Chapter: VIII

Excited State Dynamics of 6-Hydroxy Flavanone

[Diagram showing LUMO and HOMO]
Estelar
8.1 Introduction:

Nowadays, a number of research groups have focused their efforts on the development of fluorescent multiparametric probes that are simultaneously sensitive to different types of intermolecular/ intramolecular interactions [1,4]. Ability to sense the characteristics of local surroundings and detection of specific interactions viz. hydrogen bond formation and excited state proton transfer (ESPT) are important prerequisites for such probes which can be only possible when the probes are sensitive to the local characteristics of the hydrogen bond (acidity or basicity) and polarity of the surrounding medium.

Flavonoids are polyphenolic compound derivatives of benzo-pyrone which are ubiquitous in photosynthesising cells and are commonly found in fruit, vegetables, nuts, seeds, stems, flowers, tea, wine, propolis and honey.

Flavanoids are completely gratifying the requirements imposed on the multiparametric probes. These compounds are known to exhibit distinct absorption and emission bands whose intensity, spectral profile and positions have different sensitivities to perturbations from the microenvironment.

Among the numerous classes of flavonoids, flavones are characterized by 2-phenyl-1,4-benzopyrone skeleton and usually classified in terms of the numbers and positions of the hydroxyl substituents [5]. The six major subclasses of flavanoids include flavones, isoflavones, flavonols, flavanones, flavanols and anthocyanidins [6]. These compounds have been found to possess a broad spectrum of pharmacological activities and have raised considerable interest because of their potential beneficial effects on human health.

Owing to the close proximity of the –OH and carbonyl groups, an asymmetrical intramolecular hydrogen bond exists in these compounds [7-11] which makes proton transfer reaction more feasible in this system [12-14]. The occurrence of excited state intramolecular proton transfer (ESIPT) in flavanols have been first introduced by Sengupta and Kasha [15] and now ESIPT is frequently used to describe the photophysics of flavanols and related compounds [16 -21].
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In 3-hydroxy flavone (3-HF) the unusual property of fluorescing in two distinct bands in the blue (410 nm) and green (540 nm) spectral regions was observed by Sengupta et al. [15]. They noticed that blue fluorescence band is basically the mirror image of the absorption spectrum and has only a small Stokes' shift, which is typical for the emission from a large organic molecule. The green fluorescence band, however, is broad and featureless and is Stokes shifted by several thousand wavenumbers. This implies that the green emission is an outcome of significant relaxed state which has no memory of direct excited state. So, they assigned the blue emission as normal form of the excited molecule whereas, the green emission was assigned to the tautomeric species produced after ESIPT [15]. This hypothesis has been summarized by the energy level diagram, as depicted in Figure 8.1.

![Energy level scheme for 3-HF](image)

Figure 8.1 Energy level scheme for 3-HF. UV excitation of normal 3-HF leads to either blue fluorescence or excited state proton transfer (ESIPT). After ESIPT, excited tautomers emits green fluorescence [15]

Sengupta and Kasha also noticed that at room temperature, only the green tautomeric luminescence was present in methyl cyclohexane solution [15]. However, when frozen into a matrix at 77 K, excited 3-HF gives only the normal blue emission [15, 22]. They speculated that this was due to some viscosity effect where the large viscosity of the rigid matrix was shutting off some large amplitude motion of the molecule necessary for the proton transfer.
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Upon deuteration of 3-HF, a mixture of the blue and green emission was observed [15]. Protti et al. [23] have reported the hydrogen bonding effect on fluorescence characteristics of 3-HF. They have reported the role of hydrogen bond accepting as well as donating ability of the solvents on the formation of anions in 3-HF which suggests that hydrogen-bonding interactions with the solvent plays an important role in mediating the ESPT process.

In most of the flavonols such ESIPT process leads to two tautomeric forms (N and T) after electronic excitation. Flavanoids, which have ─OH group at C-3 position like 3-hydroxy flavone, 3-hydroxy flavanone, (N-N, diethyl amino)-3 hydroxy flavone, are high in fluorescence quantum yield with two distinct fluorescence emissions which are very sensitive towards surrounding media. Apart from ESIPT, solvent dipolar reorientation can also take place as important relaxation mechanism for the excited S₁ state as in the case of 7-HF [24, 25]. Besides, some polyhydroxyflavones which have ─OH functional group at fifth position (like apiganin), are regarded as nonfluorescent molecules.

In view of the above observations, one can realize that the number and position of the ─OH groups in flavonoids will have a significant effect on photochemical reactions and also on their spectroscopic properties. The polyphenol (─OH group) structure of these flavonoids make them very sensitive to the surroundings that would alter the solubility, hydrophobicity and excited state dynamical behaviour of these compounds and eventually lead to changes in their selective biological activities. Flavonoids have been proved to possess antioxidant, antimicrobial, anti-inflammatory, chemopreventive and anticancer properties [26-36]. Recently [37] the cytotoxic and apoptotic effects on HeLa cancer cells of TRAIL in combination with 6-hydroxyflavanone (6-HF) have been studied and have explained the potential mechanism by which these flavanone enhance TRAIL-induced apoptosis, and demonstrate the potential use of 6-HF in TRAIL-based anticancer therapy and prevention.

6-Hydroxy flavanone is also a member of earlier discussed class of flavanoids. It is a polyhydroxyflavanone which has hydroxy group at its 6th position. It has been reported [37] that flavanone with only the hydroxylation at C₆ has a significant cytotoxic effect in human leukemia HL-60 cells accompanied
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by the occurrence of DNA ladders, apoptotic bodies, and hypodiploid cells, characteristics of apoptosis. The replacement of a hydroxyl group (\(\text{--OH}\)) by a methoxyl (\(\text{--OCH}_3\)) group at C6 or \(\text{--OH}\) at 7\(^{th}\) position does not lead to any cytotoxic effect and there is no significant cytotoxicity of flavanone with \(\text{--OH}\) in C7-treated HL-60 cells.

In the present work, to understand the photo-induced behaviour of strong biologically active 6-HF, we have tried to reveal its excited state dynamics and some hitherto aspects of its photochemistry using fluorescence spectroscopic techniques.

