

# Photophysics of 1-hydroxy-9-fluorenone: absence of excited state intramolecular proton transfer reaction

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## Abstract

Absorption, fluorescence, fluorescence excitation spectroscopy and time dependence fluorimetric studies of 1-hydroxy-9-fluorenone (1-HFu) and 1-methoxy-9-fluorenone (1-MFu) have been studied in different solvents. Both these molecules exhibit only one small Stokes shifted and similar fluorescence band, even in ultra dry cyclohexane. This suggests that excited state intramolecular proton transfer (ESIPT) reaction is not observed in 1-HFu. The electronic structure calculations were carried out on each species using semi-empirical AM1 and CNDO/S-CI methods, as well as, hybrid density-functional theory (DFT) B3LYP with 6–31 G\*\* basis set to find out the cause for non-observance of ESIPT in 1-HFu.

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**Keywords:** 1-Hydroxy-9-fluorenone; Absorption spectrum; Fluorescence spectrum; ESIPT; Theoretical calculations

## 1. Introduction

Intramolecular hydrogen bonds (IHB) are known to have a considerable effect on the geometric, electronic, vibrational and radiationless transitional properties of the substituted aromatic molecules [1–3]. Besides its relevance in understanding the conformation in bio-molecules, the above properties have many practical utilities worthy of considerations, e.g. development of UV photo-stabilizers [4], molecular energy storage devices [5], dye lasers [6], high-energy radiation detectors [7] and fluorescent probes [8,9].

Basic conditions for observing ESIPT reactions are the presence of IHB between the acidic centers (–OH, –NH<sub>2</sub> groups) and the basic centers (>C=O, =N– groups) in the ground state (S<sub>0</sub>) and proper energy levels of the enol and the tautomer in the first excited singlet state (S<sub>1</sub>). The driving force for the proton transfer from the acidic center to the basic center is the drastic changes observed in the charge densities at these centers in S<sub>1</sub> state. Thus, the acidic center becomes stronger acid and the basic center becomes stronger base in S<sub>1</sub> state. The presence of single fluorescence band either from enol or from tautomer or the dual fluorescence from both enol and tautomer depend upon the:

(i) changes in the pK<sub>a</sub> values of the acidic and basic centers [10], (ii) energy gap between the enol and tautomer in S<sub>1</sub> state and (iii) presence of different conformers leading to or not leading to the formation of tautomer from the enol one. Thus, it is important to note that the presence of IHB between the acidic and basic centers in a molecule does not guarantee that ESIPT will occur. For example, molecules like 1-aminoanthraquinone (1-AA) [11] and 1,4-dihydroxyanthraquinone (1,4-DHA) [12] do not exhibit evidence of a strongly Stokes shifted emission (i.e. from the tautomer band).

1-HFu is a potential molecule which can exhibit ESIPT, since it possesses both acidic and basic centers and involves IHB in S<sub>0</sub>. Present study has been carried out to see whether this molecule exhibits ESIPT or not? If not, what is the mechanism for this behavior? Spectroscopic studies were also carried out on 1-MFu to help in assigning the transitions.

## 2. Materials and methods

1-HFu was procured from Aldrich Chemical Company, UK, whereas 1-MFu was prepared from 1-HFu using methyl iodide in basic medium [13]. Both these compounds were purified by repeated crystallization from ethanol. Obtaining identical fluorescence and fluorescence excitation spectra

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with different excitation and emission wavelengths respectively in any one particular solvent checked the purity of both the compounds. All the solvents, except ethanol, were either of spectroscopic grade or HPLC grade from E. Merck and were used as such. Triply distilled water was used for the preparation of aqueous solutions.

Procedure used to prepare the solutions, adjustment of pH and instruments used to record absorption, fluorescence excitation and fluorescence spectra, as well as, to measure excited state lifetimes were the same as mentioned in our recent paper [14]. Fluorescence quantum yields ( $\phi_f$ ) have been measured from solutions having absorbance less than 0.1, using quinine sulphate in 1N H<sub>2</sub>SO<sub>4</sub> as reference ( $\phi_f = 0.55$ ) [15]. Concentration of 1-HFu and 1-MFu was kept at  $2 \times 10^{-5}$  M.

### 3. Semi-empirical quantum mechanical calculations

Different species of 1-HFu and 1-MFu (Scheme 1) were considered. Different parameters, e.g. total energy ( $E$ ), dipole moment ( $\mu$ ), dihedral angle ( $\varphi$ ) and the charge densities at different basic centers of different structures of 1-MFu and 1-HFu were calculated using AM1 method (QCMP137, MOPAC 6/PC) [16] and optimizing the geometries of various species in S<sub>0</sub> state, as well as, in the S<sub>1</sub> state by taking in to account the configuration interactions (CI = 5 in MOPAC, total configurations 100). Similar parameters in the S<sub>1</sub> state with ground state geometry and in S<sub>0</sub>

state with excited state geometry were also calculated using AM1 method. These parameters depict the Franck–Condon absorption and fluorescence transitions. Relevant data are compiled in Tables 1 and 2, along with experimental data. Assignment of singlet and triplet states were made by using CNDO/S-CI method, described elsewhere [17] and values are compiled in Table 3. Charge densities in the S<sub>1</sub> state at all the basic centers have also been obtained by CNDO/S-CI method and are compiled in Table 1.

The electronic structure calculations were also performed on each species using Gaussian 98 program [18]. The geometry optimization was carried out on each species of 1-HFu and 1-MFu in S<sub>0</sub> state using DFT [19,20] B3LYP with 6–31 G\*\* [18,21] basis set. The geometry of these stationary points on S<sub>1</sub> state was calculated using configurations interaction singles (CIS) [22,23] theory with 6–31 G\*\* basis sets. Time dependent (TD) [23,24] B3LYP was also used to calculate the excited state energies at the calculated stationary point geometry in S<sub>0</sub> and S<sub>1</sub> states. Relevant data are compiled in Table 4.

