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ARTICLES

Molecular Mechanism of the Intermolecular Hydrogen Bond between 2-Piperidinoanthraquinone and Alcohol in the Excited State: Direct Observation of the Out-of-Plane Mode Interaction with Alcohol by Transient Absorption Studies

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Radiationless deactivation of 2-piperidinoanthraquinone (2PAQ) in its excited singlet state induced by an intermolecular hydrogen bond interaction was studied by picosecond and femtosecond transient absorption spectroscopy in benzene. On addition of alcohol, the transient absorption of excited 2PAQ exhibited a blue shift and was effectively quenched. Kinetic analyses of the transient decay obtained by experiments using a picosecond pulse compared well with those from dynamic fluorescence studies; the observed transient absorption was confirmed as being attributed to the excited singlet state of 2PAQ. Subpicosecond transient absorption experiments indicated that even at high concentrations of ethanol (1−3 M) in benzene the primary relaxation process was almost the same as that in neat benzene. A hydrogen-bonded excited state of 2PAQ, due to an out-of-plane mode interaction with ethanol, was successfully detected for the first time. Using detailed multicomponent analyses of the transient absorption, the spectra of both the out-of-plane mode species with λ_{max} at 570 nm and the in-plane mode species with λ_{max} at 550 nm were obtained.

1. Introduction

An excited molecule in its intramolecular charge transfer (ICT) excited state has a large dipole moment. The surrounding solvents reorientate themselves in response to the sudden change of the dipole moment to minimize the total energy of the system.[3] The solvation dynamics have been studied by analyzing the dynamic stokes shift of the fluorescence by using ultrafast time-resolved fluorescence spectroscopy.[4−10] Molecular dynamics have also been used as a powerful tool for such a study.[11−13]

Recently, transient absorption spectroscopy of the ultrafast vibrational relaxation in the electronic excited states has been reported by Kovalenko et al.[14,15] In the case of an aprotic solvent molecule, the solvent reorientation is mainly induced by a dipole−dipole interaction between the solvent molecule and the excited solute. Coumarin derivatives,[4−7] Resolfin,[8] and DCM[9] have been frequently used as probe molecules for studying the reorientation of the aprotic solvent. Because these dyes are sufficiently fluorescent and their fluorescence lifetimes are nearly insensitive to various solvents, no specific deactivation pathway is involved. On the other hand, the reorientational motion of a protic solvent is sometimes affected by a specific intermolecular hydrogen bond between the solvent molecules themselves. The electronic state of the solute is also influenced by an intermolecular hydrogen bond with the protic solvent.[16,17] Among the different types of solvent relaxational behavior, the reorientational motion of the solvent induced by a specific intermolecular interaction has attracted special attention from the viewpoint of the molecular processes involved in chemical reactions.

To understand the details of chemical reactions at the molecular level, solvent relaxation, the microscopic molecular motion of the solvent due to a specific solute−solvent interaction, is one of the key processes that needs to be studied. The microscopic relaxational motion of a solvent molecule should also govern how the vibrational energy is transferred from solute to solvent molecule and how the vibrational energy is dissipated in solution. The details of these processes are, however, not yet fully understood.

From these points of view, we have been studying radiationless deactivation of an electronically excited state induced by a specific solvation accompanying an intermolecular hydrogen-bonding interaction.[18−21] We have found that aminoanthraquinones (AAQ) and aminofluorenones (AF) having ICT excited states suffered substantial fluorescence quenching due to intermolecular hydrogen bonding in ethanol, thereby drastically reducing the fluorescence lifetimes.[18,19] The exposed contact area of the molecular surface of the hydroxyl hydrogen which is accessible to a third molecule has been shown to correlate well with the fluorescence quenching,[20] indicating that intermolecular hydrogen bonding plays a key role in the deactivation. The intramolecular charge transfer to the carbonyl group within the AAQ or AF molecules results in a sudden appearance of a negative charge on the carbonyl oxygen, and the hydroxyl group

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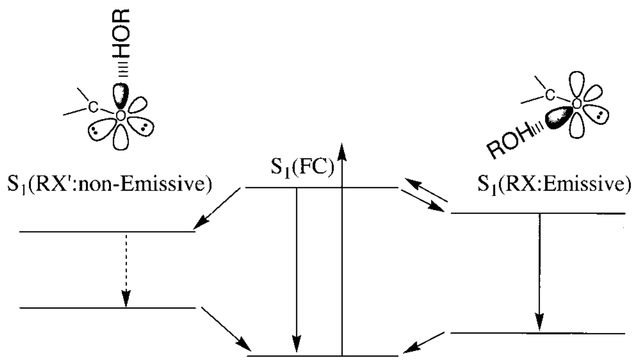
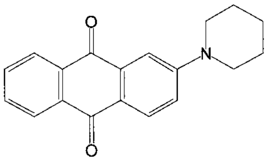


Figure 1. Simplified diagram of the relaxation processes corresponding to each hydrogen-bonding mode with alcohol.

of the alcohol clings to the carbonyl oxygen forming an intermolecular hydrogen bond which efficiently induces deactivation.

Detailed kinetic analyses of the fluorescence dynamic decay revealed that the intermolecular hydrogen bonding involved at least two species with different lifetimes. We proposed that the two modes of interaction are the following: (1) an in-plane mode; (2) an out-of-plane mode. Each is due to a specific interaction with a specific molecular orbital of the carbonyl oxygen: a p_y orbital in the former case and a $\pi^*(p_z)$ in the latter (Figure 1). The emissive relaxed state corresponding to the in-plane mode species could be definitely observed by time-resolved fluorescence spectroscopy, while the out-of-plane mode could not yet directly be detected due to its short lifetime and low emission yield. The direct detection of the out-of-plane mode species and the observation of its dynamic behavior would be very important for the understanding of the molecular mechanism involved with the energy dissipation.

In this paper, the direct detection of the nonemissive out-of-plane mode species of hydrogen-bonded 2-piperidinoanthraquinone (2PAQ) in the excited state and the observation of its dynamic behavior were attempted using transient absorption spectroscopy.



2PAQ

2. Experimental Section

2-Piperidinoanthraquinone (2PAQ) was purified as reported previously.[20] Ethanol and dry benzene were also prepared as reported. Ethanol-*O*-*d* (Aldrich, 99.5+% D) was used as received. The absorption spectra were recorded on a Shimadzu UV-2100PC spectrophotometer. To obtain the transient absorption spectrum, we used two laser photolysis systems.

For observation of the region from 1 to 20 ns, the third harmonic of a Nd^{3+}YAG laser (EKSPLA PL2143B; 355 nm, 25 ps fwhm) was used for excitation. A continuum probe light was generated by focusing the fundamental pulse of the Nd^{3+}-YAG laser onto a high-pressure Xe tube. The probe light was monitored by a streak camera (Hamamatsu, C4334) equipped with a polychrometer (CHROMEX 2501S). A single 1 ps pulse from a regenerative amplifier (PL2143B) was extracted by an InGaAs photodiode (Hamamatsu, G3476-05) and used as a pretrigger for the streak scope.

