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Proton Transfer in the Ground and Excited Electronic States of 4-Methyl-2,6-diformylphenol: Role of Alcoholic Solvents

Ranjan DAS, Sivaprasad MITRA, and Samaresh MUKHERJEE*
Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India
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The effect of alcohols on the proton-transfer processes in the ground and excited states of 4-methyl-2,6-diformylphenol (MFOH) has been investigated experimentally by steady state and time resolved emission spectroscopy. It is shown that the large Stokes-shifted fluorescence band in alcohols is due to the 4-methyl-2,6-diformylphenolate anion (MFO^-), except in the case of 1-butanol. In 1-butanol the single broad fluorescence band observed in the visible region is assigned to the partially ionized species; the emission is found to depend on the excitation wavelength. Dual emission is observed only in the case of 2,2,2-trifluoroethanol (TFE). At 77 K the emission spectrum is found to be contaminated with the phosphorescence spectrum. The spectral characteristics obtained reveal that MFOH in protic solvents exists in more than one structural form in both the ground and excited states.

The possibility of ground- and excited-state proton transfers in intramolecularly hydrogen-bonded compounds has been the subject of intense activity in recent times.[1—20] Since the idea of an excited-state intramolecular proton transfer (ESIPT) was proposed by Weller[21] in the case of methyl salicylate (MS), the phenomenon has been observed in a wide variety of compounds. It was Forster[22] who showed for the first time that the spectral changes which occur in an aromatic hydroxy compound is due to the complete transfer of a proton to an accepting base (e. g., alcohol or water). Fluorescence studies on molecules with an intramolecular hydrogen bond have confirmed the above prediction. Nagaoka et al.[23—28] studied the spectral features and dynamics of some proton-transfer processes in the S_0 state as well as in different excited electronic states of *o*-hydroxybenzaldehyde (OHBA). OHBA shows a dual fluorescence in ethanol and methanol. It has been demonstrated that OHBA predominantly exists in the form of intermolecularly hydrogen-bonded open conformers in alcohols at room temperature. At 77 K, the closed conformer of OHBA is converted into the open conformer by UV irradiation in nonpolar solvents as well as in alcohols. The main species in the S_0 state of OHBA has been shown to be an intramolecularly hydrogen-bonded closed conformer. Moreover, it has also been shown that the deformation of the benzene skeleton plays an important role in the proton-transfer process in the first excited singlet state.

The fluorescence spectrum of methyl salicylate (MS)[29—35] is characterized by two bands, the longer wavelength band having an unusually large Stokes shift. Different ground-state species have been proposed to explain the dual emission and the variation in the emission spectrum with solution polarity. It has also been found that nonradiative processes are often important in the decay of the excited states of such molecules.

4-Methyl-2,6-diformylphenol (MFOH) is a chromophore structurally related to OHBA and provides a fascinating test case for excited-state proton transfer processes and environmental effects in solution spectra in general. The present work focusses on the absorption and emission properties of MFOH by steady state and time resolved spectroscopic methods in alcoholic solvents at room temperature and 77 K. As reported later, MFOH shows a dual fluorescence in 2,2,2-trifluoroethanol (TFE), one in the visible and another in the yellow green region. However, two absorption bands and a single Stokes-shifted emission band are observed in methanol and ethanol. We have tried to identify the species responsible for the different absorptions and emissions while providing insight into the structure and dynamics involving the ground and excited states of MFOH. Studies in interacting solvents, such as alcohols and water, are particularly interesting, since the environment here offers a means of studying the proton transfer mechanism of solvated molecules.

Experimental

4-Methyl-2,6-diformylphenol (MFOH) was prepared as reported earlier.[36] 2,2,2-Trifluoroethanol (Fluka A. G.), ethanol, methanol, and 1-butanol were all of spectroscopic grade (Merck), and were used without further purification. Triton X-100 (Aldrich) was used as received. Analytical-grade sodium hydroxide and triply distilled water were used.