As it is known that most chemical reactions and biological functions take place in solution, we have undertaken the present study to investigate the photophysical and photo-chemical properties of 6-HF (scheme 8.1) in different surrounding perturbations of homogenous (solvents with varying polarity and proton donating/accepting ability) and heterogeneous (binary mixtures) environments using steady state and time resolved spectroscopy.

We have also systematically examined the spectral properties of 6-HF in presence of external agents like triethylamine (TEA) and urea (UREA) to elucidate the complete understanding of factors which may affect the photochemical properties of 6 –HF.

8.2 Results and discussion:

8.2. (1) Photophysical Properties of 6-HF in Pure Solvents

The absorption spectra of 6-HF are recorded in different nonpolar and polar solvents including series of alcohols at room temperature. Concentration of the solute was kept fixed at \(10^{-4}\)M for all measurements. No change in peak position and profile of the absorption and emission spectra are observed for different solute concentrations and hence we rule out the possibility of dimer and excimer formation at the used concentration in this study (i.e. \(10^{-4}\)M).
8.1 Introduction

8.2. (a) Absorption and Fluorescence Spectra

i. In Non-Polar Solvents:

In non-polar solvents viz. benzene (BZN) and toluene (TLN) absorption and emission maximum of 6-HF are observed at 349 nm and 420 nm respectively (Fig. 8.2) and their corresponding Stokes shift is 4844 cm\(^{-1}\). The excitation spectrum of 6-HF in these solvents is found to be dependent on monitored emission wavelength and exhibits a single peak at ~350 nm which shifts to red side on monitoring at longer emission wavelengths (Fig. 8.3). Steady state parameters of 6-HF in different solvents are summarized in Table 8.1. The fluorescence quantum yield of 6-HF is very low (i.e. 0.002 in BZN and 0.001 in TLN).

ii. In Aprotic Solvents:

From Table 8.1, it can be seen that the empirical solvent polarity parameter (\(E_T^N\)) of aprotic solvents are in the order as diethyl ether (DEE) < di-oxane (DXN) < ethyl acetate (EA) < acetone (ACTN) < acetonitrile (ACNTL). In aprotic solvents (those which were used in this study), no significant change is observed in the absorption maximum which appears at ~ 350 nm, excitation spectrum are also independent of emission wavelength (fig 8.4).

One can notice that the broad excitation spectrum with spectral width (FWHM ~20,000 cm\(^{-1}\)) may be due to overlapped spectrum of more than one species. Moreover, with increase in the polarity parameter (\(E_T^N\)), a successive red shift (Table 8.1) in the emission maximum is observed. Emission maximum varies from 410 nm in DEE (\(E_T^N = 0.117\)) to 418 nm in ACTN (\(E_T^N = 0.355\)) as shown in Fig. 8.5.

From table 8.1, it can be noticed that hydrogen bond accepting parameter (\(\beta\)) of all studied aprotic solvents is almost similar while hydrogen bond donating parameter (\(\alpha\)) is either zero or close to zero. Therefore, apparently only polarity parameter (\(E_T^N\)) can be correlated to the red shift in emission maximum in aprotic solvents.
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iii. In Polar Protic Solvents:

In protic polar solvents like MeOH and ethanol, absorption maxima are observed at around 358 nm which is relatively red shifted as compared to that observed in non-polar / aprotic polar solvents. Red shift in absorption maximum in polar protic solvent indicates a more stabilized ground state. Intermolecular hydrogen bond formation seems to be a key feature for such stabilization which results in red shift in absorption maximum [38].

Since protic solvents have very high ability of hydrogen bond acceptor, it can be anticipated that hydrogen of the hydroxyl group of 6-HF participates for intermolecular hydrogen bond formation with oxygen of the protic solvent (scheme 8.2). One can assume such intermolecular hydrogen bond formation in aprotic solvents also but it is very unlikely as the value of hydrogen bond accepting parameter of aprotic solvent is near and/or close to zero.

On the other hand, had there been such formation of hydrogen bonding in aprotic solvent then the absorption profile in aprotic solvents should have shown red shift in absorption profile. Another kind of hydrogen bonded complex in protic solvents is also feasible in which hydrogen of the protic solvent and either or both of the oxygen of 6-HF can form an intermolecular hydrogen bond (scheme 8.3). Possibility of such hydrogen bonded complex (scheme 8.3) in aprotic solvent, of course, is not reasonable.

Further, increase in Q.Y. in polar protic solvents (Table 8.4) which is almost ten times higher than the nonpolar solvents suggest that intermolecular hydrogen bonding network between solute and solvent stabilizes the system which results in less degree of freedom for solute and thus it could be a reason for decreasing the non-radiative rates and hence increase in Q.Y as compared to that in nonpolar solvents.

In MeOH, on excitation with $\lambda = 358$ nm, emission maximum is observed at ~ 470 nm (Fig 8.2). The corresponding Stokes shift is 6656 cm$^{-1}$ which is relatively very large as compared to non-polar and aprotic solvents. Such large Stokes shift could be due to large solvent reorientation relaxation which also
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indicates much higher dipole moment of 6-HF in the excited state as compared to the ground state.

Scheme 8.1 Structure of 6-Hydroxy Flavanone

Scheme 8.2

Scheme 8.3
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Figure 8.2 Absorption and emission spectra of 6-HF in different solvents.

Figure 8.3 Excitation spectrum of 6-HF in non polar solvents.
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Figure 8.4 Excitation spectrum of 6-HF in aprotic polar solvents.

