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Evidence of Ground-State Proton-Transfer Reaction of 3-Hydroxyflavone in Neutral Alcoholic Solvents

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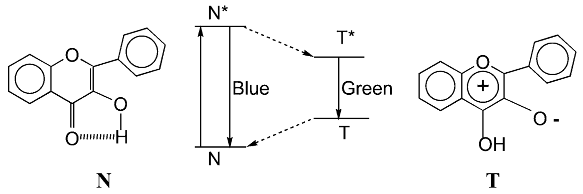
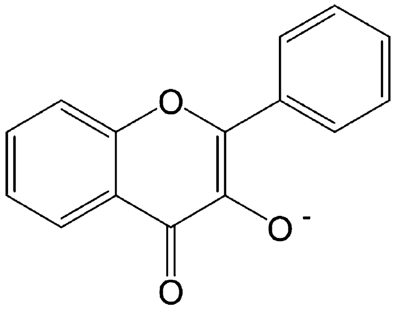
Photophysical behavior of 3-hydroxyflavone (HF), a molecule that exhibits excited-state intramolecular proton-transfer reaction and has been studied extensively in the past, has been reinvestigated in hydrogen bond donating solvents. In neat alcohols or in an acetonitrile−methanol mixture, a long wavelength absorption band ($\lambda_{max} \approx 410$ nm) has been observed for the first time. It is found that selective excitation of this band does not produce the characteristic fluorescence of the "normal" form or the tautomer; instead, an emission characterized by a featureless band ($\lambda_{max} \approx 480$ nm) is observed. The absorption and emission bands have been found to disappear completely in the presence of water. The influence of temperature suggests that the species responsible for the 410 nm absorption band is produced in higher concentrations at higher temperatures. On the basis of the present results and the available literature, the long-wavelength absorption band of HF has been attributed to its anionic form, generated in the alcoholic media by solvent mediated deprotonation of the 3-hydroxy group of the molecule in the ground state.

1. Introduction

Excited-state intramolecular proton-transfer (ESIPT) reaction is considered to be one of the simplest photoreactions of great importance in chemical and biological systems and has received a great deal of attention both experimentally and theoretically.[1] 3-Hydroxyflavone (HF) is undoubtedly one of the most extensively studied systems for understanding of the mechanism and dynamics of the intramolecular proton-transfer reactions.[1−35] Sengupta and Kasha were the first to interpret the dual fluorescence (referred to as "blue" and "green" emission) of HF as due to emission originating from the normal isomer (represented in Scheme 1 as **N**) and the tautomer (**T**).[2] According to these authors, excitation of HF, which exists in the ground state as **N**, leads to an adiabatic ESIPT reaction resulting in the formation of **T***. The "blue" fluorescence occurs from **N***, whereas the "green" one originates from **T***. Time-resolved fluorescence studies by Woolfe and Thistlethwaite and later by Itoh and co-workers have shown the dependence of the ESIPT dynamics on the nature of the solvent and temperature.[3,4] Steady-state and time-resolved studies by Barbara and co-workers revealed a biexponential proton-transfer kinetics, which was attributed to the presence of two different forms of **N** in the excited state undergoing proton-transfer reaction at different rates.[5] These authors also investigated the isotope effect on the proton-transfer reaction.[6] The effect of solvent on the proton-transfer reaction of HF was examined in detail by McMorrow and Kasha[7,8] and later by Strandjord and Barbara.[9] These studies led to an understanding of the factors that control the mechanism and dynamics of the proton-transfer reaction in HF. McMorrow and Kasha concluded that ESIPT in HF is so rapid in dry hydrocarbon solvents that the fluorescence from **N*** could not be observed even in frozen solvent at 77 K. Interestingly, these authors observed a third fluorescence band ($\lambda_{max} = 497$ nm) in methylcyclohexane at 77 K, which was attributed to the anionic form (**A**) of HF formed because of a trace of water, as an impurity in the solvent.[8] Various solvated structures of HF were invoked to account for the different fluorescence bands of HF in hydroxylic solvents. The fluorescence behavior of HF was studied in a series of alcohols by Strandjord and Barbara with a view to gaining insight into the mechanism of ESIPT of HF in alcoholic solvents.[9] These authors observed a direct correlation between the slow proton-transfer rate constant and the hydrogen bond donating ability of the solvent. It was also found that the rate constant for the slow proton-transfer process is independent of the viscosity of the solvent. Taking into consideration the available photophysical data of HF, a mechanistic model for the proton-transfer reaction was proposed that

