Solvent Effects upon Fluorescence Spectra and the Dipolemoments of Excited Molecules[*]

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Introduction

Although solvent effects upon the absorption spectra have been studied extensively, there are rather few investigations of the solvent effects upon the fluorescence spectra. These two are generally different from each other, and from the study of this difference one may expect to derive some information as to the nature of the excited state in contrast to the ground state. To accomplish this program, however, it is necessary to have a general and reliable theory upon the interaction between solute and solvent molecules. Now in 1954 Ooshika[1)] published a general theory concerning the solvent effect upon the absorption spectra and the objective of the present communication is to apply his theory to the solvent effect upon the fluorescence spectra, and to compare the two effects.

An important piece of information obtained from this comparison is that one can estimate the dipolemoment of the excited state. An independent and analogous work has already been published by Lippert[2)] employing the substances of quite a different type from ours.

Theoretical Consideration

Generally speaking, the difference of the solvent shifts between the absorption and fluorescence spectra is due to the following circumstances.

As to the absorption spectra which correspond to the energy difference between excited state and the ground state, the interaction energies between solute molecule and the solvent molecules sorrounding it are different in the ground and excited state, and this difference produces the solvent shift. Now, according to the Franck-Condon principle, the configuration of the solvent molecules around the the solute molecule does not change during the light absorption, and the above mentioned difference of the interaction energy refers to this Franck-Condon excited state[3)] and the equilibrium ground state. But the Franck-Condon excited state is in general not the most stable equilibrium state appropriate to the excited solute molecule. The equilibrium excited configuration is only reached, for example, by reorientation of the solvent molecules, which requires at least a time of the order of 10^{-11} sec., the relaxation time of molecular rotation. The life-time of the excited state, on the other hand, is known to be of the order of 10^{-8} sec., which is ample for the equilibrium configuration to be realized prior to the emission. Hence, for the fluorescence spectrum, the initial state is the equilibrium excited state. During the emission, the solvent configuration does not change, and the momentary ground state in the Franck-Condon ground state which is different from the ground equilibrium state. Thus, when the stabilization energies due to solvent effects are represented as $<\Delta E>^g_e$, $<\Delta E>^g_f$, $<\Delta E>^e_e$ and $<\Delta E>^e_f$ for the ground equiribrium and Franck-Condon state and for the excited equilibrium and Franck-Condon state, respectively, the solvent shift of absorption and fluorescence spectrum may be written as follows:

$$hc\Delta\sigma_a = <\Delta E>^e_f - <\Delta E>^g_e$$
$$hc\Delta\sigma_f = <\Delta E>^e_e - \quad \Delta E \quad ^g_f$$

which are different from each other in general.

In the case when these interaction energies are mainly contributed by dipolar interaction, it is expected that a quantitative theory will enable us to estimate the difference of the dipolemoment between the excited state and the ground state, from the data of the two solvent shifts. As such, one may use Ooshika's theory[1)] on the light absorption in solution which treats only the long range dipolar interaction between solute and solvent molecules surrounding it without taking into consideration the short range interactions such as higher polar interactions, charge transfer, hydrogen bonding, etc.

Applying the Ooshika's theory to the case where the solvent molecules surrounding the

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[*] A preliminary short communication was published in This Bulletin, 28, 690 (1955).

[1)] Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).

[2)] E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955).

[3)] N.S. Bayliss and E.G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

solute molecule are in the equilibrium configuration appropriate to the dipolemoment $\vec{\mu}_e$ of the excited solute molecule, one obtains the stabilization energy of solute molecule in its m state, $<\Delta E>^m$.

