Femtosecond–Picosecond Laser Photolysis Studies on the Mechanisms of Electron Transfer Induced by Hydrogen-Bonding Interactions in Nonpolar Solutions: 1-Aminopyrene–Pyridine Systems

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Abstract: The mechanisms of photoinduced electron transfer in 1-aminopyrene (AP, D–H)–pyridine (Pyr, A) and –methylpyridine (MePyr, A) hydrogen-bonded complexes in nonpolar hexane solutions have been investigated by means of femtosecond–picosecond laser photolysis methods. Rapid electron transfer from the S_1 state of AP to the hydrogen-bonded Pyr or MePyr converging to the equilibrium state, $(D^*\text{–H}\cdots A) \rightleftarrows (D^+\text{–H}\cdots A^-)$, has been directly observed by time-resolved transient absorption spectral measurements. The mechanism of the photoinduced electron transfer in nonpolar solvents greatly assisted energetically by specific hydrogen-bonding interactions and also dynamically by a little movement of the proton of D–H toward A in the hydrogen bond has been concluded. The charge recombination deactivation rate from the $(D^+\text{–H}\cdots A^-)$ state to the ground state has been examined for AP–Pyr and various –MePyr systems by time-resolved measurements, and it has been demonstrated that the rate constant decreases exponentially with increase of the energy gap.

Introduction

The mechanisms and dynamics of the photoinduced electron transfer (ET) or charge transfer (CT) between an electron donor (D) and acceptor (A) and related phenomena, leading to the formation of a transient ion pair (IP) or ET state, and subsequent behaviors of the IP or ET state are the most important and fundamental problems in photochemical reactions in the condensed phase.[1]

The important factors regulating the rate of photoinduced charge separation (CS) by ET and that of charge recombination (CR) of the produced geminate IP state are generally believed to be the electronic interactions responsible for ET between D and A, the free energy gap ($-\Delta G$) between the initial and final states of ET, the reorganization energies (λ) of D and A as well as the surrounding solvent, and the solvent dynamics.[2–4] In many cases, the ET reactions are interpreted by assuming a very weak electronic interaction between D and A, leading to the simple two-state model with a definite rate constant for the reaction, e.g., $(D\cdots A) \rightarrow (D^+\cdots A^-)$.

However, in the actual D/A systems in the condensed phase, depending on the magnitude of the electronic interaction as well as other factors described above, there arise various cases of different mechanisms of photoinduced CS and CR of the produced IP state,[5–8] some of which are not yet well comprehended, especially in the cases of strongly interacting systems.[8] For example, in the photoinduced CS processes of CT complexes where the electronic interaction between D and A is strong, intracomplex structural rearrangements in addition to the reorientations of the surrounding solvent molecules seem to be taking place in the course of the ET process,[5,7,8] which is quite different from the simple outer-sphere ET reaction by a very weak interaction. Namely, this CS process of the excited CT complex in polar solvents is not such a simple ET reaction but the relaxation process accompanied with a rather large intracomplex geometrical rearrangement leading to the formation of the IP (contact or compact IP, CIP) state.[5,7,8] It has been demonstrated also that various kinds of IP's including CIP's (without intervening solvent) and LIP's (loose IP's with intervening solvent molecules) of different interionic distances are formed depending on the D/A electronic interactions, $-\Delta G$ values, and solvent polarities.[5–9] These IP's show different characteristics in the subsequent reactions.[6,9]

On the other hand, it was shown first by us many years ago that the intermolecular hydrogen-bonding interaction frequently led to the quenching of fluorescence, especially when two conjugate π-electronic systems were directly combined by a hydrogen-bonding interaction.[10] We suggested the CT interaction between proton-donor (D–H) and -acceptor (A) π-electron systems via the hydrogen bond as a possible mechanism of the quenching.[10] Namely, a kind of nonfluorescent or very weakly fluorescent exciplex, $(D^+\text{–H}\cdots A^-)$, was assumed to be formed in the course of this quenching process.[10]

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Since then, more or less detailed studies on the mechanisms of the hydrogen-bonding quenching of fluorescence have been performed.[10–17] We have demonstrated first the transient ET state formation in the course of fluorescence-quenching reactions of several conjugate π-electronic proton donor–acceptor systems by means of picosecond laser spectroscopy.[1b,14–17] Detailed picosecond laser spectroscopic studies have been made in the cases of the 13*H*-dibenzocarbazole[15,17] (13DBC)–, 7*H*-dibenzocarbazole[15,17] (7DBC)–, and 1-aminopyrene[16] (AP)–pyridine (Pyr) systems in nonpolar solvents. It was confirmed that, when the ground-state hydrogen-bonded complexes, $(\mathrm{D{-}H\cdots A})$, of 7DBC–Pyr and AP–Pyr systems were excited by the 355-nm pulse of 22-ps duration (fwhm), the equilibrium state between $(\mathrm{D^*{-}H\cdots A})$ and $(\mathrm{D^+{-}H\cdots A^-})$ was attained owing to the much shorter time constants of forward and backward ET reactions between these two states compared with those of their decay to the ground state. Actually, the equilibrium was established within a ca. 10-ps time resolution of the apparatus and the concentration ratio between $(\mathrm{D^*{-}H\cdots A})$ and $(\mathrm{D^+{-}H\cdots A^-})$ was kept the same throughout the direct observation of the decay of these species by means of the picosecond time-resolved transient absorption spectral measurements.[15–17] In the case of the 13DBC–Pyr system, much slower forward–backward ET processes between the two species $(\mathrm{D^*{-}H\cdots A}) \rightleftarrows (\mathrm{D^+{-}H\cdots A^-})$, obeying the usual exciplex dynamics over the 100-ps–1-ns region, were observed because the time constants of the ET processes were comparable with those of the decay of these species to the ground state. Different behavior of the 13DBC–Pyr system from those of 7DBC– and AP–Pyr systems was ascribed to the steric hindrance in the hydrogen bonding, which was unfavorable for the ET reaction.

