(Faculty of Engineering) and Dr. J. Sato (Ejima Laboratory, Faculty of Engineering, Tohoku University) for the loan of the crystalline $AlCl_3$. The atomic absorption spectrochemical analysis for Al in the BPCl + $AlCl_3$ mixtures was carried out by the helpful advice of T. Tanaka (Department of Chemistry, Faculty of Science). This work was supported in part by a Grant-in-Aid for Scientic Research No. 58540242 from the Ministry of Education, Science and Culture, Japan.

Appendix

$R_{1,A}$ is the spin–lattice relaxation rate in the presence of chemical exchange from A to B. It is given as follows:

$$R_{1,A} = \frac{D \pm E^{1/2}}{2} \qquad \text{(A1)}$$

where

$$D = R_{1,A}^* + R_{1,B}^* + \frac{1}{\tau_A} + \frac{1}{\tau_B} \qquad \text{(A2)}$$

and

$$E = (R_{1,A}^* - R_{1,B}^*)^2 + \frac{4}{\tau_A \tau_B} \qquad \text{(A3)}$$

Under the condition that the probability for spin transfer from site A to B (or B to A), W°_{AB} (or W°_{BA}), is equal to zero, $R_{1,A}$ is equal to $R_{1,A}^*$. Because of this reason, if $R_{1,A}^*$ is larger than $R_{1,B}^*$, $R_{1,A}$ is given as $(D + E^{1/2})/2$. The other way, if $R_{1,B}^*$ is larger than $R_{1,A}^*$, $R_{1,A}$ is given as $(D - E^{1/2})/2$.

Registry No. Al, 7429-90-5; $AlCl_3$, 7446-70-0; BPCl, 1124-64-7.

Transient Absorption and Two-Step Laser Excitation Fluorescence Studies of the Excited-State Proton Transfer and Relaxation in the Methanol Solution of 7-Hydroxyflavone

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Contribution from the Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan. *Received December 19, 1983*

Abstract: The methanol solution of 7-hydroxyflavone (7-HF) exhibits dual fluorescence (λ_{max} 410 and 530 nm) with very short lifetimes at room temperature, and the 530-nm fluorescence shows two exponential decays at ~200 K (τ = <0.2 and 0.7 ns). The long-wavelength fluorescence was ascribed to the excited-state tautomer generated by the excited-state proton transfer in the hydrogen bonding complex of 7-HF with two methanol molecules (1:2), which was confirmed by the methanol concentration dependence in tetrahydrofuran of the 530-nm fluorescence intensity. The transient absorption spectra of this solution exhibit two transient absorption bands at 380 and 420 nm with short and long decay times (~400 ns and ~60 μs) in addition to the triplet–triplet absorption band (λ_{max} ~ 370 nm). These transient absorptions were attributable to two ground-state tautomers generated by the excited-state proton transfer and relaxation. The first laser excitation of 7-HF in methanol induces the formation of two unstable ground-state tautomers. The second dye laser excitation of the transient absorption bands delayed from the first one affords two considerably different two-step laser excitation (TSLE) fluorescence spectra (λ_{max} 525–530 and 515–520 nm) of the tautomers. Further, when delay times between the first and second laser pulses were varied (a variable delay technique), the decay times of two ground-state tautomers were determined to be 450 ns and 50–60 μs, which are consistent with those obtained by the transient absorption spectroscopy. These TSLE fluorescence and transient absorption spectra demonstrate that the excited-state proton transfer in the methanol solution of 7-HF may take place, forming two types of phototautomers in the excited state and also in the ground state.

Two-step laser excitation (one or two colors) fluorescence as one of the recent developments of the laser spectroscopy provides us with the reaction kinetics and dynamics of unstable molecules. Recently, a Bell Laboratories group reported the spectra and kinetics of naphthylmethyl radical by means of two-color laser-induced fluorescence experiments.[1] Further, Sitzmann, Wang, and Eisenthal have also determined reaction rate constants of the triplet diphenylcarbene with alcohols by the two-pulse experiment with UV picosecond pulses (one color).[2] At the almost same time, Itoh et al.[3] have reported transient absorption and two-step laser excitation (TSLE, two colors) fluorescence studies of the excited-state and ground-state proton transfer in the methanol solution of 7-hydroxyquinoline (7-HQ).