$$\begin{aligned}
<\Delta E>^m = & -\Big\{\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\Big\}\Big\{\frac{\vec{\mu}_e\cdot\vec{\mu}_m}{a^3} \\
& +\frac{2(D-1)}{2D+1}\,\frac{2}{a^5}\sum_{m'\mp e} \\
& \times\frac{\{\vec{\mu}_e(e|\vec{\mu}_0|m')\}\{\vec{\mu}_m(e\,\vec{\mu}_0|m')\}}{\varepsilon_{m'}-\varepsilon_e}\Big\} \\
& -\frac{1}{2}\,\frac{2(n^2-1)}{2n^2+1}\,\frac{\mu_m^2}{a^3}+\frac{2(D+1)(D-n^2)}{3(2D+n^2)D}\,\frac{kT}{a^3} \\
& \times\sum_{m'\mp m}\frac{(m\,\vec{\mu}_0|m')^2}{\varepsilon_m-\varepsilon_{m'}}+\Big\{\frac{2(D-1)}{2D+1}\Big\}^2\frac{1}{a^5} \\
& \times\sum_{m'\mp m}\frac{\{\vec{\mu}_e(m\,\vec{\mu}_0|m')\}^2}{\varepsilon_m-\varepsilon_{m'}}-\frac{1}{2}\,\frac{2(n^2-1)}{2n^2+1}\,\frac{1}{a^3} \\
& \times\sum_{m'\mp m}(m\,\mu_0|m')^2\Big\{1-\frac{\varepsilon_m-\varepsilon_{m'}}{E_g-E_n}\Big\}
\end{aligned} \tag{1}$$

Where, D, n: dielectric constant and refractive index of the solvent, ε_m: electronic energy of solute molecule in its m state, E_n: electronic energy of solvent molecule in its n state, a: cavity radius in Onsager's theory of reaction field[4), $\vec{\mu}_m$, $\vec{\mu}_0$: dipolemoment in the m state and dipole operator of solute molecule.

The meaning of each term appearing in eq. (1) is as follows: The first term is due to the orientation effect between permanent dipole of solute molecule and those of solvent molecules, the second term represents the interaction of permanent dipole of solute with induced dipoles of solvent molecules (induced by solute permanent dipole), the third term arises from the fact that the average field of the solvent due to interaction between the permanent dipoles and induced dipoles of solvent molecules (induced by solvent permanent dipoles) polarizes the solute molecule, the fourth term is attributable to the interaction between the reaction field due to the mutual orientation of the solvent molecules and the dipole induced on the solute molecule by it, and the fifth term comes from the contribution of dispersion force.

Now the formula for $<\Delta E>_e^e$ and $<\Delta E>_f^g$ can be obtained easily from (1); the solvent shift of fluorescence spectrum $hc\Delta\sigma_f$ is represented as follows:

$$\begin{aligned}
hc\Delta\sigma_f = & <\Delta E>_e^e-<\Delta E>_f^g=\frac{2(D-1)}{2D+1} \\
& \times\frac{\vec{\mu}_e\vec{\mu}_g-\vec{\mu}_e^{\,2}}{a^3}+\frac{2(n^2-1)}{2n^2+1}\,\frac{(\vec{\mu}_e-\vec{\mu}_g)^2}{2a^3} \\
& +\frac{2(D+1)(D-n^2)}{3(2D+n^2)D}\,\frac{kT}{a^3}\Big\{\sum_{m\mp e}\frac{(e\,\vec{\mu}_0|m)^2}{\varepsilon_e-\varepsilon_m} \\
& -\sum_{m\mp g}\frac{(g|\vec{\mu}_0\,m)^2}{\varepsilon_g-\varepsilon_m}\Big\}+\Big\{\frac{2(D-1)}{2D+1}\Big\}^2\frac{1}{a^6} \\
& \times\Big[3\sum_{m\mp e}\frac{\{\vec{\mu}_e(e|\vec{\mu}_0|m)\}^2}{\varepsilon_e-\varepsilon_m}-\sum_{m\mp g}\frac{\{\vec{\mu}_e(g|\vec{\mu}_0\,m)^2\}}{\varepsilon_g-\varepsilon_m} \\
& -2\sum_{m\mp e}\frac{\{\vec{\mu}_e(e\,\vec{\mu}_0\,m)\}\{\vec{\mu}_g(e|\vec{\mu}_0\,m)\}}{\varepsilon_e-\varepsilon_m}\Big] \\
& +\frac{1}{2}\,\frac{2(n^2-1)}{2n^2+1}\,\frac{1}{a^3}\Big[\sum_{m\mp g}(g|\vec{\mu}_0\,m)^2 \\
& \times\Big\{1-\frac{\varepsilon_g-\varepsilon_m}{E_g-E_n}\Big\}-\sum(e|\vec{\mu}_0|m)^2 \\
& \times\Big\{1-\frac{\varepsilon_e-\varepsilon_m}{E_g-E_n}\Big\}\Big].
\end{aligned} \tag{2}$$