SCHEME 1





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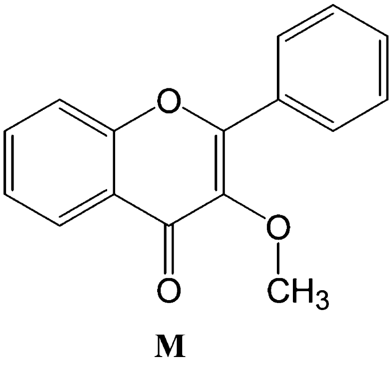
assumed the formation of 1:1 complex with the alcohol molecules.[9] Further studies on several HF derivatives suggested that the ESIPT mechanism in these systems is governed primarily by the energetic factors of the solute:solvent complex rather than by solvent reorganization dynamics.[10] Several papers have subsequently appeared dealing with various aspects of the proton-transfer reaction in HF under a variety of reaction conditions. A femtosecond time-resolved absorption and fluorescence experiment[11] suggested the presence of subpicosecond and picosecond components in all solvents. Even in methanol, a fast rise component (<125 fs, the time resolution of the instrument) has been observed in transient absorption experiment. The fast and slow components in alcohol have been attributed to the monosolvated and disolvated HF molecules, respectively. A more recent ultrafast measurement by Ameer-Beg et al.[12] however indicates that the proton-transfer reaction in HF is faster than what was found in the earlier experiments. These authors could observe a 60 fs component in ethanol. In aprotic solvents such as methyl cyclohexane and acetonitrile, ESIPT was found to be even faster. The most recent measurements on HF have been made by Bader et al.[13] From an analysis of the homogeneous bandwidth of the emission spectra of HF and its deuterated derivative in Shpol'skii matrixes (*n*-octane and *n*-octane/octanol mixtures) at 10 K, the time constant for excited-state proton-transfer reaction is estimated to be 39 ± 10 fs.[13]

It is therefore evident that though steady-state and time-resolved fluorescence properties of HF in aprotic media are fairly well understood, the mechanism of the proton-transfer reaction in hydrogen bond donating solvents is still far from clear and is a topic of further investigation. What we found difficult to comprehend is the fact that even though fluorescence measurements in hydroxylated solvents have clearly indicated the formation of complexes of various stoichiometries between HF and the solvent molecules, absorption measurements somehow have not provided any clue to the formation of the complex and on its nature. Because identification of specific absorption due to the hydrogen-bonded complex allows selective excitation of this species (without exciting the intramolecularly hydrogen bonded molecules), thereby making the fluorescence measurements in these media much simpler, we thought it appropriate to reinvestigate the absorption and fluorescence behavior of HF in alcoholic solvents.

2. Experimental Section

HF (Tokyo Kasei Co.) was recrystallized several times from methanol. The recrystallized sample was vacuum sublimed prior to photophysical measurements. The methoxy derivative (**M**) of HF was prepared by following the literature procedure.[32] The solvents used in this study (acetonitrile, ethyl acetate, diethyl ether, methanol, ethanol, 2-propanol, 1-butanol, *n*-hexane) were dried over calcium hydride or calcium oxide and distilled over magnesium turnings and iodine or sodium metal following standard procedures.[36] Triple-distilled water was used in this study. The purity of the solvents was checked (by absorption and emission measurements) prior to the photophysical studies.



M

The UV−vis absorption and fluorescence spectra of HF were recorded on a Shimadzu (UV-3101PC) spectrophotometer and SPEX (FluoroMax-3) spectrofluorometer, respectively. All fluorescence measurements were corrected for the instrumental response. Temperature-dependent absorption measurements were carried out with the help of TCC-260 thermo-electrically temperature-controlled cell holder (Shimadzu). The fluorescence lifetime of the sample was measured on a single photon counting spectrofluorometer (IBH, Model 5000). The instrument was operated with a thyratron-gated flash lamp filled with hydrogen at a pressure of 0.5 bar. The lamp was operated at a frequency of 40 kHz and the pulse width of the lamp under the operating conditions was ~1.2 ns. The decay times were estimated from the measured fluorescence decays and the lamp profile, using a nonlinear least-squares iterative fitting procedure. The goodness of the fit was evaluated from the χ^2 values and the plot of the residuals.