The fluorescence emission and fluorescence excitation spectra were recorded on a Perkin–Elmer MPF 44B fluorimeter. The electronic absorption spectra were scanned with a JASCO UV-vis spectrophotometer, (model 7850). The transient fluorescence lifetimes (τ_f) were measured with an SP-70 nanosecond spectrometer (Applied photophysics, Ltd., England) using a pulsed nitrogen lamp based on a time-correlated single-photon counting technique. All of the spectra reported are uncorrected for instrument response. The relative emission quantum yields were determined from the 480—490 nm emission in 1-butanol and 520—530 nm emission intensities in all other solvents using quinine sulfate as a standard ($\phi=0.54$), and as described earlier.[36,37] These intensities were corrected by subtracting off the intensities from sample blanks, which were identical to the samples. This corrected for any signal from scattered light or emission from impurities. This correction is almost negligible at 520—530 nm. The emission spectra are similar for all the concentration of MFOH studied (0.6×10^{-5} to 1.2×10^{-4} mol dm^{-3}) in all of the solvents used in this study.

Results and Discussion

(i) Spectral Feature in Different Alcoholic Media. The effects of the MFOH concentration in ethanol on the absorption spectra are shown in Fig. 1a. The absorption spectra of MFOH in methanol and ethanol exhibit two distinctly different bands at a certain concentration (4.0×10^{-5} mol dm^{-3}), one at 350 nm and another in the 430—440 nm region. It is noted that when the concentration of MFOH is below 2.0×10^{-5} mol dm^{-3} only the red end band is observed in ethanol (Fig. 2). However, in the case of methanol, both bands are observed, even in a very dilute solution (0.6×10^{-5} mol dm^{-3}). On the other hand, a single absorption band at 350 nm is observed in 1-butanol and TFE for all of the concentrations of MFOH studied. The species obtained at 350 nm in the ground state is considered to be an intramolecularly hydrogen-bonded closed conformer as reported earlier.[38] The absorption band covers the range 370 to 320 nm with $\varepsilon_{\max}\approx4500$ dm^3 mol^{-1} cm^{-1}. This large ε indicates that it is due to a $S_0\rightarrow{}^1(\pi\pi^*)$ transition.[39] The fluorescence spectra show a large Stokes-shifted band at 520 nm in ethanol/methanol and at 490 nm in 1-butanol. The fluorescence spectra of MFOH in TFE show dual emission at 520 and 440 nm (Fig. 1). The appearance of a large Stokes shift in the emission spectra indicates the translocation of the hydroxyl proton. Two bands were obtained in the excitation spectra of MFOH in 1-butanol, as shown in Fig. 2. The excitation spectra obtained by monitoring the 440 and 520 nm emission in TFE are different and red shifted from the absorption spectra by ca. 10 and ca. 70 nm, respectively. The distinctly different excitation spectra suggest the presence of two ground-state species. The excitation spectra in ethanol and methanol are structured and are poorly correlated with the corresponding absorption spectra. These observations indicate the complex nature of the spectra and coexistence of more than one species. It is, however, difficult to account for all of the peaks presumably arising from species which exist in a rather small amount in solution. In protic solvents MFOH may exist in different structural forms, due to solute/solvent interaction. The above mentioned observations and Fig. 1 distinctly show that these solute/solvent interacting ability are different in different solvents, and that ionization is favourable in relatively more dilute solutions.