Dipolar solvation energies for different species have been calculated using the following expression based on Onsager's theory [25].

$$\Delta E_{\text{solv}} = - \left( \frac{\mu^2}{a^3} \right) f(D) \quad (1)$$

where  $f(D) = (D - 1)/(2D + 1)$ ,  $D$  is the dielectric constant of the solvent,  $\mu$  the dipole moment of the fluorophore in the respective state and ' $a$ ' the Onsager's cavity radius. For

Table 1  
Calculated properties of 1-MFu and 1-HFu rotamers/tautomer in the ground and excited states

	1-MFu-b	1-MFu-a	1-HFu-a	1-HFu-b	1-HFu-T
$E$ (eV)	−2569.1311	−2569.1288	−2414.0829	−2413.8695	−2413.2925
$E_{\text{sol}}$ (eV)	−2569.1873	−2569.1604	−2414.1544	−2413.9627	−2413.3864
$\mu_{\text{g}}$ (D)	3.44	2.40	3.35	3.82	3.76
$\Delta E_{ij}$ (nm) (CNDO/S-CI)					
S <sub>1</sub>	340	412	343	341	429
S <sub>2</sub>	311	315	314	312	392
$\mu_{\text{e}}$ (D) (CNDO/S-CI)					
S <sub>1</sub>	3.67	4.31	2.97	3.23	6.02
S <sub>2</sub>	5.7	5.54	6.23	6.00	8.82
S <sub>1</sub> state					
$E$ (eV)	−2565.8415	−2565.7785	−2410.9997	−2410.6229	−2410.7475
$E_{\text{sol}}$ (eV)	−2565.9476	−2565.8744	−2411.1952	−2410.7827	−2410.9648
$\mu_{\text{e}}$ (D)	4.73	4.18	5.53	5.00	5.80
Charge densities					
S <sub>0</sub>					
O <sub>14</sub>	6.2553	6.2458	6.2820	6.2718	6.2570
O <sub>23</sub>	6.4312	6.4163	6.4312	6.4157	6.4817
S <sub>1</sub>					
O <sub>14</sub>	6.2557	6.2434	6.2768	6.2708	6.2666
O <sub>23</sub>	6.1115	6.1025	6.1356	6.1100	6.0736
S <sub>2</sub>					
O <sub>14</sub>	6.2427	6.2443	6.2763	6.2684	6.2764
O <sub>23</sub>	6.5145	6.5288	6.5309	6.5127	6.5126

Table 2

Assignment of excitation and fluorescence transitions of 1-MFu and 1-HFu in terms of calculated energies (eV), with and without solvation energies and experimental values

Assignment	1-Mfu-a	1-MFu-b	1-HFu-a	1-HFu-b	1-HFu-T
Excitation					
Without solvation					
Single point	3.36	3.30	3.10	3.19	2.55
CNDO/S-CI	3.65	3.01	3.61	3.64	2.89
DFT	3.14	3.06	3.13	3.08	2.75
Experimental	3.18		3.14		
With solvation					
Single point	3.31	3.20	2.96	3.12	2.42
Experimental	3.26		3.26		
Emission					
Without solvation					
Single point	3.36	3.28	3.04	3.19	2.49
Experimental	2.78		2.73		
With solvation (acetonitrile)					
Single point	3.30	3.19	2.82	3.02	2.25
Experimental	2.58		2.52		

Table 3

Energy ( $\text{cm}^{-1}$ ) of the few singlet and triplet states of 1-HFu and 1-MFu under isolated and solvated conditions (water) obtained by CNDO/S-CI method, oscillator strengths are given in parenthesis

States	Experimental			
	Cyclohexane	Singlet	Solvated singlet	Triplet
1-HFu				
$\psi_1$	25641	29128 (n, $\pi^*$ ) (0.000)	29245 (n, $\pi^*$ )	22655 ( $\pi$ , $\pi^*$ )
$\psi_2$	27973	31859 ( $\pi$ , $\pi^*$ ) (0.095)	30429 ( $\pi$ , $\pi^*$ )	25402 ( $\pi$ , $\pi^*$ )
$\psi_3$	34013	34274 ( $\pi$ , $\pi^*$ ) (0.015)	32812 ( $\pi$ , $\pi^*$ )	28032 ( $\pi$ , $\pi^*$ )
1-Mfu				
$\psi_1$	25641	29407 (n, $\pi^*$ ) (0.000)	29340 (n, $\pi^*$ )	22685 ( $\pi$ , $\pi^*$ )
$\psi_2$	28490	32141 ( $\pi$ , $\pi^*$ ) (0.092)	31340 ( $\pi$ , $\pi^*$ )	25492 ( $\pi$ , $\pi^*$ )
$\psi_3$	32894	34116 ( $\pi$ , $\pi^*$ ) (0.017)	32714 ( $\pi$ , $\pi^*$ )	28317 ( $\pi$ , $\pi^*$ )

non-spherical molecules like 1-HFu and 1-MFu. Values of 'a' have been obtained by taking 40% of the maximum length of the molecule [26] and values of 'a' obtained for 1-MFu and 1-HFu are 0.4 and 0.37 nm, respectively. Total energies including solvation energy for each species in water are compiled in Table 1.