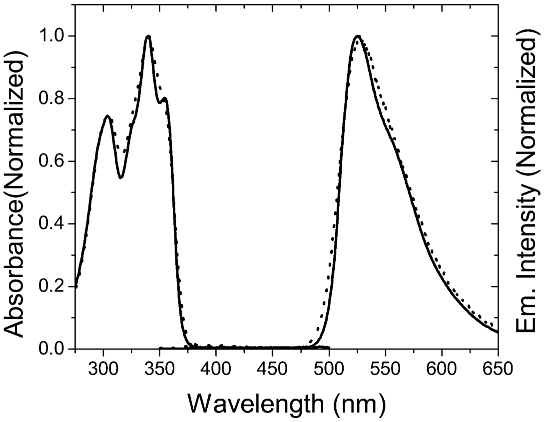


Figure 1. Absorption and fluorescence spectra of HF (4×10^{-6} M) in *n*-hexane (—) and acetonitrile (- - -). The fluorescence spectra are obtained by excitation at 345 nm. The absorption and emission intensities in the two solvents have been normalized at the respective maximum.

3. Results

3.1. Spectral Behavior in Aprotic Solvents. The absorption and fluorescence behavior of HF in nonpolar media such as *n*-hexane and in polar media such as acetonitrile are depicted in Figure 1. Except for the fact that the absorption spectrum is relatively more resolved in *n*-hexane, the spectral behavior of the system is very similar in two solvents. The onset of the absorption is observed at around 375 nm and the absorption peaks (±1 nm) are observed at 355, 340, and 304 nm. The fluorescence spectrum, on the other hand, is characterized by a highly Stokes-shifted band (λ_{max} = 526−528 nm). This spectral behavior of HF is consistent with that reported previously, according to which the absorption band is due to excitation of the form **N** and the Stokes-shifted fluorescence originates from **T***.[2]

3.2. Spectral Behavior in Protic Solvents. *3.2.1. Absorption.* Although the spectral behavior of HF in aprotic solvents is in agreement with the literature, the absorption and fluorescence behavior of the system in alcoholic media is found to be significantly different from what is reported in the literature. In

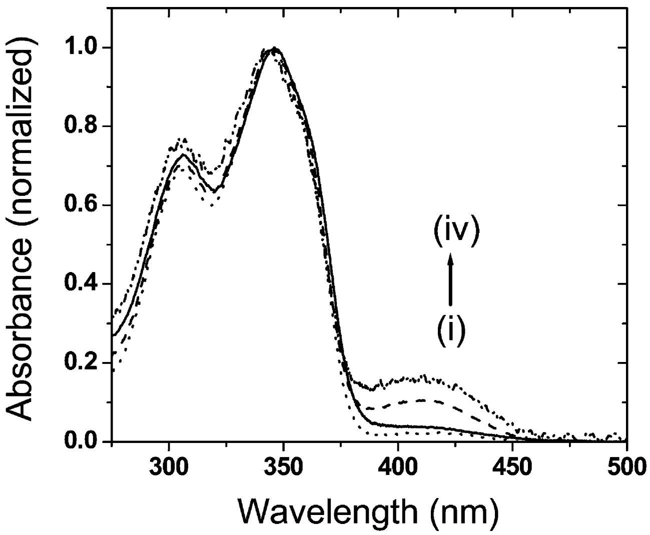


Figure 2. Absorption spectra of HF in different alcohols. The spectra labeled (i) to (iv) denote those obtained in 2-propanol, 1-butanol, ethanol, and methanol, respectively. The spectra have been normalized at their respective maximum.

