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On the Mechanism of Proton Transfer Reactions in the Excited Hydrogen Bonded Complexes

By

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The results of systematic experimental studies on the hydrogen bonding and proton transfer reactions between excited naphthol molecule and aliphatic amine molecule in non-hydroxylic solvents are described and interpreted.

The mechanism of the proton transfer process is discussed on the basis of the σ-π interaction in the hydroxy group of naphthol and the charge transfer interaction between the proton acceptor and the donor in the excited electronic state.

Les résultats d'études systématiques expérimentales sur la liaison hydrogène et les réactions de transfert de proton entre des molécules de naphtol excitées et des amines aliphatiques sont décrits et interprétés. Des solvants non-hydroxyliques sont employés.

Le mécanisme du transfert de proton est discuté sur base d'une interréaction σ-π dans la groupe hydroxyle du naphtol et d'un transfert de charge entre l'accepteur et le donneur du proton, le donneur étant en état excité.

Die Ergebnisse systematischer experimenteller Untersuchungen über Wasserstoffbrückenbindung und Protonenaustausch zwischen angeregten Naphtholmolekülen und aliphatischen Aminen werden beschrieben und interpretiert. Es werden Lösungsmittel ohne Hydroxylgruppen benutzt.

Der Mechanismus der Protonenaustauschreaktion wird diskutiert auf der Basis einer σ-π-Wechselwirkung in der Hydroxylgruppe des Naphtholmoleküls und einer charge-transfer-Wechselwirkung zwischen Protonen-Akzeptor und -Donor. Dabei befindet sich der Donor in einem angeregten Elektronenzustand.

I. Introduction

Intermolecular charge transfer and proton transfer reactions, i. e., the motion of proton associated with the change of electronic structure and vice versa in the hydrogen bonded complexes are of special interest and of great importance from the viewpoint of the basic mechanisms of the chemical reactions in solution and also from the viewpoint of the mechanisms of the electron transport in some biological systems.

The charge transfer or the delocalization nature of the hydrogen bonding interaction has been the subject of recent lively discussions. For example, Nagakura [*13*] has demonstrated that the hydrogen bond between naphthol and various proton acceptors (A) in the ground equilibrium (e.-q.) and the excited Franck-Condon (F.-C.) state, is stronger, the smaller the ionization potential of the lone pair orbital of A. This result favours the charge transfer (CT) mechanism of the hydrogen bond. Moreover, Nagakura, Tsubomura and Kaya [*14*] have interpreted the strong absorption band of hydrogen maleate anion at 2130 Å as arising from the CT through the hydrogen bond and not from the π-electron system.

On the other hand, it is well known that light absorption causes rather strong change in some molecular properties in the excited electronic state such as in the dipolemoment, hydrogen bonding ability and ionic dissociation constant [*3*–*6*, *9*, *10*, *16*]. In the case of naphthols, the hydrogen bonding ability is greater in the first excited singlet state than in the ground state and the ionic dissociation constant of *-O-H* proton is much larger in the first excited singlet state than in the ground state. These facts have been ascribed to the increased migration of π-electrons on the oxygen to the vacant π-MO's of naphthalene ring in the excited electronic state. Owing to this change in the electron distribution, the hydrogen bond energy and the shape of the potential energy surface for proton in the excited state are different from those in the ground state. Therefore, the distance between the proton donor (*D*) and *A* and also the relative position of proton in the hydrogen bond in the excited e.-q. state may be different from those in the excited F.-C. state and the ground e.-q. state. In view of these facts, one may expect an anomalously strong hydrogen bond or an ion-pair formation which can be regarded as a limiting form of a strong hydrogen bond, in the excited e.-q. state of naphthol hydrogen bonded with some strong *A* in non-polar solvent.

We have observed by fluorescence spectral measurements that the strong hydrogen bond between 2-naphthol and trethylamine in the e.-q. ground state and the excited F.-C. state shifts to an ion-pair in the excited e.-q. state from which fluorescent transition occurs [*7*, *10*]. These experimental results have been interpreted on the basis of the charge transfer mechanisms of the hydrogen bond. Although our previous interpretation seems to be correct essentially, we have undertaken more systematic studies employing various combinations of donors and acceptors [*8*, *11*] in order to make clearer the mechanism of the intermolecular proton transfer reactions in the excited hydrogen bonded complex.