Figure 8.5 Absorption and emission spectra of 6-HF in different aprotic solvents.
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Table 8.1: Solvent parameters and Steady State Parameters of 6-HF

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_T^N$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\eta$ (cP)</th>
<th>$\lambda_{abs}^{max}$</th>
<th>$\lambda_{em}^{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.099</td>
<td>0</td>
<td>0.11</td>
<td>0.56</td>
<td>349</td>
<td>420</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.111</td>
<td>0</td>
<td>0.60</td>
<td></td>
<td>349</td>
<td>420</td>
</tr>
<tr>
<td>DEE</td>
<td>0.117</td>
<td>0</td>
<td>0.47</td>
<td>0.22</td>
<td>354</td>
<td>410</td>
</tr>
<tr>
<td>Di-oxane</td>
<td>0.168</td>
<td>0</td>
<td>0.37</td>
<td>1.18</td>
<td>351</td>
<td>414</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.228</td>
<td>0</td>
<td>0.45</td>
<td>0.42</td>
<td>350</td>
<td>416</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.355</td>
<td>0.08</td>
<td>0.48</td>
<td>0.31</td>
<td>352</td>
<td>418</td>
</tr>
<tr>
<td>ACNTL</td>
<td>0.460</td>
<td>0.44</td>
<td>0.0</td>
<td>0.37</td>
<td>354</td>
<td>422</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.259</td>
<td>0.31</td>
<td>0.19</td>
<td>0.54</td>
<td>356</td>
<td>432</td>
</tr>
<tr>
<td>1-ButOH</td>
<td>0.586</td>
<td>0.84</td>
<td>0.84</td>
<td>2.54</td>
<td>360</td>
<td>465</td>
</tr>
<tr>
<td>EtOH</td>
<td>0.654</td>
<td>0.86</td>
<td>0.75</td>
<td>1.07</td>
<td>358</td>
<td>466</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.78</td>
<td>0.98</td>
<td>0.66</td>
<td>0.54</td>
<td>358</td>
<td>470</td>
</tr>
<tr>
<td>Water</td>
<td>1.0</td>
<td>1.17</td>
<td>0.47</td>
<td>0.89</td>
<td>360</td>
<td>475</td>
</tr>
</tbody>
</table>

8.2.(b) Dipole moment determination

Dipole moments of the 6-HF have been estimated using solvatochormic shift method. In this method following equations are used.

(i) Bakhshiev’s formula [39]

$$\tilde{\nu}_a - \tilde{\nu}_f = S_1 F_i(\varepsilon, \eta) + \text{Constant}$$

(8.1)

Where $\tilde{\nu}_a$ and $\tilde{\nu}_f$ are the wavenumbers (cm⁻¹) of the absorption and emission maxima respectively, $F_i$ is the (solvent polarity function) and $S_1$ is defined as follows

$$F_i(\varepsilon, \eta) = \frac{2\eta^2 + 1}{\eta^2 + 2} \left[ \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\eta^2 - 1}{\eta^2 + 2} \right]$$

(8.2)

And $S_1 = \frac{2(\mu_e - \mu_g)^2}{hc\alpha_0^3}$

(8.3)

Where $h$ is Planck’s constant, $c$ is the velocity of light in vacuum, $\mu_g$ is the dipole moment in the ground state, $\mu_e$ is the dipole moment in the excited singlet state, $\alpha_0$...
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is the Onsager cavity radius, \( \varepsilon \) is the solvent dielectric constant and \( \eta \) is the solvent refractive index.

(ii) Kawski-Chamma-Viallet's formula [40, 41]

\[
\frac{\bar{v}_a + \bar{v}_f}{2} = S_2 F_2(\varepsilon, \eta) + \text{Constant} \tag{8.4}
\]

where the meaning of the symbols is the same as in eqs. (8.1) and (8.2), except for \( F_2 \) and \( S_2 \) which are defined as follows

\[
F_2(\varepsilon, \eta) = \frac{2\eta^2 + 1}{2(\eta^2 + 2)} \left[ \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\eta^2 - 1}{\eta^2 + 2} \right] + \frac{3}{2} \left[ \frac{\eta^4 - 1}{(\eta^2 + 2)^2} \right] \tag{8.5}
\]

And \( S_2 = -\frac{2(\mu_e^2 - \mu_g^2)}{hca_0^3} \tag{8.6} \)

The parameters \( S_1 \) and \( S_2 \) can be obtained from the absorption and fluorescence band shifts (Eqs. (1) and (4)). If the ground and excited states are parallel, the following expressions are obtained on the basis of eqs. (8.3) and (8.6) [41, 42].

\[
\mu_g = \frac{S_2 - S_1}{2} \left[ \frac{hca_0^3}{2S_1} \right]^{1/2} \tag{8.7}
\]

\[
\mu_e = \frac{S_1 + S_2}{2} \left[ \frac{hca_0^3}{2S_1} \right]^{1/2} \tag{8.8}
\]

and

\[
\mu_e = \frac{S_1 + S_2}{S_2 - S_1} \mu_g; (S_2 > S_1) \tag{8.9}
\]

The value of the solute cavity radius \( (a_0) \) was calculated from the molecular volume according to Suppan's equation [43]

\[
a_0 = \left( \frac{3M}{4\pi\delta N} \right)^{1/3} \tag{8.10}
\]

Where \( \delta \) is the solid state density of solute molecule, \( M \) the molecular weight and \( N \) is the Avogadro number.

Spectral shifts \( (v_a - v_f) \) versus the solvent polarity function \( F_1 (\varepsilon, n) \) and \( (v_a + v_f) / 2 \) versus \( F_2 (\varepsilon, n) \) are shown in the Figure 8.6. We get \( \mu_g = 2.12 \) D and \( \mu_e = 6.09 \) D and change in dipole moments, \( \Delta \mu = 3.97 \) D.

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Figure 8.6 Bakhshiev (● ● ● ●) and Kawski-Chamma-Viallet (● ● ● ●) correlation between the solvent spectral shifts and solvent polarity functions for all solvents.

Higher excited state dipole moment of 6-HF also support the large solvent reorientation relaxation and thus it may be one of the factors of which is responsible for large Stokes shift.

To understand the nature of the solvent effects on the spectral feature in detail, a plot between Stokes shift ($\Delta \tilde{w}$) and solvent polarity function ($\Delta F$) is drawn using Lippert equation [44]. The standard Lippert equation is given below:

$$\tilde{w}_A - \tilde{w}_F = \frac{2}{hc} \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\eta^2 - 1}{2\eta^2 + 1} \right) \left( \frac{\mu_e - \mu_g}{a^3} \right) + \text{constant} \quad (8.11)$$

Where $F$ is the solvent polarity function described by $F = \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\eta^2 - 1}{2\eta^2 + 1} \right)$ and $\varepsilon$ and $\eta$ are the dielectric constant and refractive index of the solvent respectively. Using eq. 8.11, a plot between $\Delta \tilde{w}$ versus $F$ is shown in Fig 8.7. Deviation from the linearity suggests that in addition to general solvent effects (only solvent relaxation), specific solvent effects are also present. However excluding aprotic solvent from fitting leads to linear plot with correlation factor ~ 0.98 (fig 8.8).
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**Fig: 8.7** Plot between solvent polarity function \((F)\) and Stokes shift \((\Delta \tilde{v})\) for all solvents.