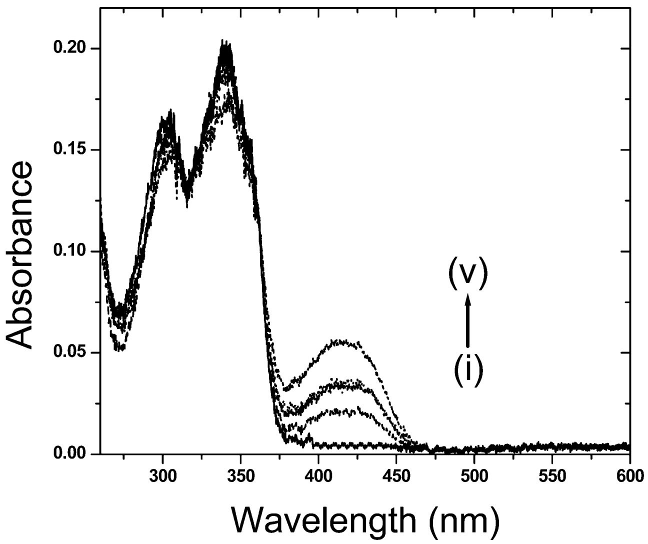


Figure 3. Effect of addition of methanol on the absorption behavior of an acetonitrile solution of HF. The concentrations of methanol in the spectra labeled (i) to (v) are (i) 0, (ii) 0.5, (iii) 1.0, (iv) 2.0, and(v) 3.0 M.

methanol, a broad absorption band is observed (Figure 2) between 400 and 450 nm ($\lambda_{\max} \approx 410$ nm) that has not been reported previously. To make sure that this absorption is not due to any impurity in methanol, we have examined the absorption behavior of the system in a few other alcohols such as ethanol, 2-propanol, and 1-butanol. As can be seen, this hitherto unobserved band of HF above 400 nm appears in all the solvents, although less prominently in other alcohols.

A long-wavelength absorption band similar to that seen in pure alcoholic solvents is also observed on addition of methanol (or other alcohols) to an acetonitrile solution of HF (Figure 3). The observation of an isosbestic point around 362 nm is suggestive of the existence of two species in the solution.

We examined the influence of temperature on the absorption behavior of HF in methanol and the results are depicted in Figure 4. With increase in the temperature the optical density (OD) at 410 nm gradually increases with concomitant decrease of the OD in the 300−350 nm region of the spectra. An isosbestic point could be observed at ~372 nm.

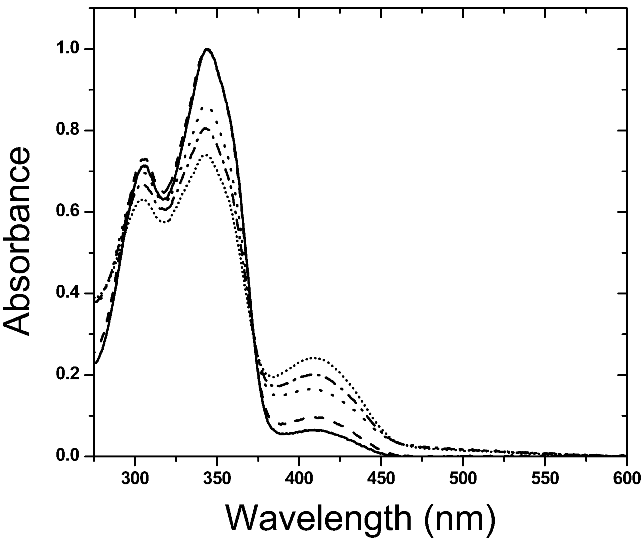


Figure 4. Temperature dependence of the absorption spectra of HF in methanol. The spectra shown in increasing order of intensity at 410 nm are obtained at temperatures 10, 20, 30, 40, and 50° C.

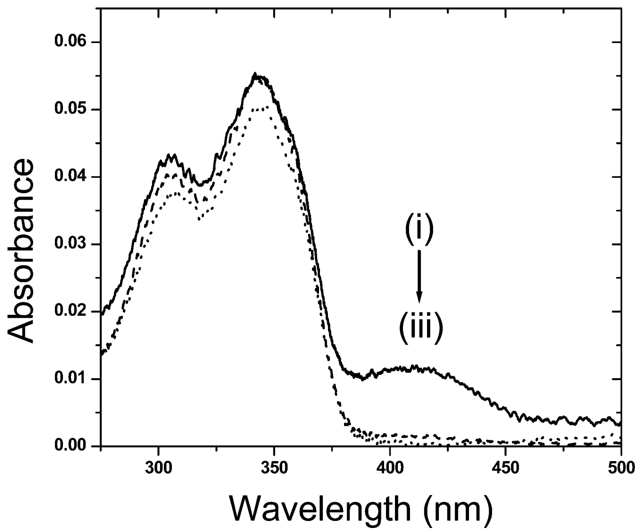


Figure 5. Influence of water on the absorption behavior of HF in methanol. The water concentration for the spectra labeled from (i) to (iii) are 0.00, 1.11, and 3.33 M, respectively.