Numerous investigations of the intra- and intermolecular excited-state proton transfer of the hydrogen bonding systems were reported by nano- and picosecond fluorescence spectroscopy as well as conventional steady-state spectroscopy.[4-11] On the other hand, the transient absorption study that may provide us with valuable information on the proton transfer not only in the excited state but also in the ground state has only been reported in a few papers.[12-14] Recently, Huston et al.[13] have reported that 2-(2-hydroxy-5-methylphenyl)benzotriazole in several solvents shows

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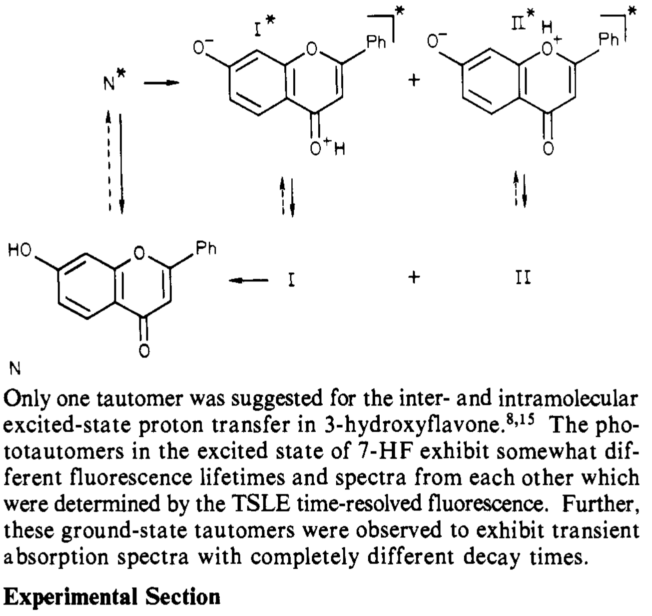
ground-state recovery in the transient absorption spectroscopy, whose recovery time is longer than the fluorescence lifetime of the phototautomer, and they have suggested the intervention of an intermediate during the relaxation of the tautomer. Further, Itoh et al.[9,15] have reported the time-resolved fluorescence, transient absorption spectra, and two-step laser excitation (TSLE) fluorescence study (including variable delay technique and the TSLE fluorescence excitation spectra) of the ground- and excited-state proton transfer in 3-methylpentane solutions of 3-hydroxyflavone and -chromone. They have demonstrated that the intramolecular excited-state proton transfer takes place from the normal form (N*) to the tautomer (T*) followed by the fluorescent relaxation to the ground-state tautomer. The ground- and excited-state tautomers in the nonpolar solvent were reported to be generated by proton transfer from 3-hydroxyl group to carbonyl oxygen of the pyrone ring. Further, the reverse proton transfer in the ground state was shown to occur from the ground-state tautomer to the normal form by TSLE fluorescence. On the other hand, Schipfer et al.[16] reported the pH-dependent fluorescence study of 7-hydroxyflavone (7-HF) and 7-methoxyflavone and that 7-HF undergoes adiabatic photodissociation in the S_1 state, forming a phototautomer in acidic methanol.

This paper presents the time-resolved fluorescence, transient absorption, and TSLE fluorescence studies in the methanol solution of 7-HF. The transient absorption spectra and TSLE fluorescence spectra at variable delay times between two laser pulses suggest that excited-state proton transfer and relaxation in 7-HF take place to afford two types of tautomers in the ground and excited states as follows:



Only one tautomer was suggested for the inter- and intramolecular excited-state proton transfer in 3-hydroxyflavone.[8,15] The phototautomers in the excited state of 7-HF exhibit somewhat different fluorescence lifetimes and spectra from each other which were determined by the TSLE time-resolved fluorescence. Further, these ground-state tautomers were observed to exhibit transient absorption spectra with completely different decay times.