**Figure 8.8** Plot between solvent polarity function \((F)\) and Stokes shift \((\Delta \tilde{v})\) excluding aprotic solvents.
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8.2.(c) Linear solvation energy relationship analysis

In addition to solvent relaxation, hydrogen bonding seems to have an additive effect on the large Stokes shift in protic solvents. Therefore, to further explore and understand the role of solvents in detail, the combined effect of solvent polarity and hydrogen bonding parameters on the Stokes shift is analysed by means of the linear solvation energy relationship (LSER) concept using Kamlet–Taft relation as follows:

\[ S = S^0 + p\pi^* + a\alpha + b\beta \]  (8.12)

where \( S \) is the value of the solvent dependent property to be modelled, \( S^0 \), a and b are the coefficients determined from the LSER analysis. The term \( \pi^* \) indicates the measure of solvent bipolarity/polarizability [45], whereas \( \alpha \) and \( \beta \) are hydrogen bond donating and accepting abilities of the solvent, respectively [46].

Using multiple linear regression analysis, fit for calculated and observed Stokes shift is found almost linear with the correlation factor of 0.97. The fitted equation with parameters is as follows:

\[ \delta_{\text{cat}} = 4844.56 + 34.18 \pi^* + 3046.20 \alpha - 1227.95 \beta \]  (8.13)

From equation 8.13, it can be seen that the coefficient of \( \alpha \) is the maximum bearing positive sign, hence it also illustrates that hydrogen bond accepting ability greatly influences the Stokes shift. Positive sign demonstrates the increasing shift (towards red side). On the other hand, negative coefficient of \( \beta \) exhibits decreasing shift, which has been well observed in experimental data.

In table 8.1 one can notice that if the value of \( \alpha \) is zero, then with increase in value of \( \beta \), blue shift in emission maximum (less Stokes shift) is observed. As expected, polarity shows a positive correlation, however, with less contribution as compared to other parameters of the solvent. Therefore, from LSER analysis and the linear plot (figure 8.9) of stoke shift vs HBA (Hydrogen bond accepting ability), it can be inferred that hydrogen bond accepting ability of the solvent is the decisive property for the Stokes shift of 6-HF.
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Figure 8.9 Plot between alpha and Stokes shift ($\Delta \nu$) for all solvent.

8.2.(d) Lifetime measurement

Decay times of 6-HF at room temperature for various emission wavelengths in different solvents have been shown in figure 8.10 and the corresponding data are given in Table 8.2 & 8.3. It can be seen from the table that the decay shows a double exponential fit for all solvents in which shorter decay component of ~ 0.5 ns is almost constant and presents in all aprotic polar and nonpolar solvents while the longer decay component ~4.5 ns is highly sensitive to polarity, viscosity and proticity of the medium.

i. In non polar solvents:

In nonpolar solvents, fluorescence decays are found to be best fitted with double exponential function with decay components of ~ 0.8 ns and ~ 4.5 ns. Higher value of excited state dipole moment as compared to its ground state dipole moment, it is evident that it posses different excited state geometry.
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![Figure 8.10 Decay curve of 6-HF in nonpolar and aprotic solvents.](image)

Table 8.2: Fluorescence decay parameters of 6-HF in the nonpolar and aprotic polar solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{ex}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\tau_1$ (ns)</th>
<th>a1</th>
<th>$\tau_2$ (ns)</th>
<th>a2</th>
<th>$\chi^2_1$</th>
<th>$\chi^2_2$</th>
<th>$\tau_{\text{avg}}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>350</td>
<td>420</td>
<td>0.89</td>
<td>0.47</td>
<td>4.92</td>
<td>0.53</td>
<td>-</td>
<td>1.14</td>
<td>3.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440</td>
<td>0.703</td>
<td>0.15</td>
<td>4.528</td>
<td>0.85</td>
<td>-</td>
<td>1.06</td>
<td>3.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470</td>
<td>0.699</td>
<td>0.08</td>
<td>4.623</td>
<td>0.92</td>
<td>-</td>
<td>1.09</td>
<td>4.321</td>
</tr>
<tr>
<td>Dioxane</td>
<td>350</td>
<td>420</td>
<td>0.36</td>
<td>0.67</td>
<td>1.93</td>
<td>0.33</td>
<td>4.08</td>
<td>1.08</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440</td>
<td>0.83</td>
<td>0.79</td>
<td>2.06</td>
<td>0.26</td>
<td>2.76</td>
<td>1.18</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470</td>
<td>0.25</td>
<td>0.56</td>
<td>2.47</td>
<td>0.44</td>
<td>2.10</td>
<td>1.00</td>
<td>1.23</td>
</tr>
<tr>
<td>EtA</td>
<td>355</td>
<td>440</td>
<td>0.48</td>
<td>0.46</td>
<td>2.63</td>
<td>0.54</td>
<td>3.76</td>
<td>1.08</td>
<td>1.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470</td>
<td>0.34</td>
<td>0.46</td>
<td>2.55</td>
<td>0.54</td>
<td>1.89</td>
<td>1.03</td>
<td>1.54</td>
</tr>
</tbody>
</table>
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Further, decay behaviour of 6-HF can be explained as continuous model, which accounts only for the solvent relaxation / time dependent spectral shift. Therefore, shorter decay component can be attributed to the decay time of Frank Condon (FC) state / locally excited (LE) state. On the other hand longer decay component corresponds to relaxed state after structural /conformational changes followed by solvent relaxation. For the conformity of continuous model of decay behaviour, time resolved spectra (TRES) are generated as shown in Fig.8.11 which clearly shows the time dependent fluorescence Stokes shift (TDFSS) can be seen which is known to occur due to solvent relaxation process [47].

![TRES for 6HF in benzene](image)

*Figure 8.11 TRES in Benzene.*

Further, adopting the procedure of DeToma and coworkers [48, 49], the Bakhshiev [50] formulation of solvent relaxation can be used to obtain some information about the relaxation.