On the other hand, the solvent shift of absorption spectrum is[1).

$$\begin{aligned}
hc\Delta\sigma_a = & <\Delta E>_f^e-<\Delta E>_e^g=\frac{2(D-1)}{2D+1} \\
& \times\frac{\mu_g^2-\vec{\mu}_g\vec{\mu}_e}{a^3}-\frac{2(n^2-1)}{2n^2+1}\,\frac{(\vec{\mu}_e-\vec{\mu}_g)^2}{a^3} \\
& +\frac{2(D+1)(D-n^2)}{3(2D+n^2)D}\,\frac{kT}{a^3}\Big\{\sum_{m\mp e}\frac{(e\,\vec{\mu}_0\,m)}{\varepsilon_e-\varepsilon^m} \\
& -\sum_{m\mp g}\frac{(g|\vec{\mu}_0|m)^2}{\varepsilon_g-\varepsilon_m}\Big\}+\Big\{\frac{2(D-1)}{2D+1}\Big\}^2\frac{1}{a^6} \\
& \times\Big[3\sum_{m\mp g}\frac{\{\mu_g(g|\mu_0|m)\}^2}{\varepsilon_m-\varepsilon_g}-\sum_{m\mp e}\frac{\{\vec{\mu}_g(e|\vec{\mu}_0\,m)\}^2}{\varepsilon_m-\varepsilon_e} \\
& -2\sum_{m\mp g}\frac{\{\vec{\mu}_g(g|\vec{\mu}_0|m)\}\{\vec{\mu}_e(g|\vec{\mu}_0|m)\}}{\varepsilon_m-\varepsilon_g}\Big] \\
& +\frac{1}{2}\,\frac{2(n^2-1)}{2n^2+1}\,\frac{1}{a^3}\Big[\sum_{m\mp g}(g\,\vec{\mu}_0\,m)^2 \\
& \times\Big\{1-\frac{\varepsilon_m-\varepsilon_g}{E_n-E_g}\Big\}+\sum_{m\mp e}(e|\vec{\mu}_0\,m)^2 \\
& \times\Big\{1-\frac{\varepsilon_m-\varepsilon_e}{E_n-E_g}\Big\}\Big].
\end{aligned} \tag{3}$$

From (2) and (3) we obtain:

$$hc(\Delta\sigma_f-\Delta\sigma_a)=-\Big[\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\Big]$$

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4) L. Onsager, *J. Am. Chem. Soc.*, 58, 1486 (1936).

$$\times\frac{(\vec{\mu}_e-\vec{\mu}_g)^2}{a^3}+\left\{\frac{2(D-1)}{2D+1}\right\}^2\frac{1}{a^3}$$

$$\times\Big[3\sum_{m\neq e}\frac{\{\vec{\mu}_e(e|\vec{\mu}_a|m)\}^2}{\varepsilon_e-\varepsilon_m}+3\sum_{m\neq g}\frac{\{\vec{\mu}_g(g|\vec{\mu}_0|m)\}^2}{\varepsilon_g-\varepsilon_m}$$

$$-\sum_{m\neq g}\frac{\{\vec{\mu}_g(g|\vec{\mu}_0|m)\}^2}{\varepsilon_g-\varepsilon_m}-\sum_{m\neq e}\frac{\{\vec{\mu}_g(e|\vec{\mu}_0|m\})^2}{\varepsilon_e-\varepsilon_m}$$

$$-2\sum_{m\neq e}\frac{\{\vec{\mu}_e(e|\vec{\mu}_0|m)\}\{\mu_g(e|\vec{\mu}_0|m)\}}{\varepsilon_g-\varepsilon_m}$$

$$-2\sum_{m\neq g}\frac{\{\vec{\mu}_g(g(\vec{\mu}_0|m)\}\{\vec{\mu}_e(g|\vec{\mu}_0|m)\}}{\varepsilon_g-\varepsilon_m}\Big]. \tag{4}$$