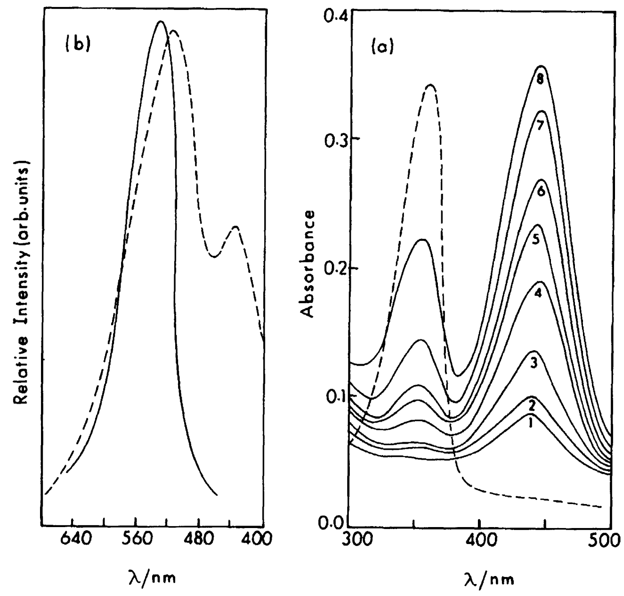


Fig. 1. Absorption (a) and emission (b) spectra of MFOH at room temperature. (a): in ethanol [—], [MFOH] (1 to 8) $=8.5\times10^{-6}$ to 1.0×10^{-4} mol dm^{-3} and TFE [- - -], [MFOH] $=2.5\times10^{-5}$ mol dm^{-3}. (b): in ethanol [—] and TFE [- - -], [MFOH] $=8.5\times10^{-5}$ mol dm^{-3}, $\lambda_{\text{exc}}=360$ nm.

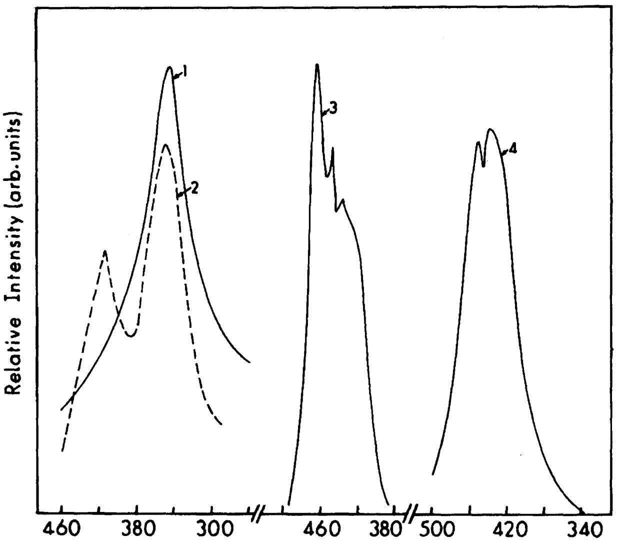


Fig. 2. Fluorescence excitation spectra in TFE (1), 1-butanol (2), ethanol (3), and methanol (4). The spectra are obtained by monitoring at 520 nm in ethanol and methanol, 440 nm in TFE, and 490 nm in 1-butanol respectively. [MFOH] $=1.2$ to 2.0×10^{-5} mol dm^{-3}.

The shapes of the emission spectra in 1-butanol and TFE depend markedly on the excitation wavelength (Fig. 3). At different excitation wavelengths the fluorescence spectrum either comprises two peaks or one peak, presumably resulting from the overlap of emissions from two different species. These observations also suggest that MFOH is present in more than one structural form in both the ground and excited states in 1-butanol, as well as in TFE, though a single ab-

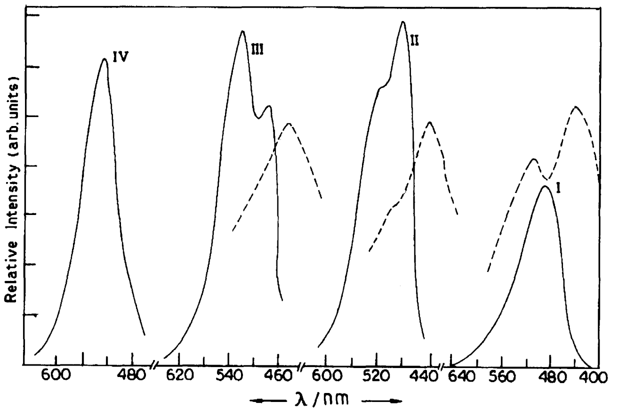


Fig. 3. Emission spectra in 1-butanol [—], TFE [- - -]. λ_{exc}, 380 (I), 400 (II), 420 (III), and 440 (IV) nm; [MFOH]$=2.1\times10^{-4}$ and 2.5×10^{-5} mol dm^{-3} for 1-butanol and TFE, respectively. The intensity is arbitrary in each case.