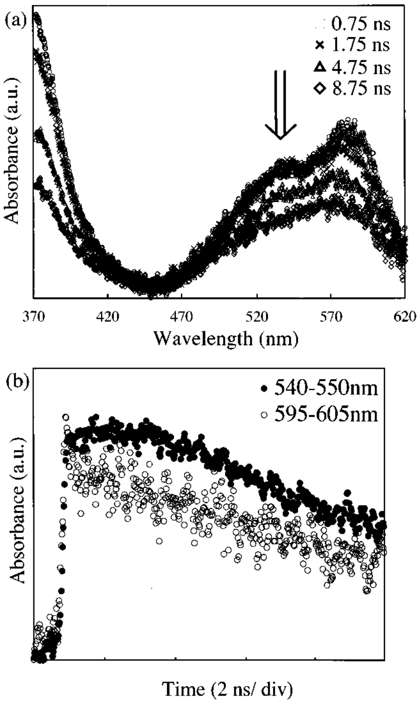


Figure 2. (a) Transient absorption spectra of 2PAQ in benzene with 0.02 M ethanol at 0.75, 1.75, 4.75, and 8.75 ns after excitation. The gate width is 0.5 ns. (b) Transient decay profiles at 540−550 nm (●) and 595−605 nm (○).

For the measurements in time regions shorter than 1 ns, a double-beam subpicosecond pump−probe method was adopted, the details of which were described elsewhere.[22,23] The delayed second harmonic of a Ti−sapphire laser (400 nm, 1 kHz) was used as the pumping light. Femtosecond supercontinuum pulses generated by the fundamental were used to probe the absorbance change in the 500−620 nm. After interaction with the sample, the supercontinuum probe pulses were recorded with a dual photodiode array. At the same time, supercontinuum pulses not passing through the sample were also detected for reference. Wavelength-dependent signals were obtained at every time step of 4 ps (200 ps/full scale), 0.96 ps (48 ps/full scale), and 0.24 ps (12 ps/full scale). Signals taken every 8 nm, between 500 and 620 nm, were averaged to obtain a decay profile. The instrument response function and time zero at each probe wavelength were estimated by optical Kerr effect cross correlation, in which neat *o*-dichlorobenzene was used as the active medium. The full width at half-maximum of the instrument response function was 0.55−0.65 ps. The decay profiles were not deconvoluted. The probe pulse energy was <80 nJ. The diameter of the pump and probe pulse at the sample position were 0.3 and 0.2 mm, respectively. No signal was detected in neat benzene without 2PAQ by the pico- and subpicosecond measurement conditions employed in this study.

3. Results and Discussion

3.1. Measurements Using Picosecond Pulses and Assignment of Transients. The transient absorption spectrum and the transient decay curve obtained upon excitation of 2PAQ in benzene including ethanol (0.02 M) using the third harmonic of a Nd^{3+}YAG picosecond laser pulse under an aerated condition are shown in Figure 2. At this ethanol concentration, formation of a ground-state hydrogen-bonded complex of 2PAQ with ethanol is negligible.[20] The transient decay is thus considered to reflect the dynamic process of the excited 2PAQ

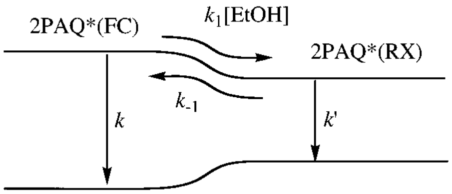


Figure 3. Two excited-states diagram including the original fluorescent state 2PAQ* and only one relaxed state 2PAQ*(RX). The rate constants k, k_1, k_{-1}, and k' denote the deactivation rate constant from 2PAQ* to the ground state, the forward relaxation rate constant from 2PAQ* to 2PAQ*(RX), the backward process from 2PAQ*(RX) to 2PAQ*, and the deactivation rate constant from 2PAQ*(RX) to the ground state, respectively.

in the solution. A rise and decay of the transient (470−570 nm) was observed in the shorter wavelength region, whereas only two component decays were observed in the longer wavelength region (580−620 nm), within the time delay of 10 ns (Figure 2b). These dynamic processes could not be observed in the absence of ethanol. The two-step process in the time range is understood as forming a hydrogen-bonded complex in the excited state from a Franck−Condon state of 2PAQ. Assuming only one relaxed state formed by the interaction with ethanol, the state diagram in Figure 3 was obtained, as reported previously.[20] Each rate constant can be estimated by a two-component analysis[24] of the transient decay in Figure 2b. Each concentration of the Franck−Condon state and the relaxed state of 2PAQ with ethanol are expressed by eqs 1 and 2, respectively.

$$[\text{2PAQ*(FC)}](t) = A\exp(-\lambda_1 t) + B\exp(-\lambda_2 t) \qquad (1)$$

$$[\text{2PAQ*(RX)}](t) = C\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \qquad (2)$$

$$\lambda_{2,1} = 0.5[k + k_1[\text{EtOH}] + k_{-1} + k' \mp \{(k + k_1[\text{EtOH}] - k_{-1} - k')^2 + 4k_{-1}k_1[\text{EtOH}]\}^{1/2}]$$

Here [2PAQ*(FC)] and [2PAQ*(RX)] denote the concentrations of the excited 2PAQ in the Franck−Condon state and the relaxed state with ethanol, respectively. k_1, k, k_{-1}, and k' are the corresponding rate constants in Figure 3. The preexponential terms $A-C$ are functions of the time constants, λ_1 and λ_2, and the concentration of ethanol. The sum and product of the time constants λ_1 and λ_2 are dependent on the ethanol concentration as expressed in eqs 3 and 4. The slope obtained from a plot of them affords the rate constants k_1 and k'.

$$\lambda_1 + \lambda_2 = k + k' + k_{-1} + k_1[\text{EtOH}] \qquad (3)$$

$$\lambda_1\lambda_2 = k(k_{-1} + k') + k'k_1[\text{EtOH}] \qquad (4)$$

The apparent Stern−Volmer constant in the steady-state fluorescence quenching experiment can be expressed as eq 5, assuming the relaxed state is almost nonemissive. The Stern−Volmer constant is written as in eq 6. The rate constant k_{-1} thus can be obtained from the relation of eq 6 and the rate constant k_q obtained from the steady-state fluorescence quenching experiment and the lifetime of the excited 2PAQ in benzene.

$$\Phi_0/\Phi = 1 + K_{SV}[\text{EtOH}] \qquad (5)$$

$$K_{SV} = k_q/k = k_1k'/k(k' + k_{-1}) \qquad (6)$$

The results obtained by the two-component fitting analyses of the transient absorption decay at 540−550 nm were compared with those estimated from the time-resolved fluorescence decay analyses in Table 1. Some contribution of T_n-T_1 absorption along with experimental error may be the reason for the small discrepancy.[25] The results in Table 1 clearly indicate that the transient absorption in Figure 2 is due to 2PAQ in its singlet excited state and its dynamic behavior reflects the relaxation process induced by its interaction with ethanol.