In the present report, we shall try to give a more rigorous and clearer interpretation of the observed results.

II. Experimental Results and Interpretations

Although the details of the experimental results have been described elsewhere [*10*, *11*], some of them will be given here for convenience's sake. The results of the measurements in which 2-naphthol was used as *D* and ammonia and various alkylamines were used as *A*'s seem to be particularly useful for theoretical discussions. The values of the spectral shifts of 2-naphthol (in unit of cm^{-1}) due to *D-A* complex formation in various solvents are in the table, where $\delta\tilde{\nu}_a$ and $\delta\tilde{\nu}_f$ represent the shift of the absorption and fluorescence spectra, respectively, and mono-, di-, tri-n-butylamine and triethylamine are respectively abbreviated as *MBA*, *DBA*, *TBA* and *TEA*.

Because the $\delta\nu_a$ values for *TEA* and *TBA* in non-polar solvents are quite large, the hydrogen bond in the e.-q. ground and the F.-C. excited state seems to be very strong in these cases. Nevertheless, these spectral changes still indicate the normal hydrogen bonding interactions. However, the $\delta\tilde{\nu}_f$ values due to 1:1 complex formation are anomalously large and this fact indicates that an extraordinary strong hydrogen bond or an ion-pair is formed in the excited e.-q. state. When *A* is *TEA*, the $\delta\tilde{\nu}_f$ value becomes larger with the increase of the solvent polarity. This fact supports the possibility of the ion-pair formation because the ion-pair

Table. *Absorption and fluorescence spectral shifts caused by D-A interaction. D: 2-naphthol*

A	Solvent	$\delta\tilde{\nu}_a$	$\delta\tilde{\nu}_f$	$\delta\tilde{\nu}_f'$	I_A (eV)
NH_3	cyclohexane	500	810	5500	10.154
MBA	cyclohexane	590	960	5700	8.71
	benzene	430	~ 560	5400	
DBA	cyclohexane	590	1040	4700	7.69
	benzene	430	—	4300	
TEA	cyclohexane	590	2700 (1340)		7.5
	benzene	370	4000		
TBA	cyclohexane	590	3000		(7.1)*
	benzene	—	3900		

* estimated by extrapolation.

is stabilized by the surrounding solvent molecules to the greater extent in the more polar solvent. Furthermore, as it is shown in Fig. 1, we can observe an approximate linear relation between the $(\delta\tilde{\nu}_f - \delta\tilde{\nu}_a)$ values of 2-naphthol-*TEA* system and the values of $\left(\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1}\right)$ of the solvents [*4*, *5*], where D and n are the static dielectric constant and the refractive index of the solvent, respectively. This result seems to be an evidence for the ion-pair formation in the excited state. Although it might be possible to estimate the dipolemoment of the ion-pair from this linear relation, the fact that the π-electron system is mainly concerned with the electronic transition and the electronic structure of the ion-pair is concerned with the σ-electron system of A and both of the σ- and the π-electron system of D complicates the interpretation of the observed results.

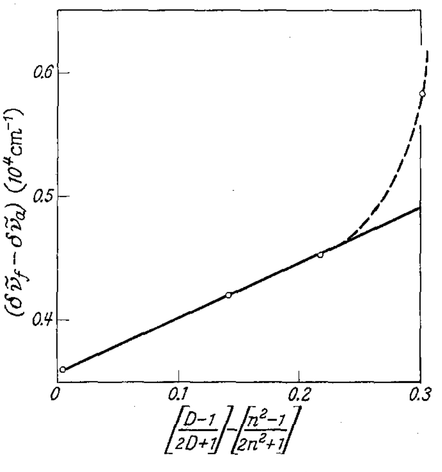


Fig. 1. $\delta\tilde{\nu}_f - \delta\tilde{\nu}_a$ vs. $\left(\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1}\right)$ relation for the 2-naphthol-*TEA* system. Solvents: (1) benzene, (2) monochlorobenzene, (3) dichloroethane, (4) acetonitrile

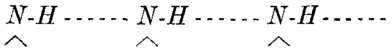
It should be noted here that in the case of acetonitrile solution the deviation from the linear relation is quite large. Therefore, it might be argued that the ionic dissociation in the sense:

$$(R\text{-}O^- \text{-----} H\text{-}N^+(R')_3)_{solv.} \rightarrow (R\text{-}O^-)_{solv.} + (H\text{-}N^+(R')_3)_{solv.}$$

occurs during the lifetime of the excited state, in this very polar solvent, or the strong interaction between the ion-pair and the surrounding acetonitrile molecules cannot be represented by the simplified dielectric theory.