Experimental Section

Materials. 7-Hydroxyflavone was synthesized according to the literature[17] and purified by repeated recrystallizations from spectrograde ethanol and by sublimation in vacuo. Spectrograde methanol and THF (Nakarai) were used without further purification.

Fluorescence Lifetimes and Transient Absorption Spectra. Fluorescence lifetimes were determined by the same method as described previously.[9,18] For the determination of two short lifetimes of the 530-nm fluorescence, the longest wavelength region (~550 nm) was collected to remove the contribution of the 400-nm fluorescence. Transient absorption spectra were determined by using an excimer laser (Lambda Physik EMG-50E, 308 nm) and a monitoring Xe flash lamp. For the determination of the very long-lived transient absorption, a steady Xe lamp with a synchronously operated shutter with the excimer laser was used as a monitoring light source.[19]

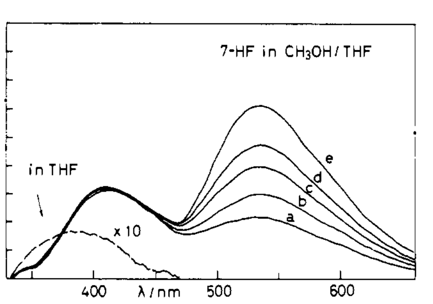


Figure 1. Fluorescence spectra of 7-HF (5.0×10^{-5} M) in CH_3OH/THF mixed solution at room temperature (20 °C). CH_3OH concentration in THF: (a) 45%, (b) 53.7%, (c) 63.3%, (d) 72.2%, (e) 90%.

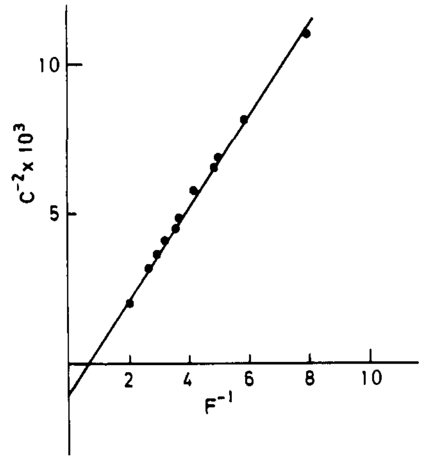


Figure 2. Plots of C^{-2} vs. F^{-1} at room temperature (20 °C), where C and F are concentration of CH_3OH in THF and fluorescence intensity at 530 nm, respectively.

Two-Step Laser Excitation Fluorescence Spectra and Variable Delay Technique. The excimer laser was used as the first excitation light source. The second N_2 laser-pumped dye laser (Molectron UV-12 and DL-14) was synchronously operated with the excimer laser by a pulse generator and a variable delay circuit (delay time, 0–70 μs). The TSLE fluorescence signal was detected by a HTV 1P28 photomultiplier, which was operated with subnanosecond response time. The signal was detected by Taktronix oscilloscope 7904 (7A19 and 7B85) which was triggered by a second laser pulse detected with a biplaner phototube (HTV R617-02). The TSLE fluorescence spectra were constructed with the oscilloscope signal vs. wavelengths. The TSLE fluorescence was confirmed by the following manner so that the signal could not be detected without the first laser pulse and also without the second one. The lifetimes of the ground-state transients were determined from TSLE fluorescence intensities, which were detected by the second excitation pulse (386, 406, 420, and 440 nm) delayed at variable delay times from the first pulse.

Results and Discussion

Fluorescence and Transient Absorption Spectroscopies. The methanol-containing tetrahydrofuran (THF) solution of 7-HF shows dual fluorescence at 400–430 nm and 500–530 nm at room temperature, though the THF solution is faintly fluorescent. The intensity ratio of the longer wavelength fluorescence to the shorter increases with increasing methanol concentration as shown in Figure 1. Figure 2 shows the plots of C^{-2} vs. F^{-1}, where C is the concentration of methanol in THF and F is the intensity of the 530-nm fluorescence. The linear plots suggest that the 530-nm fluorescence may be attributable to the following 1:2 interaction (probably H-bonding) of 7-HF with methanol molecules: 7-HF + $2(CH_3OH) \rightleftarrows$ 7-HF$(CH_3OH)_2$.[20,21] The equilibrium constant (K) of the 1:2 complex formation was obtained to be 1.1×10^{-3} M^{-2} at room temperature.