TABLE 1: Rate Constants of 2PAQ in the Two-state Model

method	k_1 (10^{10} M^{-1} s^{-1})[c]	k_1 (10^8 s^{-1})[d]	k (10^8 s^{-1})[e]
fluorescence[a]	1.2	9.6	5.3
transient abs[b]	1.1	5.2	3.3

[a] Reference 20. [b] Transient absorption decays of 2PAQ at 540−550 nm. [c]Determined from the slope of $\lambda_1 + \lambda_2$ vs [EtOH] plot. [d]Calculated from eq 6. [e]Determined from the slope of $\lambda_1\lambda_2$ vs [EtOH] plot.

3.2. Measurements in Neat Solvents Using Femtosecond Pulses: Specific and Nonspecific Solvation. ***Transient Absorption in Benzene.*** The transient absorption spectrum and its decay upon excitation of 2PAQ in benzene using the second harmonic (400 nm) of a femtosecond Ti−sapphire laser pulse are shown in Figure 4. A very fast rise (e.g. Figure 4b, opened circle) or decay (e.g. Figure 4b, closed circle) around 3.7 ps was observed at every wavelength. Maroncelli et al. reported that even a nonpolar solvent like benzene has very fast multiexponential relaxation time constants.[4,5] Of the reported ultrafast relaxations of benzene, the slowest one was observed in the present study due to the time step of 0.24 ps of the system.

Hydrogen-Bonded Complex between 2PAQ and Ethanol in the Ground State. 1-or 2-substituted anthraquinone derivatives are known to form ground-state hydrogen-bonded complexes with alcohols.[26] The UV−vis spectral change of 2PAQ in benzene upon addition of ethanol is shown in Figure 5. Very interestingly, the spectrum changed in two steps with increasing ethanol concentration: the absorption peak of 2PAQ at 460 nm first gradually shifted to the red, and then at much higher concentrations of ethanol (above 8.5 M) the peak shifted to the blue. The complex formation constant was estimated using the Benesi−Hildebrand treatment for the absorption intensity at 370 nm,[25] where ΔOD, ϵ_D, and ϵ_{D-A} denote the absorbance change at the observed wavelength and extinction coefficient of 2PAQ and the hydrogen-bonded complex, respectively. [2PAQ], [EtOH], and K_{eq} are concentrations of 2PAQ and ethanol and the complex formation constant, respectively.

$$\frac{1}{\Delta\text{OD}} = \frac{1}{(\epsilon_D - \epsilon_{D-A})[\text{2PAQ}]}\left(1 + \frac{1}{K_{eq}[\text{EtOH}]}\right) \qquad (7)$$

A linear plot was obtained for a concentration of ethanol below 6 M as shown in Figure 6a. This indicates that 2PAQ and ethanol form a 1:1 complex over that concentration range. The red shift of the spectrum of the hydrogen-bonded complex suggests that the excited state is more stabilized by complex formation than the ground state.

The hydrogen bonding of ethanol with aminoanthraquinones could involve three modes of interaction: (1) a donating hydrogen bond interaction with the carbonyl oxygen of 2PAQ; (2) a donating interaction with the amino nitrogen; (3) an accepting interaction with the amino hydrogen atoms. The third possibility can be excluded, because the 2PAQ has no amino hydrogen. The second possibility, the hydrogen bonding with the amino nitrogen, should induce a blue shift of the spectrum, which is supported by molecular orbital calculations. The red shift of the spectrum thus strongly supports the first possibility that hydrogen bonding of ethanol with the carbonyl oxygen of 2PAQ is involved.

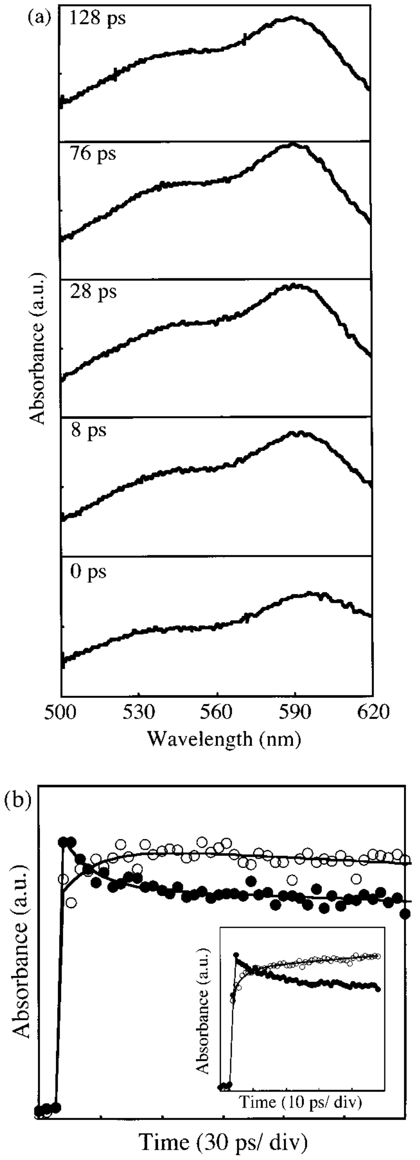


Figure 4. (a) Transient absorption spectra of 2PAQ in benzene at 0, 8, 28, 76, and 128 ps after excitation (400 nm, 4 ps time interval). (b) Transient absorption decay profile in benzene at 613−620 nm (●) and 501−509 nm (○). The inset shows the transient profile in the shorter time region (10 ps/div).

At higher concentrations of ethanol (above 6 M), the Benesi−Hildebrand plot drastically changed (Figure 6b). Although no definite conclusion can be made involving such a high concentration of ethanol due to the possible change in the polarity of the solvent from benzene and the self-aggregation of ethanol, 2PAQ may partly form a 1:2 complex with ethanol.

Transient Absorption in Ethanol. The transient absorption spectrum and its decay behavior in ethanol were drastically different from those in benzene as shown in Figure 7. Two kinds of solvent relaxation were observed in neat ethanol. A fast decay (1.9 ps) observed in the longer wavelength region of 613−620 nm corresponded well with a rapid rise (1.8 ps) in the 565−572 nm region. In the shorter wavelength region of 501−509 nm another slow rise (~30 ps) was distinctly observed. In the entire wavelength region, the decay of the transient with a time constant around 60 ps was also observed. The 60 ps decay coincides well with the fluorescence lifetime (60 ps) of 2PAQ in ethanol, indicating that the transient can be assigned as 2PAQ in its excited singlet state.

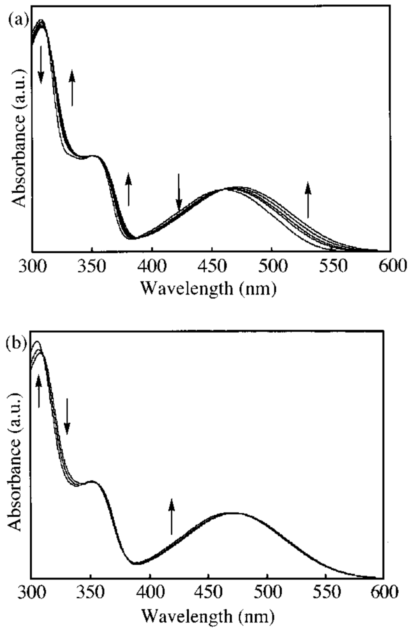


Figure 5. Changes in the UV−vis absorption of 2PAQ in benzene upon addition of ethanol: (a) [ethanol] = 0, 0.85, 1.7, 3.4, 6.4 M; (b) [ethanol] = 8.5, 13.6, 17.0 M (neat ethanol).