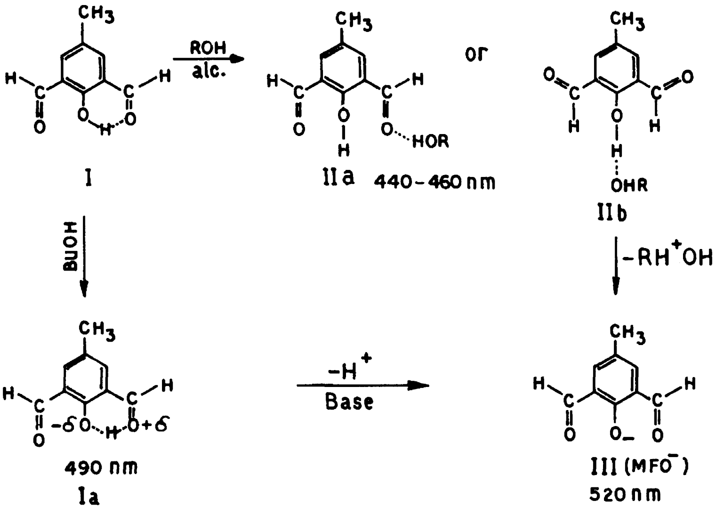
sorption band is obtained in these solvents. The single absorption and emission band in the case of 1-butanol can be interpreted as being the result of a superposition of different absorptions and emissions arising from different structural forms.

To interpret the spectral features, an attractive Scheme for different types of proton-transferred species of MFOH can be represented in Scheme 1. **I** in Scheme 1 can not directly transfer proton intramolecularly because its intramolecular hydrogen bond is weakened by the presence of a strong hydrogen-bonding interaction with an alcoholic acceptor. In this Scheme an intermediate state (**II**) is assumed to occur before an actual proton transfer. For this open conformer, two different structures (**IIa** and **IIb**) can be considered. Our theoretical analysis using the AM1 technique[40] shows that the energy difference between **IIa** and **IIb** was about 0.2 kcal mol^{-1}. Since the energy difference between the two forms is low, and there is no bulky group attached to C=O group, it seems that the rotation of the formyl group in MFOH is probable. Thus, MFOH is able to attain structure **IIb**.

The dual-emission bands and a single absorption band in TFE (Fig. 1) presumably imply incomplete ionisation or weaker interaction of MFOH with TFE, and that the formation of a hydrogen-bonded complex (open conformer **II**, Scheme 1) is probable in addition to **III** in the excited state. This weaker proton-accepting ability is invariably due to the presence of electronegative fluorine atoms in TFE. The two absorption bands observed in methanol and ethanol clearly indicate the presence of two species, the MFO$^-$ ion (430-440 nm) in addition to the closed conformer **I** (350 nm), in the ground state. This is not reflected in the emission spectra. In the excited state, i. e. in the more solvated state, the single emission band in methanol and ethanol exhibits a single component (MFO$^-$) which is found to be independent of the excitation wavelength. This situation may occur if the molecule rearranges upon excitation to only one radiative from (**III**). Extensive solvation seems to be responsible for the appearance of such a large single Stokes-shifted band. Another possible interpretation of the single emission in ethanol and methanol is that the fluorescence of the open conformer (**II**) is very weak and, hence, only the fluorescence of the anionic species (**III**) is observed. This is quite possible because the intersystem crossing in nπ^* carbonyls is often very efficient, as in the case of OHBA.[25]

The emission spectrum in 1-butanol is in a higher energy region than in methanol and ethanol. Therefore, the species responsible for this emission is more energetic and less stable than MFO$^-$. In a simple interpretation, it can be said that the resonance in the phenyl group should favour a partial negative charge on the oxygen atom of the OH group and a positive charge on the carbonyl group (**Ia** in Scheme 1). The most plausible explanation for the occurrence of the partially ionic species is that the bulky alkyl group in 1-butanol causes a steric effect that increases the proton-transfer barrier in MFOH. Moreover, due to a steric effect the bulky alkyl group may be twisted out-of the plane. As a result, the electron-releasing ability of the group towards the oxygen atom is affected. Hence, 1-butanol should be less basic and its hydrogen-bonding ability less compared to methanol and ethanol. It is likely that analogous effects should also be operative in the excited state. However, the steric effect is much less due to the increased polarity of the medium in the excited state and by the addition of base (section below). It should be noted that in a very weak proton-accepting solvent, such as 1-butanol, fluorescence should be observed in the visible region.[19,32]

