Remark on the Solvent Effects upon the Electronic Spectra of Naphthalene Derivatives

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In one of our previous papers[1] we reported on the absorption and fluorescence spectra of naphthylamines and isomeric aminobenzoic acids in various organic solvents. This sort of study, in which the effects of solvents on both the absorption and fluorescence spectra are investigated, is important in order to obtain detailed information on the electronic structures of complex aromatic molecules as well as on the nature of the molecular interaction in solutions.

It has been observed that the hydrogen bonding between the solute and the solvent molecules, especially that between the alcohol and amino nitrogen of naphthylamines or aminobenzoic acids, affects the electronic spectra of the latter two quite remarkably. This fact has been ascribed to the rearrangement of the hydrogen bond between the solute and solvent molecules during the lifetime of the excited solute molecule.

In the present report, we shall describe additional experimental findings concerning the electronic spectra of some aromatic hydrocarbon derivatives, such as naphthylamines, naphtholate ions and aniline in aqueous and alcohol solutions; we shall also discuss the rearrangement of the solute-solvent interaction in the excited state and the role of the Franck-Condon principle in the spectral shifts.

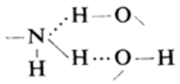
Experimental

The details of the apparatus for the measurement of the absorption and fluorescence spectra have been described elsewhere.[1-3] The samples of the solutes were the same as were used before.[1,3]

Experimental Results and Discussion

The Importance of the Franck-Condon Principle in the Solvent Shifts of π-π^* Spectra.— As has been demonstrated in our previous report,[1] the solute-solvent interactions in alcohol solutions affect the absorption spectra of naphthylamines only slightly, whereas they cause a very large red shift of the fluorescence spectra compared to the case of *n*-hexane or cyclohexane solutions.

The hydrogen-bonding interaction in alcohol solutions of naphthylamines probably involves the following types of hydrogen bonds:



The hydrogen bond of the $-\text{H}-\text{H}\cdots\text{O}<$ type (type D) causes a red shift of the absorption spectrum, whereas the $-\underset{\text{H}}{\text{N}}\cdots\text{H}-\text{O}\diagdown$ type (type A) hydrogen bond causes a blue shift of the absorption spectrum; this is because the former is favorable while the latter is unfavorable to the charge migration from the substituent to the aromatic ring.

The hydrogen-bonding interaction of the A type is certainly much weaker in the excited

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[1] N. Mataga, This Bulletin, 36, 654 (1963).

[2] N. Mataga, Y. Torihashi and Y. Kaifu, *Z. physik. Chem. N. F.*, 34, 379 (1962).

[3] N. Mataga and Y. Kaifu, *Mol. Phys.*, in press.

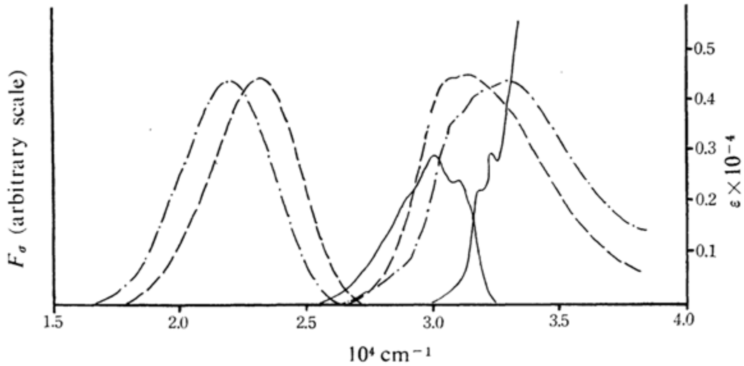

Fig. 1. Absorption and fluorescence spectra of α-naphthylamine in various solvents. Solvents: —— 60% (weight) H_2SO_4, ——— Ethanol, —·— H_2O (neutral). Concentrations of solute: 2×10^{-3} mol./l. in 60% H_2SO_4 and ca. 0.8×10^{-4} mol./l. in the other solvents.