The methanol solution of 7-HF also exhibits a similar dual fluorescence to that of 90% methanol solution, as shown in Figure 1e. Therefore, 7-HF seems to be in the 1:2 H-bonding state with

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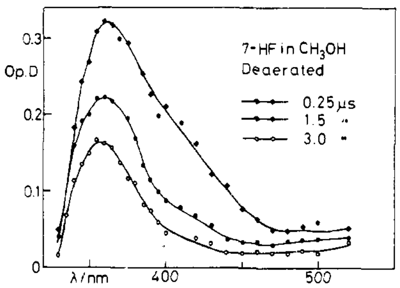

Figure 3. Transient absorption spectra of a methanol solution of 7-HF (5.0×10^{-5} M, deaerated) depicted at 0.25-, 1.5-, and 3.0-μs delay after a laser pulse (308 nm). The light path length is 10 mm. The solution was stirred during measurement.

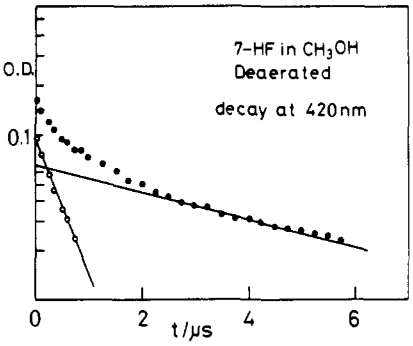

Figure 4. Decay cruve of transient absorption (Figure 3) at 420 nm. The short and long decay time components are due to the ground-state tautomer and the triplet–triplet absorption, respectively.

two methanol molecules. The excitation spectra of the dual fluorescence in CH$_3$OH are identical with an absorption spectrum, which implies that the dual fluorescence of 7-HF is attributable to the photoexcitation of the H-bonding complex (1:2) of 7-HF with methanol. If the 530-nm fluorescence is ascribed to the excited-state proton transfer as reported previously, two methanol molecules may be required for the formation of the excited-state tautomer of 7-HF. Therefore, the dual fluorescence spectra in methanol solution of 7-HF may be ascribed to the excited-state normal form being H-bonded with methanol molecules and to the excited-state tautomer generated from this normal form. The fluorescence decay profiles of both fluorescences in methanol solution at room temperature, which are almost identical with those of the excitation pulse, suggest that both fluorescence lifetimes are less than ~200 ps. At low temperature (~200 K), however, two exponential decays of the 530-nm fluorescence were observed without rise time, while the lifetime of the shorter wavelength fluorescence (~400 nm) was still less than ~200 ps. The fluorescence lifetimes monitored at 550–650 nm were determined to be <0.2 ns and 0.7 ns at 216 K. This suggests that there seem to be two types of phototautomers generated in the excited-state proton transfer of 7-HF in methanol, though more accurate determination of fluorescence decay is impossible within the limits of the nanosecond spectroscopy at the present stage. Therefore, this argument was confirmed by the TSLE time-resolved fluorescence spectra and lifetimes, as will be mentioned later.