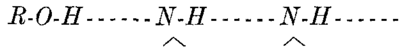
When ammonia, *MBA* and *DBA* are used as A and when $0.01 < [A] < 0.1$mol/l, the intensity of the fluorescence band of the 1:1 *D-A* complex decreases and at the same time a new fluorescence band appears at much longer wavelength region and the shift from the fluorescence band maximum of free *D* is given in the table ($\delta\tilde{\nu}'_f$). However, the absorption spectrum shows only the change due to 1:1 hydrogen bonding interaction even at this high concentration of *A*. The [*A*] value where this long wavelength fluorescence band begins to appear is smaller in the case of *MBA* than *DBA*.

The dipolemoment of the aliphatic amine decreases in the order: mono- > di- > tri-, and such hydrogen bonding interaction as shown below is possible in the case of mono- and di-alkylamines but impossible in the case of the trialkylamine.



$$N\text{-}H\cdots\cdots N\text{-}H\cdots\cdots N\text{-}H\cdots\cdots$$

Therefore, in the case of ammonia and mono- and di-alkylamines, the 1:1 *D-A* complex may be further solvated by amines including the dipole-dipole, dipole-polarization interaction and the hydrogen bonding interaction as indicated below, during the lifetime of the excited state. Thus, the ion-



$$R\text{-}O\text{-}H\cdots\cdots N\text{-}H\cdots\cdots N\text{-}H\cdots\cdots$$

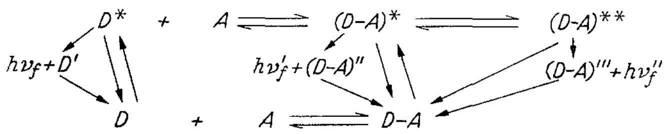
pair formation occurs being assisted by the solvation and at the same time the ion-pair is stabilized considerably by this solvation, which leads to the long wavelength fluorescence band.

The hydrogen bonding interaction between amine molecules may be rather weak. However, the amine molecule directly hydrogen bonded to naphthol may be polarized rather strongly in the excited state and this change of the electronic structure of the amine molecule will affect the next one in the hydrogen bonded chain------. In this way, the ion-pair formation by the cooperative process becomes feasible. Although the dielectric constant of the liquid ammonia or the pure amine liquid (primary and secondary) is rather small compared with that of acetonitrile, the $\delta\tilde{\nu}'_f$ values in the former solvents are very large. This fact seems to indicate that the short range molecular interactions in the associating solvent is very important for the ion-pair formation process as described above.

The intermolecular proton transfer process assisted by solvation such as demonstrated here, may be closely related to the ionic dissociation processes of excited molecules in aqueous solution, where the proton transfer occurs quite easily because of the very large dielectric constant of the solvent and the very extensive hydrogen bonding in the solvent.

As shown in the table, $\delta\tilde{\nu}_f$ or ($\delta\tilde{\nu}_f - \delta\tilde{\nu}_a$) of 2-naphthol in cyclohexane is larger the smaller the ionization potential of the lone pair orbital of A (I_A). This result favours the CT mechanism [*12*–*15*] of hydrogen bonding, particularly in the excited state. Accordingly, the observed proton transfer reaction in the excited state may be interpreted on the basis of this CT mechanism of hydrogen bonding.

The general plan of the processes involved in the hydrogen bonding and ion pair formation may be given by the following reaction scheme:



(1)

In (1), D^* and $(D\text{-}A)^*$ represent the free D and the hydrogen bonded $D\text{-}A$ pair in the first excited singlet state, respectively, $(D\text{-}A)^{**}$ denotes the ion-pair or the very strongly hydrogen bonded pair in the excited e.-q. state, D', $(D\text{-}A)''$ and $(D\text{-}A)'''$ represent respectively the free D, the hydrogen bonded $D\text{-}A$ pair and the ion-pair or the very strongly hydrogen bonded pair in the F.-C. ground state.