It should be noted here that, if we assume the usual ET mechanism by weak interaction for these systems, the ET reaction, $(\mathrm{D^*{-}H\cdots A}) \rightarrow (\mathrm{D^+{-}H\cdots A^-})$, should be much slower even in the 7DBC–Pyr and AP–Pyr systems because $-\Delta G$ values for ET of these systems in nonpolar solvents are estimated to be ca. -1.1 and -0.95 eV, respectively. The observed rapid ET in these systems indicates that the $-\Delta G$ value becomes approximately zero or positive even in nonpolar solvents, owing to the decrease of ionization potential of D–H and the increase of the electron affinity of A by the hydrogen-bonding interaction.[15,16] The hydrogen-bonding interaction between these D–H and A molecules in the excited state is stronger than in the unexcited state due to the much larger extent of intramolecular CT from the $-\mathrm{NH_2}$ or >N–H group to the aromatic hydrocarbon rings. The larger extent of intramolecular CT will make the proton in the hydrogen bond shift toward A, which will further lower the ionization potential of the D–H π-electron system and enhance the electron affinity of the π-electron system of A, facilitating the photoinduced ET,[15,16] as discussed in detail later in this article. It should be noted here, however, that a complete proton transfer coupled with ET in these hydrogen-bonded systems does not take place but only a slight shift of proton toward A in the hydrogen bond which assists greatly photoinduced ET is possible. We cannot observe the spectrum due to the neutral radical $\mathrm{D^\bullet}$ produced by complete proton transfer coupled with ET but only the $\mathrm{D^+}$–H cation radical-like spectrum superposed on the $S_n \leftarrow S_1$ spectrum of D–H in these excited hydrogen-bonded complexes.[15,16]

Moreover, the electronic interaction responsible for ET between $\mathrm{D^*}$–H and A may be considerably stronger due to the hydrogen-bonding interaction than in the case of the outer-sphere ET by weak electronic interaction, leading to some different mechanisms of the reaction. That is, the nature of the donor–acceptor interaction in the excited-state dynamics of the present systems might be somewhat analogous to but will be more specific than that of the CT complexes.

The crucial importance of the specific nature of the hydrogen-bonding interaction in the excited-state dynamics is also evident from the fact that the quenching in hexane solution of the AP–Pyr system is diffusion-controlled while the quenching rate constant in acetonitrile solution of the same system is 2 orders of magnitude smaller than that in hexane solution,[16] probably owing to the hindering of the hydrogen-bonding interaction between AP and Pyr due to the solvation of both of them by strongly polar acetonitrile.[16]

It should be pointed out here that, in addition to the above described systems, aromatic hydroxy compounds–azaaromatic systems are also typical ones showing hydrogen-bonding quenching of fluorescence.[10] However, results of our unpublished transient absorption spectral studies on the 1-pyrenol–Pyr system with picosecond laser spectroscopy did not show the formation of the ET state but indicated mainly the very rapid decay of the 1-pyrenol S_1 state.[18] Presumably, the photoinduced ET reaction in the hydrogen-bonded pair induces ultrafast deactivation to the ground state in this system contrary to the case of the above described aromatic amine–Pyr systems. However, investigation on the excited-state dynamics of the 1-pyrenol–Pyr system by measurements with higher time resolution is necessary for the further elucidation of the quenching mechanism.

The above described characteristics of the photoinduced CT or ET in the hydrogen-bonding systems may be interesting and important from the viewpoint of the ET theories in general and also in view of the mechanisms of ET taking place in nonpolar or only slightly polar protein media in biological systems. Accordingly, in order to elucidate more details of the photoinduced ET mechanisms in the hydrogen-bonding systems, we have examined the ET processes in the hydrogen-bonding complexes of AP with Pyr and various methyl-substituted Pyr's in nonpolar solvents and also CR decay of the produced ET state by means of the femtosecond–picosecond laser spectroscopy, results of which are reported in this paper. We have made similar studies on the hydrogen-bonded systems of 1-pyrenol–Pyr and -methyl-substituted Pyr's, results of which will be reported in a subsequent paper.[19]

Experimental Section

Method. A microcomputer-controlled picosecond laser photolysis system with a repetitive mode-locked $\mathrm{Nd^{3+}}$:YAG laser was used for transient absorption spectral measurements in the 10-ps to a few-nanosecond region.[20] The third harmonic pulse with a 22-ps fwhm was used for exciting the sample. For the measurements of spectra in the shorter time region, a femtosecond laser photolysis system was used.[7,21] The second harmonic pulse (355 nm) of the "Pyridine-1" dye laser (710 nm) with a 500-fs fwhm was used for excitation. The overall time resolution of the apparatus was ≤0.5 ps.[8a] Fluorescence decay curves were measured by means of a time-correlated single-photon-counting method using a synchronously pumped, cavity-dumped dye laser (second harmonic of "Pyridine-1") exciting at 355 nm.[21] The response time of this apparatus was 30-ps fwhm. SALS at the Osaka University Computation Center was used for the least-squares analysis of the observed decay curves.

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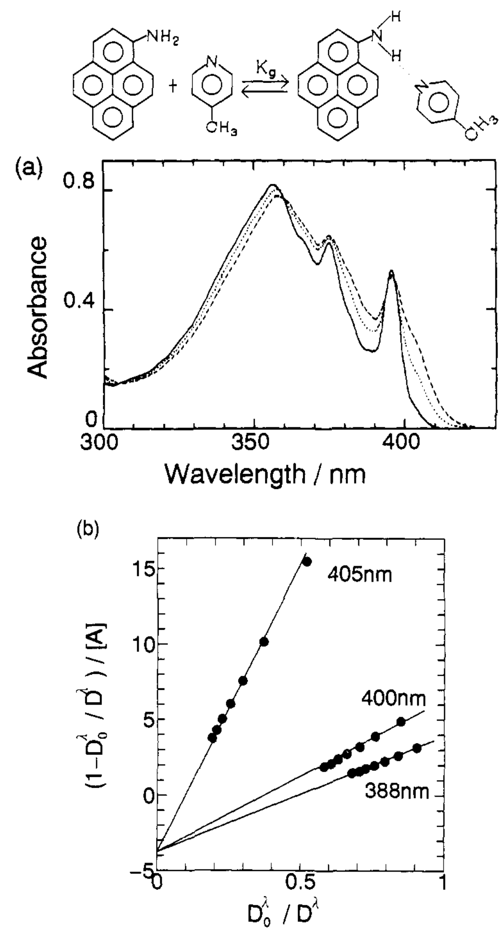

Figure 1. (a) Ground-state absorption spectra of the AP–4MePyr system in hexane solution: [AP] = 4.1 × 10^{-5}M; [4MePyr] = 0 M (—), 9.3 × 10^{-2} M (···), 0.217 M (- - -). (b) Analysis of the 1:1 hydrogen-bonding equilibrium by means of eq 1.

Materials. 1-Aminopyrene (AP) (Tokyo Kasei) was recrystallized twice from ligroin and sublimated under vacuum. Pyridine (Pyr) was Merck spectrograde and was used without further purification. 2-Methylpyridine (2MePyr), 4-methylpyridine (4MePyr), 2,6-dimethylpyridine (DMePyr), and 2,4,6-trimethylpyridine (TMePyr) (Wako GR grade) were carefully distilled before use. Hexane and acetonitrile were Merck spectrograde and were used without further purification. Sample solutions for measurements were deaerated by freeze–pump–thaw cycles.

