fluorescence emitting from the ion pair complex of α -naphthol with triethylamine originates from the 1L_a state and not from the 1L_b state. Thus energy level inversion between 1L_b and 1L_a bands is evident.

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