According to Bakhshiev, at any wavenumber (\(\vec{\nu}\)), the time-resolved emission I (\(\vec{\nu},t\)) can be described as a product of the decay of the total fluorescence intensity I(t) and a normalized time-dependent spectral relaxation \(\rho(\vec{\nu}_m(t),\vec{\nu})\).

\[
I(\vec{\nu},t) = I(t)\rho(\vec{\nu}_m(t),\vec{\nu}).
\] (8.14)
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where \( \bar{\nu}_m(t) \) is the centre of gravity of the emission spectrum or the emission maximum for a gaussian shape, it is assumed to shift to lower energy in an exponential fashion as a function of solvent relaxation time \( \tau_R \)

\[
\bar{\nu}_m(t) = \bar{\nu}_\infty + (\bar{\nu}_0 - \bar{\nu}_\infty)e^{-t/\tau_R}
\]

(8.15)

where \( \bar{\nu}_0 \) and \( \bar{\nu}_\infty \) represent the emission maxima for \( t = 0 \) and \( t = \infty \) respectively.

The nature of curve of decay in \( \bar{\nu}_m(t) \) with time is exponential and the solvent relaxation time \( \tau_R \) calculated using eqn. (8.15) is about 0.84 ns which is close to the value of shorter decay time. As the decay time of LE state and \( \tau_R \) are comparable, therefore, both decay times from LE and relaxed could be observed in the fluorescence decay.

The TRES observations confirm that the decay in nonpolar solvents originates from two conformers for which distribution analysis may give a better insight. Reasonable results for benzene are obtained for different emission wavelengths. Results of distribution analysis are presented in fig 8.12.

![Distributional analysis of 6-HF in Benzene.](image)

Figure 8.12 Distributional analysis of 6-HF in Benzene.
8.2 Results and discussion

The results clearly indicate that two types of decaying components are present which are well separated from each other and well distributed as some width of distribution is also dependant on the statistical precision of the data.

The wide distribution of long lived component for emission monitored from 420 nm to 500 nm is indicative of being differentially influenced by polarity or viscosity. The shorter component is not so distributed and is more like the case for Frank Condon state in any medium. This supports the assumption that short lived component has its origin from frank Condon state. The mean life time (C.G.) of the distribution profiles of components also corresponds to the results of global component analysis results.

ii. In polar aprotic /aprotic solvents:

Lifetime measurements for aprotic solvents show some interesting results. Average lifetime in aprotic solvent also shows dependency on the steady state spectral shift (stoke shift). Interestingly, 6-HF has longer lifetime in such solvents which have highly stokes shifted spectral behaviour. It can be seen from a linear plot of average lifetime ($<\tau>$) vs. stoke shift (fig 8.13).
8.2 Results and discussion

Moreover, in aprotic solvents like ethyl acetate, dioxane and acetone, similar to non-polar solvents fluorescence decay curves are found to be best fitted with the double exponential function with decay times $\tau_1 \sim 0.3$ ns and $\tau_2 \sim 2.5$ ns. In contrast to non-polar solvents values of the both shorter ($\tau_1$) and longer decay component ($\tau_2$) are less. Here, one can notice that the viscosity of benzene (0.60 cP) is higher than the viscosity of DEE (0.20cP) and ethyl acetate (0.40 cP) on the other hand the corresponding polarity parameter $E^P$ are comparable.

It seems that decrease in the value of decay times in aprotic solvents could be due to less viscosity of the aprotic solvents as compared to non-polar solvents. In the comparable polarity region of non-polar and aprotic medium viscosity shows dominating effect on the decay behaviour. Subsequently, we observed that in alcohols with increase in viscosity, shorter decay component increases from 0.7 ns (in MeOH) to 1.1 ns in Octanol while the longer decay component increases from 4.5 ns (in MeOH) to 12.0 ns in Octanol (fig 8.14).

![Figure 8.14 Fluorescence decay profiles of 6-HF in protic solvents.](image)
### Table 8.3 Fluorescence decay parameters of 6-HF in the alcohols.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\lambda_{ex}$ (nm)</th>
<th>$\tau_1$ (ns)</th>
<th>$a_1$</th>
<th>$\tau_2$ (ns)</th>
<th>$a_2$</th>
<th>$\chi^2$</th>
<th>$\tau_{avg}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>355</td>
<td>500</td>
<td>0.71</td>
<td>0.21</td>
<td>4.58</td>
<td>0.79</td>
<td>1.07</td>
<td>3.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470</td>
<td>0.70</td>
<td>0.23</td>
<td>4.53</td>
<td>0.77</td>
<td>1.02</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440</td>
<td>0.65</td>
<td>0.26</td>
<td>4.50</td>
<td>0.74</td>
<td>1.00</td>
<td>3.50</td>
</tr>
<tr>
<td>Ethanol</td>
<td>355</td>
<td>500</td>
<td>0.60</td>
<td>0.13</td>
<td>6.63</td>
<td>0.87</td>
<td>1.13</td>
<td>5.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470</td>
<td>0.68</td>
<td>0.15</td>
<td>6.61</td>
<td>0.85</td>
<td>1.02</td>
<td>5.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440</td>
<td>0.69</td>
<td>0.18</td>
<td>6.60</td>
<td>0.82</td>
<td>1.00</td>
<td>5.53</td>
</tr>
<tr>
<td>Propanol</td>
<td>355</td>
<td>470</td>
<td>1.31</td>
<td>0.27</td>
<td>10.95</td>
<td>0.73</td>
<td>1.02</td>
<td>8.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>1.23</td>
<td>0.17</td>
<td>10.94</td>
<td>0.83</td>
<td>1.08</td>
<td>9.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440</td>
<td>1.10</td>
<td>0.18</td>
<td>10.73</td>
<td>0.82</td>
<td>1.04</td>
<td>9.00</td>
</tr>
<tr>
<td>Heptanol</td>
<td>355</td>
<td>470</td>
<td>1.23</td>
<td>0.10</td>
<td>9.85</td>
<td>0.90</td>
<td>1.00</td>
<td>8.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>1.00</td>
<td>0.09</td>
<td>9.47</td>
<td>0.91</td>
<td>1.01</td>
<td>8.70</td>
</tr>
<tr>
<td>Octanol</td>
<td>355</td>
<td>500</td>
<td>1.22</td>
<td>0.16</td>
<td>12.81</td>
<td>0.84</td>
<td>1.04</td>
<td>10.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470</td>
<td>1.03</td>
<td>0.11</td>
<td>12.43</td>
<td>0.89</td>
<td>1.02</td>
<td>11.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440</td>
<td>1.01</td>
<td>0.13</td>
<td>11.96</td>
<td>0.87</td>
<td>1.00</td>
<td>10.54</td>
</tr>
</tbody>
</table>