The transient absorption spectra of the methanol solution (deaerated) were measured by the excimer laser excitation (308 nm) and a monitoring flash lamp, as shown in Figure 3. The considerably long- and short-lived absorption bands were observed in the 370- and 430-nm regions, as seen in Figure 3. Figure 4 shows the decay curve of the transient absorption monitored at 430 nm. From the decay curve and spectra, the decay times of the former and latter absorptions were determined to be 5 μs and ~400 ns. The decay time of the former band is dependent on the aeration, while the latter is independent. Hamanoue et al.[22] reported triplet–triplet absorption bands of flavone at 365–370 and 640–650 nm and suggested them for the lowest triplet state with π–π^* character. Therefore, the former band may be attributable to the triplet–triplet absorption band of 7-HF. Since lifetimes of the normal and two tautomer forms in the excited state are both subnanoseconds at room temperature, as mentioned above, the transient absorption band at 430 nm with τ = 400 ns seems to be ascribed tentatively to the ground-state tautomer. Furthermore, the very long-lived transient absorption was also observed in the somewhat shorter wavelength region (370–390 nm) by using a monitoring steady lamp as shown in Figure 5. This transient absorption was ascribed to another long-lived ground-state tautomer. These assignments of the transient absorption bands to the ground-state tautomers were confirmed by the variable delay technique of the TSLE fluorescence spectra, as will be mentioned later.

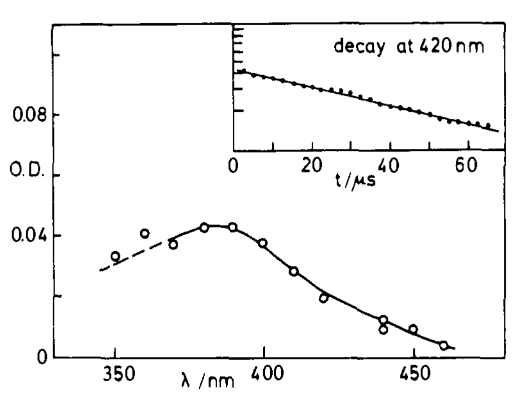

Figure 5. Transient absorption spectrum of a methanol solution of 7-HF (5.0×10^{-5} M, deaerated) depicted at 10-μs delay after a laser pulse (308 nm), and a decay curve monitored at 420 nm using a steady Xe lamp. The solution was stirred during measurement.

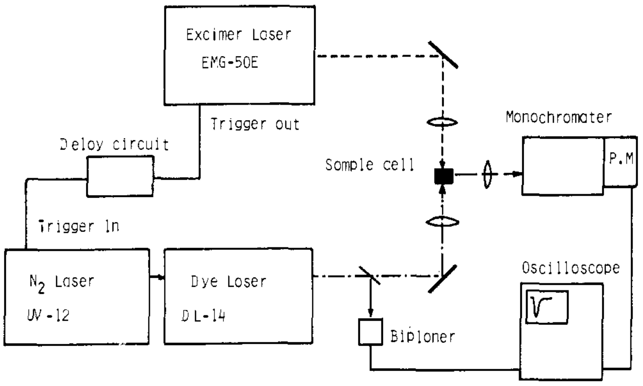

Figure 6. Experimental setup of the two-step laser excitation fluorescence.

Two-Step Laser Excitation Fluorescence Spectroscopy. In order to confirm the transient absorption bands with two different decay times which were tentatively ascribed to the short- and long-lived ground-state tautomers mentioned above, the TSLE fluorescence spectra of methanol solution of 7-HF were measured at room temperature. If transient absorption bands are exclusively excited within their lifetimes by the second laser pulse of these absorption wavelengths, the TSLE fluorescence spectra and lifetimes of the tautomers should be observed.[3,15,18] The block diagram of the TSLE fluorescence detection is shown in Figure 6. After the first excimer laser excitation of the methanol solution which generates the ground-state tautomers through the excited-state proton transfer and relaxation, the TSLE fluorescence spectra and lifetimes were determined by the second laser excitations at the different delay times. These time-resolved TSLE fluorescence spectra and decay times exhibit the respective fluorescence properties of the excited-state tautomers generated from ground-state tautomers with different lifetimes. Figure 7 shows these time-resolved fluorescence spectra (TSLE) at the delay times of 100 ns and 3 μs. These TSLE fluorescence spectra are con-

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[22] Hamanoue, K.; Nakayama, T.; Miyake, T.; Teranishi, H. *Chem. Lett.* **1981**, 39.