The influence of water on the long wavelength absorption band is found to be quite interesting. In the presence of a small concentration of water (~1 M), the new absorption band disappears almost completely. Figure 5 illustrates the influence of water on the absorption behavior of HF.

3.2.2. Fluorescence. The fluorescence behavior of HF in alcoholic media is also found to be different from that reported previously. We found that the fluorescence spectrum of HF is dependent on the excitation wavelength. Figure 6 depicts the excitation wavelength dependence of the fluorescence spectrum of HF. Although excitation at 305 nm produces the dual emission bands (with maxima at 405 and 527 nm) reported in the literature, a third emission band, which appears as a shoulder at around 480 nm, can also be seen. Excitation at 410 nm, however, results only in the formation of the 480 nm band. The fluorescence lifetime of this emitting species in methanol, measured from the decay profile obtained on excitation at 410 nm, is estimated to be ~2.0 ns. The decay profile corresponding to the 480 nm emission was also examined by exciting the sample at 305 nm. However, we could not resolve any rise time

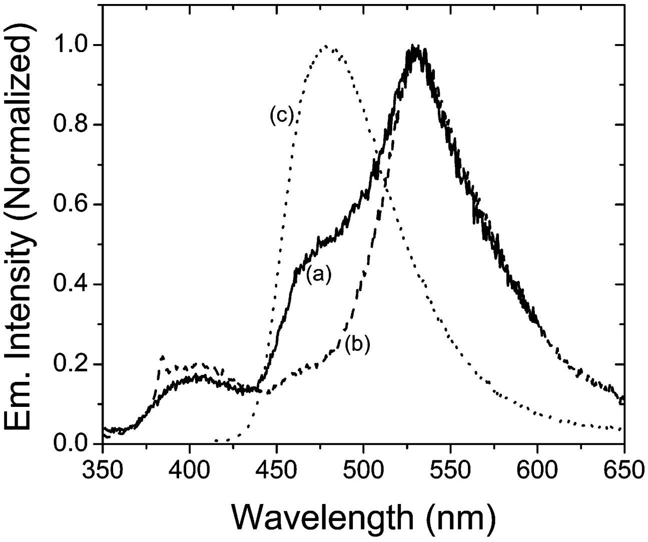


Figure 6. Excitation wavelength dependence of the fluorescence spectrum of HF in methanol. Spectra labeled (a), (b), and (c) are obtained on excitation at 305, 345, and 410 nm, respectively.

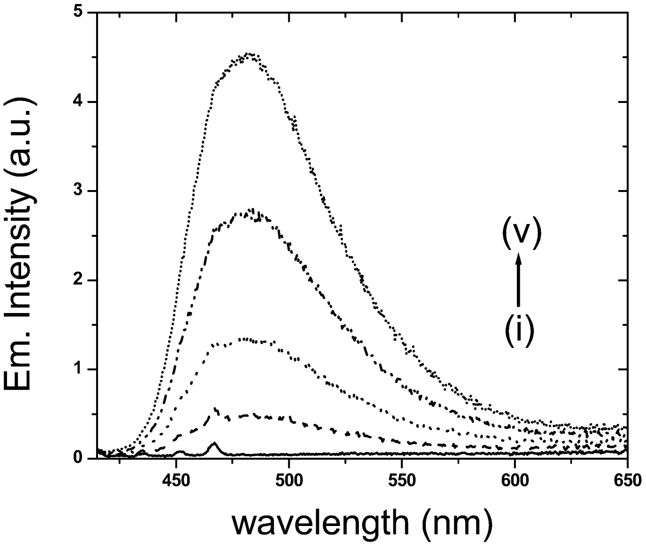


Figure 7. Effect of addition of methanol on the fluorescence behavior of HF in acetonitrile ($\lambda_{ex} = 410$ nm). The concentrations of methanol in the spectra labeled (i) to (v) are as follows: (i) 0, (ii) 0.5, (iii) 0.7, (iv) 1.0, and (v) 1.2 M

that may suggest that 480 nm species is produced on excitation of a second species.

