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Solvent and concentration effects on the steady state fluorescence of fluorenone

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Abstract

The electronic absorption and steady state fluorescence spectra of fluorenone in the regions 280–340 and 320–420 nm respectively have been obtained at room temperature for various concentrations in a series of non-polar and polar solvents. The effects of fluorenone concentration in various solvents in the range 10^{-6}–10^{-3} M on the spectral properties are discussed. In addition to the monomer fluorescence, we have also observed another fluorescence band at longer wavelength in the region 420–600 nm which has been ascribed to excimer formation. The monomer and excimer fluorescence lifetimes of fluorenone in typical solvents such as benzene and acetonitrile have been determined experimentally. By combining our results of steady state fluorescence and measurements of fluorescence lifetimes with previously reported studies of laser-induced fluorescence, the mechanism of excimer formation has been explained. The absence of excimer formation in hexane, cyclohexane and alcohols is discussed.

Keywords: Solvent effects; Concentration effects; Steady state fluorescence; Fluorenone

1. Introduction

Fluorenone exhibits some rather unique spectroscopic and photochemical properties that have made it the subject of several investigations. For example, assignments of states [1,2], the interpretation of solvent effects on the spectra, luminescence yields and lifetimes [3–5] and laser flash photolytic measurements [6] have already been reported in the literature. The existence of delayed fluorescence of fluorenone in acetonitrile has been attributed to excimer formation by laser-induced fluorescence [6]. Also, to understand the nature of solvent effects on the photophysics of fluorenone, the basic photophysical parameters as a function of temperature in the range 180–340 K in five different solvents have been extensively studied [7]. These studies show clearly the solvent and temperature dependence of the rates of the dominant photophysical processes. Solvent- and temperature-dependent studies of fluorenone derivatives with electron-donating and electron-withdrawing substituents have been reported recently [8].

From a survey of the literature it has been found that there are no detailed reports on the excimer fluorescence of fluorenone under steady state excitation. In this paper we will discuss our results on the steady state excimer fluorescence in *non-polar solvents* such as hexane, cyclohexane, dioxane, benzene and toluene, *polar aprotic solvents* such as chloroform, tetrahydrofuran, dichloromethane, acetonitrile and dimethyl formamide and *polar protic solvents* such as butanol, propyl alcohol and methanol.

By combining our results of steady state fluorescence and measurements of fluorescence lifetimes of the monomer and excimer with previously reported studies of laser-induced fluorescence, the mechanism of excimer formation has been explained on the basis of a triplet–triplet annihilation process.

2. Experimental details

2.1. Chemicals

Fluorenone obtained from Aldrich Chemical Company has been used in our investigations directly without further purification. The solvents used are of spectroscopic grade and were obtained from E-Merck Ltd.

2.2. Spectral measurements

UV absorption spectra of fluorenone in various concentrations (10^{-6}–10^{-3} M) in non-polar and polar solvents have been recorded at room temperature using a Hitachi U3400 spectrophotometer. Fluorescence spectra of fluorenone in the

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Table 1
Spectral characteristics of fluorenone

Solvent	Absorption maxima λ (nm) [log ε]	Fluorescence maxima λ (nm) [fluorescence intensity (a.u.)]	
		Monomer peak	Excimer peak
Non-polar			
Hexane	310.1 [2.676], 289.9 [3.467]	341.0 [72.00]	–
Cyclohexane	310.9 [2.661], 290.5 [3.511]	347.0 [81.70]	–
Dioxane	306.3 [3.158], 292.5 [3.479]	347.5 [13.40]	484.25 [95.15]
Benzene	307.6 [3.293], 291.9 [3.737]	351.0 [13.20]	486.00 [90.60]
Toluene	307.0 [3.298], 293.5 [3.847]	354.0 [14.00]	488.50 [92.35]
Polar			
Chloroform	307.8 [2.832], 294.9 [3.125]	355.50 [15.30]	501.00 [92.70]
Tetrahydrofuran	306.1 [3.101], 292.1 [3.389]	356.50 [30.30]	493.75 [104.25]
Dichloromethane	307.6 [3.063], 293.2 [3.389]	359.25 [10.40]	508.25 [89.50]
Acetonitrile	306.5 [3.003], 292.4 [3.294]	346.75 [13.05]	504.5 [94.00]
Dimethyl formamide	308.5 [3.323], 292.7 [3.737]	359.25 [90.10]	507.5 [86.70]
Alcohol			
Butanol	312.8 [2.720], 293.9 [2.776]	350.00 [78.09]	–
Propyl alcohol	– 291.4 [4.255]	346.00 [133.5]	–
Methanol	306.5 [2.255], 291.7 [3.463]	353.00 [90.55]	–

same concentration range in various solvents have been recorded at room temperature using a Perkin–Elmer LS5b luminescence spectrometer under excitation at 308 nm. Fluorescence lifetimes for the same concentrations in benzene and acetonitrile have also been measured at room temperature using an Applied Photophysics nanosecond spectrometer under excitation at 308 nm. All these spectra have been recorded under excitation at 308 nm because we intend to further investigate the transients using an XeCl excimer laser (308 nm) as a source of excitation