All the discussions given above are on the basis of long range dipolar interaction between solute and solvent molecules. The theory, therefore, is not appropriate to the system with the specific short range interactions. For the consideration of such short range interactions, it may be necessary to compute the quantum mechanical interaction energy for each special pair of solute and solvent molecules, and, in fact, the general treatment as shown above may not be allowed. Even in the limit of the approximation of dipolar interaction, it is practically a very complicated and difficult problem to apply to this case Kirkwood's theory[5] which is a higher approximation than Onsager's[4], taking into consideration the correlation of nearest neighbour dipoles.

Now, consider the case of solutes such as naphtholes in the solvents such as acetic acid esters, where hydrogen bond is formed between solute and solvent molecules but for solvent molecules Onsager's approximation may be fairly well applicable. Put a hydrogen bonded solute molecule in the cavity in dielectric continuum, and apply to this system the Onsager's approximation.

Then one may be able to separate approximately the interaction energy of solute molecule with solvent molecules surrounding it as follows:

$$<\Delta E>^m_{f\cdot e}=<\Delta E(s)>^m_{f\cdot e}+<\Delta E(l)>^m_{f\cdot e} \tag{5}$$

Where, s and l indicate the terms arising from short range interaction due to hydrogen bonding and long range dipolar interaction, respectively. The superscript m represents that $<\Delta E>_m$ is the interaction energy in the m state of solute molecule, and subscript f or e means the Franck-Condon or equilibrium state.

From (5), the solvent shifts of fluorescence and absorption spectra can be written as follows:

$$\left.\begin{aligned}hc\Delta\sigma_f&=(<\Delta E(s)>^e_e+<\Delta E(l)>^e_e)\\&\quad-(<\Delta E(s)>^g_f+<\Delta E(l)>^g_f)\\hc\Delta\sigma_a&=(<\Delta E(s)>^e_f+<\Delta E(l)>^e_f)\\&\quad-(<\Delta E(s)^g_e+<\Delta E(l)>^g_e)\end{aligned}\right\} \tag{6}$$

From (6) we obtain:

$$\begin{aligned}hc(\Delta\sigma_f-\Delta\sigma_a)=&[(<\Delta E(l)>^e_e+<\Delta E(l)>^g_e)\\&-(<\Delta E(l)>^e_f+<\Delta E(l)>^g_f)]\\&+[(<\Delta E(s)>^e_e+<\Delta E(s)>^g_e)\\&-(<\Delta E(s)>^g_f+<\Delta E(s)>^g_f)]\end{aligned} \tag{7}$$

The first term in square bracket in (7) is formally equated to the right hand side of (4), where, however, all the quantities associated with solute molecule must be replaced by those of hydrogen bonded solute. The second term is unknown but we may estimate this experimentally as will be mentioned later.

When the associating liquids such as alcohols are used as solvents, owing to the short range interactions between solvent molecules themselves, applicability of Onsager's theory, becomes much doubtful.

Experimental

According to the idea mentioned above, we have examined the fluorescence and absorption spectra of β-methylnaphthalene, β-naphthyl methyl ether, and α-, β-naphthols in various organic solvents. Fluorescence spectra were photographed with Hilger E_2 type spectrograph and the peaks of fluorescence spectra were visually observed. Absorption spectra were measured with Beckman Quartz spectrophotometer, and also photographed with Hilger E_2 type spectrograph. The solvents used were *n*-hexane, benzene, toluene, acetic acid esters, and alcohols.

α-, β-naphthols and β-naphthyl methyl ethers were the same samples as used before[6], methylnaphthalene was kindly supplied by Shionogi & Co., Ltd. and distilled under the atmosphere of dry nitrogen before use.

n-hexane and acetic acid esters were the same samples as described before[6], benzene, toluene and butanol were extra pure grade and used without further purification. Ethanol was 99% in purity.