### Table 8.4 Viscosity effect on radiative and non-radiative rates of 6-HF.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\eta$ (cP)</th>
<th>$E_n^H$</th>
<th>$\tau_{avg}$ (ns)</th>
<th>$\tau_{rad}$ (ns)</th>
<th>$k_r$ ($\times 10^7$ s$^{-1}$)</th>
<th>$k_{nr}$ ($\times 10^7$ s$^{-1}$)</th>
<th>Quantum Yield $\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.6</td>
<td>0.762</td>
<td>3.65</td>
<td>12.97</td>
<td>7.71</td>
<td>310.89</td>
<td>0.0242</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.2</td>
<td>0.654</td>
<td>5.72</td>
<td>16.79</td>
<td>5.95</td>
<td>151.54</td>
<td>0.0377</td>
</tr>
<tr>
<td>Propanol</td>
<td>1.9</td>
<td>0.617</td>
<td>8.35</td>
<td>24.20</td>
<td>4.13</td>
<td>42.28</td>
<td>0.069</td>
</tr>
<tr>
<td>Heptanol</td>
<td>5.8</td>
<td>0.549</td>
<td>8.49</td>
<td>41.11</td>
<td>2.43</td>
<td>29.20</td>
<td>0.076</td>
</tr>
<tr>
<td>Octanol</td>
<td>8.2</td>
<td>0.537</td>
<td>11.17</td>
<td>36.99</td>
<td>2.70</td>
<td>39.53</td>
<td>0.084</td>
</tr>
</tbody>
</table>
8.2 Results and discussion

A plot for alcohols between deactivation rate \((k = 1 / \langle \tau \rangle)\) and viscosity \((\eta)\) also suggests that decay rates are sensitive towards viscosity (fig. 8.15). Tredwell and Kreary [51] have shown that viscosity is related to fluorescence lifetime by the relation:

\[
\tau_f = C \times (\text{Viscosity})^\gamma
\]

Where \(C\) is a constant and \(\gamma\) (gamma) shows the viscosity power dependence. Using this relation, the log-log plot of the fluorescence lifetime and viscosity for different alcohols gives a straight line (fig 8.16) and the estimated value of \(\gamma\) is approximately equal to 0.4. The high value of gamma indicates here that viscosity has a strong effect on the deactivation path of the excited 6-HF. Table 8.4 also shows the variation in non-radiative rates and quantum yields on increasing viscosity.

![Figure 8.15 Plot between deactivation rate and viscosity in alcohols.](image)

Further, for the estimation of decay behaviour of 6-HF in polar medium TRES was generated (fig 8.17) which do not exhibit any TDFSS. The decay constants and spectral data in polar media support the continuous relaxation behaviour. In general polar medium, solvent relaxation time is much faster than the non-polar medium. Therefore, somehow appearance of TDFSS in TRES depends
8.2 Results and discussion

on the time resolution of the system. Probably in our case, time resolution of the system is not sufficient to observe TDFSS in polar medium like MeOH.

Figure 8.16 A log-log plot of fluorescence lifetime against viscosity for 6-HF in alcohols.

Figure 8.17 TRES in MeOH.
8.2 Results and discussion

8.2.(e) Photophysical Properties of 6-HF in Binary Solvent Mixtures

It is well known that an appropriate choice of solvents can accelerate or inhibit a chemical reaction by changing their kinetics and mechanism. In particular, in a binary system, solvent molecules may have different chemical structure and physical properties (e.g. dielectric constant and refractive index). In continuation to our work to explore the factor affecting photophysical properties of 6-HF, we have tried to explore the change in equilibrium and thus in the photochemical reaction in binary solvents.

Here, we have chosen different solvent mixtures of toluene-acetonitrile and DEE-methanol to compare the photophysical response of 6-HF. The uniqueness of these mixtures is that the polar components acetonitrile and methanol have similar dielectric constants and refractive indices but methanol can form hydrogen bonds while acetonitrile cannot. In the same manner toluene and DEE both are nonpolar but toluene has no hydrogen bond accepting ability while DEE has high hydrogen accepting ability. So the explicit factor which is responsible for Stoke’s shift can be easily demonstrated which can also be useful to demonstrate the hydrogen bond forming ability of 6-HF.

Fluorescence behaviour of 6-HF has been observed in toluene-acetonitrile mixture. The absorption maxima of 6-HF shifts to a small extent (~ 4 nm) at different compositions of the solvent mixtures. Moreover, the fluorescence emission maxima shift ~ 4 nm when the mole fraction of the aprotic component (i.e. acetonitrile) is increased and correspondingly the empirical polarity [ET (30)] of the solvent mixture is increased. Interestingly the fluorescence intensity gets enhanced ~ 10 times on increasing the polarity. Figure 8.18 displays the dependence of intensity of the fluorescence emission maxima on the mole fraction of acetonitrile. Observed results suggest that the polarity of a solvent does not affect the magnitude of stokes shift but it has a great influence on nonradiative rates and consequently on quantum yield of 6-HF which are supposed to be high on increasing the polarity of medium.
8.2 Results and discussion

![Figure 8.18 Emission spectrum of 6-HF in toluene acetonitrile binary mixture.](image)

In case of DEE – Methanol mixture, absorption maxima of 6-HF shifts to a large extent ~10 nm at different compositions of the solvent mixtures. Moreover, the fluorescence emission maximum shifts bathochromically when the mole fraction of the protic component (i.e. MeOH) is increased. Figure 8.19 displays the dependence of stokes shift ~ 70 nm of the fluorescence emission maxima on the mole fraction of MeOH at each composition.