(ii) Effects of Electron Donors. Upon the addition of a base such as Triton X-100 or aqueous alkali, the intensity of the 430—440 nm absorption band increases with a concomitant decrease in the intensity of the 350 nm band in methanol and ethanol. In the excited state the intensity of the 520 nm band increases without any change in the position of the band by the addition of a base. Similar phenomena were also observed when aqueous NaOH was added to a water solution of MFOH. These facts indicate that the long-wavelength absorption band and the emission band at 520 nm must have arise in from the phenolate anion (MFO$^-$). In the presence of a base, MFO$^-$ becomes more solvated, and probably forms a hydrogen-bonded ion pair, or the population of the anionic species increases. It therefore, seems plausible that MFOH undergoes deprotonation to form MFO$^-$ in methanol and ethanol in both the ground and excited state. A pertinent point is that in a protic solvent a significant population of anionic species is expected, depending on the protolytic strength of the medium.[41—43] The anion or hydrogen bonded ion pair formed may give rise to an



Scheme 1.

increased fluorescence or quantum yield (Table 1).

A good number of earlier studies concerning an intramolecularly hydrogen-bonded compound suggested that the phenolic proton can undergo complete transfer to a proton-accepting solvent resulting in an excited state phenolate anion, which is responsible for a large Stokes shift. It may be mentioned that in a similar study Acuña et al.[19,32)] detected the phenolate ion as a third component in water and lower alcohols. Thistlethwaite and Woolfe[41,44,45)] pointed out that the phenolic proton can undergo an intermolecular proton transfer to the solvent molecules, resulting in an excited-state phenolate anion. An intramolecular proton transfer does not occur in alcoholic solvents, since its intramolecular hydrogen bond is almost broken by the presence of a strong intermolecular hydrogen bonding in protic solvents.

It was also observed in this study that by the addition of a base, the 490 nm band in 1-butanol shifts to the 520 nm region with some gain in intensity. Hence, the steric effect due to a bulky group is less in the excited state and in the presence of a base. This shift was also observed upon increasing the excitation wavelength (Fig. 3). A model that can be used to rationalize the results in 1-butanol is represented in Scheme 1 as **I**→**Ia**→**III**. In this case the immediate precursor to a proton transfer may be assumed to be a partially ionized species (**Ia**) in a relatively weak proton-accepting solvent, such as 1-butanol. **Ia** can undergo an intermolecular proton transfer, since its intramolecular hydrogen bond is almost broken in the presence of a base in the excited state, and since this ionic state is now bound at a longer O–H distance like OHBA. It was shown in our earlier study that the large Stokes-shifted emission band of MFOH in cyclohexane shifted to the 440—460 nm region upon the addition of a base.[38)] This was clearly due to an exciplex-type interaction between MFOH and the base, and the formation of a hydrogen-bonded complex i.e. the open conformer. The 440 nm region band in TFE may safely be assigned as being due to the open conformer **II**.

Table 1. Lifetime of the Excited MFOH (τ_f), Fluorescence Quantum Yield (ϕ_f) and Decay-Rate Constants (k_f^r, k_f^{nr})

Solvent	τ_f/ns	ϕ_f	$k_f^r/s^{-1}\times10^{-7}$	$k_f^{nr}/s^{-1}\times10^{-8}$
Methanol	4.5	0.41	9.1	1.3
Ethanol	5.5	0.46	8.1	1.1
1-Butanol	4.9	0.22	4.5	1.5
TFE (440 nm)	2.7	0.20	7.1	2.8
TFE (520 nm)	4.2	0.28	6.7	1.7
Triton X-100 + Ethanol	5.8	0.51	8.6	0.8

(iii) Emission Spectra in Rigid Media at 77 K. Figure 4 shows the emission spectra of MFOH at 77 K. The emission in TFE shows that it is contaminated by the phosphorescence spectrum. It comprises the superposition of a Stokes-shifted fluorescence and a phosphorescence spectrum, as was observed in the case of OHBA[25)] in nonpolar solvents. In the case of methanol and ethanol, the fluorescence is replaced by a blue phosphorescence at 77 K. It is observed that as the temperature is raised the phosphorescence intensity gradually decreases, because of phosphorescence quenching; only fluorescence is observed at room temperature. The presence of phosphorescence in the fluorescence spectra seems to be due to the presence of an intersystem crossing in the proton-transfer process of MFOH. This is characteristic of a triplet $\pi\pi^*$ aromatic carbonyl of benzaldehyde type. As was suggested by Nagaoka et al.,[46)] the blue phosphorescence is likely to be due to the open conformer **II**. Both conformers **IIa** and **IIb** (Scheme 1) can give rise to phosphorescence in these solvents.