TABLE I. THE WAVE NUMBERS OF THE BAND MAXIMA OF ANILINE, α- AND β-NAPHTHYLAMINES IN ETHANOL AND IN AQUEOUS SOLUTIONS (IN UNITS OF 10^4 cm^{-1})

Solvent	Aniline		α-Naphthylamine		β-Naphthylamine	
	σ_a^m	σ_f^m	σ_a^m	σ_f^m	σ_a^m	σ_f^m
EtOH	3.52	2.95	3.13	2.31	2.96	2.46
H_2O	3.58	2.91	3.30	2.19	3.02	2.43

state,[*1] while that of the D type is a little stronger in the excited state than in the ground state. The former circumstance is related to the fact that the basicity of the amino nitrogen is much weaker in the excited state than in the ground state, as has been demonstrated by Förster[4)] in the case of naphthylamines in an aqueous solution. Moreover, the type D hydrogen bond may be strengthened by the cooperative interaction between alcohol molecules in the hydrogen-bonded chain.

These hydrogen-bonding interactions, as well as the dipole-dipole and dipole-polarization interactions with the surrounding solvent molecules, which are much stronger in the excited state than in the ground state, may cause the very large $\Delta\sigma$ value (the wave number difference between the maxima of the absorption, (σ_a^m), and of the fluorescence spectra, (σ_f^m), respectively) of the alcohol solution.

The effects of the solute-solvent interactions on the spectral shifts described above may be far greater in the aqueous solution than in the alcohol solution because of the more extensive hydrogen bonding interactions and dipolar interactions in the former solution.

As an example of very large spectral shifts in the hydroxylic solvent, the absorption and fluorescence spectra of α-naphthylamine in ethanol and water (neutral), together with those in 60% (weight) sulfuric acid solution, are shown in Fig. 1. In the last solvent, the amino nitrogen is protonated in both the ground state and the fluorescence state.

The wave numbers of the band maxima of α- and β-naphthylamines in ethanol and in an aqueous solution are collected in Table I. The wave numbers of the band maxima of naphthylamines in some of the other organic solvents have been given elsewhere.[1)]

As can be seen from Fig. 1 and Table I, the σ_a^m values of naphthylamines in aqueous (neutral) solutions are greater than those in alcohol solutions, whereas the σ_f^m values in the aqueous solutions are much smaller than those in alcohol solutions. Therefore, the $\Delta\sigma$ value is quite large in the aqueous solution. For example, $\Delta\sigma\sim11100$ cm^{-1} in the aqueous

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[*1] In the potential energy curve for the type A hydrogen bonding which was given in our previous report (Fig. 7 of Ref. 1), the equilibrium distance between the proton donor and the acceptor in the case of the type A hydrogen bond was assumed to be larger in the excited state than in the ground state. However, this assumption is rather doubtful. Because the extent of the charge migration from the nitrogen lone pair orbital to the ring is much greater in the excited state than in the ground state, the lone pair orbital may be more contracted in the excited state than in the ground state. Accordingly, the equilibrium distance between the donor and the acceptor may be a little smaller in the excited state than in the ground state. This circumstance is analogous to the case of the blue shift of the absorption and the red shift of the emission in the n-π spectra shown by Krishna and Goodman (V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **33**, 381 (1960)), although the extent of the orbital contraction may be smaller in the present case than in the case of the n-π^* transition.

4) Th. Föster, *Z. Elektrochem.*, **54**, 531 (1950).

neutral solution compared to ~8200 cm^{-1} in ethanol and ~4800 cm^{-1} in *n*-hexane in the case of α-naphthylamine.*2 This wave number difference is greater, the larger the sum of the Franck-Condon destabilization energies in the excited and ground states. The present experimental results, which demonstrate the blue shift of the absorption spectrum and the large red shift of the fluorescence spectrum in a more polar solvent, indicate that the Franck-Condon principle, including the various solute-solvent interactions, plays a very important role in the solvent shifts of the electronic spectra.

Table I also contains the σ_a^m and σ_f^m values of aniline in ethanol and in the aqueous neutral solution. We can observe from Table I that the solvent shifts of the spectra in this case are quite analogous to those in the case of naphthylamines.