Results and Discussion

Hydrogen-Bonding Effects upon Ground-State Absorption and Stationary Fluorescence Spectra. The ground-state equilibrium constants (K_g) of 1:1 hydrogen-bonding for AP–Pyr and AP–methyl-substituted Pyr (MePyr) pairs in hexane at room temperature (22 ± 2 °C) were obtained to be ca. 2–4 M^{-1} from the analysis of the concentration effect of added Pyr's on the AP absorption spectrum.

As an example, the ground-state absorption spectrum of AP and the effect of the addition of 4MePyr on it in hexane solutions are shown in Figure 1a. The absorption bands show a little red shift owing to the larger stabilization of the excited state due to the hydrogen-bonding interaction. This spectral change can be analyzed by eq 1 on the basis of the 1:1 hydrogen bonding,[10] as shown in Figure 1b. In eq 1, $K_g = [D\text{–}H\cdots A]/[D\text{–}H][A]$ for the

$$(1 - D_0^{\lambda}/D^{\lambda})/[A] = -K_g + (\epsilon_c^{\lambda}/\epsilon_{D\text{–}H}^{\lambda})K_g(D_0^{\lambda}/D^{\lambda}) \quad (1)$$

equilibrium D–H + A ⇄ (D–H···A), as indicated in Figure 1a, ϵ_C^λ and $\epsilon_{D\text{–}H}^\lambda$ are molar extinction coefficients of (D–H···A) and D–H at a wavelength λ, respectively, and D_0^λ and D^λ are absorbances at λ in the absence and presence of A, respectively.

Table I. Fluorescence-Quenching Rate Constants of the AP–Pyr and AP–MePyr Systems in Hexane Solutions

quencher	$k_q(10^{10}\ M^{-1}\ s^{-1})$	quencher	$k_q(10^{10}\ M^{-1}\ s^{-1})$
Pyr	1.2	DMePyr	0.82
2MePyr	1.0	TMePyr	0.54
4MePyr	0.86		

Since the quenching of AP fluorescence by added Pyr's takes place in the concentration regions of Pyr's where the AP absorption spectrum is not affected by the hydrogen-bonding interaction, the bimolecular quenching rate constant (k_q) was obtained by analysis with a simple Stern–Volmer equation. The obtained k_q values in hexane solutions at room temperature are shown in Table I. The k_q values are rather close to the diffusion-controlled one but a little smaller especially in the case of TMePyr. Although the reason for this decrease of k_q by methyl substitution of pyridine is not clear at the present stage of the investigation, some steric restriction at the encounter of MePyr's with excited AP and a decrease of electron affinity of Pyr by methyl substitution might lead to such a result.

Although we cannot recognize practically the fluorescence of free AP at very high concentrations (~1 M) of added Pyr and MePyr's in hexane solution, we can observe a weak and red-shifted fluorescence band of the hydrogen-bonded complexes. The red-shifted band shows a peak at 420–430 nm and a shoulder around 450 nm. Although we have not determined the quantum yield of this red-shifted fluorescence, its relative yield increases with an increase of the number of the substituted methyl groups and also roughly with the lowering (more negative value) of the reduction potentials of pyridines. On the basis of the time-resolved absorption and fluorescence spectral measurements on these hydrogen-bonded systems, as demonstrated in the next section, we can conclude that this red-shifted fluorescence is emitted from the equilibrium state between the locally excited (LE) state, (D^*–H···A), and the ion pair (IP) state, (D^+–H···A^-), of the hydrogen-bonded complex. Therefore, the above result of the dependence of relative fluorescence yield on the number of the substituent methyl groups seems to indicate the decrease of the nonradiative decay rate from the equilibrium state with the lowering of the reduction potential of Pyr, of which more details will be discussed later.

Femtosecond–Picosecond Transient Absorption and Time-Resolved Fluorescence Studies on Photoinduced Charge Separation (CS) and Charge Recombination (CR) of the Produced Ion Pair (IP) State in Hydrogen-Bonded Systems. Time-Resolved Transient Absorption Spectral Studies. Time-resolved transient absorption spectra of the AP–Pyr system in hexane solution excited with a 500-fs laser pulse at 355 nm are indicated in Figure 2a, where most of AP molecules are hydrogen bonded with Pyr in the ground state. We show in Figure 2b also the absorption spectrum of the S_1 state of AP (AP^*)[16] and that of the AP cation radical (AP^+)[16] for the purpose of comparison. Immediately after excitation, the transient absorption spectrum showed a maximum (at 520 nm) and band shape very similar to those of the $S_n \leftarrow S_1$ spectrum of AP in hexane solution, as indicated in Figure 2b. Therefore, the absorption spectrum in the top frame in Figure 2a may be ascribed to the excited state localized in the AP part, (D^*–H···A).

With increase of the delay time, a shoulder arises in the 470–480-nm region which may be ascribed to the absorption band of AP^+ in the IP state, (D^+–H···A^-), in view of the fact that the AP cation radical shows an absorption spectrum with a maximum at 475 nm, as indicated in Figure 2b. It should be noted here that the absorption band of AP^+ in Figure 2b is rather sharp because it was observed in the rigid matrix at 77 K. It will be a little broader in solution at room temperature. Transient absorption spectra at 20 ps as well as at 8 ps are very similar to those at longer delay times which were obtained with picosecond laser

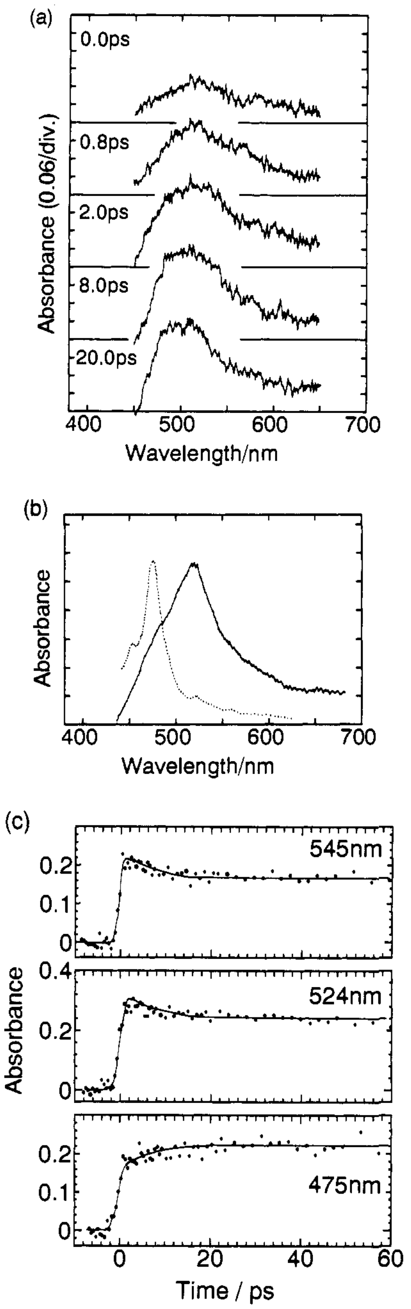

Figure 2. (a) Time-resolved transient absorption spectra of the AP–Pyr system in hexane solution excited with a 500-fs laser pulse at 355 nm: [AP] = 5 × 10^{-5} M; [Pyr] = 1 M. Delay times from the exciting laser pulse are indicated in the figure. (b) The absorption spectrum of the AP cation radical produced by γ radiolysis in a *sec*-butyl chloride matrix at 77 K (···)[16] and the $S_n \leftarrow S_1$ spectrum of AP in hexane solution (—)[16] for comparison with the time-resolved spectra in (a). (c) Time profiles of transient absorbances at 545, 524, and 475.

spectroscopy using a 22-ps pulse.[16] At still longer delay times, the transient absorption spectra showed single exponential decay with time constant τ_d = 235 ps and the spectral band shape was the same as that in the 10-ps region during the course of the decay.