At 77 K the open conformer emission in TFE is markedly suppressed. This indicates that the open con-

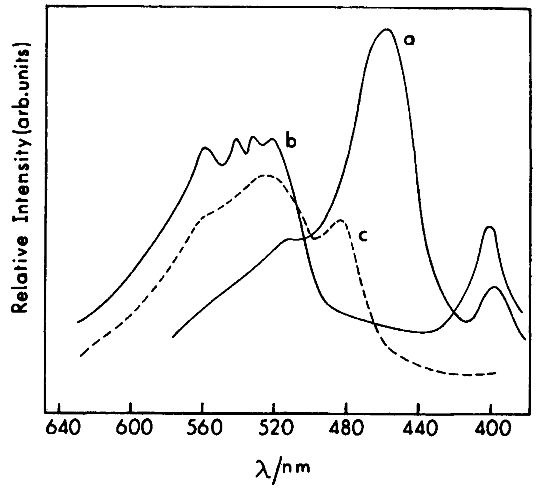


Fig. 4. Emission spectra at 77 K in 1-butanol (a), TFE (b), and ethanol (c). [MFOH]=4.5×10^{-5} to 1.0×10^{-4} mol dm^{-3}.

former is less stable and more energetic than that giving rise to anion emission (520 nm). At low temperature the population of the more energetic conformer **II** is small; this explains the suppression of **II** at 77 K.[47] The open conformer emission in methanol and ethanol may be very weak, even at room temperature. Therefore, the emission of conformer **II** is not observed in ethanol and methanol.

(iv) Rate Constants for Fluorescence Decay. We have also studied fluorescence decays. A typical decay profile of MFOH in ethanol in the presence of Triton X-100 is given in Fig. 5. The emission showed a single exponential decay in the presence and absence of a base. This suggests that the anion emission originates from the MFOH molecule in the same environment, even in presence of a base. The lifetime values increased in the presence of a base, as shown in Table 1. The fluorescence decay-rate constants $k_f(=1/\tau_f)$ are given as the sums of the radiative and nonratiative decay rate constants (k_f^r and k_f^{nr} respectively). From nanosecond measurements and quantum yields of the fluorescence we have estimated the decay rates of the fluorescence species (MFO$^-$) using the following equations:

$$1/\tau_f = k_f = k_f^r + k_f^{nr};\quad k_f^r\tau_f = \phi_f;\quad k_f^{nr} = k_f - k_f^r \qquad (1)$$

These values are given in Table 1. The rate constants are considerably different from that of $k_f^r \approx 10^8$ and $k_f^r \approx 10^9$ s^{-1} reported for MS and OHBA,[19,26,29] respectively, in spite of the similarity in the molecular structure. The low values of the rate constants clearly indicate that both the radiative and nonradiative processes in MFOH are much slower than in MS and OHBA. This slow process points to the fact that the excited-state proton-transfer process of MFOH is not essentially barrier free. The fluorescence quantum yields (ϕ_f) are relatively higher than MS and OHBA, and less than unity. From Table 1 it can be seen that the nonradiative decay constants (k_f^{nr}) are always higher than the radiative decay constants (k_f^r). The conversion of the fluorescence spectrum to the phosphorescence type should be very slow, as mentioned earlier.[38] Therefore, the proton transfer in the S_1 state or the intersystem crossing from the S_1 state to the triplet state may be responsible for the decay of the S_1 state.