3. Results and discussion

The absorption and fluorescence spectra of fluorenone in all the solvents for various concentrations in the range 10^{-6}–10^{-3} M reveal that two fluorescence bands exist. At lower concentrations the band at shorter wavelength is found to be predominant over the band at longer wavelength. With increasing concentration the intensity of the second band at longer wavelength is seen to increase, while the band at shorter wavelength is gradually suppressed. This phenomenon has been observed in all the solvents except hexane, cyclohexane and alcohols at higher wavelength for any concentration.

Based on these observations, the additional fluorescence band observed at longer wavelength is expected to be due to excimer formation. This will be discussed further to establish its existence.

3.1. Absorption and fluorescence spectra of fluorenone

The peak wavelengths of absorption and fluorescence of fluorenone (λ_a and λ_f) along with the molecular absorption coefficients (log ε) and fluorescence intensities of both monomer and excimer for a typical concentration of 10^{-3} M are listed in Table 1 for all the solvents. Fig. 1 shows the absorption spectra for fluorenone in non-polar (hexane and benzene), polar aprotic (chloroform) and polar protic (methanol) solvents for the concentration of 10^{-3} M. The absorption spectrum shows two prominent bands at 290 and 310 nm in all the solvents. In the case of alcohols the absorption spectrum itself is broadened. This shows that there are specific solute–solvent interactions between the carbonyl atom of fluorenone and the OH group of alcohols. The fluorescence spectra of fluorenone in hexane, benzene, chloro-

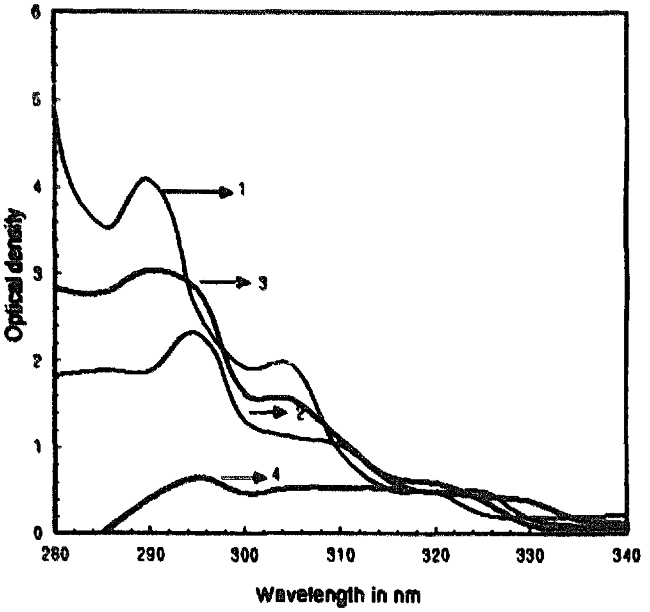

Fig. 1. Electronic absorption spectra of fluorenone (10^{-3} M) in various solvents: 1, hexane; 2, benzene; 3, chloroform; 4, methanol.

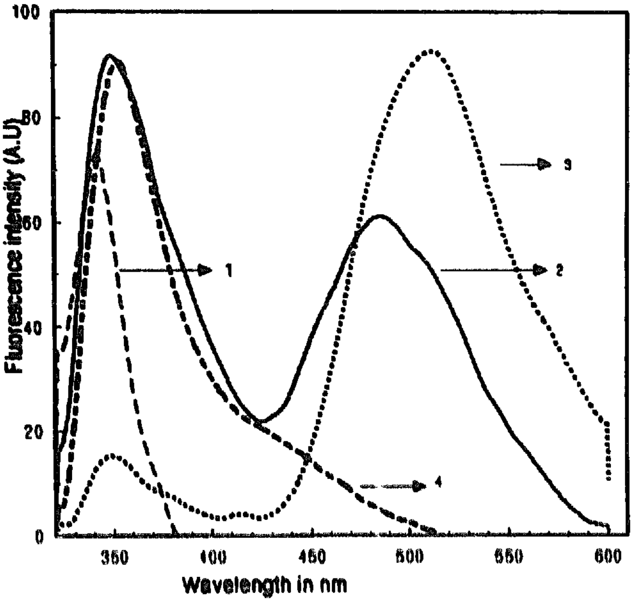

Fig. 2. Fluorescence spectra of fluorenone (10^{-3} M) in various solvents: 1, hexane; 2, benzene; 3, chloroform; 4, methanol.

