SHORT COMMUNICATION

The Solvent Effect on Fluorescence Spectrum. Change of Solute-Solvent Interaction during the Lifetime of Excited Solute Molecule

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The solvent effect on absorption spectrum is determined by the equilibrium ground state and the Franck-Condon excited state, while that of fluorescence spectrum depends upon the equilibrium excited state and the Franck-Condon ground state¹⁾. Therefore, the spectral shift of fluorescence due to the solvent effect may differ in general from that of absorption, and it is expected that from the investigation of this difference some informations may be derived concerning the excited electronic structure. But the theoretical treatment of the solvent effect of fluorescence spectrum seems not to have been undertaken so far. Now it was found that a reasonable formula for the difference of the spectral shifts between absorption and fluorescence conld be derived by applying Ooshika's theory²⁾ concerning the light absorption in solution to the case of fluorescence. The formula obtained is as follows.

$$hc(\varDelta\sigma_f-\varDelta\sigma_a)\cong-\left\{\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\right\}\frac{(\vec{\mu}_e-\vec{\mu}_g)^2}{a^3}+\left\{\frac{2(D-1)}{2D+1}\right\}^2\frac{1}{a^3}\Big[3\sum_{e\neq m}\frac{\{\vec{\mu}_e(e|\vec{\mu}_0|m\}^2}{\varepsilon_e-\varepsilon_m}$$
$$+3\sum_{m\neq g}\frac{\{\vec{\mu}_g(g|\vec{\mu}_0|m)\}^2}{\varepsilon_g-\varepsilon_m}-\sum_{m\neq g}\frac{\{\vec{\mu}_e(g|\vec{\mu}_0|m)\}^2}{\varepsilon_g-\varepsilon_m}-\sum_{m\neq e}\frac{\{\vec{\mu}_g(e|\vec{\mu}_0|m)\}^2}{\varepsilon_e-\varepsilon_m}-\sum_{m\neq e}\frac{\{\vec{\mu}_e(e|\vec{\mu}_0|m)\}\{\vec{\mu}_g(e|\vec{\mu}_0|m\}}{\varepsilon_e-\varepsilon_m}$$
$$-2\sum_{m\neq g}\frac{\{\vec{\mu}_g(g|\vec{\mu}_0|m\}\{\vec{\mu}_e(g|\vec{\mu}_0|m)\}}{\varepsilon_g-\varepsilon_m}\Big] \qquad (1)$$

$\varDelta\sigma_f$, $\varDelta\sigma_a$; Wave number shifts of fluorescence and absorption spectra.
D, n; Dielectric constant and refractive index of the solvent.
$\vec{\mu}_e$, $\vec{\mu}_g$; Dipolemoments in the excited and ground states.
a: Radius of the cavity in Onsager's Theory³⁾.
ε_m: Electronic energy of the solute molecule in m state.
$\vec{\mu}_0$: Dipole operator.

The second term of Eq. (1) is relatively small in its order of magnitude compared with the first term, and can be neglected in the first approximation:

$$-hc(\varDelta\sigma_f-\varDelta\sigma_a)\simeq\left\{\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\right\}\frac{(\mu_e-\mu_g)^2}{a^3} \qquad (2)$$

This equation represents the effect of orientation polarization, and it is noteworthy that, if it really holds, it enables us to estimate the dipolemoment of the excited molecule.

In order to test the applicability of the equation, we have measured the spectral shifts of α- and β-naphthols and β-naphthyl methyl ether in various solvents. It must be noted that, in the case of α- and β-naphthols, the hydrogen bond is formed between the solute and solvent molecules in most cases. Hence a short range interaction due to hydrogen bonding must be taken into account in addition to a long range dipole interaction. But the contribution of the former to $(\varDelta\sigma_f-\varDelta\sigma_a)$ is negligibly small as was already confirmed by the measurement in mixed solvent⁴⁾.

The results obtained conform fairly well to with the Eq. (2) in all cases. If one assumes a∼3 A for β-naphthyl methyl ether, the value of $\vec{\mu}_e-\vec{\mu}_g$ is calculated to be ∼0.5 D, from the inclination of a straight plot.

This enlargement of dipolemoment in the excited state may plausibly be due to the increase of electron migration in the excited state, because the value agrees fairly well with the one theoretically calculated by Baba⁵⁾ for phenol on the analogous assumption.

Quite recently, Lippert*⁶⁾ has made the treatment similar to ours regarding the

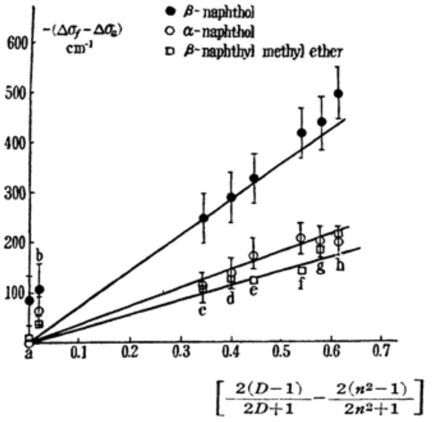

Fig. 1. $(\Delta\sigma_f-\Delta\sigma_a)\sim\left[\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\right]$: relation for naphthols and β-naphthyl methyl ether.

Solvents

a, benzene; b, toluene; c, butyl acetate; d, ethyl acetate; e, methyl acetate; f, butanol; g, ethanal; h, methanol.

spectral shifts of 4-dimethylamino-4′-nitrostilbene and 4′-cyanostilbene, etc., and estimated the dipolemoments of these molecules in the excited state.

But the application of Onsager's theory to such long molecules would be too rough to except the satisfactory agreement between theory and experiment. Really, this agreement is much better in our case. The approximate nature of the theory, however, still does not allow the exact quantitative discussion of the problem, and a more refined theory should be needed. Full details of data and discussions will soon be published.

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1) See for example: N. S. Bayliss and E. G. McRae *J. Phys. Chem.*, 58, 1002 (1954).

2) Y. Ooshika, *Rep. Kobayashi Inst. Phys. Research*, 2, 99 (1952), ibid., 3, 54 (1953); *J. Phys. Soc. Japan*, 9, 594 (1954).

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

4) N. Mataga, Y. Kaifu, and M. Koizumi, (to be published in this Bull.)

5) H. Baba, *Monograph Ser. Research Inst. Applied Electrocity*, Hokkaido, No. 4 61 (1954).

6) E. Lippert. *Z. Naturforsch.*, 10a, 541 (1955).

* After we had finished the present work, Dr. Lippert, informed us of this work by a private communication which was kindly given to Mataga.