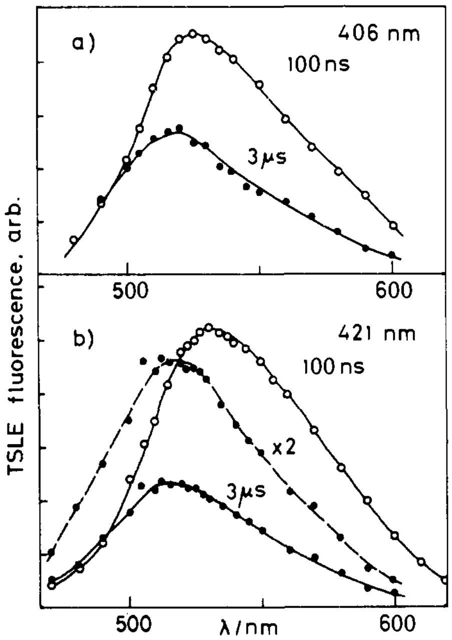

Figure 7. TSLE time-resolved fluorescence spectra of a methanol solution of 7-HF (3.0×10^{-5} M). The second excitation wavelengths are (a) 406 nm and (b) 421 nm; delay times are 100 ns and 3 µs from the first excitation laser pulse (308 nm).

siderably similar to the steady-state fluorescence spectrum of the tautomer. However, it is noteworthy that these TSLE time-resolved fluorescence spectra determined at different delay times are significantly different from each other. The spectrum at the shorter delay time appears in the longer wavelength region than that at the longer delay time. The fact suggests that the longer wavelength fluorescence (λ_{max} 525–530 nm) may originate from the shorter lived ground-state tautomer and the shorter wavelength fluorescence (515–520 nm) from the long-lived one. Since no difference of the TSLE fluorescence lifetimes between two different delay times can be observed at room temperature because of too short lifetime, the lifetimes were measured at low temperature (~200 K). The TSLE fluorescence lifetime at the delay time of 3 µs was determined to be approximately 0.7 ns at ~200 K, while that of the delay time of 100 ns remained less than <0.2 ns.[23] This TSLE fluorescence lifetime is consistent with that obtained by the conventional pulse excitation within experimental error. Therefore, these TSLE fluorescence spectra shown in Figure 7 are ascribed to two different types of the excited-state tautomers. A schematic energy diagram of these two types of tautomers both in the ground and excited states are shown in Figure 8.

The TSLE fluorescence intensities at 530 nm were plotted vs. delay times between two laser pulses, as shown in Figure 9. This figure demonstrates that there are two unstable species with short and long lifetimes (~400 ns and 60–70 µs) in the ground state. Further, the ratio of the short- and long-lifetime components increases with changing the second laser wavelength in the order 406, 421, and 440 nm, which implies that the short-lived tautomer has the long-wavelength absorption band and the long-lived one has the shorter wavelength band. These decay times of the ground-state tautomers determined by this TSLE variable delay technique are quite consistent with those of the transient absorption spectra mentioned above. It is unlikely that the excitation of the triplet–triplet absorption band (360–370 nm) may induce the tautomer fluorescence or triplet–triplet fluorescence. Therefore, the transient absorption and TSLE fluorescence suggest that two types of different excited-state tautomers, I* and II*, are formed in the excited-state proton transfer, though the respective fluorescence lifetimes were observed only at low temperature, as mentioned above. Schipfer et al.[16] reported that 7-HF in methanol undergoes proton transfer in the S_1 state, forming a phototautomer, where 7-HF may pick up a proton at the carbonyl oxygen from solvent and release one at 7-hydroxyl group. Further, Itoh and Fujiwara[15] have reported the TSLE fluorescence study of the intramolecular excited-state proton transfer in benzene solutions of 3-HF and 3-HC and intervention of the long-lived ground-state tautomer, where a proton transfers from 3-OH group to carbonyl oxygen in the pyrone ring. Therefore, it is proposed that the long-lived tautomer (τ = 60–70 µs) may be ascribed to tautomer I, with the shorter one to tautomer II, where a proton seems to transfer from the solvent to the ether oxygen of the pyrone ring and to be released from 7-hydroxyl group to the solvent. This seems to be reasonable because II is more labile than I, probably both in the ground and excited states. These spectroscopic data are summarized in Table I.