The above results indicate that the time-dependent spectral change observed in the early stage, as shown in Figure 2a, represents the rapid forward and backward ET reactions between the LE state, (D^*–H···A), and the IP state, (D^+–H···A^-), leading to the formation of an equilibrium mixture of the two species, because their decay to the ground state is much slower compared with the ET reactions between them, as described already in the Introduction to some extent on the basis of our previous picosecond laser photolysis studies on 7DBC–Pyr and AP–Pyr systems.[15,16]

Table II. Values of τ_e^{-1} and τ_d^{-1} for AP–Pyr and AP–MePyr Hydrogen-Bonded Complexes in Hexane Determined by Time-Resolved Spectral Measurements and Values of the Energy Gap for the Photoinduced CS ($-\Delta G_{CS}$) and Those between the Electron-Transfer State and the Ground State ($-\Delta G_{IP}$) of the Complexes

quencher	τ_e^{-1} (s^{-1})	$\tau_{d,a}$ (s^{-1})[a]	$\tau_{d,f}^{-1}$ (s^{-1})[b]	$-\Delta G_{CS}$ (eV)	$-\Delta G_{IP}$ (eV)
Pyr	(2.0 ± 0.5) × 10^{11}	4.3 × 10^9	4.4 × 10^9	–0.94	4.07
2MePyr	(1.3 ± 0.2) × 10^{11}	1.8 × 10^9	2.4 × 10^9	–0.98	4.11
4MePyr	(1.0 ± 0.1) × 10^{11}	1.2 × 10^9	1.3 × 10^9	–1.04	4.17
DMePyr	(9.0 ± 2.0) × 10^{10}	1.0 × 10^9	1.1 × 10^9	–1.03	4.16
TMePyr	(8.0 ± 2.0) × 10^{10}	4.4 × 10^8	4.6 × 10^8	–1.09	4.22

[a] $\tau_{d,a}^{-1}$: determined by the time-resolved transient absorption spectral measurements on the equilibrium state. [b] $\tau_{d,f}^{-1}$: determined by the measurements of fluorescence decay curves of hydrogen-bonded complexes.

The dynamics of the equilibrium-state formation from the LE state of the hydrogen-bonded complex may be given approximately by the reaction scheme of eq 2 from the reasoning described above. From this scheme, [LE(t)] and [IP(t)] are given as shown in eqs 3 and 4, respectively, where $\tau_e = (k_1 + k_{-1})^{-1}$ and [LE(t)] + [IP(t)] = [LE(0)].

$$\mathrm{LE}(t) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{IP}(t) \tag{2}$$

$$[\mathrm{LE}(t)] = k_1\tau_e[\mathrm{LE}(0)]\{1 + (k_1/k_{-1}) \exp(-t/\tau_e)\} \tag{3}$$

$$[\mathrm{IP}(t)] = k_1\tau_e[\mathrm{LE}(0)]\{1 - \exp(-t/\tau_e)\} \tag{4}$$

The time profiles of the observed transient absorbances at 545, 524, and 475 nm are indicated in Figure 2c. On the basis of eqs 3 and 4, the transient absorbance $D_\lambda(t)$ at a wavelength λ may be given by eq 5, where ϵ_{LE}^λ and ϵ_{IP}^λ are respectively the molar

$$\begin{aligned} D_\lambda(t) &= \epsilon_{LE}^\lambda[\mathrm{LE}(t)] + \epsilon_{IP}^\lambda\,[\mathrm{IP}(t)] \\ &= \tau_e[\mathrm{LE}(0)]\{(k_{-1}\epsilon_{LE}^\lambda + k_1\epsilon_{IP}^\lambda) + \\ &\qquad k_1(\epsilon_{LE}^\lambda - \epsilon_{IP}^\lambda) \exp(-t/\tau_e)\} \end{aligned} \tag{5}$$

extinction coefficients of LE and IP states at wavelength λ. At $t = 0$, $D_\lambda(0) = \epsilon_{LE}^\lambda[\mathrm{LE}(0)]$ and, at a sufficiently long delay time, $D_\lambda(t)$converges to $D_\lambda(\infty) = \tau_e[\mathrm{LE}(0)](k_{-1}\epsilon_{LE}^\lambda + k_1\epsilon_{IP}^\lambda)$.

Observed time profiles show considerable instrument-limited absorbance rises before the decay or further rises converging to the formation of the equilibrium state. The fast rise of the absorbance can be ascribed to the LE state, (D^*–H···A), which has considerable absorbance at these wavelengths, as can be seen from the reference spectrum in Figure 2b. After the initial fast rise, the absorbance shows decay at 524 as well as 545 nm converging to the equilibrium-state absorbance $D_\lambda(\infty)$, which corresponds to the fact that $\epsilon_{LE}^\lambda > \epsilon_{IP}^\lambda$ at these wavelengths, while the absorbance at 475 nm shows a rise converging to the equilibrium value $D_{475}(\infty)$, which means that $\epsilon_{IP}^\lambda > \epsilon_{LE}^\lambda$ at 475 nm. The time constants τ_e obtained from these absorbance decay and rise profiles agree with each other in accordance with the prediction by eq 5 (see Table II for the τ_e values).