## 4. Results

### 4.1. Absorption spectrum

Absorption spectrum of 1-MFu in different solvents can be divided into three regions, i.e. long wavelength (LW) band

Table 4

Calculated properties of 1-HFu and 1-MFu in ground and excited state, obtained with the help of TD (DFT) method

Characteristics	1-MFu-a	1-MFu-b	1-HFu-a	1-HFu-b	1HFu-T
B3LYP					
E/Hartrees	-689.9548	-689.9571	-650.6651	-650.6508	-650.6425
$\mu_g/D$	2.05	3.44	3.49	3.85	4.2
Transition energies, nm (nature of transitions)					
T1	505 ( $\pi$ , $\pi^*$ )	486 ( $\pi$ , $\pi^*$ )	510 ( $\pi$ , $\pi^*$ )	484 ( $\pi$ , $\pi^*$ )	866 ( $\pi$ , $\pi^*$ )
T2	450 (n, $\pi^*$ )	481 (n, $\pi^*$ )	458 ( $\pi$ , $\pi^*$ )	478 (n, $\pi^*$ )	585 ( $\pi$ , $\pi^*$ )
T3	444 ( $\pi$ , $\pi^*$ )	425 ( $\pi$ , $\pi^*$ )	412 (n, $\pi^*$ )	417 ( $\pi$ , $\pi^*$ )	470 (n, $\pi^*$ )
T4	368 ( $\pi$ , $\pi^*$ )	366 ( $\pi$ , $\pi^*$ )	373 ( $\pi$ , $\pi^*$ )	366 ( $\pi$ , $\pi^*$ )	359 ( $\pi$ , $\pi^*$ )
S <sub>0</sub> -S <sub>1</sub>	395 ( $\pi$ , $\pi^*$ )	405 (n, $\pi^*$ )	397 ( $\pi$ , $\pi^*$ )	403 (n, $\pi^*$ )	451 ( $\pi$ , $\pi^*$ )
S <sub>0</sub> -S <sub>2</sub>	385 (n, $\pi^*$ )	375 ( $\pi$ , $\pi^*$ )	367 (n, $\pi^*$ )	373 ( $\pi$ , $\pi^*$ )	434 ( $\pi$ , $\pi^*$ )
S <sub>0</sub> -S <sub>3</sub>	347 ( $\pi$ , $\pi^*$ )	339 ( $\pi$ , $\pi^*$ )	355 ( $\pi$ , $\pi^*$ )	330 ( $\pi$ , $\pi^*$ )	431 (n, $\pi^*$ )

Table 5

Absorption band maximum ( $\lambda_{\max}^{ab}$ , nm) and molar extinction coefficients ( $\log \epsilon_{\max}$ ) of 1-MFu in different solvents

Solvent	$\lambda_{\max}^{ab}$ (log $\epsilon_{\max}$ )							
Cyclohexane	400 sh	390 (3.18)	380 sh	351 (3.60)	336 (3.57)	304 (3.55)	291 (3.53)	280 (3.40)
Ether	400 sh	391 (3.26)	380 sh	352 (3.64)	340 (3.62)	305 (3.50)	292 (3.49)	282 (3.36)
Dioxane	–	392 (3.28)	380 sh	354 (3.67)	340 (3.65)	305 (3.52)	293 (3.46)	282 (3.33)
Ethyl acetate	–	392 (3.30)	380 sh	354 (3.67)	340 (3.65)	305 (3.46)	293 (3.46)	282 (3.32)
Acetonitrile	–	394 (3.30)	380 sh	354.5 (3.69)	340 (3.66)	306 (3.43)	294 (3.40)	282 (3.29)
<i>n</i> -Butanol	–	395 (3.32)	–	356 (3.70)	–	309 (3.36)	296 (3.52)	285 (3.26)
2-Propanol	–	395 (3.32)	–	356 (3.70)	–	309 (3.38)	296 (3.38)	285 (3.30)
<i>n</i> -Propanol	–	395 (3.32)	–	356 (3.70)	–	309 (3.38)	296 (3.38)	285 (3.30)
Ethanol	–	–	380 (3.44)	356 (3.70)	–	307 (3.37)	294 (3.33)	283.5 (3.24)
Methanol	–	–	380 (3.50)	356 (3.73)	–	307 (3.34)	294 (3.32)	283.5 (3.23)
Water pH 6.9 (neutral)	–	–	380 (3.61)	359 (3.73)	–	311 (3.34)	297 (3.29)	286 (3.20)

[1MFu] =  $2 \times 10^{-5}$  M.

greater than 380 nm, middle wavelength (MW) band in the range of 336–350 nm and short wavelength (SW) band below 330 nm. SW absorption band has sharp structure with vibrational frequency of  $1410 \pm 50 \text{ cm}^{-1}$  and structure is retained even in most polar and protic solvent water. Both MW ( $\bar{\nu}_{\text{vib}} = 1270 \text{ cm}^{-1}$ ) and LW ( $\bar{\nu}_{\text{vib}} = 660 \text{ cm}^{-1}$ ) absorption bands become diffuse with increase in polarity and protic nature of the solvents. All the three band systems are slightly red shifted and molecular extinction coefficients of nearly all the bands increase under the similar conditions. Full width at half the maximum height (FWHM) of the combined MW and LW absorptions bands (difficult to separate) is the maximum in cyclohexane ( $5540 \text{ cm}^{-1}$ ) and decreases with increase in polarity of the solvents. FWHM is nearly similar ( $4480 \text{ cm}^{-1}$ ) in all the polar protic solvents. Relevant data are compiled in Table 5.

Similar study was also carried out for 1-HFu in different solvents and relevant data are compiled in Table 6. Similarities between absorption spectra of 1-MFu and 1-HFu are the presence of three band systems, nearly similar vibrational structure ( $1390 \pm 50 \text{ cm}^{-1}$ ) in SW absorption band and invariance of SW absorption band maxima to the solvent polarity and protic nature. On the other hand differences observed in the absorption spectra of 1-HFu and 1-MFu are: (i) MW absorption band is broad and structure less even in non-polar solvents, whereas structure observed in LW ab-

sorption band is different from that of 1-MFu, (ii) LW and MW absorption bands get diffuse with increase in solvent polarity and hydrogen bond donor capacity, whereas  $\epsilon_{\max}$  of both the band systems (measured at  $\sim 355$  and  $380 \text{ nm}$ ) is nearly invariant under similar conditions and, (iii) FWHM of the combined band systems ( $\sim 355$  and  $380 \text{ nm}$ ) is nearly similar in all the solvents ( $\sim 5780 \text{ cm}^{-1}$ ), except in water where it decreases to  $5400 \text{ cm}^{-1}$ . These observations suggest that MW and LW absorption bands in 1-HFu are influenced by the presence of IHB, which is not possible in 1-MFu.