If we take the spectrum in such non-polar aliphatic hydrocarbons as *n*-hexane and cyclohexane as a reference, then the sum of the Franck-Condon destabilization energies resulting from the solute-solvent interactions in the excited and ground states may be expressed as the difference between the $\Delta\sigma$ value in a polar solvent and that in the hydrocarbon solvent. The Franck-Condon destabilization energy of aniline in an aqueous solution amounts to 3400 cm^{-1}. This value is much smaller than the corresponding quantity for α-naphthylamine (6300 cm^{-1}), although it is larger than that for β-naphthylamine (2900 cm^{-1}).

The Similarity of the Electronic Spectra of Naphtholate Ions to Those of Naphthylamines. —Before ending the present article, we would like to note the similarity between the electronic spectra of naphtholate ions in the aqueous solution and those of naphthylamines in the aqueous solution. The conjugation power of $-O^-$ seems to be only a little larger than that of the amino group, as one can see from the electronic absorption spectra of many aromatic hydrocarbon derivatives which have $-O^-$ and $-NH_2$ substituents. Actually, the most appropriate values of the Coulomb parameter for the calculation of Hückel MO's seem to be 0.8[5] for $-O^-$ and 1.2[6] for the amino nitrogen.

The σ_a^m values of α- and β-naphtholate ions are 30300 cm^{-1} and 29000 cm^{-1} respectively*3. These σ_a^m values are smaller than the corresponding values of naphthylamines, in accordance with the stronger conjugation power of $-O^-$ than the amino group. However, the $\Delta\sigma$ values for the naphtholate ions (9300 cm^{-1} for the α-isomer and 5200 cm^{-1} for the β-isomer) are rather close to those of naphthylamines. The value for the β-naphthol molecule in an aqueous solution is 2200 cm^{-1}, which is much smaller than that of the ion (α-naphthol molecule is not fluorescent in an aqueous solution).

Thus, although the wave numbers of the maxima of both the absorption and the fluorescence spectra of naphtholate ions are a little smaller than those of naphthylamines, the spectra of each isomer of naphtholate ions and naphthylamines are similar to each other and the characteristics[1] of the spectrum of each isomer are well maintained in naphtholate ions as well.

Summary

The importance of the Franck-Condon principle in the solvent shifts of $\pi-\pi^*$ spectra has been discussed with reference to aniline and naphthylamines in alcohol and aqueous solutions. The blue shift of the absorption spectra and the red shift of the fluorescence spectra in these polar solvents have been interpreted in terms of the Franck-Condon destabilization energies, including the solute-solvent hydrogen bonding interactions and the dipolar interactions. In addition to this, the similarity of the electronic spectra of naphtholate ions to those of naphthylamines has been pointed out with reference not only to the absorption spectra but also to the fluorescence spectra.

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*2 As has been discussed in the previous report,[1] the fluorescent state of α-naphthylamine is plausibly ^1L_a, although the lowest absorbing singlet state seems to be ^1L_b. In the case of β-naphthylamine, ^1L_b is the relevant excited state for both light absorption and fluorescence. Therefore, the σ_a^m value indicated in the text for α-naphthylamine is that of ^1L_a.

5) N. Mataga, This Bulletin, 36, 1109 (1963).

6) H. Baba, ibid., 34, 76 (1961); H. Baba and S. Suzuki, ibid., 34, 82 (1961).

*3 As has been discussed in Ref. 1, the ^1L_a band shifts strongly to the red in constrast to the ^1L_b band, which shifts to the red only slightly upon the substitution of an electron-donating group at the α position.

The ^1L_b band of α-naphtholate ion is overlapped by the ^1L_a band more extensively than that of α-naphthylamine because the red shift of the ^1L_a band relative to that of the ^1L_b band is greater for the $-O^-$ substitution than for the amino substitution. In view of this, the σ_a^m value for α-naphtholate ion indicated in the text can quite plausibly be assigned to ^1L_a.