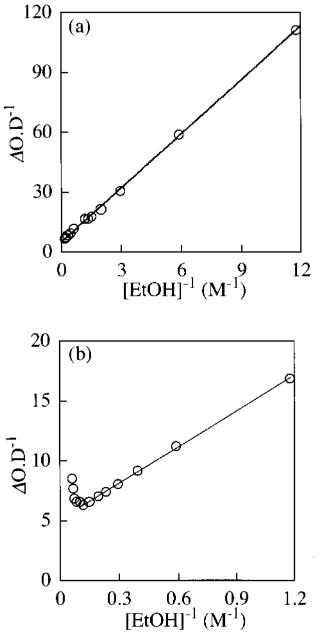


Figure 6. Benesi−Hildebrand plot of 2PAQ and ethanol in benzene: (a) a wide ranging ethanol concentration region ([EtOH] = 0.085−10.5 M); (b) a high ethanol concentration region ([EtOH] = 0.85−17 M).

The decay profile at all wavelengths was successfully analyzed by curve fitting, showing three time constants for two relaxations in the excited singlet state and one deactivation from the relaxed singlet state. The results are shown in Table 2. The two relaxation times obtained coincided well with those reported for Coumarin 153 by analyzing the time correlation function of a dynamic stokes shift.[4]

Alcohols have been reported to have three kinds of relaxation times corresponding to (1) a microscopic rotational motion of the OH group, (2) a unimolecular rotational diffusion, and (3) a rotational diffusion caused by cleavage of hydrogen bonds with other alcohols among clusters.[28] Yoshihara et al. reported that Coumarin 102 exhibited three relaxation times of 0.18, 1.96, and 15.36 ps for the time-resolved fluorescence dynamics in

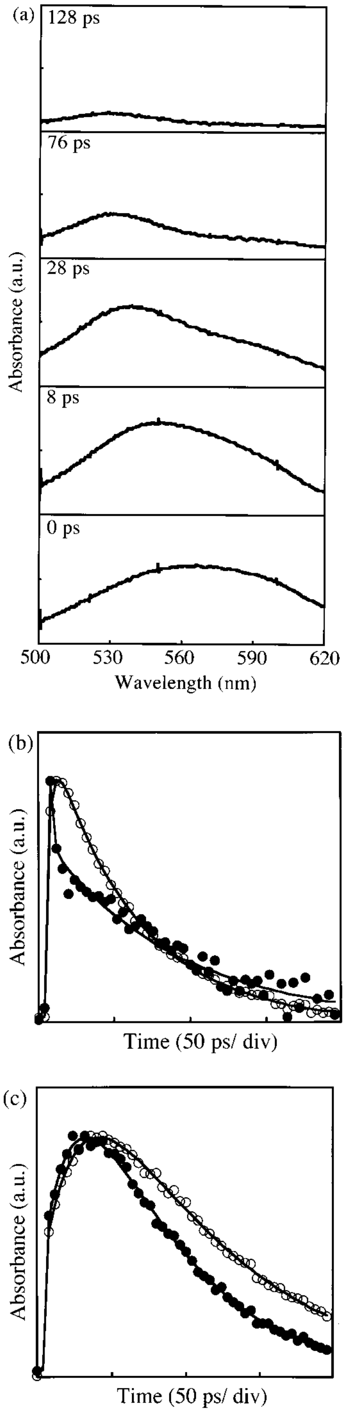


Figure 7. (a) Transient absorption spectra of 2PAQ in ethanol at 0, 8, 28, 76, and 128 ps after excitation (400 nm, 4 ps time interval). (b) Transient absorption decay profile in ethanol at 613−620 nm (●) and 557−564 nm (○). (c) Transient absorption decay profile at 501−509 nm in ethanol (●) and ethanol-*O-d* (○).

methanol.[27] They also observed a deuterium isotope effect of ca. 10% for the third relaxation time. The two relaxation times observed in the present study could thus correspond to the slower two relaxations involving a unimolecular rotational diffusion and a rotational diffusion caused by cleavage of hydrogen bonds with other alcohols among clusters.

The slower relaxation time (27 ps) exhibited a deuterium isotope effect of 10% as indicated in Table 2, corresponding well with the report by Yoshihara et al. The deactivation lifetime of the relaxed state of the excited 2PAQ also had a deuterium isotope effect (Table 2). Some anthraquinone derivatives have been reported to undergo proton transfer in their excited states.[30,31] Though to make a distinct discrimination between a proton transfer and a hydrogen bonding interaction is rather difficult, a proton transfer generally has a larger deuterium isotope effect. The effect on the deactivation of the excited 2PAQ is pretty small at a factor of 1.5 (Table 2). This strongly suggests that hydrogen bonding is actually involved in the deactivation of the excited 2PAQ as previously reported.[18]

TABLE 2: Relaxation Time and Lifetime of 2PAQ in Benzene and Ethanol

solvent	relaxation time (ps)		lifetime (ps)
benzene	3.7 ± 0.2[a]		c
ethanol	1.7 ± 0.3[a]	27[b]	60 ± 2[d]
ethanol-*O-d*	1.7 ± 0.3[a]	31[b]	90 ± 7[d]

[a] Averaged value of the analyzed relaxation time of the transient absorption decay profile at 10 wavelengths from 509 to 589 nm excited with a subpicosecond laser pulse (12 ps/full scale, not shown). [b] Analyzed relaxation time of transient decay at 501−509 nm (48 ps/full scale, not shown). [c]Lifetime is too long to be analyzed for this time scale. [d]Averaged value of the analyzed lifetime at 12 wavelength regions from 500 to 589 nm.

Transient Absorption of 2PAQ at High Concentrations of Ethanol in Benzene. At a low concentration of ethanol in benzene the excited 2PAQ relaxed to the hydrogen-bonded state and deactivation from the relaxed state had a moderate lifetime of 1.9 ns (5.3×10^8 s^{-1} in Table 1) as described above. On the other hand, in neat ethanol a much faster deactivation with a lifetime of 60 ps was confirmed, also by transient absorption decay. In the previous study by time-resolved fluorescence, the species having the longer lifetime (1.9 ns) was assigned as the in-plane mode hydrogen-bonded complex in the excited state and that with the shorter lifetime was presumed to be due to the out-of-plane mode species.[20] The out-of-plane mode species, however, has not been directly detected in benzene.