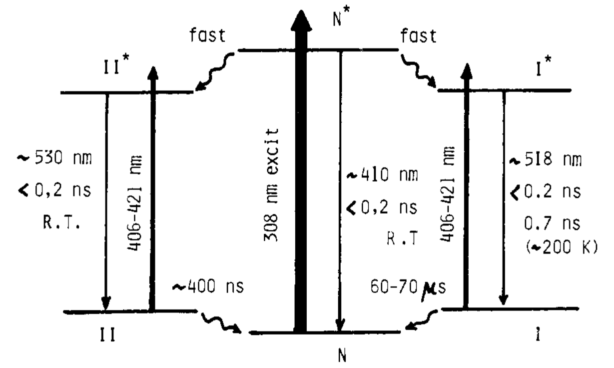

Figure 8. Schematic energy diagram of phototautomers of 7-HF both in the ground and excited states.

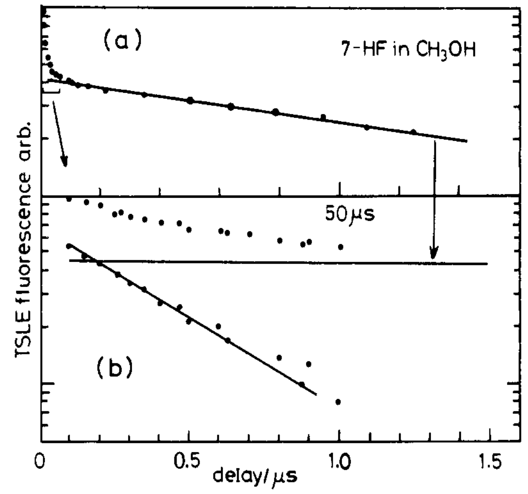

Figure 9. (a) TSLE fluorescence intensity (530 nm) vs. variable delay times of the second laser pulse (421 nm) after the first one (308 nm) of the methanol solution of the 7-HF (3.0×10^{-5} M) at room temperature. (b) Expanded time scale of (a).

Concluding Remarks. Woolfe and Thistlethwaite[8] have reported intermolecular excited-state proton transfer in alcoholic solution of 3-HF in addition to the intramolecular interaction. Further, Strandjord et al.[10] have reported the temperature and solvent dependence of this proton transfer. On the other hand, Itoh et al.[9] and Itoh and Fujiwara[15] have reported nanosecond fluorescence and transient absorption and TSLE fluorescence studies on intramolecular proton transfer in the ground and excited states of 3-HF and 3-HC, as mentioned above. In these papers, it was concluded that the proton transfer takes place from the 3-OH group to carbonyl oxygen. In the methanol solution of 7-HF, however, the TSLE fluorescence (time-resolved) as well as conventional determination of fluorescence lifetime at low temperature suggest that there are two types of tautomers not only in the excited state but also in the ground state. As for these tautomers, the phototautomers I* and II* (I and II) were tentatively proposed

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[23] Double exponential decays (τ = <0.2 and 0.7 ns) of the 530-nm tautomer fluorescence were detected both at 100-ns and 5-µs delay times (~200 K). The long-lifetime component (τ = 0.7 ns) increased more at the longer delay time (5–20 µs) than at 100 ns.

Table I. Fluorescence Maxima and Lifetimes of the Excited-State Tautomers I* and II*, and Transient Absorption Maxima and Lifetimes of the Ground-State Tautomers I and II

	excited-state tautomers		ground-state tautomers	
	I*	II*	I	II
fluores				
λ_{max}	530 nm			
τ	0.65 ns[a]	<0.2 ns[a]		
TSLE fluores	518 nm[b]	530 nm[b]		
τ	0.7 ns[c]	<0.2 ns[c]		
τ			60–70 μs[d]	400 ns[d]
trans absorp			380 nm	420 nm
τ			65 μs	380 ns