Interestingly, on addition of 2% Methanol in DEE, emission maxima shift by ~ 60 nm with 20 times increment in its fluorescence intensity while in pure methanol, the emission maximum is shifted by ~10 nm. Also the quantum yield of maximum (2%) added composition of methanol was higher than the quantum yield of 6-HF in pure methanol.

This observation indicates that the compounds behave unlikely in pure solvents and binary solvent mixtures and may experience additively dielectric enrichment. Fluorescence decay measurements were also recorded which support the steady state observations. On increasing the content of methanol in DEE, lifetime gets enhanced ~12 times (table 8.5) for (added 2%) maximum
8.2 Results and discussion

concentration of methanol which confirm the formation of more stabilized hydrogen bonded complex in presence of methanol.

![Figure 8.19 Emission spectrum of 6-HF in presence DEE-MeOH binary mixture.](image)

**Table 8.5 Decay parameters of 6-HF in DEE in presence of MeOH**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{ex}$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\tau_1$ (ns)</th>
<th>*$\alpha_1$</th>
<th>$\tau_2$ (ns)</th>
<th>*$\alpha_2$</th>
<th>$\chi_2^2$</th>
<th>$\chi_1^2$</th>
<th>$\tau_{avg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEE+0%</td>
<td>410</td>
<td>0.438</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>1.02</td>
<td>-</td>
<td>0.438</td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>470</td>
<td>0.709</td>
<td>23%</td>
<td>-</td>
<td>4.533</td>
<td>77%</td>
<td>-</td>
<td>1.02</td>
<td>3.653</td>
</tr>
<tr>
<td>DEE+0.1%</td>
<td>410</td>
<td>0.653</td>
<td>61%</td>
<td>2.825</td>
<td>39%</td>
<td>-</td>
<td>1.03</td>
<td>1.501</td>
<td></td>
</tr>
<tr>
<td></td>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEE+0.3%</td>
<td>430</td>
<td>0.518</td>
<td>48%</td>
<td>3.367</td>
<td>52%</td>
<td>-</td>
<td>1.10</td>
<td>1.919</td>
<td></td>
</tr>
<tr>
<td>DEE+0.5%</td>
<td>430</td>
<td>0.547</td>
<td>36%</td>
<td>4.285</td>
<td>64%</td>
<td>-</td>
<td>1.08</td>
<td>2.939</td>
<td></td>
</tr>
<tr>
<td>DEE+0.8%</td>
<td>440</td>
<td>0.541</td>
<td>29%</td>
<td>5.186</td>
<td>71%</td>
<td>-</td>
<td>1.00</td>
<td>3.961</td>
<td></td>
</tr>
<tr>
<td>DEE+1.0%</td>
<td>450</td>
<td>0.548</td>
<td>24%</td>
<td>6.223</td>
<td>76%</td>
<td>12.8</td>
<td>1.00</td>
<td>4.993</td>
<td></td>
</tr>
<tr>
<td>DEE+1.2%</td>
<td>450</td>
<td>0.432</td>
<td>19%</td>
<td>6.869</td>
<td>81%</td>
<td>2.39</td>
<td>1.07</td>
<td>5.195</td>
<td></td>
</tr>
<tr>
<td>DEE+1.5%</td>
<td>460</td>
<td>0.511</td>
<td>14%</td>
<td>7.141</td>
<td>86%</td>
<td>3.82</td>
<td>1.09</td>
<td>6.190</td>
<td></td>
</tr>
<tr>
<td>DEE+2.0%</td>
<td>460</td>
<td>0.451</td>
<td>10%</td>
<td>7.511</td>
<td>90%</td>
<td>1.91</td>
<td>1.07</td>
<td>6.825</td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>470</td>
<td>0.709</td>
<td>23%</td>
<td>4.533</td>
<td>77%</td>
<td>-</td>
<td>1.02</td>
<td>3.653</td>
<td></td>
</tr>
</tbody>
</table>
8.2 Results and discussion

8.2.(f) Photophysical Properties of 6-HF in presence of proton accepting agents:

To further elucidate the effect of hydrogen bonding, we have systematically investigated the interaction of 6-HF with triethylamine (a strong hydrogen bonding agent/strong proton acceptor) in dioxane. 6-HF exhibits dual fluorescence in dioxane in presence of TEA.

Interestingly, absorption gets red shifted ~5 nm (350 nm to 355 nm) in presence of TEA (0.001 M) while in emission spectrum; a new band develops at ~510 nm (green), along with 410 nm (blue) band. The changes in the fluorescence spectra of 6-HF in the presence of TEA concentrations are shown in Fig 8.20.

![Figure 8.20 Emission spectrum of 6-HF in presence of TEA at $\lambda_{ex}$=360 nm.](image)

It can be seen that the intensity of normal emission band (410 nm) of 6-HF decreases with addition of TEA in Dioxane. Tentatively, deprotonated or excited state intermolecular proton transfer (ESPT) species is expected for the origin of largely Stokes’s shifted green band. The main objective of the investigation is to probe whether the deprotonation or ESPT takes place in the ground state or in the excited state. Therefore, attention is focused on large stokes shifted emission band.
8.2 Results and discussion

Further, we have supposed that in neat solvent, the dioxane molecules are not sufficient for hydrogen bonding or proton abstraction from 6-HF but with the addition of TEA, 6-HF may be hydrogen bonded due to high proton accepting ability and force the formation of a complex between the hydrogen of hydroxy group and nitrogen of TEA held together by a hydrogen bond. In the presence of TEA, deprotonation either in the ground state or in the excited state may take place. Red shifted absorption spectrum may be due to hydrogen bonded complex. Had there been an anion formation in the ground state due to deprotonation, the absorption spectrum in the presence of TEA should have shown similar profile as observed at pH 13. At pH 13, 6-HF shows a highly red shifted absorption profile with maximum ~ 396 nm.

Scheme 8.5

Further, in the presence of TEA, the identical excitation spectra for both blue and green bands clearly reveal that an excited state reaction occurs in presence of TEA. A model for ESIPT is proposed as shown in scheme 8.5 for dioxane-TEA system. Initially, ground state hydrogen bonded complex may be formed in presence of TEA and these complexes may get excited and during the excited state lifetime a fast ESPT reaction may take place between hydroxyl group of 6-HF and nitrogen of amine and the resultant product may emit at 510 nm.
8.2 Results and discussion

However, for ruling out the possibility of deprotonated species in the ground state, decay behaviour of green emission is very important.