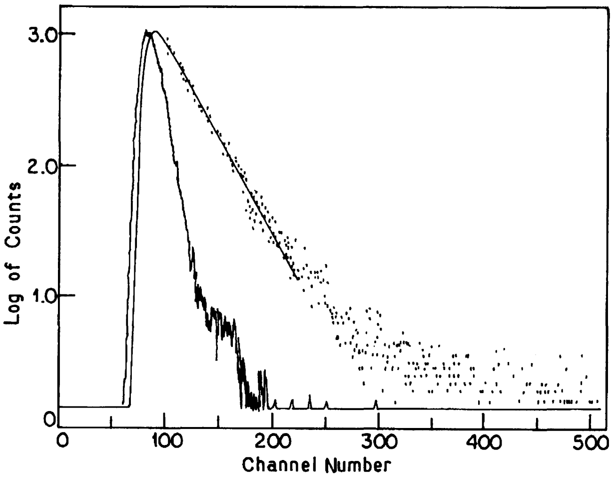


Fig. 5. Typical decay profile (λ_{exc}=530 nm) in ethanol+Triton X-100. The solid curve represents the best computer-fit of the experimental points to a single exponential decay. The lamp profile is denoted by broken lines (resolution 0.167 ns/channel).

Conclusion

The spectra of MFOH in alcoholic solvents illustrate the complex origin of the emission which may arise from some coexisting species in the ground state. These states may originate from the corresponding ground-state forms, or may be produced upon electronic excitation. All of these isomeric forms may be available due to the solute–solvent interaction, which may bring their energy levels closer together.[48] In the case of TFE, dual emission with a large energy gap is obtained from the absorption band. The appearance and disappearance of red band (Fig. 1) with the concentration of MFOH indicate self-association in solution.

The alkyl groups in alcohols have a +**I** effect and are able to release electrons towards it's oxygen atom so that it becomes negatively charged. This negative charge makes the alcohols proton acceptors. Due to the presence of electron-withdrawing fluorine atoms in TFE and bulky alkyl groups in 1-butanol, the electron-releasing ability of TFE and 1-butanol is less than ethanol. However, the emission spectra show that the modes of interaction in TFE and 1-butanol are different. The relative concentration of the conformers depend more or less on the nature of specific and nonspecific interactions with the solvent and, in some cases, on the excitation wavelength as well. However, a comparison of the spectral characteristics when passing from solvent to solvent, clearly demonstrates the significance of solvent effect. Finally, the conclusion that can be drawn from these results is that the reaction coordinate that is involved in this slow rate must be at least partly due to the motion of the proton associated with an intermolecular hydrogen bonding between MFOH and alcohols.

References

1) T. C. Swinney and D. F. Kelley, *J. Phys. Chem.*, **95**, 10369 (1991).

2) D. McMorrow and M. Kasha, *J. Phys. Chem.*, **88**, 2235 (1984).

3) P. F. Barbara, P. K. Walsh, and L. E. Brus, *J. Phys. Chem.*, **93**, 488 (1989).

4) E. Caldin and V. Gold, "Proton-Transfer Reaction," Chapman and Hall, London (1975).

5) D. Huppert, M. Gutmann, and K. Kaufmann, *Adv. Chem. Phys.*, **47**, 643 (1981).

6) J. Heldt and M. Kasha, *J. Mol. Liq.*, **41**, 305 (1989).

7) A. J. G. Strandjord and P. F. Barbara, *J. Phys. Chem.*, **89**, 2355 (1985).

8) S. Yamauchi and N. Hirota, *J. Am. Chem. Soc.*, **110**, 1346 (1988).

9) H. K. Sinha and S. K. Dogra, *Chem. Phys.*, **102**, 337 (1986).

10) M. Itoh and Y. Fujiwara, *J. Am. Chem. Soc.*, **107**, 1561 (1985).

11) A. U. Acuña, A. Costela, and J. M. Muñoz, *J. Phys. Chem.*, **90**, 2807 (1986).

12) M. Kondo, *Bull. Chem. Soc. Jpn.*, **52**, 521 (1979).

13) S. R. Flom and P. F. Barbara, *J. Phys. Chem.*, **89**, 4489 (1985).

14) P. F. Barbara, P. M. Rentzepis, and L. E. Brus, *J. Am. Chem. Soc.*, **102**, 5631 (1980).