Experimental Results and Discussions

The experimental results are shown in Table I, where σ^m_a is the position of the longest wave length peak of absorption spectra which is most prominent in all cases.

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[5] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

[6] N. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **29**, 115 (1956).

TABLE I

σ_f^m AND σ_a^m VALUES FOR NAPHTHALENE DERIVATIVES (σ IN cm^{-1})

		β-Methylnaphthalene			β-Naphthyl methyl ether			α-Naphthol			β-Naphthol		
Solvent	$\left[\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\right]$	σ_f^m	σ_a^m	$(\sigma_a^m-\sigma_f^m)$	σ_f^m	σ_a^m	$(\sigma_a^m-\sigma_f^m)$	σ_f^m	σ_a^m	$(\sigma_a^m-\sigma_f^m)$	σ_f^m	σ_a^m	$(\sigma_a^m-\sigma_f^m)$
n-Hexane	~0	29810	31340	1530	29070	30550	1480	30710	31090	380	29800	30460	660
Benzene	~0	29690	31270	1580	28930	30420	1490	30600	30980	380	29550	30290	740
Toluene	0.026	29670	31280	1610	28910	30430	1520	30540	30990	450	29510	30280	770
Butyl acetate	0.345	29810	31330	1520	28930	30520	1590	30460	30950	490	29220	30130	910
Ethyl acetate	0.398	—	—	—	28930	30540	1610	30460	30980	520	29210	30160	950
Methyl acetate	0.444	—	—	—	28950	30550	1600	30420	30980	560	29200	30180	980
Butanol	0.540	29760	31350	1590	28900	30530	1630	30330	30920	590	29110	30180	1070
Ethanol	0.582	29760	31350	1590	28880	30550	1670	30370	30950	580	29120	30220	1100
Methanol	0.616	—	—	—	28840	30560	1720	30380	30960	580	29110	30270	1160

while σ_f^m is that of the strongest or the most clearly observable peaks of fluorescence spectra, and are shown schematically in Fig. 1.

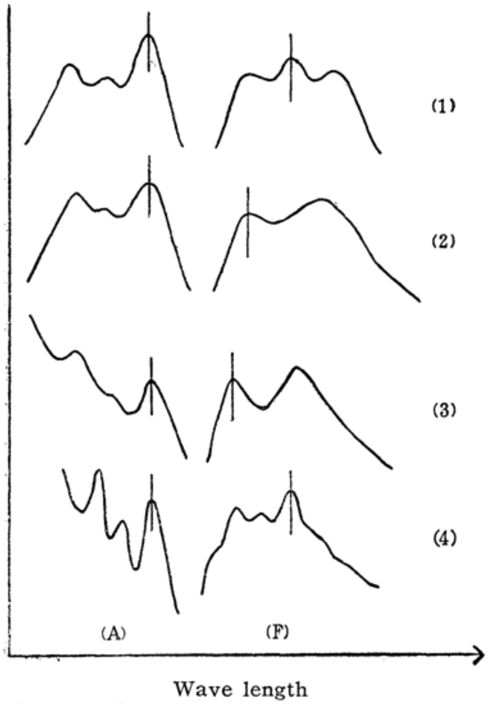

Fig. 1. Schematic diagrams of absorption and fluorescence spectra, the vertical lines showing the chosen peaks. (A), absorption (F), fluorescence; (1), β naphthylmethylether; (2), β naphthol; (3), β naphthol; (4), β methylnaphthalene.

For the comparison of the theory developed in II with the experimental results, the shifts of O–O bands should be employed, but it is very difficult to determine them exactly especially for such large molecules as naphthols. Hence it is necessary at first to consider the difference between O–O band on one hand and σ_a^m, σ_f^m on the other.

When σ_f^m and σ_a^m are used instead of O–O bands, equation (4) can easily be rewritten as follows.