On the other hand, it is well-known that, when aromatic molecules in solution are excited to the electronic state with a significant amount of excess vibrational energy, broad absorption bands are observed immediately after the excitation, and the broad bands undergo sharpening and blue shifting in the course of the vibrational cooling on a 10-ps time scale according to many

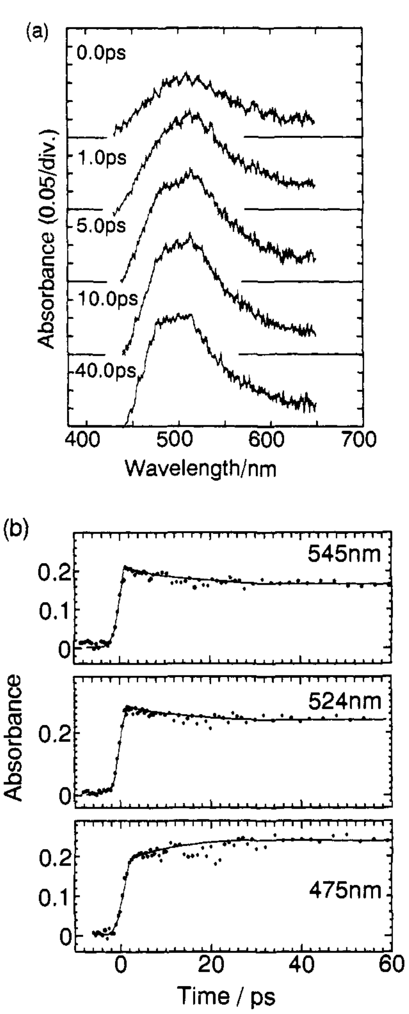

Figure 3. (a) Time-resolved transient absorption spectra of the AP–DMePyr system in hexane solution excited with a 500-fs laser pulse at 355 nm: [AP] = 5 × 10^{-5} M; [DMePyr] = 1 M. Delay times from the exciting laser pulse are indicated in the figure. (b) Time profiles of transient absorbances at 545, 524, and 475 nm.

investigations made so far.[20b,22] Therefore, it might be possible that such time-dependent modifications of the band shape and shift of the peak positions of the band due to the vibrational cooling affect considerably the analysis of the time profiles in the present study.

We have observed the absorbance decay not only at 545 nm but also at 524 nm near the peak position of the $S_n \leftarrow S_1$ band of AP where one might observe the absorbance rise due to the sharpening of the band or a quite different τ_e value from that at 545 nm if the vibrational cooling effect is significant. However, we have observed approximately the same value of the decay time constant τ_e at 524 and 545 nm and moreover it was the same as the rise time constant at 475 nm. These results indicate that vibrational cooling does not affect seriously the present results.

Similar time-resolved transient absorption spectra have been observed also in the case of the AP–MePyr systems in hexane solution. As an example, the results of the AP–DMePyr system are indicated in Figure 3. The absorbance decay has been observed both at 524 and 545 nm, and the time constants obtained at three different wavelengths agree with each other in accordance with eq 5. Therefore, the effect of vibrational cooling on the analysis of the absorbance time profiles seems to be small also in this case.

We can see that the time-dependent change of the spectral shape due to the electron transfer from the excited AP to DMePyr in the hydrogen-bonded pair seems to be a little slower compared with that of the AP–Pyr system. Actually, the time constant τ_e has been confirmed to be a little longer. It has been confirmed also that the transient absorption at longer delay times shows single exponential decay with time constant τ_d = 975 ps without changes of the spectral shape in the course of decay. Similar results have been obtained also for other AP–MePyr systems.

The values of $\tau_{d,a}^{-1}$ (obtained from the transient absorption measurement) as well as τ_e^{-1} are indicated in Table II together with the free energy gap for the photoinduced charge separation (CS) process between the LE and the IP states ($-\Delta G_{CS}$) as well as that between the IP and the ground states ($-\Delta G_{IP}$) for the charge recombination (CR) process.

Values of $-\Delta G_{CS}$ and $-\Delta G_{IP}$ in hexane solution have been estimated by means of eqs 6, 7, and 8, where ΔE_{00} is the S_1–S_0

$$-\Delta G_{CS} = \Delta G_{IP} + \Delta E_{00} \qquad (6)$$

$$-\Delta G_{IP} = E(\text{D–H}/\text{D}^+\text{–H}) - E(\text{A}^-/\text{A}) - e^2/\epsilon R + \Delta G_S \qquad (7)$$

$$\Delta G_S = (e^2/2)(1/R^+ + 1/R^-)(1/\epsilon - 1/\epsilon_r) \qquad (8)$$

energy gap of AP, $E(\text{D–H}/\text{D}^+\text{–H})$ and $E(\text{A}^-/\text{A})$ are the oxidation potential of AP[16] and reduction potentials of Pyr's[23] measured in polar solvents with dielectric constant ϵ_r, respectively, R is the center to center distance between the cation and anion, assumed to be 7 Å, and ΔG_S is the sum of the correction terms of the solvation energies calculated with the Born formula for the cation and anion with radii R^+ and R^-, respectively, in a solvent with dielectric constant ϵ.

Usually, $-\Delta G_{CS}$ values give a rough measure for the feasibility of electron transfer in the excited state. However, with such a large endothermicity ($-\Delta G_{CS} \sim -1$ eV) of reaction, as indicated in Table II, the rapid population of the ET state taking place with a time constant of several picoseconds–ca. 10 ps, as actually observed here, may be impossible from the viewpoint of the conventional electron-transfer theories in the condensed phase.[2] Presumably the present type of hydrogen-bonding interaction in the excited state will exert a large and specific effect on energetics and dynamics of electron transfer leading to almost zero or positive values of $-\Delta G_{CS}$, as mentioned already in the Introduction to some extent. A more detailed discussion on the photoinduced electron-transfer mechanism in this hydrogen-bonded system will be given later in this paper.

It should be noted here that, although the value of τ_e^{-1} increases a little with decrease of the endothermicity of the reaction, its order of magnitude does not change by this small change of the $-\Delta G_{CS}$ value. On the other hand, the rate constant τ_d^{-1} of the decay from the LE $\rightleftarrows$ IP equilibrium state to the ground state shows a much larger change for the same amount of small change in the energy gap $-\Delta G_{IP}$. In the case of $\tau_e^{-1} = k_1 + k_{-1}$, k_1 will increase but simultaneously k_{-1} will probably decrease a little with decrease of the endothermicity or increase of the exothermicity of the LE → IP process, leading to the rather small change of τ_e^{-1} with the change of $-\Delta G_{CS}$. Contrary to this, the decay from the equilibrium state to the ground state is a "one-way" reaction with a large energy gap leading to the much higher sensitivity of $\tau_{d,a}^{-1}$ to the change of the energy gap. A more detailed discussion on the mechanism of the energy gap dependence of $\tau_{d,a}^{-1}$ will be given in the next subsection.

Time-Resolved Fluorescence Studies. As described in the previous section concerning the ground-state absorption and stationary fluorescence spectra, at high concentrations of added Pyr and MePyr's (~1 M), where practically no fluorescence of

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(22) (a) Greene, B. I.; Hochstrasser, R. M.; Weiseman, R. B. *J. Chem. Phys.* **1979**, *71*, 544. (b) Anderson, R. W. *Picosecond Phenomena II*; Springer-Verlag: Berlin, 1980; p 163. (c) Elsaesser, T.; Kaiser, W. *Annu. Rev. Phys. Chem.* **1991**, *42*, 83. (d) Schultz, K. E.; Russell, D. J.; Harris, C. B. *J. Chem. Phys.* **1992**, *97*, 5431. (e) Miyasaka, H.; Hagihara, M.; Okada, T.; Mataga, N. *Chem. Phys. Lett.* **1992**, *188*, 259.