15) K. K. Smith and K. J. Kaufmann, *J. Phys. Chem.*, **85**, 2895 (1981).

16) R. S. Becker, C. Lenoble, and A. Zein, *J. Phys. Chem.*, **91**, 3517 (1987).

17) N. P. Ernsting, *J. Am. Chem. Soc.*, **107**, 4564 (1985).

18) N. P. Ernsting, *J. Phys. Chem.*, **89**, 4932 (1985).

19) J. Catalán, F. Toribio, and A. U. Acuña, *J. Phys. Chem.*, **86**, 303 (1982).

20) K. Ding et al., *J. Phys. Chem.*, **87**, 1184 (1983).

21) A. Weller, *Prog. React. Kinet.*, **1**, 189 (1961).

22) T. Forster, *Z. Electrochem.*, **54**, 42 (1950).

23) S. Nagaoka, U. Nagashima, N. Ohta, M. Fujita, and T. Takemura, *J. Phys. Chem.*, **92**, 166 (1988).

24) S. Nagaoka, *J. Photochem. Photobiol.*, **A40**, 185 (1987).

25) S. Nagaoka, N. Hirota, M. Sumitani, and K. Yoshihara, *J. Am. Chem. Soc.*, **105**, 4220 (1983).

26) S. Nagaoka, M. Fujita, T. Takemura, and H. Baba, *Chem. Phys. Lett.*, **123**, 489 (1986).

27) S. Nagaoka and U. Nagashima, *Chem. Phys.*, **136**, 153 (1989).

28) U. Nagashima, S. Nagaoka, and S. Katsumata, *J. Phys. Chem.*, **95**, 3532 (1991).

29) K. K. Smith and K. J. Kaufmann, *J. Phys. Chem.*, **82**, 2286 (1978).

30) L. A. Heimbrook, J. E. Kenny, B. E. Kohler, and G. W. Scott, *J. Phys. Chem.*, **87**, 280 (1983).

31) P. M. Felker, W. R. Lambert, and A. H. Zewail, *J. Chem. Phys.*, **77**, 1603 (1982).

32) A. U. Acuña, J. Catalán, and F. Toribio, *J. Phys. Chem.*, **85**, 241 (1981).

33) J. Goodman and L. E. Brus, *J. Am. Chem. Soc.*, **100**, 7472 (1978).

34) A. Mordzinski and A. Grabowska, *Chem. Phys. Lett.*, **90**, 122 (1982).

35) E. Hoshimoto, S. Yamauchi, N. Hirota, and S. Nagaoka, *J. Phys. Chem.*, **95**, 10229 (1991).

36) R. Ray and S. Mukherjee, *Indian J. Chem., Sect. A*, **28A**, 545 (1989).

37) S. Mukherjee, *Bull. Chem. Soc. Jpn.*, **60**, 1119 (1987).

38) S. Mitra, R. Das, and S. Mukherjee, *Chem. Phys. Lett.*, **202**, 549 (1993).

39) C. J. Selisker, *J. Mol. Spectrosc.*, **53**, 140 (1974).

40) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985)

41) G. J. Woolfe and P. J. Thistlethwaite, *J. Am. Chem. Soc.*, **102**, 6917 (1980).

42) W. Klöpffer, *Acv. Photochem.*, **10**, 311 (1977).

43) W. Klöpffer and G. Naundorf, *J. Lumin.*, **8**, 457 (1974).

44) P. J. Thistlethwaite and G. J. Woolfe, *Chem. Phys. Lett.*, **63**, 401 (1979).

45) G. J. Woolfe and P. J. Thistlethwaite, *J. Am. Chem. Soc.*,**103**, 3849 (1981).

46) S. Nagaoka, N. Hirota, M. Sumitani, K. Yoshihara, E. L. Kochany, and H. Iwamura, *J. Am. Chem. Soc.*, **106**, 6913 (1984).

47) K. Das, N. Sarkar, D. Majumdar, and K. Bhattacharyya, *Chem. Phys. Lett.*, **198**, 443 (1992).

48) F. Toribio, J. Catalán, F. Amat, and A. U. Acuña, *J. Phys. Chem.*, **87**, 817 (1983).