In ethanol, 2PAQ is surrounded by many ethanol molecules. Multiple ethanol molecules could thus interact with the excited 2PAQ to simultaneously form both the in-plane mode and the out-of-plane mode species. Such a doubly interacted species may have the short lifetime of the out-of-plane-mode one. That is, in ethanol the in-plane mode species with the longer lifetime would be “masked” by the short-lifetime species (out-of-plane-mode one) and therefore not be detected, while, at a low concentration of ethanol in benzene, the out-of-plane mode species again cannot be detected due to the deactivation of the species occurring faster than its formation (rate = [ethanol] × rate constant (diffusion controlled one as a maximum limit)). Detection of the out-of-plane mode species having the fast deactivation is thus expected to be possible by increasing the concentration of ethanol to shorten the rise time of formation of the species to less than 60 ps. The rise time would be ca. 100 ps for 1 M ethanol and ca. 30 ps for 3 M ethanol, because the rate constant for hydrogen-bonding formation between ethanol and the excited 2PAQ is estimated to be mostly diffusion controlled.[20] At 1 M ethanol the out-of-plane mode species may not be explicitly observed, but it could be detected at 3 M ethanol in benzene.

The purpose of the present study is to detect both the in-plane mode and the out-of-plane mode species in benzene and verify the previous assumptions. The transient absorption spectrum of 2PAQ was observed in benzene with high concentrations of ethanol (1 and 3 M). At high concentrations of ethanol 2PAQ forms mainly a 1:1 complex with ethanol as indicated by the straight line of the Benesi−Hildebrand plot below 6 M of ethanol in Figure 6; 38% and 64% of the ground-state 2PAQ

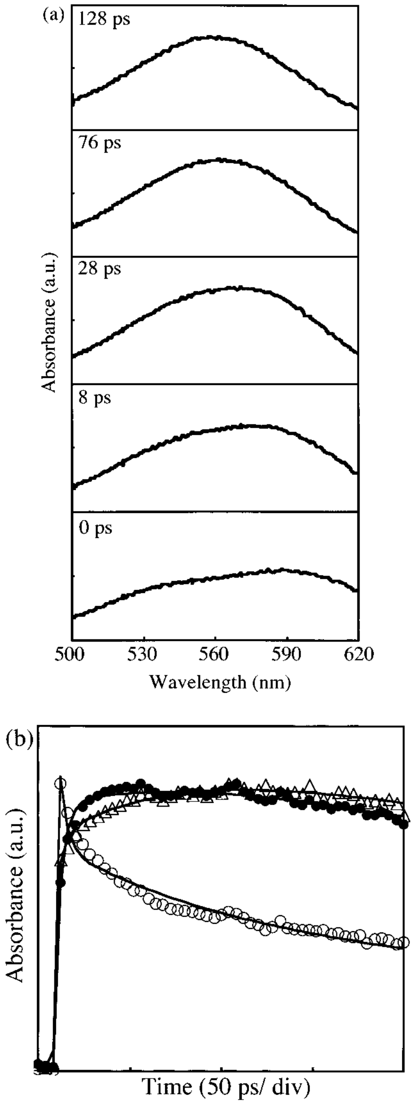


Figure 8. (a) Transient absorption spectra of 2PAQ in benzene with 1 M ethanol at 0, 8, 28, 76, and 128 ps after excitation (400 nm,4 ps time interval). (b) Transient absorption decay profile at 613−620 nm (○), 565−572 nm (●), and 501−509 nm (△).

formed the complex at ethanol concentrations of 1 and 3 M, respectively, because the formation constant is 0.6 M^{-1}.

The transient spectra and their decay profiles are shown in Figures 8 and 9. The spectral changes are very drastic. In the case of 1 M ethanol in benzene, the time-resolved transient absorption spectrum exhibited a rapid blue shift while losing the structure of the initial excited 2PAQ in the Franck−Condon state. The spectrum in the case of 3 M ethanol was already structureless, even immediately following the laser pulse. The decay profiles showed other interesting aspects. The rise profile at 501−509 nm within 12 ps after the laser pulse is shown in Figure 10. Very interestingly, the rise profiles of the signal immediately following the laser pulse were almost the same between those for neat benzene and benzene with ethanol (1 and 3 M). On the other hand, the rise was apparently different in neat ethanol. These observations strongly suggest that 2PAQ suffers the same primary solvent relaxation as that in benzene and is surrounded by benzene molecules even at rather high concentrations of ethanol. A hypothesis of diffusional collision between ethanol and 2PAQ should be valid in this case.

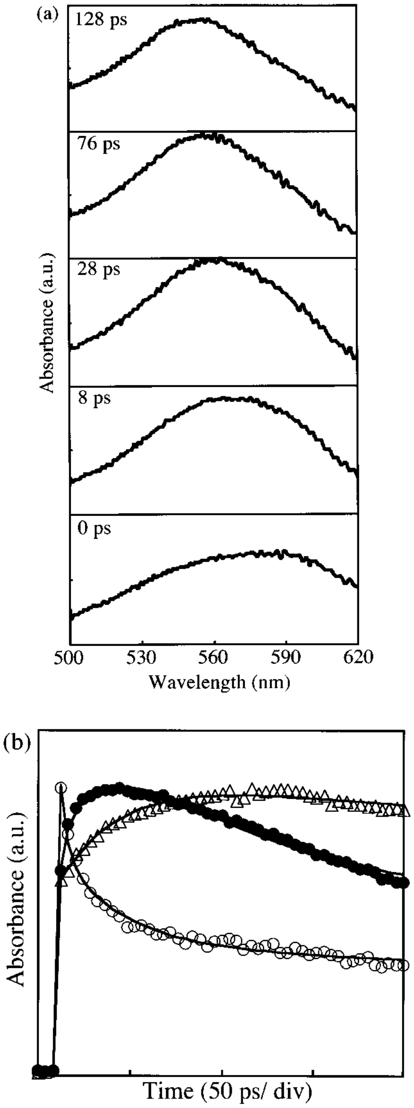


Figure 9. (a) Transient absorption spectra of 2PAQ in benzene with 3 M ethanol at 0, 8, 28, 76, and 128 ps after excitation (400 nm,4 ps time interval). (b) Transient absorption decay profile at 613−620 nm (○), 565−572 nm (●), and 501−509 nm (△).

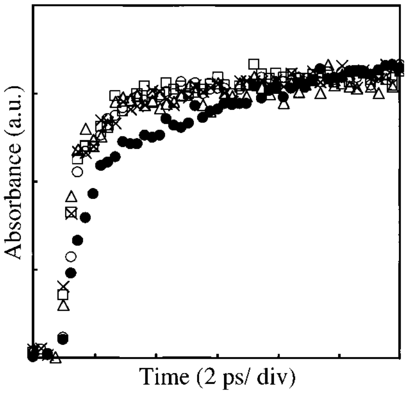


Figure 10. Rise profiles of 2PAQ in several solutions at short time intervals: (○) in neat benzene; (●) in neat ethanol; (□) in 0.5 M of ethanol in benzene; (△) in 1 M of ethanol in benzene; (×) in 3 M of ethanol in benzene.