Although only the green fluorescence due to the tautomer (**T***) is observed in acetonitrile, addition of methanol indeed produces the 480 nm emission band that is observed in neat alcoholic solutions. This effect has been illustrated in Figure 7.

The influence of trace amount of water on the fluorescence behavior of HF is illustrated in Figure 8. As can be seen, the 480 nm emission band disappears almost completely in the presence of 1 M water.

4. Discussion

We were somewhat puzzled initially to figure out how a simple absorption band (though weak in intensity) could be missed by others, particularly when taking into consideration the large volume of investigations made on the current system.[1−35] We had to carry out several control experiments to rule out the possibility that the absorption is not due to any impurity in the sample/solvent and to convince ourselves that the new absorption band, which can be crucial to the dynamics and mechanism of excited-state proton-transfer reaction in alcoholic solvent, is indeed a real one. It is only when we observed that the new absorption vanishes completely in the presence of a trace amount of water that we realized others might have missed this absorption because of the presence of a small amount of water in the alcohol. Literature clearly shows that though utmost care was taken to ensure that the hydrocarbon solvents were free from hydroxylic impurities, no purification procedure was adopted for methanol.[8]

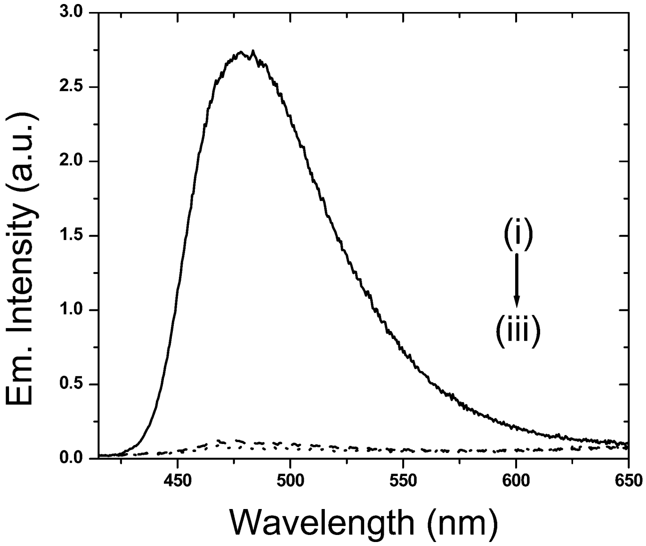
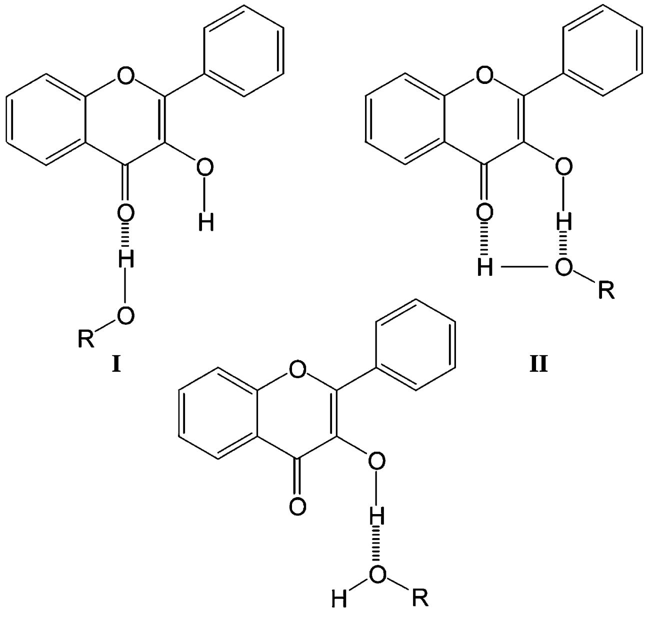


Figure 8. Effect of addition of water on the fluorescence spectrum of HF in methanol ($\lambda_{ex} = 410$ nm). The concentration of water in the spectra labeled from (i) to (iii) are 0.00, 2.22, and 3.33 M, respectively.