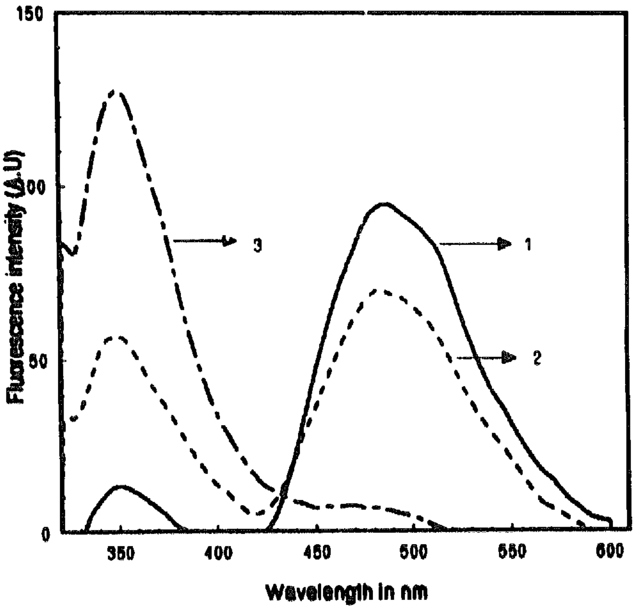

Fig. 3. Variation in fluorescence spectrum of fluorenone in benzene with concentration: 1, 1.1×10^{-3} M; 2, 1.1×10^{-4} M; 3, 1.1×10^{-5} M.

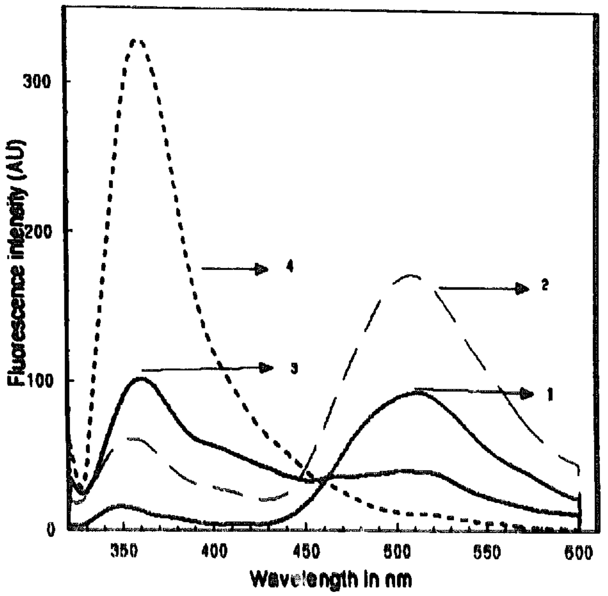

Fig. 4. Variation in fluorescence spectrum of fluorenone in chloroform with concentration: 1, 1.1×10^{-3} M; 2, 1.1×10^{-4} M; 3, 1.1×10^{-5} M; 4, 1.1×10^{-6} M.

form and alcohols are shown in Fig. 2. We have not observed any additional fluorescence band at longer wavelength in hexane, cyclohexane and alcohols. In all the other solvents two fluorescence bands have been observed.

In order to understand the existence of the second band of fluorescence at longer wavelength, the effect of concentration on the fluorescence spectra has been investigated. Figs. 3 and 4 show the effect of typical variations in concentration of fluorenone in benzene and chloroform respectively. With an increase in concentration from 10^{-6} to 10^{-3} M we found that there is a drop in the intensity of the fluorescence band at shorter wavelength, while the band at longer wavelength started increasing in intensity in all these solvents.

There is also a possibility of the occurrence of fluorescence at longer wavelength due to charge transfer states, in which case there should be a regular trend in the increase or decrease in intensities of these bands with increasing or decreasing concentrations. The existence of the additional fluorescence band at longer wavelength is expected to be due to excimer formation. This can be established by following the reasons and observations given below.