$-hc(\sigma_f^m-\sigma_a^m)=hc(\delta\sigma_f+\delta\sigma_a)+\{$right hand side of (4)$\}$ (8) where $\delta\sigma_f$ and $\delta\sigma_a$ are the wave number differences between O–O bands and the peaks in the fluorescence and absorption spectra, respectively. Now the experimental results show that the solvent shifts of spectra take place as a whole; in other words, both the fluorescence and absorption spectra have respectively the same shape with the same interval between peaks irrespective of the solvents employed. Hence it may be allowed to put $(\delta\sigma_f+\delta\sigma_a)=$const. for one solute molecule.

Next, the theoretical formula (4) can be made much simpler for naphthalene derivatives, because the first term is far greater than the remaining terms in the order of magnitude. Thus a rough estimation for the given solvents mentioned in III, gives,

first term $\lesssim 10^{-13}-10^{-14}$ erg.
second term $\lesssim 10^{-17}-18^{-18}$ erg.

Therefore eq. (8) becomes

$$-hc(\sigma_f^m-\sigma_f^m)\cong\text{Const.}+\left[\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\right]\times\frac{(\overrightarrow{\mu_e}-\overrightarrow{\mu_g})^2}{a^3} \tag{9}$$

Lastly the second term of (7) must be estimated when the hydrogen bond is formed between solute and solvent molecules. As reported already[6)], we have compared the fluorescence and absorption spectra of α-, β-naphthols in pure *n*-hexane on one hand and in *n*-hexane added with acetic acid esters on the other and confirmed that $\Delta\sigma_f$ and $\Delta\sigma_a$ due to hydrogen bonding is nearly equal. Hence second term in (7) in the present case may be neglected in comparison with the first term.

After all, the theory can be tested by (9) using the data tabulated in Table I. The result is that (9) is fairly well satisfied by all the experimental data as shown in Fig. 2.

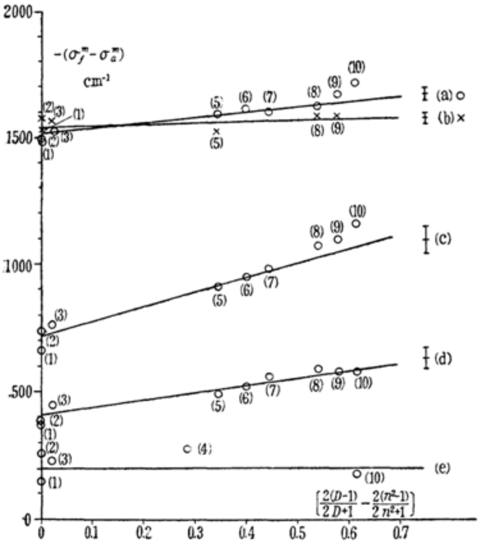

Fig. 2. $(\sigma_f^m-\sigma_a^m)\sim\left[\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\right]$ relation for naphthalene derivatives and anthracene*.

Solutes: (a), β-naphthylmethylether; (b), β-methylnaphthalene; (c), β-naphthol; α-naphthol; (e) anthracene.

Solvents; (1), *n*-hexane; (2), benzene; (3), toluene; (4) chlorobenzene; (5), butylacetate; (6), ethylacetate; (7), methylacetate; (8), butanol; (9), ethanol; (10), methanol.

The veitical lines in the right hand of figure indicate the ranges of probable errors,

* Data from Ref. (9).

Thus it can be concluded that the orientation polarization is in fact the most prominent factor for the difference of solvent shifts of fluorescence and absorption.

The values for alcohols seem to show some systematic deviations, but the experimental errors are too large for us to say definitely.

From the inclination of these lines, $\frac{(\vec{\mu}_e-\vec{\mu}_g)^2}{a^3}$ can be calculated as follows:

β-naphthol: $\sim 9\times10^{-14}$ erg.
α-naphthol: $\sim 5\times10^{-14}$ erg.
β-naphthyl methyl ether: $\sim 3\times10^{-14}$ erg.
β-methylnaphthalene: $\lesssim 4\times10^{-15}$ erg.