Because the long-wavelength absorption can be observed only in alcoholic solvents (pure alcohols or mixed solvent containing alcohol), the hydrogen bond donating ability of the solvent is likely to be responsible for the formation of the species that contribute to this absorption. This is corroborated by the fact that this long-wavelength absorption could not be observed in solvents that are well-known hydrogen bond acceptors (such as diethyl ether and ethyl acetate). A further support for this conjecture comes from the observation that the intensity of the 410 nm band decreases as follows: methanol > ethanol > 1-butanol > 2-propanol. This order is in fact identical with the hydrogen bond donating ability[37] of the solvent molecules.

Taking note of the isosbestic point in acetonitrile−methanol mixed solvent and the discussion made in the previous paragraph, one can perhaps attribute the 410 nm absorption to a 1:1 complex formed between HF and alcohol molecules and speculate structures such as **I** or **II** for the complex. **III** is ruled out as a possibility as the solvent molecule does not play the role of a hydrogen bond donor in this structure.

However, there are a few problems in attributing the 410 nm absorption band to one of the two 1:1 complexes. The main difficulty is the following: We found that the methoxy derivative of HF (**M**) does not show the long-wavelength absorption band in alcoholic solvents. Had the 410 nm absorption band been due to a 1:1 complex in which the solvent acts as a hydrogen bond donor (as in **I** or **II**), **M** should have exhibited this absorption in alcoholic solvents. A second difficulty is the interpretation of the observed effect of the temperature on the absorption spectrum of HF. An increase in temperature should have led to the dissociation of the complex (**I** or **II**) resulting in a reduction in the intensity of the long-wavelength band. However, the effect of temperature on the



I **II**

III

absorption intensity at 410 nm is exactly opposite to what is expected from the hydrogen-bonded complex. A third difficulty is to find a suitable explanation for the disappearance of the absorption band in the presence of water. Because water is a better hydrogen bond donor (vide later) than the alcohols, one would have expected a more intense 410 nm band in water.

Clearly, 1:1 complexation between HF and hydrogen bond donating solvents cannot account for some of the crucial observations made in this paper and one needs a different assignment for the 410 nm absorbing species. We take into consideration that the species, which absorbs at 410 nm emits at around 480 nm. Although no absorption band of the kind observed here has been reported in the past, a number of workers have reported an emission band similar to the one described here. McMorrow and Kasha[8] attributed this type of emission, observed in MCH glass (at 77 K), to the anion (**A**) of HF, formed as a result of the presence of water as impurity in the solvent. Brucker and Kelly,[34] on the other hand, attributed a similar emission band of 3HF in the argon:methanol matrix at 30 K to a monosolvated tautomer. Interestingly, while studying the proton-transfer reaction in the HF/ammonia complex at 10 K, Brucker and Kelly[35] observed a fluorescence excitation band around 400 nm that resembles the present absorption band. These authors attributed this band to the HF anion (**A**), formed as a result of proton transfer from 3HF to the $(NH_3)_n$ cluster in the ground state.

Taking into consideration the literature and our observation that the absorption and emission spectra of the anion, **A**, generated in alkaline methanolic solution of HF are very similar to the spectra we have observed in alcoholic media, we assign the 410 nm absorbing species to **A** that emits at 480 nm. This implies that HF undergoes solvent mediated deprotonation reaction in alcoholic media in the ground state (Scheme 2). The extent of anion formation has been evaluated by estimating the equilibrium constant, K_a by monitoring the changes in the absorbance at 410 nm following addition of methanol to an acetonitrile solution of HF. Using data from Figure 3 and molar extinction coefficient of **A** at 410 nm as 1.44×10^4 M^{-1} cm^{-1} (estimated from the absorbance at 410 nm in a KOH (excess) added alcoholic solution of known concentration of HF), the K_a value ($\pm$ 15%) is found to be 2.9×10^{-7}. This suggests that the extent of ionization of HF is rather small.