3.2. *Excimer fluorescence of fluorenone*

It is also observed that at lower concentrations the first band of fluorescence due to the monomer predominates over the excimer fluorescence. In dilute solutions the average separation of solute molecules is too great to allow an appreciable proportion of the excited molecules to encounter a second solute molecule within the lifetime of the excited state. Hence the excimer formation in dilute solutions is very small. As the concentration increases, the average separation between solute molecules becomes too small to allow the interaction for excimer formation [9].

In order for emission to occur from the excimer, it must be formed within the lifetime of the excited states [10,11]. To understand the formation of the excimer, we have measured the fluorescence lifetimes of both monomer and excimer in concentrations of 10^{-3} and 10^{-5} M of fluorenone in benzene and acetonitrile. Keeping the excitation wavelength at 308 nm and the emission at the peaks of the monomer and excimer fluorescence, the decay has been recorded and analysed using the deconvolution technique, assuming an exponential decay. Fig. 5 shows the typical pump pulse and fluorescence decay

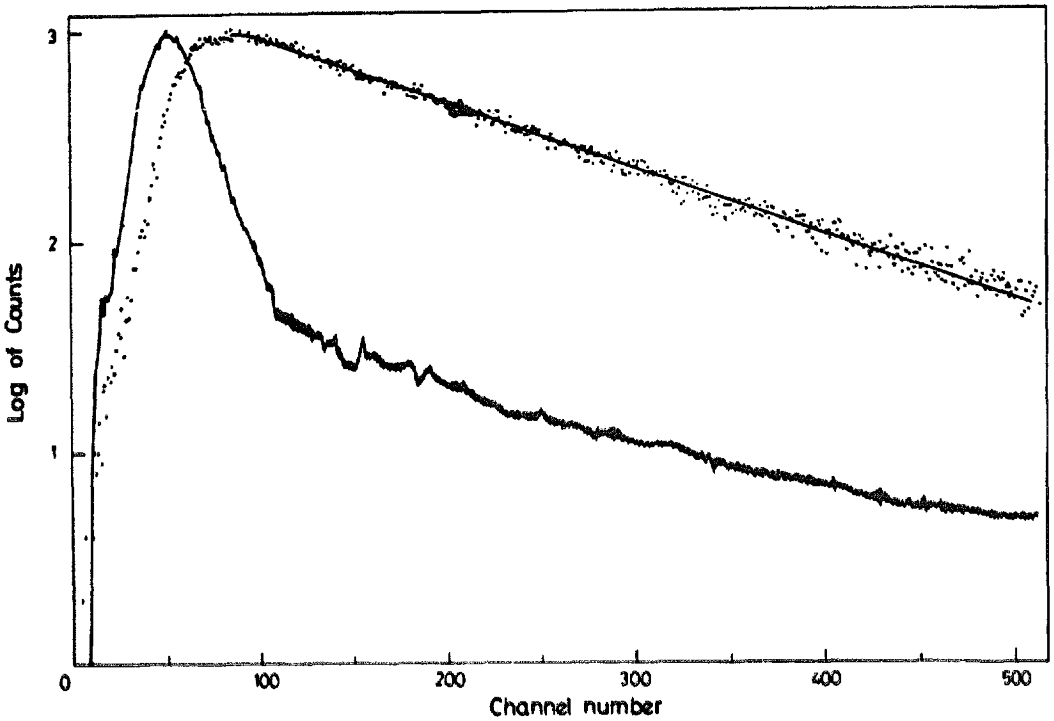

Fig. 5. Typical pump pulse and fluorescence decay of excimer fluorescence of fluorenone (10^{-3} M) in acetonitrile.

of the excimer fluorescence of fluorenone in acetonitrile for the concentration of 10^{-3} M. The lifetimes of the excimer fluorescence in benzene and acetonitrile are found to be 4.9 and 8.83 ns respectively. The lifetimes of the monomer fluorescence in benzene and acetonitrile are found to be 10.36 and 9.66 ns respectively. From the lifetime measurements it is observed that the lifetime of the excimer fluorescence is within that of the monomer. Also, we observed the fluorescence decay of only the monomer in dilute solutions (10^{-5} M) and of only the excimer at higher concentrations (10^{-3} M) using excitation with a nitrogen pulsed lamp in the nanosecond spectrometer. This again confirms the formation of the excimer at higher concentrations.