#### 4.2. Fluorescence spectrum

Fluorescence band maximum ( $\lambda_{\max}^f$ ), fluorescence quantum yield ( $\phi_f$ ) and FWHM of 1-MFu have been compiled in Table 7. Unlike absorption spectrum, only one fluorescence band is observed and it is very sensitive to solvent polarity and protic nature. A large red shift observed in  $\lambda_{\max}^f$  under similar conditions, suggest that large changes are observed in polarity or in geometry of 1-MFu on excitation to  $S_1$  state.  $\phi_f$  increases from  $6.3 \times 10^{-5}$  in cyclohexane to 0.02 in ethanol and then decreases in methanol and water. Similar to that of absorption spectrum, FWHM decreases with increase in the polarity of the solvents. In all the polar/protic solvents, FWHM is nearly similar ( $3620 \pm 60 \text{ cm}^{-1}$ ). It is also observed that FWHM of the fluorescence band is smaller

Table 6

Absorption band maxima ( $\lambda_{\max}^{ab}$ , nm) and molar extinction coefficients ( $\log \epsilon_{\max}$ ) of 1-HFu in different solvents

Solvent	$\lambda_{\max}^{ab}$ (log $\epsilon_{\max}$ )							
Cyclohexane	418 sh	396 (3.39)	379 sh	357.5 (3.69)	306 (3.47)	294 (3.49)	282 (3.39)	
Ether	–	396 (3.36)	380 sh	356 (3.66)	306 (3.41)	294 (3.43)	282 (3.34)	
Dioxane	–	396 (3.32)	380 sh	356 (3.65)	306 (3.41)	294 (3.46)	283 (3.38)	
Ethyl acetate	–	396 (3.32)	380 sh	355 (3.65)	306 (3.39)	293 (3.41)	283 (3.32)	
Acetonitrile	–	396 (3.34)	380 sh	355 (3.67)	306 (3.41)	294 (3.42)	283 (3.33)	
<i>n</i> -Butanol	–	395 (3.39)	380 sh	356 (3.65)	308 (3.37)	296 (3.41)	283 (3.32)	
2-Propanol	–	395 (3.41)	380 sh	356 (3.67)	307 (3.39)	295 (3.43)	283 (3.35)	
<i>n</i> -Propanol	–	395 (3.42)	380 sh	356 (3.66)	308 (3.39)	295 (3.42)	283 (3.32)	
Ethanol	–	396 (3.40)	380 sh	356 (3.66)	306 (3.41)	293 (3.43)	282 (3.35)	
Methanol	–	–	380 (3.54)	356 (3.70)	306 (3.39)	295 (3.40)	283 (3.32)	
Water pH 4.1 (neutral)	–	–	380 (3.54)	356 (3.70)	308 (3.39)	295 (3.38)	284 sh	

[1HFu] =  $2 \times 10^{-5}$  M.

Table 7

Fluorescence band maxima ( $\lambda_{\max}^f$ , nm), fluorescence quantum yield ( $\phi_f$ ), lifetime ( $\tau$ , ns) and FWHM of 1-HFu and 1-MFu in different solvents

Solvent	1-HFu				1-MFu			
	$\lambda_{\max}^f$	$\phi_f$	$\tau$	FWHM	$\lambda_{\max}^f$	$\phi_f$	$\tau$	FWHM
Cyclohexane	446, 467	0.0129	1.24	3600	454	0.000064	–	–
Ether	455, 478	0.022	2.39	3600	458	0.00013	–	–
Dioxane	483	0.0284	3.38	3580	465	0.00049	–	4070
Ethyl acetate	485	0.0383	5.48	3585	467	0.0006	–	3980
Acetonitrile	495	0.053	9.67	3510	481	0.0073	2.1	3620
<i>n</i> -Butanol	513	0.022	5.22	3570	510	0.023	7.27	3550
2-Propanol	513	0.024	5.50	3600	507	0.029	8.52	3560
<i>n</i> -Propanol	515	0.021	4.82	3590	512	0.021	6.93	3530
Ethanol	516	0.0197	4.85	3600	513	0.020	5.98	3530
Methanol	521	0.012	3.61	3620	521	0.0111	3.92	3620
Water pH 4.1	549	0.0017	–	3640	550	0.00163	–	3690
Cyclohexane (+0.139 M TFE)	501	0.02	4.49	3850	495	0.0198	4.17	3654

$\lambda_{\text{exc}} = 400 \text{ nm}$ ,  $[1\text{-HFu}] = [1\text{-MFu}] = 2 \times 10^{-5} \text{ M}$ .

than that of the absorption spectra. It could be either due to the more rigid structure of the molecule in  $S_1$  state or the absorption spectra may be composite spectra of two-band system.  $\lambda_{\max}^f$  and  $\phi_f$  remain invariant when excitation wavelengths ( $\lambda_{\text{exc}}$ ) used is 350 and 400 nm. This is consistent with the fact that the relaxation times of the solvents used are shorter than the lifetime of 1-MFu.

Few similarities between the fluorescence spectra of 1-HFu and 1-MFu recorded in different solvents are that  $\lambda_{\max}^f$  of 1-HFu is also very large red shifted with increase in polarity and protic nature of the solvents.  $\lambda_{\max}^f$ ,  $\phi_f$  and FWHM of 1-HFu and 1-MFu are nearly similar in protic solvents. Differences between the fluorescence spectra of 1-HFu and 1-MFu are that: (i) fluorescence spectra of 1-HFu in cyclohexane and ether possess structure of vibrational frequency of  $\sim 1000 \text{ cm}^{-1}$ , which is similar to that

observed in LW absorption band. This reflects a mirror image symmetry and suggests that emitting and absorbing states are the same, (ii) in any respective solvent  $\phi_f$  of 1-HFu is larger than that observed in 1-MFu, (iii) increase in the  $\phi_f$  of 1-MFu is much larger ( $\sim 100$ -fold in going from cyclohexane to acetonitrile) than that observed in 1-HFu in similar set of solvents (similar increase in 1-HFu is only four-fold), (iv)  $\phi_f$  of 1-HFu decreases in protic solvents in comparison to that in acetonitrile, whereas  $\phi_f$  of 1-MFu increases up to ethanol and then decreases in methanol and water and (v) lastly FWHM decreases in 1-MFu in going from non-polar to polar/protic solvents, whereas it remains nearly invariant in 1-HFu under the similar conditions. Relevant data are compiled in Table 7. Fluorescence spectra of 1-HFu in some selected solvents are shown in Fig. 1.