In the longer wavelength region (613−620 nm) the slow decay profile (1.9 ns) observed after a delay time of ca. 80 ps, when the primary relaxation is already completed, did not depend on the concentration of ethanol (Figures 8 and 9). The decay profile at the transient signal (1.9 ns) in the shorter wavelength region (501−509 nm) in the same time region also

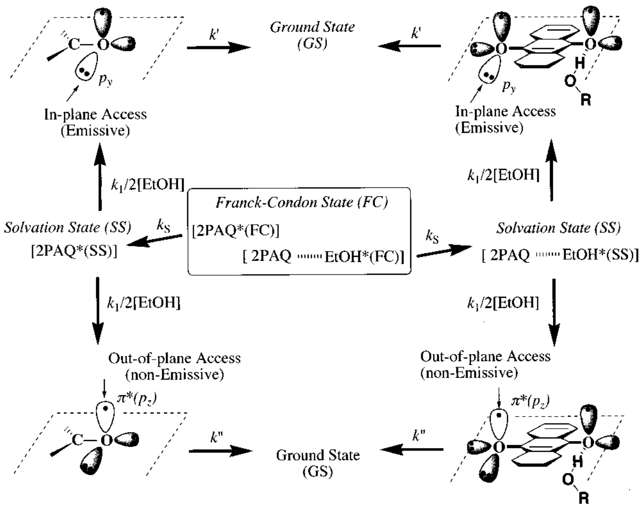


Figure 11. Simplified kinetic scheme proposed for the system in which both free 2PAQ and the 2PAQ−ethanol complex exist in the ground state. The rate constants k_S, k_1, k', and k'' denote the relaxation rate constant by solvent (benzene) obtained from Table 2, the diffusion-controlled rate constant by ethanol, the decay rate constant for in-plane mode interactions of the complex, and the decay rate constant for out-of-plane mode interactions of the complex.

seemed to be independent of ethanol concentration (Figures 8 and 9). These results indicate that the same species, having rather long lifetimes around 1.9 ns, are formed by interaction with 1 or 3 M ethanol and are observed at these wavelength regions. On the other hand, a very drastic effect related to ethanol concentration was observed in the region of 565−572 nm. A clear rise and decay profile was observed for 3 M ethanol (Figure 9b)! Such a profile was not so evident in the case of 1 M ethanol (Figure 8b), but the tendency was apparently observed.

These results clearly indicate that a species with a short lifetime should exist in this region (565−572 nm). By increase of the concentration of ethanol, an out-of-plane mode species with a shorter lifetime than the in-plane mode species (1.9 ns) was successfully detected in the region of 565−572 nm as expected! As hypothesized previously, the relaxation processes in Figure 11 can be depicted as two species having different modes of interaction with 2PAQ. One of the two species is the in-plane mode species having a longer lifetime, which has a hydrogen-bonding interaction on the p_y orbital of the carbonyl oxygen of 2PAQ, the same as the ground state hydrogen-bonded complex. The other one is possibly the out-of-plane mode species which interacts on the $\pi^*(p_z)$ orbital and only exists in the excited state.

To simplify the analysis without losing the essential points, the following assumptions were adopted: (1) The out-of-plane mode species derived from both the unimolecular 2PAQ (2PAQ*(out-of-plane)) and the hydrogen-bonded complex of 2PAQ in the ground state with the in-plane mode species (2PAQ*−EtOH(out-of-plane)) all have the same lifetimes. (2) The in-plane mode species formed from both the unimolecular 2PAQ (2PAQ*(in-plane)) and the hydrogen-bonded complex of 2PAQ in the ground state with the in-plane mode species (2PAQ*−EtOH(in-plane)) also have the same lifetimes.

The decay profiles at every wavelength were computer-fitted for four components assuming that (1) the rate constant of the ethanol interaction with the excited 2PAQ is diffusion controlled, (2) the deactivation lifetime of all of the out-of-plane mode species is 60 ps, which is the fluorescence lifetime in ethanol, (3) the lifetime of all of the in-plane mode species is 1890 ps, as adopted in Table 1, and (4) the primary solvent relaxation time immediately following the laser pulse is that in benzene (3.7 ps). Reasonably good fits (correlation coefficient = 0.95−0.99) using four preexponential parameters for the four component decay were obtained for the entire wavelength region (500−612 nm).

Upon excitation of the free 2PAQ and the hydrogen-bonded 2PAQ in the ground state having an in-plane mode, the excited molecule would undergo the processes depicted as follows:

$$\text{2PAQ*(FC)} \xrightarrow{k_s} \text{2PAQ*(SS)} \tag{8}$$

$$\text{2PAQ*−EtOH(FC)} \xrightarrow{k_s} \text{2PAQ*−EtOH(SS)} \tag{9}$$

$$\text{2PAQ*(SS)} \xrightarrow{\alpha k_1[\text{EtOH}]} \text{2PAQ*(in-plane)} \tag{10}$$

$$\text{2PAQ*(SS)} \xrightarrow{\beta k_1[\text{EtOH}]} \text{2PAQ*(out-of-plane)} \tag{11}$$

$$\text{2PAQ*−EtOH(SS)} \xrightarrow{\alpha k_1[\text{EtOH}]} \text{2PAQ*−EtOH(in-plane)} \tag{12}$$

$$\text{2PAQ*−EtOH(SS)} \xrightarrow{\beta k_1[\text{EtOH}]} \text{2PAQ*(out-of-plane)} \tag{13}$$

$$\text{2PAQ*(in-plane)} \xrightarrow{k'} \text{2PAQ(GS)} \tag{14}$$

$$\text{2PAQ*(out-of-plane)} \xrightarrow{k''} \text{2PAQ(GS)} \tag{15}$$

$$\text{2PAQ*−EtOH(in-plane)} \xrightarrow{k'} \text{2PAQ(GS)} \tag{16}$$

$$\text{2PAQ*−EtOH(out-of-plane)} \xrightarrow{k''} \text{2PAQ(GS)} \tag{17}$$

Here k_S, αk_1, βk_1, k', and k'' denote the rate constants for solvent relaxation in benzene, interaction with ethanol to form the relaxed hydrogen-bonded complex with in-plane mode in the excited state, one with the out-of-plane mode, deactivation of the in-plane mode species, and deactivation of the out-of-plane mode species, respectively. $\alpha + \beta = 1$. Assuming that ethanol forms the in-plane mode species and out-of-plane one in equal opportunity, $\alpha = \beta = 0.5$. The concentration of each species can then be written as the following:

$$[\text{2PAQ*(FC)}] = [\text{2PAQ*(FC)}]_0 \exp(-k_s t) \tag{18}$$

$$[\text{2PAQ*−EtOH(FC)}] = [\text{2PAQ*−EtOH(FC)}]_0 \exp(-k_s t) \tag{19}$$

$$[\text{2PAQ*(SS)}] = \frac{k_s[\text{2PAQ*(FC)}]_0}{k_1[\text{EtOH}] - k_s}(\exp(-k_s t) - \exp(-k_1[\text{EtOH}]t)) \tag{20}$$

$$[\text{2PAQ*−EtOH(SS)}] = \frac{k_s[\text{2PAQ*−EtOH(FC)}]_0}{k_1[\text{EtOH}] - k_s}(\exp(-k_s t) - \exp(-k_1[\text{EtOH}]t)) \tag{21}$$