![Figure 8.21 decay profile of 6-HF in presence of TEA.](image)

Further, to confirm the excited state proton transfer, the fluorescence decay data were recorded for both the emissions in presence of TEA. At shorter emission band (410 nm), fluorescence decay was best fitted with single exponential function with decay components of 0.7 ns while for ~ 510 nm decay is fitted with biexponential with decay component 0.85 ns and 2.8 ns. The decay curves are shown in Fig. 8.21.

It can be clearly seen from the decay profile that a rise time should be observed for the second emission band at 510 nm but due to low resolution of instrument, it was not possible to record the rising component. It is reasonable to assume that a fast ESPT has occurred. The observed phenomena can be understood as in presence of TEA, complexation process is expected to accelerate the tautomerization process at the excited state by increasing the electron density on the OH group and strengthening the intermolecular hydrogen bond between nitrogen of TEA and hydrogen of hydroxyl group.
8.2 Results and discussion

Again, upon complexation, normal emission is also observed, also some molecules undergo ESPT and emit as green band. Our results indicate that photo-chemical properties of 6-HF are modulated in presence of amines. Such study can explore photo-reactions in biological system which contains amines as a functional group like amino acids (major constituents of proteins).

8.2.(g) Effect of UREA on fluorescence of 6-HF

To further extend our study to probe the origin of green band in presence of TEA fluorescence properties of 6-HF in the presence urea (which is also proton accepting) are studied in different solvents.

It has been observed that optical density as well as fluorescence of 6-HF is enhanced in dioxane in presence of UREA. No changes in the absorption maximum have been observed even after addition of high concentration of UREA. Interestingly, the fluorescence emission in dioxane is red shifted ~ 15 nm on addition of UREA. Spectral nature of 6-HF in presence of UREA is depicted in figure 8.22.

This behaviour is entirely different from earlier discussed interaction of TEA with aprotic solvent. Here it seems that no ESPT takes place in presence of urea.

However, red shifted emission spectrum suggests that hydrogen bond formation with urea takes place in the excited state only. Interestingly, no shift in absorption in presence of UREA indicates that hydrogen bonding between urea and 6-HF either doesn’t exist or is very weak and hydrogen bonded complexes are formed only in the excited state which stabilizes the excited state.

Decay curve of 6-HF in presence of UREA is depicted in figure 8.23. When the emission is monitored at ~ 420 nm, the decay fits with a bi-exponential function with components around 0.68 ns and 1.62 ns having contribution 32% and 68% respectively. With increase in UREA concentration, the amplitude of shorter decay component decreases while the contribution of longer decay component increases.
8.2 Results and discussion

It is noticed that both the lifetimes vary with increasing UREA concentration and at the highest urea concentration (5 × 10^{-2} M) both shorter and longer decay components are 1.16 ns and 7.60 ns respectively. Increase in decay component with increase in urea concentration suggest towards more stabilized excited state due to intermolecular hydrogen bond formation between 6-HF and UREA.

Unlike previous observation in TEA, UREA seems to have less tendency to attract protons as compared to TEA.

![Figure: Emission spectrum of 6-HF in presence of UREA.](image-url)

On the other hand, the behaviour for methanol in presence of UREA is quite different. On keeping the solute concentration fixed and increasing UREA concentration, absorption spectrum does not show any change in presence of UREA. No shift in emission spectrum is observed although the intensity gets enhanced. In ACN three folds and in MeOH two fold enhancements in the fluorescence intensity is observed with increased concentration of UREA.
8.2 Results and discussion

Figure 8.23 Decay Parameters of 6-HF in presence of UREA in Acetonitrile.

Figure 8.24 Emission spectrum of 6-HF in methanol in presence of UREA.
8.2 Results and discussion

The enhancement in the fluorescence intensity can be viewed in fig. 8.24. No significant change is observed in decay times in the presence of UREA (figure 8.25). The possible reason is that MeOH is itself a good proton acceptor therefore addition of UREA does not alter the equilibrium of the system.

The present study of interaction of UREA with 6-HF is quite useful for detection of trace amount of UREA.

![Figure 8.25 Decay parameters of 6-HF in presence of UREA.](image)

8.3 Conclusion:

Steady state and transient studies of 6-Hydroxy Flavanone (6-HF) have been studied in pure solvents, binary mixtures and in the presence of proton accepting solvents. Comparison of absorption spectra and fluorescence excitation spectrum indicate that the structure of 6-HF is highly sensitive for electronic excited state. Absorption maxima shift to a small extent on changing the hydrogen bond ability of the solvent or varying the composition of the binary solvent mixtures.
8.3 Conclusion

On the contrary, the fluorescence emission maximum is largely dependent on the nature of the solvent or the composition of the solvent mixture. 6-HF undergoes a large change in dipole moment on excitation. The fluorescence decay is bi-exponential in all the solvents. The fluorescence lifetime is highly dependent on viscosity of the medium and increases with increase in the viscosity of the solvent.

Photophysical study of 6-HF is mostly dependent on the HBD acidity/basicity of the solvent and have minimal influence of polarity on the stokes shift of fluorescence maximum. 6-HF undergoes dielectric enrichment in DEE-methanol solvent mixture, whereas, for toluene-acetonitrile solvent mixture this is not the case. Such observations indicate a special interaction of the compound with protic solvent which originates from intermolecular hydrogen bonding.

As it is known that excited state proton transfer is most fundamental reaction in chemistry and biology, the observed results of fast ESPT reaction in dioxane on addition of TEA suggest that presence of TEA makes ESPT process more feasible. Such study is the demonstration of a proton migration in the excited state without water, however to make it more clear ultrafast experiments still needed to be carried out. These distinct features of 6-HF make it a good candidate to probe the microenvironmental surroundings.

Changes in excited state dynamics of 6-HF with UREA are rationalized in terms of hydrogen bond formation in the excited state in aprotic medium while in protic medium no such effect was observed. Photophysical properties of 6-HF with urea reveal that such system may be useful for the detection for the trace amount of UREA.
8.4 References:

8.4. Reference

8.4. Reference