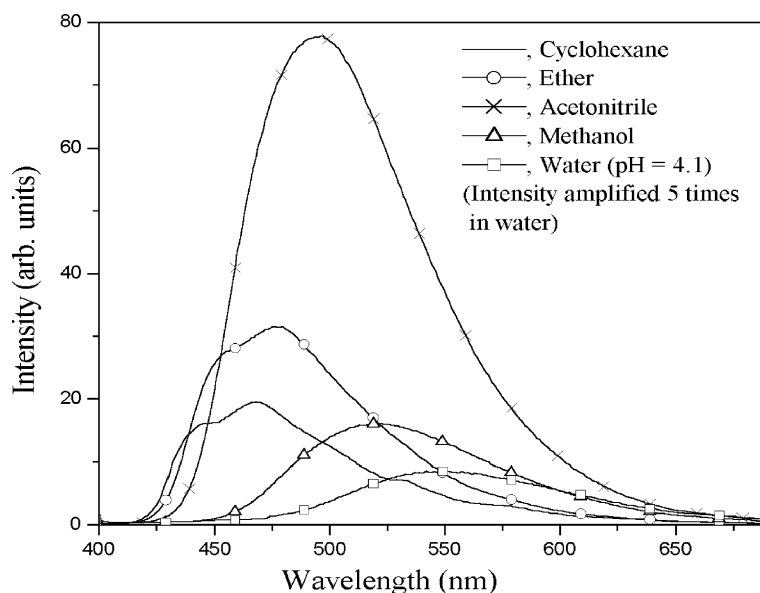


Fig. 1. Fluorescence spectrum of 1-HFu in some selected solvents: (—) cyclohexane; (—○—) ether; (—×—) acetonitrile; (—△—) methanol; (—□—) water (pH 3),  $[1\text{-HFu}] = 2 \times 10^{-5} \text{ M}$ .

### 4.3. Fluorescence excitation spectrum

Fluorescence excitation spectra of 1-MFu were recorded in different solvents and at emission wavelengths in the range of 400–600 nm. In each case fluorescence excitation spectra resemble with each other and also with absorption spectra in the respective solvents. Similar to absorption spectra, LW fluorescence excitation band is also composite spectra of two bands. This is reflected by a very large FWHM (in the range of 6400–5250  $\text{cm}^{-1}$ ) in different solvents. FWHM decreases with increase in polarity and protic nature of the solvents as observed in case of absorption spectra. In order to find out whether fluorescence excitation spectra is a composite spectra, we have tried to simulate the fluorescence excitation spectra and found out that fluorescence excitation spectrum in each solvent is a mixture of two bands, having maximum at  $355 \pm 3$  and  $400 \pm 3$  nm, resembling with MW and LW absorption bands. FWHM of each band is nearly similar in all the solvents and can be described by  $4950 \pm 150$  and  $2680 \pm 130 \text{ cm}^{-1}$ , respectively. In other words, the fluorescence spectrum in each solvent is broader than that of LW fluorescence excitation spectrum.

Fluorescence excitation spectrum of 1-HFu was also recorded under the similar conditions as done for 1-MFu. Similar characteristics of the fluorescence excitation bands of 1-HFu were also observed as noted for 1-MFu, except that FWHM of LW fluorescence excitation band of 1-HFu is nearly similar in non-polar and polar/aprotic solvents and then increase with increase in the protic nature of the solvents. This suggests that IHB in 1-HFu is retained even in the first set of solvents and thus does not change the geometry of the molecule in different solvents. On the other hand in polar/protic solvents, competition is there between the IHB and intermolecular hydrogen bonding and thus broad-

ening the fluorescence excitation spectrum. All these observations suggest that the absorbing and the emitting species are similar and these species emit from the same state.

### 4.4. Lifetimes

Excited state lifetimes of 1-MFu and 1-HFu were measured in different solvents by using  $\lambda_{\text{exc}} = 354 \text{ nm}$ , whereas the  $\lambda_{\text{em}}$  were the fluorescence band maxima in the respective solvents. Fluorescence intensity in each case followed a single exponential decay with  $\chi^2 = 1 \pm 0.1$  and good autocorrelation functions. Fig. 2 represents a typical fluorescence decay profile of 1-HFu in acetonitrile and relevant data are compiled in Table 7.

## 5. Discussion

### 5.1. Assignment of the emitting state

Data of Table 1 suggests that both the rotamers, 1-MFu-b and 1-MFu-a are nearly equally stable under isolated conditions in  $S_0$  state. 1-MFu-b is slightly more stable than 1-MFu-a by  $2.6 \text{ kJ mol}^{-1}$  when dipolar solvation energy is included. Results of DFT calculations also predict the similar results except that 1-MFu-b is  $6 \text{ kJ mol}^{-1}$  more stable than 1-MFu-a in  $S_0$  state under isolated conditions. Since barrier height for the inter-conversion of 1-MFu-b to 1-MFu-a is only  $6 \text{ kJ mol}^{-1}$  in  $S_0$  state, both the rotamers of 1-MFu can be present in  $S_0$  state. On the other hand, 1-HFu-b and 1-HFu-T are nearly  $20.6$  and  $76.3 \text{ kJ mol}^{-1}$ , respectively more unstable than the rotamer 1-HFu-a under isolated conditions and their instability decreases ( $18.5$  and  $74.1 \text{ kJ mol}^{-1}$ , respectively) when dipolar solvation