III. Theoretical Discussions

A symbolic representation of the various electronic states of the $D\text{-}A$ system may be as follows.

$$\begin{array}{lcl}
\text{Separated Pair} & & \text{Bonded Pair} \\
\Psi_0^0:[(\Pi_0^0)\cdot(\Sigma_{D0}^0)]+[\Sigma_{A0}] & \longleftrightarrow & \Psi^0:[(\Pi^0)\cdot(\Sigma_D^0)\cdot(\Sigma_A)] \\
\Psi_0^1:[(\Pi_0^1)\cdot(\Sigma_{D0}^1)]+[\Sigma_{A0}] & \longleftrightarrow & \Psi^1:[(\Pi^1)\cdot(\Sigma_D^1)\cdot(\Sigma_A)] \\
\vdots & & \vdots \\
\Psi_{CT0}^0:[({}^-\Pi_0^0)\cdot({}^-\Sigma_{D0}^0)]+[{}^+\Sigma_{A0}] & \longleftrightarrow & \Psi_{CT}^0:[({}^-\Pi^0)\cdot({}^-\Sigma_D^0)\cdot({}^+\Sigma_A)] \\
\Psi_{CT0}^1:[({}^-\Pi_0^1)\cdot({}^-\Sigma_{D0}^1)]+[{}^+\Sigma_{A0}] & \longleftrightarrow & \Psi_{CT}^1:[({}^-\Pi^1)\cdot({}^-\Sigma_D^1)\cdot({}^+\Sigma_A)] \\
\vdots & & \vdots
\end{array} \tag{2}$$

In (2), (Π) represents the π-electron system of D and Σ_D and Σ_A represent the σ-electron system of D and A, respectively. In the present case, the relevant Σ_D is mainly localized in the $O\text{-}H$ group and Σ_A is the lone pair of the amine molecule. The superscripts, 0, 1, ------ represent the ground state, 1st excited singlet state, etc., respectively. Although the electronic excitation is mainly concerned with the π-electron system, σ-electron system of D is also affected by this excitation. The CT interaction in the sense,

$$R\text{-}O\text{—}H\text{--------}N(R')_3 \longleftrightarrow R\text{-}O^-\text{----}H\text{————}N^+(R')_3$$

is mainly localized in Σ_D and Σ_A. However, the π-electron system of D is evidently affected by this CT and this circumstance is represented by the symbol $({}^-\Pi)$ in (2).

The energy difference between Ψ_{CT} and Ψ may be written as follows:

$$\begin{aligned}
\Delta E_{CT}^0 &= E(\Psi_{CT}^0)-E(\Psi^0)\approx I_A-A_D^0-V^0(D^-\text{---}A^+)-\delta\varepsilon_\pi^0-\delta H_s^0 \\
\Delta E_{CT}^1 &= E(\Psi_{CT}^1)-E(\Psi^1)\approx I_A-A_D^1-V^1(D^-\text{---}A^+)-\delta\varepsilon_\pi^1-\delta H_s^1
\end{aligned} \tag{3}$$

In (3), A_D is the electron affinity of Σ_D and from the reasoning described above, A_D represents mainly the electron affinity of $O\text{-}H$ σ-bond. $-V(D^-\text{---}A^+)$ is the interaction energy between the components of the pair and $-\delta\varepsilon_\pi$ is the change of π-conjugation energy caused by the CT interaction. $-\delta H_s$ is the difference between the solvation energies in Ψ_{CT} and Ψ states, respectively. Owing to the increased migration of π-electrons on the oxygen to the vacant π-MO's of naphthalene ring in the excited state, $A_D^1 > A_D^0$ and $\delta\varepsilon^1{}_\pi > \delta\varepsilon_\pi^0$. Probably, $V^0(D^-\text{---}A^+) \sim V^1(D^-\text{---}A^+)$ and $\delta H_s^0 \sim \delta H_s^1$. Therefore, $\Delta E_{CT}^1 < \Delta E_{CT}^0$. For the purpose of the present discussion, it may be sufficient to approximate the stationary state electronic wave function of the hydrogen bonded complex by the linear combination of Ψ and Ψ_{CT}.