(23) Mietes, L.; Zuman, P. *Electrochemical Data*; John Wiley: New York, 1974; Part 1, Vol. 1.

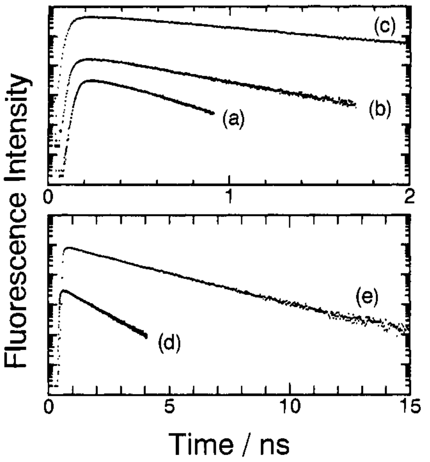
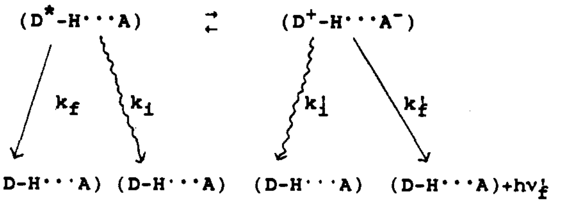


Figure 4. Decay curves of red-shifted fluorescence of AP–Pyr and –MePyr hydrogen-bonded complexes in hexane: (a) Pyr, (b) 2MePyr, (c) 4MePyr, (d) DMePyr, and (e) TMePyr. Concentrations of pyridines were 1 M.

free AP can be recognized, a weak and red-shifted broad fluorescence band of the hydrogen-bonded complexes can be observed in the 400–500 nm region. Although it is not clear whether this broad emission band involves contributions from the electron-transfer state (that is, the CT fluorescence) or not, it may be assigned to the $(D^*\text{–}H\cdots A) \rightleftarrows (D^+\text{–}H\cdots A^-)$ equilibrium state on the basis of the results and discussion in the previous subsection. In order to further confirm this, we have measured the decay curve of this emission band by the single-photon-counting method with a picosecond dye laser for excitation.

In Figure 4, we show the observed decay curves which can be well reproduced by a single exponential decay function, and the inverse of the obtained time constants $\tau_{d,f}^{-1}$ are collected in Table II together with the $-\Delta G_{IP}$ values. Evidently, the $\tau_{d,f}^{-1}$ values obtained by the fluorescence decay curve measurements agree satisfactorily with those determined by the time-resolved absorption measurements, which confirms the above assignment of the red-shifted fluorescence band to the $(D^*\text{–}H\cdots A) \rightleftarrows (D^+\text{–}H\cdots A^-)$ equilibrium state.

Four pathways as indicated in eq 9 may be possible for the deactivation process from this equilibrium state. One might suppose that there is another reaction pathway of the dissociation of the excited hydrogen-bonding complex. However, since almost all AP are hydrogen bonded with Pyr in the ground state and hydrogen-bonding interaction becomes stronger in the excited state, practically no such dissociation $(D^*\text{–}H\cdots A) \rightarrow D^*\text{–}H + A$ may take place. Actually no fluorescence of free AP can be detected in the present experimental conditions. The ionic dissociation, $(D\text{–}H^+\cdots A^-) \rightarrow D\text{–}H^+ + A^-$, is much more difficult than the dissociation of the neutral pair in nonpolar solution. Therefore the possible reaction pathways are limited to those indicated in eq 9.



(9)

Since the hydrogen-bonding interaction with a partner which does not have a conjugate π-electron system and is not capable of electron-transfer interaction does not affect significantly the deactivation process of the excited molecule as many previous results indicate,[10,15-17] $k_f + k_i$ may be close to that of D–H itself in the absence of acceptor. The observed fluorescence lifetime of AP in hexane is 12.5 ns, which is much longer than τ_d. Because the radiative transition probability k_f' from the IP state due to intermolecular electron transfer is usually small ($\leq 10^6\ s^{-1}$)[1], the τ_d value seems to be determined mainly by k_i'.

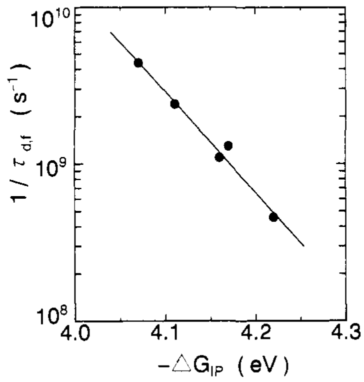


Figure 5. Dependence of $\log(\tau_{d,f}^{-1})$ on the energy gap $-\Delta G_{IP}$.

Although the energy gap $-\Delta G_{IP}$ between the IP state and the ground state as given in Table II is fairly large, the actual value of $-\Delta G_{IP}$ seems to be much smaller because the hydrogen-bonding interaction lowers the energy of the IP state formed by the electron transfer and, moreover, the electron transfer induces the shift of the proton in the hydrogen bond toward the acceptor, which stabilizes further the IP state and also will destabilize the ground state considerably, as will be discussed in detail in the next section. These effects of the hydrogen-bonding interaction decrease $-\Delta G_{IP}$, facilitating the nonradiative transition to the ground state. At any rate, results in Table II indicate that the rate of the nonradiative CR decay decreases with increase of the energy gap $-\Delta G_{IP}$, and $\log(\tau_{d,f}^{-1})$ is approximately proportional to $-\Delta G_{IP}$ as demonstrated in Figure 5. From the above arguments, the result in Figure 5 suggests the relation $\log(k_i') \propto -|\Delta G_{IP}|$, which is in accordance with the radiationless transition theory[24] or somewhat similar to the CR decay of the strongly interacting compact ion pairs.[8,9c,24c,d]

Mechanisms of Photoinduced Electron Transfer in Hydrogen-Bonded Systems in Nonpolar Solvent. From the above results and discussion, we can conclude that the AP–Pyr hydrogen-bonded systems in hexane solution undergo rapid photoinduced ET from AP to Pyr, converging to the formation of the $(D^*\text{–}H\cdots A) \rightleftarrows (D^+\text{–}H\cdots A^-)$ equilibrium state within ca. 10 ps. The free energy gap $-\Delta G_{CS}$ for the CS reaction $(D^*\text{–}H\cdots A) \rightarrow (D^+\text{–}H\cdots A^-)$ has been estimated to be ca. −1 eV by using the usual method. For the very rapid establishment of the equilibrium state between the LE and the IP states, $-\Delta G_{CS}$ should not be such a large negative value.