The ratio of the intensities of fluorescence of the excimer and monomer (I_D/I_M) shows a linear behaviour with concentration, indicating that the two processes compete with each other. The heat of formation of the excimer (ΔH^*) should be greater than RT. It has been estimated using the relation [9]

$$h(\bar{\nu}_M - \bar{\nu}_D) = -\Delta H^* + E_r \qquad (1)$$

where $\bar{\nu}_M$ and $\bar{\nu}_D$ are the peak wavenumbers of the monomer and excimer fluorescence respectively and E_r is the activation energy for formation of the excimer, which is generally of the order of 12–18 kJ mol^{-1}. It is found that the value of $-\Delta H^* + E_r$ for fluorenone in benzene is 84.32 kJ mol^{-1}, which is very much greater than RT (2.49 kJ mol^{-1}). This facilitates the formation of the excimer.

From X-ray studies it has already been reported [12,13] that the fluorenone molecule is of planar structure. At higher concentrations there is a possibility of very high molecular overlap leading to the formation of the excimer.

The absorption spectrum of fluorenone in the different solvents as a function of concentration shows that Beer's law is still valid and there is no change in the shape of the absorption spectrum. This shows that the excimer is highly dissociative in the ground state. In the case of hexane, cyclohexane and alcohols we have not observed the excimer fluorescence. The quantum yields of fluorenone in propanol and cyclohexane are very low compared with those in other solvents and are reported [3] to be 0.0027 and 0.0005 respectively. The reported [14] values of the fluorescence lifetime in cyclohexane and alcohols are found to be very low compared with those in other solvents and are in the range 1.1–1.8 ns. The absence of excimer formation in these solvents is expected to be due to their shorter lifetime. Also, in alcohols there is hydrogen bond formation between the solute and solvents, which may be responsible for the absence of excimer formation. Weak interactions between solute molecules may be responsible for the absence of the excimer in the case of the low polarity solvents hexane and cyclohexane.

3.3. Mechanism of excimer formation

In the steady state studies the excimer formation is confirmed by the concentration effect. From the fluorescence lifetime measurements the fact that the lifetime of the excimer is found to be shorter than that of the monomer again confirms the existence of the excimer. In the transient studies the excimer emission is indicated by the delayed fluorescence emission. There are three different well-known delayed emissions which can occur: phosphorescence, E-type delayed emission and P-type delayed emission. The absence of phosphorescence [1] even in rigid media rules out the first possibility of delayed emission.

Using picosecond time-resolved spectroscopy, Kobayashi and Nagakura [5] succeeded in outlining a consistent picture of the energy level diagram of fluorenone in both polar and non-polar solvents. From their assignments of singlet and triplet levels of fluorenone the energy separation between singlet and triplet levels is found to be greater than *RT*. This rules out the second possibility of E-type delayed fluorescence.

The possibility of P-type delayed emission has been confirmed by laser-induced fluorescence studies [6] of fluorenone in nitrogen-saturated acetonitrile, in which a delayed emission band in the range 400–600 nm after 4 μs of excitation has been observed. This type of delayed emission has been explained by Parker and coworkers [15,16], who have proposed a mechanism for P-type delayed emission based on a triplet–triplet annihilation process. The process of triplet–triplet annihilation [17] consists of transfer of energy from one triplet to another to form an excited dimeric species as follows:

$$\begin{array}{ccccc} T+T & \longrightarrow & S_2^* & \longrightarrow & S_1+S_0 \\ & & \downarrow & & \downarrow \\ & & S_0+S_0+h\nu_e & & S_0+h\nu_d \\ & & \text{(excimer} & & \text{(delayed} \\ & & \text{emission)} & & \text{emission)} \end{array}$$

Here S_2^* is the excimer and S_1 and S_0 are the first singlet state and ground state respectively. The first step of triplet–triplet annihilation is the excimer emission observed by steady state fluorescence. The second step is the delayed emission observed by laser-induced fluorescence. It is interesting to mention here that we have also observed an emission band in the same region in the steady state excitation which can be ascribed to excimer formation.

4. Conclusions

The photophysics of fluorenone in solutions shows some unique features as a consequence of the solvent and concentration dependence. We have observed an additional fluorescence band at the longer wavelength side of the monomer fluorescence in all the solvents except hexane, cyclohexane and alcohols under steady state excitation at 308 nm. The appearance of this band has been ascribed to the formation of an additional electronic excited singlet state by the annihilation of two triplet state molecules following a delayed P-type fluorescence. The delayed fluorescence band observed under pulsed laser excitation at 308 nm reported in Ref. [6] gives good support for the occurrence of the additional band at the same wavelength in our steady state excitation. The existence of the second electronic state has been established by lifetime measurements. We have not observed any additional fluorescence bands apart from the monomer fluorescence in the solvents hexane, cyclohexane and alcohols owing to their shorter lifetime and also possibly to solute–solvent interactions.

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