$$\Phi(r,s) \approx c_1(s)\,\Psi(r,s)+c_2(s)\,\Psi_{CT}(r,s), \tag{4}$$

where r and s represent the electronic and nuclear coordinates, respectively. In our problem, s represents approximately the coordinate of proton in the hydrogen bond. The probability density of Ψ_{CT} in this electronic wave funktion is larger in the excited state than in the ground state because $\Delta E^1_{CT} < \Delta E^0_{CT}$. However, this probability density seems to be not very large in the excited F.-C. state because the $\delta\tilde{\nu}_a$ value does not so much depend upon the I_A value as the $\delta\tilde{\nu}_f$ value does. Nevertheless, because of the CT from Σ_A to Σ_D (namely, from the lone pair orbital of nitrogen to the antibonding orbital of *O-H* group) in the excited F.-C. state, the potential energy for proton may be a little modified and this modification will bring out a little displacement of proton toward nitrogen. This small displacement of proton induces stronger migration of π-electrons on the hydroxy group to the naphthalene ring, i. e. the larger $\delta\,\varepsilon^1_\pi$ value and then stronger CT, i. e. the greater probability density of Ψ_{CT} in (4) which accelerates the displacement of proton, and so on, until the final excited e.-q. state is arrived at. Of course, smaller I_A value is favoured for this interaction process, because the increase of $\delta\,\varepsilon^1_\pi$ value due to the displacement of proton is the more effective to increase the CT interaction the smaller the I_A value.

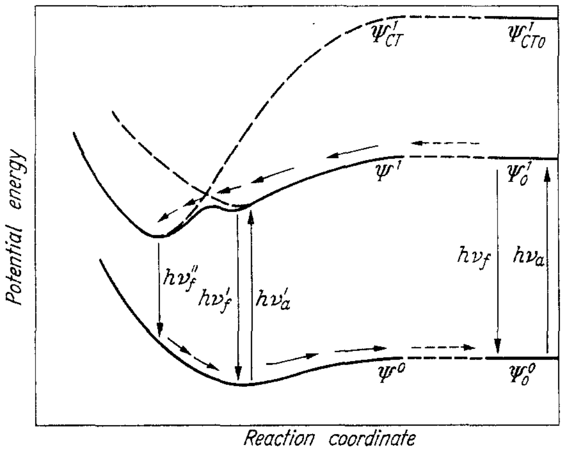


Fig. 2

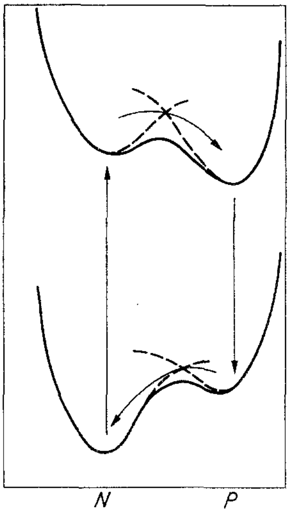


Fig. 3

Fig. 2. Potential energy curves for the hydrogen bonding and the ion-pair formation process

Fig. 3. Double minimum potential energy curves for the motion of proton in the lowest excited singlet and the ground state, respectively

The effect of the solvation upon the ion-pair formation which is represented by δH_s in (3) in a rather formal way, seems to be quite important. δH_s includes various interaction energies between the ion-pair and the surrounding solvent molecules such as long range dipolar interactions and short range interactions of more specific nature. The difference between the $\delta\,\tilde{\nu}_f$ values of 2-naphthol-*TEA* system in benzene and cyclohexane, respectively, seems to be quite remarkable in that the latter type interactions probably play a dominant role in the case of the benzene solution but not in the case of cyclohexane solution. In any way, the larger δH_s value is favourable for the greater probability density of Ψ_{CT} in (4).

Thus, the proton transfer reaction may be a coupled process of $\Pi - \Sigma_D$ interaction, the $\Sigma_A \rightarrow \Sigma_D$ CT interaction and the displacement of proton, and the readjustments of the surrounding solvent molecules.