The present results indicate that the hydrogen-bonding interaction plays an important role in stabilizing the IP state, as we have qualitatively discussed already. Namely, the hydrogen-bonding interaction will decrease the ionization potential of AP and increase the electron affinity of the proton acceptor facilitating the ET from AP to Pyr. The important role of the hydrogen-bonding interaction in lowering the ionization potential of the proton donor has been actually confirmed by measuring the effect of the hydrogen-bonding interaction of DBC (dibenzocarbazole) with Pyr on its photoionization threshold in a low-temperature matrix.[25] It has been demonstrated that the hydrogen-bonding interaction lowers the ionization potential by ca. 0.8 eV. A quite similar result can be expected also in the case of the AP–Pyr system and, with increase of the electron affinity of pyridine by

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[24] (a) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145. (b) Freed, K. J.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272. (c) Meyer, J. T. *Prog. Inorg. Chem.* **1983**, *30*, 389. (d) Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850.

[25] Martin, M. M.; Grand, D.; Ikeda, N.; Okada, T.; Mataga, N. *J. Phys. Chem.* **1984**, *88*, 167.

the hydrogen-bonding interaction, the stabilization energy of the IP state due to the hydrogen-bonding interaction will amount to ca. 1 eV.

Moreover, the hydrogen-bonding interaction between AP and Pyr in the excited state is stronger than in the ground state due to the much larger extent of the intramolecular CT from the amino group to the pyrene ring. The larger extent of intramolecular CT leading to the increase of the acidity of N–H proton will make the proton in the hydrogen bond shift toward the acceptor, which will further accelerate the intramolecular CT of AP and lower the ionization potential of the π-electron system of AP and enhance the electron affinity of the π-electron system of Pyr due to the approach of the proton to the ring nitrogen. Owing to these effects, the energy gap $-\Delta G_{CS}$ in the excited state will become almost zero or positive to make the fast ET reaction possible, where the rapid proton movement seems to play a crucial role.

It should be noted here that the above interpretation on the mechanisms of the photoinduced ET between the directly hydrogen-bonded conjugate π-electronic chromophores seems to be supported by the results of ab initio MO CI studies[26] upon model systems such as aniline–Pyr and phenol–Pyr, which predict that one-electron transfer from D*–H to the hydrogen-bonded A takes place when the D–H proton is moved to the vicinity of the middle point between N···N or O···N. According to the results of this calculation, the position of the shifted proton where the ET takes place corresponds to the barrier maximum of the potential energy curve plotted against the proton shift. The calculations of the excited states were made mainly by taking into account all singly excited configurations, but the results of a more extensive CI calculation considering also doubly and triply excited configurations indicated the decrease of barrier height leading to the rapid electron transfer.

Of course, the behaviors of the actual hydrogen-bonding systems we are studying by ultrafast spectroscopy may not necessarily be the same as the results of this MO CI calculation. Although the geometrical structures of D–H and A molecules as well as the N···N or O···N distance were fixed in this calculation, some structural rearrangements such as the change of N···N and O···N distances, bond distances and angles in the D–H and A, and torsional motions around the single bond between the pyrene ring and the amino group, etc., coupled with the ET process and the proton movement might modify the shape of the potential energy surface further facilitating the ET process. Nevertheless, the main feature of the reaction mechanism that the photoinduced ET is greatly assisted by the hydrogen-bonding interaction and by the proton shift in the hydrogen bond will be analogous to the results of the above model.

In addition to the above results, the results of the calculation on the ground state of those hydrogen-bonded systems indicate that a large destabilization of the ground state takes place by the proton movement toward the ring nitrogen of pyridine, which facilitates the nonradiative deactivation from the IP state as discussed above qualitatively.

Relation of Photoinduced ET Reactions Facilitated by Proton Shifts in Hydrogen-Bonding Systems to Photoinduced Proton-Transfer Reactions. The above described mechanism of photoinduced ET and CR deactivation of the IP state coupled with a proton shift in the hydrogen-bonding systems seems to have a close relation with the photoinduced proton-transfer (PT) phenomena.[27] We give a brief discussion on this problem in the following.

It is well-known that such aromatic hydroxy compounds as 2-naphthol (NpOH)[28] or 1-pyrenol (PyOH)[29] hydrogen bonded with a relatively strong proton acceptor like an aliphatic amine can undergo quite easily photoinduced PT reactions, $(D^*\text{–H}\cdots A) \rightarrow (D^{-*}\cdots H\text{–}A^+)$, even in nonpolar or only slightly polar aprotic solvents. For example, ultrafast laser photolysis studies on PyOH–triethylamine (TEA) hydrogen-bonding systems in benzene and also several polar solvents showed that the photoinduced PT in these systems took place with time constant of ca. 1 ps.[29] This fast excited-state PT between the hydrogen-bonded proton donor and acceptor seems to be induced by the intramolecular CT from the n orbital of the hydroxy group to the π orbitals of the pyrene ring, which is enhanced considerably by photoexcitation, leading to the larger acidity of the O–H group in the excited state. This mechanism of photoinduced PT appears to be analogous to the shift of the proton from D*–H toward the hydrogen-bonded A, which we have assumed to facilitate greatly the electron transfer, $(D^*\text{–H}\cdots A) \rightarrow (D^+\text{–H}\cdots A^-)$, for the AP–Pyr system as discussed above.

However, aromatic amines such as 2-naphthylamine (NA)[10d] and AP[30] hydrogen bonded with TEA in nonpolar or slightly polar solvents do not show such an excited-state proton transfer as in the cases of NpOH–TEA and PyOH–TEA systems, but only a slight shift of the fluorescence band due to the hydrogen-bonding interaction, corresponding to the smaller acidity of the aromatic amine as a proton donor compared to that of the aromatic hydroxy compounds, even though the extent of the photoinduced CT from the n orbital of the substituent group to the aromatic hydrocarbon π orbitals in the former is larger than that in the latter.

In accord with this fact, complete PT coupled with the photoinduced CS (charge separation) due to the ET reaction does not take place in the AP–Pyr system in nonpolar solution because we can observe only the transient absorption spectrum due to the AP cation radical in the IP state $(D^+\text{–H}\cdots A^-)$ superposed on the $S_n \leftarrow S_1$ spectrum of AP in the LE state, $(D^*\text{–H}\cdots A)$, in the course of the ET reaction, $(D^*\text{–H}\cdots A) \rightarrow (D^+\text{–H}\cdots A^-)$, as well as in the equilibrium state. If complete PT takes place following ET, we should observe the formation of the neutral radical pair, $(D^+\text{–H}\cdots A^-) \rightarrow (D^\bullet\cdots H\text{–}A^\bullet)$, for which, however, no evidence was available in our previous study on the AP–Pyr system[16] as well as in the present investigation. Namely, the transient absorption spectra due to the equilibrium mixture of LE and IP states disappeared completely with the decay time of $\tau_{d,a}$ and no transient absorption spectra due to the dissociated neutral radicals were observed.