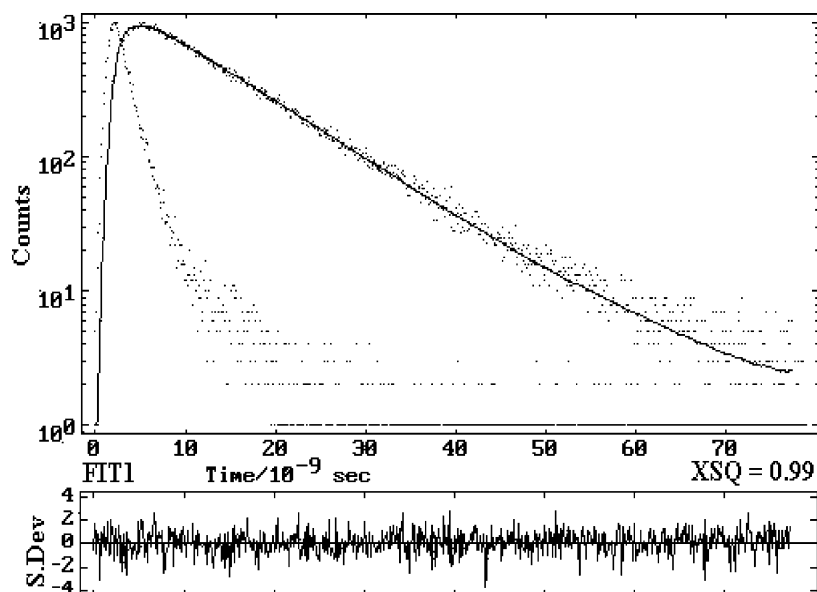


Fig. 2. Fluorescence decay profile of 1-HFu in acetonitrile.  $\lambda_{\text{exc}} = 354 \text{ nm}$ ,  $\lambda_{\text{em}} = 496 \text{ nm}$ ,  $[1\text{-HFu}] = 1 \times 10^{-3} \text{ M}$ .

energy is taken in to account. DFT calculations also support the AM1 results except that these numbers are 38 and 59 kJ mol<sup>-1</sup>, respectively in S<sub>0</sub> state under isolated conditions. In other words one can neglect the presence of rotamer 1-HFu-b and 1-HFu-T in S<sub>0</sub> state in comparison to 1-HFu-a. This is quite consistent with the structure of 1-HFu-a, which involves IHB. Further barrier height for the inter-conversion of rotamer of 1-HFu-a to 1-HFu-b is also quite large (29.5 kJ mol<sup>-1</sup>, AM1 method) in S<sub>0</sub> state. In other words it may be concluded that 1-MFu can be present as both the rotamers, where as 1-HFu will be only as 1-HFu-a. This is supported by the following observations. (i) Transitions energies (excitation and emission) predicted by a single point method and TD (DFT) calculations (Table 2) agree nicely with the experimentally determined ones for 1-MFu. Although absorption transitions cannot distinguish between 1-HFu-a and 1-HFu-b, emission transition supports 1-HFu-a preferably over 1-HFu-b. On the other hand, agreement between the transitions obtained by CNDO/S-CI method and experimental ones is not that good. This could be because CNDO/S-CI neglects many of the overlap integrals and thus does not include electron correlations effectively, where as TD (DFT) does that. (ii) Only one fluorescence band and only one type of fluorescence excitation spectra were observed at different λ<sub>exc</sub> or λ<sub>em</sub>. (iii) Fluorescence decay profile follows a single exponential decay in each case and in each solvent. Lifetimes so observed are independent of λ<sub>exc</sub> and λ<sub>em</sub>. It may be mentioned here that either equilibrium is achieved among the rotamers 1MFu-a and 1MFu-b in S<sub>1</sub> state or the difference between the lifetimes of the two rotamers is too small to be distinguished by our instrument This is also consistent with the barrier height observed for the inter-conversion of the two rotamers of each molecule in the S<sub>1</sub> state, i.e. barrier height for the inter-conversion of 1-MFu-b (1-HFu-a) to 1-MFu-a (1-HFu-b) increases from 6 kJ mol<sup>-1</sup> (29.5 kJ mol<sup>-1</sup>) to 11.0 kJ mol<sup>-1</sup> (35.3 kJ mol<sup>-1</sup>), thus making their inter-conversion more improbable in the S<sub>1</sub> state in comparison to that in S<sub>0</sub> state.

Having established that only one rotamer for 1-HFu and two rotamers for 1-MFu are present in the system, we would like to explain our results by comparing them with those obtained by CNDO/S-CI and TD (DFT) calculations, as these calculations are a useful method for considering complex photo-physical processes [27] as regards to assignment of the transitions. CNDO/S-CI calculations for all the species have shown that S<sub>1</sub> state is of n, π\* in character and S<sub>2</sub> is of π, π\*, both under the isolated conditions and when dipolar solvation energy is included (Table 3). Gap between the two singlet states decrease by a factor of 2–2.5 under the polar environments. As expected the oscillator strength for the first transition is zero and finite for the second one. Gap between the two singlet states in case of 1-MFu (2730 cm<sup>-1</sup>) and 1-HFu (2190 cm<sup>-1</sup>) is much smaller than that observed in case of 9-Fu (7000 cm<sup>-1</sup>), suggesting that charge transfer interactions are taking place from the methoxy and hydroxy