$$\begin{aligned}[\text{2PAQ*(in-plane)}] = {} & \frac{k_s k_1[\text{EtOH}][\text{2PAQ*(FC)}]_0}{2(k' - k_s)(k_1[\text{EtOH}] - k_s)} \exp(-k_s t) \\ & - \frac{k_s k_1[\text{EtOH}][\text{2PAQ*(FC)}]_0}{2(k' - k_1[\text{EtOH}])(k_1[\text{EtOH}] - k_s)} \exp(-k_1[\text{EtOH}]t) \\ & + \frac{k_s k_1[\text{EtOH}][\text{2PAQ*(FC)}]_0}{2(k' - k_s)(k' - k_1[\text{EtOH}])} \exp(-k't)\end{aligned} \tag{22}$$

$$[\text{2PAQ*(out-of-plane)}] = \frac{k_s k_1[\text{EtOH}][\text{2PAQ*(FC)}]_0}{2(k'' - k_s)(k_1[\text{EtOH}] - k_s)} \exp(-k_s t) - \frac{k_s k_1[\text{EtOH}][\text{2PAQ*(FC)}]_0}{2(k'' - k_1[\text{EtOH}])(k_1[\text{EtOH}] - k_s)} \exp(-k_1[\text{EtOH}]t) + \frac{k_s k_1[\text{EtOH}][\text{2PAQ*(FC)}]_0}{2(k'' - k_s)(k'' - k_1[\text{EtOH}])} \exp(-k'' t) \quad (23)$$

$$[\text{2PAQ*}-\text{EtOH(in-plane)}] = \frac{k_s k_1[\text{EtOH}][\text{2PAQ*}-\text{EtOH(FC)}]_0}{2(k' - k_s)(k_1[\text{EtOH}] - k_s)} \exp(-k_s t) - \frac{k_s k_1[\text{EtOH}][\text{2PAQ*}-\text{EtOH(FC)}]_0}{2(k' - k_1[\text{EtOH}])(k_1[\text{EtOH}] - k_s)} \exp(-k_1[\text{EtOH}]t) + \frac{k_s k_1[\text{EtOH}][\text{2PAQ*}-\text{EtOH(FC)}]_0}{2(k' - k_s)(k' - k_1[\text{EtOH}])} \exp(-k' t) \quad (24)$$

$$[\text{2PAQ*}-\text{EtOH(out-of-plane)}] = \frac{k_s k_1[\text{EtOH}][\text{2PAQ*}-\text{EtOH(FC)}]_0}{2(k'' - k_s)(k_1[\text{EtOH}] - k_s)} \exp(-k_s t) - \frac{k_s k_1[\text{EtOH}][\text{2PAQ*}-\text{EtOH(FC)}]_0}{2(k'' - k_1[\text{EtOH}])(k_1[\text{EtOH}] - k_s)} \exp(-k_1[\text{EtOH}]t) + \frac{k_s k_1[\text{EtOH}][\text{2PAQ*}-\text{EtOH(FC)}]_0}{2(k'' - k_s)(k'' - k_1[\text{EtOH}])} \exp(-k'' t) \quad (25)$$

Here, $[\text{2PAQ*(FC)}]_0$ and $[\text{2PAQ-EtOH*(FC)}]_0$ are the concentrations of free 2PAQ and hydrogen-bonded 2PAQ in the ground state at time zero, respectively. The observed transient absorption can be expressed as eq 26:

$$\begin{aligned}
\Delta\text{OD} = {} & \epsilon_a[\text{2PAQ(FC)}] + \epsilon_b[\text{2PAQ*(SS)}] + \epsilon_c[\text{2PAQ*(in-plane)}] + \epsilon_d[\text{2PAQ*(out-of-plane)}] + \epsilon_e[\text{2PAQ*}-\text{EtOH(FC)}] + \\
& \epsilon_f[\text{2PAQ*}-\text{EtOH(SS)}] + \epsilon_g[\text{2PAQ*}-\text{EtOH(in-plane)}] + \epsilon_h[\text{2PAQ*}-\text{EtOH(out-of-plane)}] \\
= {} & \left[\begin{array}{l} \epsilon_a[\text{2PAQ*(FC)}]_0 + \epsilon_e[\text{2PAQ*} - \text{EtOH(FC)}]_0 \\ + \dfrac{k_s(\epsilon_b[\text{2PAQ*(FC)}]_0 + \epsilon_f[\text{2PAQ*}-\text{EtOH(FC)}]_0)}{k_1[\text{EtOH}] - k_s} \\ + \dfrac{k_s k_1[\text{EtOH}](\epsilon_c[\text{2PAQ*(FC)}]_0 + \epsilon_g[\text{2PAQ*}-\text{EtOH(FC)}]_0)}{2(k' - k_s)(k_1[\text{EtOH}] - k_s)} \\ + \dfrac{k_s k_1[\text{EtOH}](\epsilon_d[\text{2PAQ*(FC)}]_0 + \epsilon_h[\text{2PAQ*}-\text{EtOH(FC)}]_0)}{2(k'' - k_s)(k_1[\text{EtOH}] - k_s)} \end{array}\right] \exp(-k_s\text{t}) \\
& - \left[\begin{array}{l} \dfrac{k_s(\epsilon_b[\text{2PAQ*(FC)}]_0 + \epsilon_f[\text{2PAQ*-EtOH(FC)}]_0)}{k_1[\text{EtOH}] - k_s} \\ + \dfrac{k_s k_1[\text{EtOH}](\epsilon_c[\text{2PAQ*(FC)}]_0 + \epsilon_g[\text{2PAQ*}-\text{EtOH(FC)}]_0)}{2(k' - k_1[\text{EtOH}])(k_1[\text{EtOH}] - k_s)} \\ + \dfrac{k_s k_1[\text{EtOH}](\epsilon_d[\text{2PAQ*(FC)}]_0 + \epsilon_h[\text{2PAQ*}-\text{EtOH(FC)}]_0)}{2(k'' - k_1[\text{EtOH}])(k_1[\text{EtOH}] - k_s)} \end{array}\right] \exp(-k_1[\text{EtOH}]\text{t}) \\
& + \left[\frac{k_s k_1[\text{EtOH}](\epsilon_c[\text{2PAQ*(FC)}]_0 + \epsilon_g[\text{2PAQ*}-\text{EtOH(FC)}]_0)}{2(k' - k_s)(k_1[\text{EtOH}] - k_s)}\right] \exp(-k' t) \\
& + \left[\frac{k_s k_1[\text{EtOH}](\epsilon_d[\text{2PAQ*(FC)}]_0 + \epsilon_h[\text{2PAQ*}-\text{EtOH(FC)}]_0)}{2(k'' - k_s)(k_1[\text{EtOH}] - k_s)}\right] \exp(-k'' t) \quad (26)
\end{aligned}$$

Here ϵ_a–ϵ_h denote the extinction coefficients for each species.

A curve fit for a decay profile involving four components has eight parameters and thus might involve substantial error. To reduce the number of free parameters, the four different time constants for each species were carefully determined by experiment as described above. The rest of the parameters, the four preexponential terms in eq 26, were taken as free parameters during the curve fitting. To obtain reference spectra for the in-plane and out-of-plane mode species, the following assumptions were also adopted: (1) all of the in-plane mode species had the same spectrum ($\epsilon_c = \epsilon_g$) as did all of the out-of-plane species ($\epsilon_d = \epsilon_h$); (2) the spectral change due to the primary solvent relaxation of benzene was negligible ($\epsilon_a = \epsilon_b$).