When it is assumed that the adiabatic approximation holds for the whole process of this hydrogen bonding and ion-pair formation reaction, the effective potential energy curves for the *D-A* interaction process and the motion of proton may be given as indicated in Fig. 2 and 3, respectively. The reaction coordinate in Fig. 2 involves the distance between the *D* and the *A* molecule and also the relative position of proton in the hydrogen bond. The actual proton transfer reaction proceeds presumably in the way as indicated by the arrows.

In the ordinary simple MO calculation, it is assumed that the *O-H* group of naphthol contributes two electrons to the π-system of *D*. Furthermore, the interactions between the π-electrons and the σ-electrons are assumed to be inductive, i. e., π-electrons move in the field due to the nuclei, inner electrons and the σ-electrons, and at the same time, the π-electrons together with the nuclei and the inner electrons form the field for the σ-electrons. Actually, however, σ-π separability does not hold exactly because the exchange interaction between the π-electron and the σ-electron systems is possible. In the case of the trigonal hybrid AO's of aromatic hydrocarbon skeleton, this exchange interaction may not be very large. However, in the *O-H* group, the σ-π exchange interaction may not be so small. Accordingly, it might be possible that the effect of the CT interaction on the π-electronic state of *D* is more direct than it is described above. Anyhow, the σ-π interaction, either in the sense of the electrostatic or the exchange interaction, plays an important role in the proton transfer process.

IV. Remarks on the Double Minimum Potential for the Motion of Proton in the Excited State

According to the BORN-OPPENHEIMER approximation [*1*, *2*], the electronic stationary state energies of a molecular system for various fixed nuclear coordinates form the effective potential energy surface for the nuclear motion. Therefore, the Hamiltonian for the proton in the hydrogen bond may be written as:

$$H_N = T_N + E_{el}(s) \tag{5}$$

where T_N is the kinetic energy and,

$$\begin{aligned} E_{el}(s) = \langle \Phi(r,s) \,|\, H_{el}(s) \,|\, \Phi(r,s) \rangle = c_1^2(s) \langle \Psi(r,s) \,|\, H_{el}(s) \,|\, \Psi(r,s) \rangle + \\ + c_2^2(s) \langle \Psi_{CT}(r,s) \,|\, H_{el}(s) \,|\, \Psi_{CT}(r,s) \rangle + \\ + 2\, c_1(s)\, c_2(s) \langle \Psi(r,s) \,|\, H_{el}(s) \,|\, \Psi_{CT}(r,s) \rangle. \end{aligned} \tag{6}$$

The wave function Φ_l for the vibrational stationary state of proton in the *O-H* or $H\text{-}N^+ \leqslant$ bond may be the solution of the following Schrödinger equation,

$$H_N \varphi_l(s) = E^l_{\text{vib.}} \varphi_l(s), \tag{7}$$

and the total wave function for an electronic and vibrational stationary state may be written as,

$$\chi(r,s) \sim \Phi(r,s) \cdot \varphi(s). \tag{8}$$

In the present approximation, the potential energy for the motion of proton near the initial position (*N* in Fig. 3) may be determined mainly by Ψ in (4). In the ground state, $C_1 \gg C_2$, which means the initial position is fairly stable. In the excited F.-C. state, this stability may decrease a little, because of a little stronger CT interaction than in the ground state. In the course of the proton transfer process, the order of the magnitude of the coefficients in (4) may be reversed. The potential energy for the motion of proton in the excited e.-q. state (*P* in Fig. 3) may be determined mainly by Ψ_{CT} in (4).

The time dependent wave function $\varphi_l\,(s,\ t)$ for the proton in the proton transfer process may be expanded in terms of $\varphi_l\,(s)$'s as follows,

$$\varphi_l\,(s,t)\ \approx\ \sum_l C_l\,\varphi_l\,(s)\exp\left(-i\,E^l_{\mathrm{vib.}}\,t/\hbar\right), \tag{9}$$

where the summation includes not only the vibrational wave functions near the position *N* in Fig. 3 but also those near the position *P*.