groups with the parent molecule. As expected, these interactions are smaller in 1-MFu and 1-HFu as compared to those in 1- and 3-amino-9-fluorenone (1-AFu, 3-AFu) [28]. This is reflected by the larger value of ε<sub>max</sub> for 1-AFu (6 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) in methanol than that for 1-HFu (3 × 10<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). On the other hand TD (DFT) calculations predict different results, i.e. S<sub>1</sub> and S<sub>2</sub> states for 1-HFu-a and 1-MFu-a are of π, π\* and n, π\* in nature, respectively, but n, π\* and π, π\* in character for 1-HFu-b and 1-MFu-b. As mentioned earlier since TD (DFT) and single point calculations have provided better agreement with the experimental results, we will accept these assignments and will discuss the present results to support these findings. (i) Electron donating group increase the energy of n, π\* state and lowers that of π, π\* state, thereby increasing a charge transfer character in the lower excited singlet state. Further reversal in energies of 1-HFu-a and 1-MFu-a as compared to 1-HFu-b and 1-MFu-b is caused by IHB. IHB with the lone pair of carbonyl oxygen will stabilize the nonbonding electrons and this increases the n, π\* transition energy. In 1-MFu-a, a weak IHB will be provided by methyl proton and this is reflected by only a small gap (660 cm<sup>-1</sup>) between π, π\* and n, π\* states in comparison to large gap (2060 cm<sup>-1</sup>) observed for 1-HFu-a. (ii) ε<sub>max</sub> observed for the LW absorption band of 1-MFu and 1-HFu is nearly two order of magnitude larger than that observed for n, π\* transition. Increase in ε<sub>max</sub> for both the molecules with increase in polarity of the solvents is due to the fact that polarity in the solvents will increase the gap between the n, π\* and π, π\* states of 1-HFu-a and 1-MFu-a and thus decrease the participation of n, π\* state in S<sub>1</sub>, whereas in case of 1-MFu-b increase in the participation of π, π\* state will take place or reversal of states may occur. (iii) φ<sub>f</sub> observed for 1-HFu even in non-polar solvents is quite large, where as for 1-MFu even though it is quite small in non-polar solvents but it is reasonable in polar solvents and is nearly similar to that of 1-HFu in polar/protic solvents. (iv) Large increase in fluorescence band maximum with solvent polarity suggests the presence of large charge transfer character in S<sub>1</sub> state and increase in μ<sub>e</sub> as observed in Lippert's plot (see part II).

Based on the above discussion, it may be concluded that only 1-HFu-a is present in the system and possesses π, π\* state as S<sub>1</sub>. Both the rotamers of 1-MFu can be present in the system in non polar solvents having n, π\* and π, π\* as S<sub>1</sub> state for 1-MFu-b and 1-MFu-a, respectively but π, π\* state in polar aprotic and protic solvents.

## 5.2. Excited state proton transfer reaction

Even though 1-HFu and 1-MFu are structurally different (1-HFu involves IHB in the S<sub>0</sub> state, whereas 1-MFu does not), similar trend observed in ε<sub>max</sub><sup>f</sup>, φ<sub>f</sub> and FWHM of both the molecules in each solvent suggest that the fluorescence from 1-HFu and 1-MFu follow the similar mechanism, fluorescence is occurring from the same excited singlet state and the solute solvent interactions are similar. Small Stokes

shifts ( $2500\text{ cm}^{-1}$  in 1-MFu and  $1700\text{ cm}^{-1}$  in 1-HFu-a) observed in non-polar solvents further suggest that hardly any change is observed in the geometry of the molecules on excitation to  $S_1$  state and fluorescence can be assigned to normal emission band. In conclusion ESIPT is not taking place in 1-HFu.

In order to explain the non-occurrence of ESIPT in 1-HFu, we have tried to carry out the semi-empirical and ab initio quantum mechanical calculations and the results are as follows. (i) As mentioned earlier, 1-HFu-a is more stable than 1-HFu-b ( $20.6\text{ kJ mol}^{-1}$  by AM1 method and  $37.6\text{ kJ mol}^{-1}$  by DFT method) in  $S_0$  state. This suggests the presence of IHB in  $S_0$  state, but is not as strong as present in salicylic acid ( $\sim 45\text{ kJ mol}^{-1}$ ) [29] and in other similar molecules. Although IHB strength increases to  $29.7\text{ kJ mol}^{-1}$  (AM1 method) in  $S_1$  state, it is still not very strong. This is also reflected by the larger IHB distance ( $0.228\text{ nm}$  in  $S_0$  state) between the hydroxyl proton and carbonyl oxygen. (ii) Hardly any change in the charge density has occurred on carbonyl oxygen atom in  $S_1$  and  $S_2$  states, suggesting that no increase in the basicity of carbonyl group has taken place. (iii) Scheiner [30] has shown recently through his theoretical studies on excited state proton transfer in small model systems that the barrier height for the ESIPT process follows the trend as  ${}^3n, \pi^*1n, \pi^*3\pi, \pi^*1\pi, \pi^*$  states. Although in our case  $\pi, \pi^*$  is the lowest singlet state but the contribution from the  $n, \pi^* S_2$  state can not be completely ruled out as it is separated by  $2060\text{ cm}^{-1}$  only. This may not allow a large decrease in the activation barrier for the conversion of 1-HFu-a to 1-HFu-T in  $S_1$  state. This has also been shown in the following paragraph.

Conversion of 1-HFu-a to 1-HFu-T in  $S_0$  and  $S_1$  states can be thought as arising from proton transfer from hydroxy