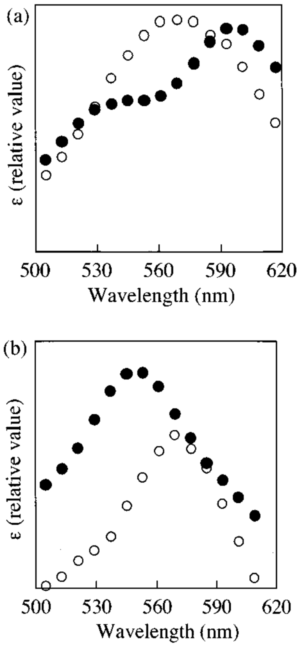


Figure 12. (a) Extinction coefficients for the two Franck−Condon states at 14 wavelengths (500−620 nm) obtained from kinetic analysis: (●) free 2PAQ* obtained from the transient absorption spectra in benzene; (○) 2PAQ*−EtOH calculated using eq 27 (see text). (b) Extinction coefficients at 14 wavelengths (500−620 nm) obtained from kinetic analysis (eq 26): (●) in-plane mode species; (○) out-of-plane mode species.

At first, the reference spectrum, ϵ_e, of the Franck−Condon excited state of the hydrogen-bonded complex (2PAQ−EtOH*(FC)) was estimated. The ratio of the extinction coefficients at the excitation wavelength (400 nm) for the free 2PAQ to the hydrogen-bonded 2PAQ at 3 M ethanol was estimated to be 17:20. Thus, the initial concentration ratio of the free 2PAQ in the Franck−Condon state ($[\text{2PAQ*(FC)}]_0$) to the Franck−Condon excited hydrogen-bonded complex ($[\text{2PAQ*-EtOH(FC)}]_0$) can be calculated to be 32:68, using the ground-state hydrogen complex formation constant, K_{eq}, and [EtOH]. The transient absorption for $t = 0$ for 3 M ethanol in benzene can be expressed as eq 27, where $[\text{2PAQ*(FC)}]_0$ and $[\text{2PAQ*}-\text{EtOH(FC)}]_0$ denote the initial concentrations of the excited free 2PAQ in the Franck−Condon state and the Franck−Condon excited hydrogen-bonded complex having an in-plane mode, respectively.

$$A(0, \lambda) = \epsilon_a[\text{2PAQ*(FC)}]_0 + \epsilon_e[\text{2PAQ*}-\text{EtOH(FC)}]_0 \quad (27)$$

The relative extinction coefficient ϵ_a can be taken as the transient absorption spectrum at $t = 0$ in benzene. Using eq 27, the estimated ϵ_a, and the ratio of the two Franck−Condon states concentrations, the extinction coefficient ϵ_e of the Franck−Condon excited hydrogen-bonded complex (2PAQ*−EtOH) was calculated as shown in Figure 12a. The spectrum is very similar to the transient spectrum at $t = 0$ in ethanol. This seems quite reasonable, because almost all of the ground-state 2PAQ forms a 1:1 hydrogen-bonded complex in ethanol.

The reference spectra of the in-plane mode species (ϵ_c) and the out-of-plane species (ϵ_d) were thus determined using the preexponential factors derived from eq 26, following the assumptions described above. The two reference spectra are shown in Figure 12b. The in-plane mode species has a spectrum very similar to that of the transient spectrum observed in the time region greater than 140 ps for 3 M ethanol in benzene as indicated in Figure 9. This strongly supports the validity of the results obtained in the kinetic analysis and seems quite reasonable, because in the time region greater than 140 ps the out-of-plane mode species should have already disappeared, leaving only the in-plane species. The blue shifts seen in spectra of both the hydrogen-bonded species in the excited state and the Franck−Condon state could be explained by stabilization of those states by the hydrogen bonding. The $\lambda_{\max}$ of the spectra follow the order Franck−Condon state > out-of-plane mode species > in-plane mode species. The order is also in accord with the drastic blue shift seen in the actual transient spectrum, because the out-of-plane mode species with the short lifetime and moderate blue shift disappears faster leaving the in-plane mode species dominant in the shortest wavelength region.

One may ask the simple question why does the out-of-plane mode species deactivate faster than the in-plane mode one? One possible explanation might be a difference in the vibrational mode involved in the intermolecular hydrogen bond and radiationless deactivation. From the viewpoint of a radiationless transition from the S_1 level of 2PAQ, the hydrogen-bonded relaxed state should be the initial state for the transition. A bending motion of the carbonyl would effectively couple with the out-of-plane type intermolecular hydrogen bond resulting in a large energy dissipation. The bending mode in this case could be called a promoting mode with the hydrogen bond being an accepting mode in the radiationless transition. On the other hand, the in-plane mode type intermolecular hydrogen bond may not be able to couple with the bending motion or even a stretching mode of the carbonyl. These hypotheses are expected to be verified in future studies using a detailed vibrational analysis of the excited hydrogen-bonded species and time-resolved Raman spectroscopy.

One further question is whether the two species with different modes of interaction interconvert with each other in the excited state. The out-of-plane mode species and the in-plane mode species are configuration isomers, and they should be interconvertible with each other. The experimental results, however, clearly indicate that the two species can be separately detected as described above. Furthermore, any temperature effect on the fluorescence deactivation from in-plane mode species was not observed in the temperature range 284−320 K. This means that the rate of interconversion is sufficiently slow enough to allow deactivation from each species. A theoretical calculation using PM3 indicates that the two species are stabilized by ca. 5 kcal/mol compared to free 2PAQ* by intermolecular hydrogen bonding with ethanol and that appreciable activation energy exists for the interconversion.[32]

Though very interesting and suggestive results were obtained in this study, some questions still remain for 2PAQ due to problems involving the presence of the two carbonyls within the molecule. A model molecule having only one carbonyl, such as an aminofluorenone derivative, would be promising for elucidating the molecular mechanism involved in deactivation through a specific solvation by an intermolecular hydrogen-bonding interaction. We have already studied the photophysical characteristics of aminofluorenones by time-resolved fluorescence spectroscopy and have reported results very similar to those for AAQ.[19,21] A transient absorption study of aminofluorenones is now in progress.

4. Conclusions

The relaxation process of an excited 2-piperidinoanthraquinone with ethanol has been studied by picosecond and femtosecond transient absorption spectroscopy. A hydrogen-bonded species with an out-of-plane mode interaction, which had been postulated but not previously directly detected by a time-resolved fluorescence spectroscopy, was successfully detected for the first time. The reference spectra for four species were determined: (1) the Franck−Condon excited state of 2PAQ; (2) the Franck−Condon excited state of hydrogen-bonded 2PAQ; (3) the excited hydrogen-bonded complex of 2PAQ and ethanol with out-of-plane mode interaction; (4) the excited hydrogen-bonded complex of 2PAQ and ethanol with in-plane mode interaction.

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References and Notes

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