The velocity of the proton transfer depends on the magnitude of the interaction elements between $\varphi_l\,(N)$'s and $\varphi_l\,(P)$'s. Such an interaction may be the stronger the larger the anharmonicity of the stretching vibration. The stronger CT interaction between Σ_D and Σ_A makes the *O-H* bond weaker and the force constant of the *O-H* stretching smaller. In this way, if the potential energy surface becomes more shallow in the excited state, anharmonicity of the stretching vibration may increase. If the anharmonicity of the *O-H* stretching vibration is increased considerably, the higher order interactions between the electronic motion and the motion of proton may be possible, which takes part in the proton transfer process. In this case, a vibronic wave function for the system may be written as,

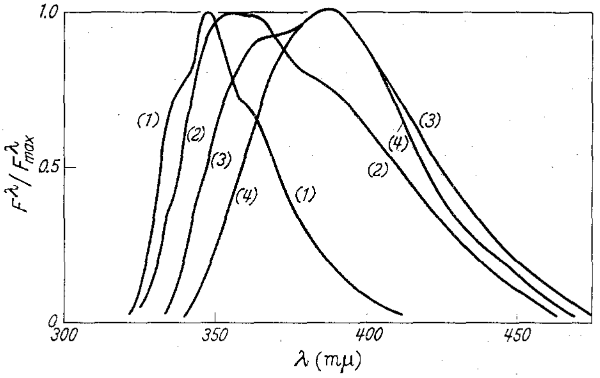


Fig. 4. Fluorescence spectra of 2-naphthol and 2-naphthol-*TEA* complex in aliphatic hydrocarbon solvents. Solvents: (1) ~ (3) cyclohexane, (4) *MP*. Concentration of 2-naphthol: (1) ~ (3) 2.0 × 10^{-4} mol/l, (4) 1.8 × 10^{-4} mol/l, Concentration of *TEA*: (1) 0, (2) 0.012 mol/l, (3) 0.20 mol/l, (4) 2.2 × 10^{-4} mol/l and 7.0 × 10^{-4} mol/l. Temperature: (1) ~ (3) ~ 15° C, (4) — 180° C

$$\begin{aligned}\chi\,(r,s) &\approx \sum_{i,l} a_{il}\,\Phi_i\,(r,s)\cdot\varphi_l\,(s)\\ &= \sum_{j,l} b_{jl}\,\Psi_j\,(r,s)\cdot\varphi_l\,(s)\end{aligned} \tag{10}$$

where *i*, *j*, and *l*, denote various electronic states and vibrational excited states, respectively. However, we cannot assess the importance of such a higher order effect at the present stage of investigation.

As it has been already described in III, the *P* position in the excited e.-q. state of 2-naphthol-*TEA* complex in cyclohexane seems to be not so stable as indicated in Fig. 3. In benzene and in the polar solvents, the circumstance may be close to that illustrated in Fig. 3, i. e. the population at position *N* may be practically neglected in the excited e.-q. state. However, in the case of the cyclohexane solution, this population seems to be considerable because the fluorescence spectrum seems to have actually two components (one of which corresponds to the transition at *N* and the other to that at *P*)*, at room temperature, as shown in

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* $\delta\bar{\nu}_f$ value which corresponds to the transition at *N* is shown in the bracket in the table.

Fig. 4. This result may be ascribed to the instability of the ion-pair in cyclohexane compared with that in benzene and polar solvents.

The fluorescence spectra of 2-naphthol and its complex with *TEA* in methylcyclohexane and isopentane mixture (3:1 in volume, abbreviated as *MP*) is practically the same as those in cyclohexane, respectively. In the fluorescence spectrum of this *D-A* complex in *MP* at − 180° C, short wavelength component seems to be much decreased compared to the case of the fluorescence at room temperature, as shown in Fig. 4. Accordingly, even in the aliphatic hydrocarbon solvent, the ion-pair may be more stable than the normal hydrogen bonded complex, in the excited state.

In one of our previous reports [*10*], it has been concluded that, in the case of the cyclohexane solution, an extraordinary strong, almost symmetrical hydrogen bond seems to be formed in the excited e.-q. state, which may probably lead to the broadness of the fluorescence band of 2-naphthol-*TEA* complex. However, this conclusion should be replaced by the more detailed one as described above.

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