proton to carbonyl oxygen with simultaneous distribution of charge density in and around the six member hydrogen bonded ring. One can also consider it as hydrogen atom transfer. In either case, one requires to identify the reaction coordinate and calculate the potential energy change along this reaction coordinate. We have chosen to vary the O–H distance and optimize rest of the structural parameters for each  $r_{\text{O-H}}$  distance to get the potential energy and plot is given in Fig. 3. It is clear from Fig. 3 and as mentioned earlier that rotamer 1-HFu-a is stable in comparison to 1-HFu-T (by  $76.3\text{ kJ mol}^{-1}$  by AM1 method and  $59.3\text{ kJ mol}^{-1}$  by DFT method) and the barrier height for this inter-conversion of 1-HFu-a to 1-HFu-T is  $159.2\text{ kJ mol}^{-1}$  (AM1 method) in  $S_0$  state. Similar potential energy plot, drawn using TD (DFT) calculations and shown in Fig. 4, gives a shallow minimum for the tautomer structure with activation barrier height as  $218\text{ kJ mol}^{-1}$  in  $S_0$  state. This suggests that the intramolecular proton transfer in  $S_0$  state is unviable under thermal conditions. The potential energy curve for the inter-conversion of 1-HFu-a to 1-HFu-T in  $S_1$  state was also constructed by presetting the  $r_{\text{O-H}}$  distance as done in the  $S_0$  state and optimizing the geometry of the molecule using AM1 method by taking in to account the configuration interactions ( $\text{CI} = 5$  in MOPAC) and TD (DFT) calculations. Unlike in many similar molecules [14,29,30], 1-HFu-T is unstable even in  $S_1$  state. Though the barrier height decreases from  $159.2$  to  $97.6\text{ kJ mol}^{-1}$  in AM1 calculations and  $218$  to  $162\text{ kJ mol}^{-1}$  by TD (DFT) calculations in  $S_1$  state, it is still very large as compared to experimental values, as well as, those obtained for other molecules by using these calculations ( $\sim 20\text{--}40\text{ kJ mol}^{-1}$ ). In other words based on thermodynamic and kinetic parameters, ESIPT is unviable in  $S_1$  also and only the normal Stokes shifted fluores-

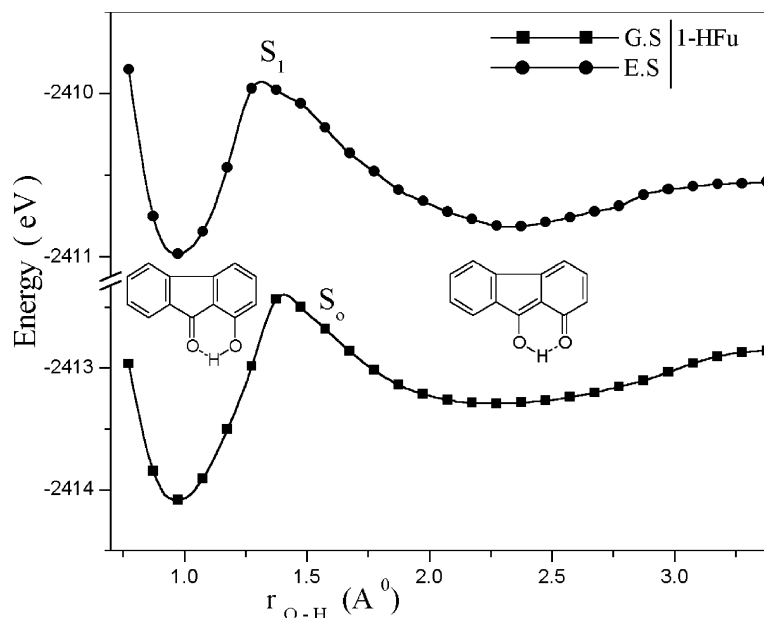


Fig. 3. Potential energy surface for the intramolecular proton transfer process of 1-HFu in  $S_0$  and  $S_1$  states under isolated conditions and using AM1 method.



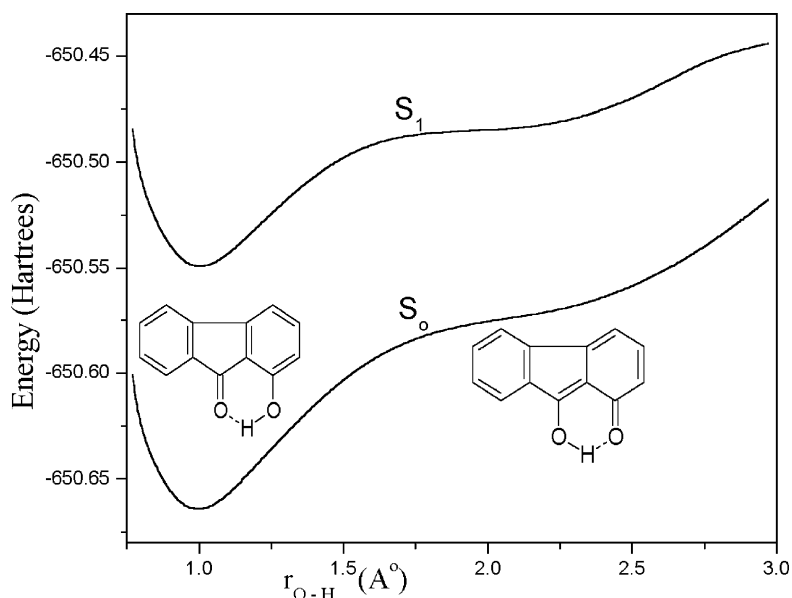


Fig. 4. Potential energy curve for the intramolecular proton transfer process of 1-HFu in  $S_0$  and  $S_1$  states under isolated conditions and using TD (DFT) calculations.

cence band is observed. Lastly, even though the conversion of 1-HFu-a to 1-HFu-T may be very fast in  $S_1$  state, emission from the tautomer may not be observed due to very fast intersystem crossing rate from  $\pi$ ,  $\pi^*$   $S_1$  state to  $n$ ,  $\pi^*$   $T_3$  state which is only separated by  $900\text{ cm}^{-1}$  (Table 4). This is an allowed process according to El Sayed's rule [31]. A similar behavior was also observed in 1-AA [11], 1,4-DHA [12], 1-AFu [28], methyl 1-hydroxy-2-naphthoate [32] and methyl 2-hydroxy-carbazole 1-carboxylate [33].

In conclusion it may be mentioned here that all the parameters are unfavorable for the ESIPT in 1-HFu, e.g. (i) IHB strength is small in  $S_0$  state, (ii) IHB distance (0.228 nm) between the hydroxyl proton and the carbonyl oxygen is quite large, (iii) change in the charge density on the carbonyl oxygen is nearly zero on excitation, (iv) even though the first singlet state is  $\pi^*$ , it has some contribution from  $n$ ,  $\pi^*$   $S_2$ . (v) ESIPT is endothermic even in  $S_1$  state and the barrier height for the conversion of normal molecule to phototautomer is quite large.

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