SCHEME 2

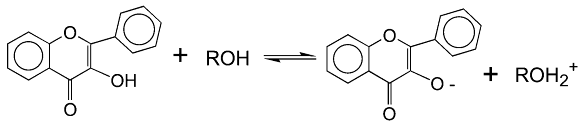


TABLE 1: Kamlet−Taft's Hydrogen Bond Donor Acidity (α) and Hydrogen Bond Acceptor Basicity (*β*) Parameters,[a] Collected from Ref 38

solvents	*β*	α
diethyl ether	0.47	0.00
ethyl acetate	0.45	0.00
acetonitrile	0.31	0.19
formamide	(0.55)[b]	0.71
2-propanol	(0.95)	0.76
ethanol	(0.77)	0.83
methanol	(0.62)	0.93
water	0.47[c]	1.17
2,2,2-trifluoroethanol	0.00	1.51

[a] Vide ref 39. [b] Values in the parenthesis are less certain. [c] From ref 40.

In this context we take note of an earlier paper wherein Parthenopoulos and Kasha report anion formation of HF in neutral medium.[31] The formation of **A** in a neutral solvent, formamide, was attributed to greater hydrogen bond donating ability of this solvent compared to the others such as acetonitrile or alcohol.[31] However, though the hydrogen bond donating ability of formamide is greater than that of acetonitrile, most of the alcohols are stronger hydrogen bond donors compared to formamide[38] and, hence, should have formed the anion, **A**. Moreover, according to the explanation offered, **A** should have been formed in water, known to be the strongest hydrogen bond donor.

Having observed the anion **A** in alcoholic media, we examine how the proton abstracting ability of the alcohols compare with that of the other solvents, where the 410 nm absorption band could not be observed and, also, whether it is possible for the alcohol molecules to abstract proton from HF in the ground state. That the proton abstracting ability of the alcohols is superior to other solvents is evident from Table 1 in which the hydrogen bond donating and accepting abilities of some of the solvents pertinent to this investigation are collected from the literature.[38] The proton abstracting ability of the solvents, as assessed from the hydrogen bond acceptor basicity parameter,[39] *β*, increases in the following order: acetonitrile < ethyl acetate ≈ diethyl ether < alcohols. We note that formamide, where anion formation has been observed previously, has a *β* value of 0.55, higher than that of acetonitrile, ether, and ethyl acetate. To address to the second question of whether the alcohols can abstract a proton from HF, we take note of the fact that aromatic hydroxy compounds are in general stronger acids compared to aliphatic hydroxy compounds. Because HF contains an electron withdrawing carbonyl group adjacent to the hydroxy group, one can expect it to be an even stronger acid, making the generation of anion possible in alcoholic media. Perhaps the most important question that needs to be answered here is why the anion disappears in the presence of water. It is evident from Table 1 that the hydrogen bond acceptor basicity (*β*) of water is not as good as that of the alcohols and, also, the hydrogen bond donor acidity (α) of water is the highest among all the solvents. It is therefore quite likely that the equilibrium shown in Scheme 2 is displaced toward the left in the presence of water. It is for the same reason, the anion formation could not be observed in

2,2,2-trifluoroethanol, a solvent with a high α value, but with a β value of zero (vide Table 1).

Even though we have unambiguously established that the anionic form (**A**) of HF, generated by ground-state proton-transfer reaction, is responsible for the long-wavelength absorption band, we find that the intensities of the 410 nm band in various alcoholic solvents do not commensurate with the hydrogen bond acceptor basicity values. Instead, the intensities are closely related to the hydrogen bond donating ability of the solvents. This observation implies that the formation of anion in neutral solvents is governed by two factors. First, formation of a hydrogen-bonded complex between HF and the solvent, where the solvent acts as a hydrogen bond donor. This is followed by abstraction of the hydroxy proton of HF, where the hydrogen bond acceptor basicity (β) of the solvent plays a decisive role. Although the first step may not be favored by an increase of temperature, the second step that involves the abstraction of proton from HF is expected to be facilitated by an increase in temperature. The observed temperature dependence implies that the influence of temperature is more pronounced for the second step.

5. Conclusion

We have identified for the first time a long-wavelength absorption band of 3-hydroxyflavone, an extensively studied system, in alcoholic media. A detailed study of the influence of various factors on the absorption and fluorescence behavior reveals that the absorption is due to the generation of the anionic form of the molecule in the ground state via solvent mediated deprotonation of the 3-hydroxy group.

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