In view of the much higher feasibility of the aromatic hydroxy compound–aliphatic amine system for photoinduced PT compared with that of the aromatic amino compound–aliphatic amine system, it might be possible that the former system undergoes complete proton transfer coupled with photoinduced ET leading to the formation of the neutral radical pair. In this respect, it should be noted here that the results of the above described MO CI calculation on the photoinduced ET in the model of aniline–Pyr and phenol–Pyr hydrogen-bonded complexes indicate a little larger proton shift coupled with ET in the case of the phenol–Pyr system,[26] suggesting the above described possibility of the neutral radical pair formation. According to our recent femtosecond laser photolysis studies on PyOH–Pyr and PyOH–MePyr systems in nonpolar solutions,[19] however, neutral pyrenoxy radical

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(26) Tanaka, H.; Nishimoto, K. *J. Phys. Chem.* **1984**, *88*, 1052.

(27) For some papers of recent studies on photoinduced PT reactions, see e.g.: (a) Barbara, P. F., Trommsdorff, H. P., Eds. Spectroscopy and Dynamics of Elementary Proton Transfers in Polyatomic Systems. *Chem. Phys.* **1989**, *136*, 153–360. (b) Barbara, P. F., Nicol, M., El-Sayed, M. A., Eds. Michael Kasha Festschrift. *J. Phys. Chem.* **1991**, *95*, 10215–10524.

(28) (a) Mataga, N.; Kaifu, Y. *J. Chem. Phys.* **1962**, *36*, 2804. (b) Mataga, N.; Kawasaki, Y.; Torihashi, Y. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 358. (c) Mataga, N.; Kaifu, Y. *Mol. Phys.* **1963**, *7*, 137. (d) Mataga, N.; Kawasaki, Y.; Torihashi, Y. *Theor. Chim. Acta* **1964**, *2*, 168.

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(30) Miyasaka, H.; Kamada, K.; Mataga, N. Unpublished work.

formation cannot be observed but only the rapid decay of the LE state with a time constant of ca. 10 ps takes place. Presumably, immediately after the ET coupled with a moderate amount of proton shift, ultrafast large-scale proton movement toward the acceptor will take place in these systems, which induces a large destabilization of the ground state, resulting in an ultrafast nonradiative back ET transition to the ground state.[19]

It should be noted here that there are also well-known examples of such intramolecular photoinduced PT reactions as observed in the case of benzothiazole compounds[31] and 3-hydroxyflavone,[32] etc., where the PT process is much faster (with a time constant of ca. 100 fs) than that of PyOH–TEA system. In these cases, the intramolecular photoinduced PT from the hydroxy group to N or O of the acceptor group is greatly facilitated by the closely coupled rearrangements of electronic charge distribution, which take place quite readily through the conjugate π-electronic chromophores directly mediating between the proton donor and acceptor groups.

From the above discussions, one may conclude that photoinduced PT in hydrogen-bonding systems is facilitated by the shift or rearrangement of the electronic charge distribution in the conjugate π-electronic chromophore linked directly to the proton donor group in the case of intermolecular PT, while intramolecular PT is facilitated by the rearrangement or shift of electronic charge distribution in the conjugate π-electronic chromophores linked directly to both the proton donor and acceptor groups. On the other hand, the photoinduced ET in intermolecular hydrogen-bonding systems where both proton donor and acceptor have conjugate π-electronic systems directly coupled to the hydrogen bond is greatly assisted by the hydrogen-bonding interaction and by a little movement of proton toward the acceptor, which is induced by the shift or rearrangement of the electronic charge distribution caused by the photoexcitation.

In the case of the AP–Pyr system studied in the present work, photoinduced PT has a close connection with the mechanism which regulates photoinduced ET. Nevertheless, PT coupled with photoinduced ET does not occur but only a slight movement of proton toward the acceptor takes place, which greatly assists the ET process in the case of the AP–Pyr system. Contrary to this, immediately after the photoinduced ET taking place by the mechanism similar to that in the AP–Pyr system, a large scale proton shift toward the acceptor in the PyOH–Pyr hydrogen-bonding complex seems to occur, leading to the complete quenching of fluorescence by the ultrafast crossing from the ET state to the ground state. It must be noticed here, however, that mere photoinduced PT without an ET process cannot lead to such a complete quenching of fluorescence. The PyOH–TEA hydrogen-bonding system where no ET from the proton donor to the acceptor can take place undergoes adiabatic photoinduced PT, producing the fluorescent state ($PyO^{-*}\cdots H{-}N^{+}(C_2H_5)_3$).

Concluding Remarks. In this work, we have confirmed that the AP–Pyr and –MePyr hydrogen-bonded complexes in hexane solutions undergo photoinduced ET between the hydrogen-bonded donor (AP) and acceptor (pyridines) by directly observing with femtosecond–picosecond laser spectroscopy that the excitation is initially localized on AP (LE state) and rapid ET from excited AP to the hydrogen-bonded acceptor to form the IP state and converging to the equilibrium state, $(D^*{-}H\cdots A) \rightleftarrows (D^+{-}H\cdots A^-)$, takes place within ca. 5–10 ps. In these systems, however, no orientations of polar solvent coupled with the ET process are possible and the free energy gap $-\Delta G_{CS}$ for the LE → IP reaction estimated by the usual procedure for the outer-sphere electron-transfer reaction shows large negative values of ca. 1 eV.

In order to understand that, in spite of the large negative $-\Delta G_{CS}$ values, the rapid ET actually takes place, one must invoke a large specific effect of the hydrogen-bonding interaction in lowering the ionization potential of proton donor D–H and in enhancing the electron affinity of the proton acceptor A in these conjugate π-electronic donor–acceptor systems. On the basis of the present experimental results and some results of theoretical calculations,[26] we can conclude that the hydrogen-bonding interaction can stabilize the IP state, $(D^+{-}H\cdots A^-)$, by more than 1 eV and also that a little movement of the proton toward A in the S_1 state greatly facilitates the ET by lowering the energy of the IP state. It has been concluded also that this proton movement greatly destabilizes the ground state, facilitating the nonradiative deactivation of the LE $\rightleftarrows$ IP equilibrium state to the ground state through the IP state.

Thus, the mechanism of the photoinduced ET due to the strong donor–acceptor interaction in the hydrogen-bonded system studied here is quite different from the usual one due to the weak donor–acceptor interaction in polar solutions. The "proton switching" of electron transfer by a slight shift of the proton in the systems studied here will provide an interesting example of the new mechanisms of electron transfer reactions.

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