If one puts $\vec{\mu}_e-\vec{\mu}_g\sim 0.5$ and a$\sim$3 Å, then $\frac{(\vec{\mu}_e-\vec{\mu}_g)^2}{a^3}$ becomes ca. 10^{-14} erg, which is near the value for β-naphthyl methyl ether. Thus for this compound the dipolemoment in the excited state is about 0.5 D. larger than in the ground state.

Of course such an evaluation would be valuable only for the estimation of the order of magnitude.

Next some discussions will be given about the value of $\vec{\mu}_e-\vec{\mu}_g$. No doubt this difference originates from π electron systems and most certainly the electron migration from substituent may be predominant in determing this value. Hence it may be reasonable to put in the first approximation,

$$\vec{\mu}_e-\vec{\mu}_g\simeq\vec{\mu}_e^{\,mig}-\vec{\mu}_g^{\,mig}$$

The effect of hydrogen bonding in the case of α-, β-naphthols would not alter the relative order,

$$(\vec{\mu}_e-\vec{\mu}_g)^{mig}_{\beta\text{-naphthol}}>(\vec{\mu}_e-\vec{\mu}_g)^{mig}_{\alpha\text{-naphthol}}$$

Thus the increments of dipolemoments in the excited state due to the enhanced electron migration are in the order of magnitude, 0.5–1 D. for β-naphthyl methyl ether and α-, β-naphthols.

It is to be noted here that a theoretical computation of migration dipole in the ground and excited state of phenol was done by Baba[7] using the theory of Sklar[8]. The increment $(\mu_e^{mig}-\mu_g^{mig})$ which he obtained is 0.3 D., which shows that the contribution of electron migration to the dipole increase in the excited state can be fairly large.

The value for β-methylnaphthalene, $\lesssim 4\times10^{-15}$ erg. given above is only provisional as an upper limit, and it is certain that this compound has much smaller dipole increment in the excited state as compared with those of naphthols and β-naphthyl methyl ether.

It may be expected from the present theory, that a nonpolar molecule with high symmetry such as anthracene does not show any effect as shown above.

In fact, the data reported by Sambursky and Wolfsohn[9], as plotted in Fig. 2, do not show any such effect. They interpreted the

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[7] H. Baba, *Monograph Ser. Research Inst. Applied Electricity Hokkaido Univ.*, No. 4, 61 (1954).

[8] A.L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

[9] S. Sambursky and Wolfsohn, *Trans. Far. Soc.*, **36**, 427 (1940).

difference of solvent shifts in fluorescence and absorption spectra as due to the dipolemoment produced in the excited anthracene molecule, but it is quite certain from the present analysis that their conclusion is wrong.

As to somewhat larger deviations from the straight line, they may perhaps be due to some short range interaction specific to each solvent molecule. An anthracene molecule is larger than a naphthalene molecule, and for larger molecules even when they have symmetrical structure with a uniform charge distribution for the entire molecule, some short range interaction may arise from the local charge unbalance which may be produced in the excited state.

The results obtained by Lippert[2] for 4-dimethylamino-4′-nitrostilbene, 4-dimethylamino-4′-cyanostilbene and dimethylnaphthenrhodine, show some deviations, rather larger than ours, from the theoretical line. He has recently made a quite different attack on the problem and confirmed that his results are quite reasonable[10].

One of the authors (N. M.) wishes to express his thanks to Mr. T. Yamaguchi of Osaka University for his discussions.

Summary

A general formula for the difference of solvent shifts of fluorescence and absorption spectra in the approximation of long range dipolar interaction was derived using Ooshika's theory of light absorption in solution.

Measurements of fluorescence and absorption spectra of some naphthalene derivatives in various organic solvents were undertaken, and the data were analysed by the theoretical formula. The formula reproduces the experimental data satisfactorily, and from this fact it was concluded that the most predominant factor which determines the difference of solvent shifts of fluorescence and absorption spectra of these molecules is the interaction energy between solute and solvent molecules due to orientation polarization. The incremental values of dipolemoments in the excited state were estimated, and those for α-, β-naphthols and β-naphthyl methyl ether were interpreted as due to the increase of electron migration from the substituent in the excited state.

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[10] E. Lippert, *Z. physiked Chem.*, N. F., 6, 125, (1956).