[a] Determined at ~200 K. [b] Determined by the TSLE time-resolved fluorescence spectra as mentioned in the text. [c] Determined by the same method as (b) at 200 K. [d] Determined by the variable delay technique of the TSLE fluorescence at room temperature.

as mentioned above. If these two types of tautomers may be generated in the excited state, there may be two respective H-bonding conformers in the ground state prior to the photoexcitation: H-bonding to carbonyl and ether oxygens of the pyrone ring in addition to the 7-hydroxyl group.[24] In the excited-state proton transfer of 4-methylumbelliferone, Shank et al.[25] suggested the protonation of the ring oxygen (pyrylium structure) of the α-pyrone ring as well as on the carbonyl oxygen. Since the pyrylium structure of 7-HF (II) seems to be more labile than the other (I), the short-lived tautomer in the ground state may be ascribed to structure II and the long-lived one to structure I. The observed decay times of the ground-state tautomers may reflect the reaction rates of the reverse proton transfer to the parent molecule in the ground state, because no significant photochemical reaction of 7-HF was observed to take place in the deaerated methanol solution. Therefore, the reverse proton transfer seems to take place faster in the tautomer II than I. On the other hand, if the interconversion between two tautomers is possible, the decay time of the short-lived tautomer II might include the interconversion rate of II to I. However, the reverse proton transfer of this tautomer II to the parent molecule N may be predominant compared with the interconversion to the other tautomer (II → I), though the possibility of the interconversion between two tautomers in the ground state as well as in the excited state can not be entirely removed at the present stage. These arguments at least for the excited state will be confirmed by picosecond spectroscopy.

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Registry No. 7-HF, 6665-86-7; methanol, 67-56-1.

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[24] According to this argument, the 410-nm fluorescence shown in Figure 1 might consist of two fluorescence spectra of these conformers superimposed. However, the spectral confirmation is impossible at the present stage.

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Solvation Structure of Silver Ions and Atoms in Acetonitrile

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Abstract: Electron spin-echo modulation studies have been carried out for Ag atoms and Ag^{2+} ions in X-irradiated frozen acetonitrile solution of $AgClO_4$ to deduce the solvation-shell geometry for these paramagnetic species and the parent Ag^+ ions. The results indicate that the solvation structure of the Ag^{2+} ion is the same as that of the parent Ag^+ ion except for the solvation-shell radii. Four acetonitriles are bonded to the Ag^{2+} or Ag^+ ion in a square-planar configuration by side-on coordination with their molecular dipoles oriented perpendicular to the plane. The distances from the Ag^{2+} ion and the Ag^+ ion to the center of the $C\equiv N$ bonds are estimated to be 0.20 and 0.23 nm, respectively. The solvation structure of the Ag atom is slightly different from that of the Ag^+ ion. Four acetonitriles are bonded to the Ag atom in a tetrahedral configuration by side-on coordination. The acetonitriles are not bonded to the silver atoms and ions through nonbonding orbitals on the $C\equiv N$ nitrogens, but σ-bonded through bonding π orbitals on the $C\equiv N$ bonds, because the energy of the nonbonding orbitals is lower than that of the π orbitals. The reason for preferential solvation of Ag^+ ions by acetonitrile in acetonitrile/water mixtures is discussed.

In mixed solvent, ions are preferentially solvated by one of the solvent components. This phenomenon is known as preferential solvation or selective solvation. Since the study of preferential solvation is not only of physicochemical interest but also of importance for elucidating chemical reactions in solutions,[2] many methods have been developed for determining the ratio of the solvent components in the solvation shell. These include conductance measurements, optical spectra measurements, NMR measurements,[3] and ESR measurements.[4,5]

One of the most typical examples of preferential solvation is Ag^+ ions in acetonitrile/water mixture. Acetonitrile generally solvates metal ions very weakly,[6] so that most metal ions are preferentially solvated by water. However, Strehlow and Koepp found that half of the water molecules around the Ag^+ ions is replaced by acetonitrile in the mixed solvent of 20 mol % acetonitrile at room temperature.[7] Alesbury and Symons studied the ESR spectra of Ag atoms and Ag^{2+} ions formed by electron gain

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