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Effects of Intermolecular Hydrogen-bonding on the Luminescence Properties of Acetophenone. Characterization of Emission States

Suniti Kumar GHOSHAL, Susil Kumar SARKAR, and Gouranga Sundar KASTHA*
Optics Department, Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700032, India

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The effects of intermolecular hydrogen-bond formation by protic solvents on the absorption and luminescence properties of acetophenone have been investigated. It has been concluded from analysis of the $T \leftarrow S_0$ absorption, phosphorescence excitation spectra and the emission characteristics that the lowest triplet state of acetophenone in its vapor phase and in nonpolar as well as in moderately polar solvents (*e.g.*, ethanol, EPA *etc.*) is of n-π^* character. In rigid polar media, acetophenone exhibits a very weak ${}^1\pi$-$\pi^* \rightarrow S_0$ fluorescence and a weak ${}^3\pi$-$\pi^* \rightarrow S_0$ phosphorescence superposed with the principal ^{3}n-$\pi^* \rightarrow S_0$ emission. A progressive enhancement of both of these emissions with increasing polarity of the solvent has been observed. It is shown that the fluorescence and the dual phosphorescence emissions from acetophenone in rigid polar media arise as a result of decreased efficiencies of the spin-orbit and vibronic coupling interactions due to intermolecular hydrogen-bond formation by the protic solvents.

In spite of extensive spectroscopic[1—18] and photophysical[19—21] studies ambiguity remains concerning the assignment of the lowest triplet state of acetophenone. The phosphorescent state of acetophenone in glassy nonpolar and moderately polar media (*e.g.*, ethanol, EPA) at 77 K has been shown to possess a n-π^* character by several investigators[1—6] and a π-π^* character by others.[7,8] More recently, Mathews and Lytle[9] characterized it as n-π^* and π-π^* type in polar (ethanol, methanol) and nonpolar media, respectively, at 77 K. In the case of pure acetophenone crystal, π-π^* assignment was made of its lowest triplet state on the basis of polarized phosphorescence-excitation spectra[11] and PMDR studies,[12] and n-π^* assignment on the basis of $T \leftarrow S_0$ absorption[10] and the polarization and Zeeman splitting measurement of the $T \leftarrow S_0$ absorption.[13]

As regards the origin of dual phosphorescence emissions in rigid polar media, the phenomenon has been interpreted on the basis of various assumptions.[14,17] Koyanagi *et al.*[6] proposed a model of highly distorted (triple minimum) potential surface in the lowest triplet state of acetophenone in order to explain its dual phosphorescence. A non-interacting density of states model has been postulated to account for the phenomenon. In each case a close proximity of the ^{3}n-π^* states has been assumed as an essential prerequisite for the occurrence of dual phosphorescence emission, but little information is given on the relative positions of the triplet levels in environments pertinent to the problem. The dual phosphorescence is observed in rigid polar media and H-bond acceptor properties of the aromatic ketones[5,22,23] but the possibility that this phenomenon could be associated with the solute–solvent intermolecular H-bonding interaction has not be considered.

Though the fluorescence activation of several aromatic aldehydes, ketones and other carbonyl compounds in protic media is well known[24] no investigation seems to have been made on the possibility of fluorescence activation in the case of acetophenone.

In view of the significance of luminescence properties of aromatic carbonyls in hydrogen bonding media and the conflicting assignment of the lowest triplet state of acetophenone, a detailed investigation on the absorption and emission characteristics of this aromatic ketone has been carried out. This study was carried out in order to obtain information on the relative positions of the n-π^* and π-π^* levels of acetophenone under various conditions, and to examine the effect of intermolecular H-bonding on the photophysical behavior of this phenyl alkyl ketone.

Experimental

Materials. Acetophenone (EGA-Chemie, West Germany) was purified by repeated fractional distillation till no impurity could be detected with a flame ionization detector column (Hewlett-Packard, Model 5730A). Spectrograde ethanol, ether, isopentane, and 3-methylpentane (3-MP) of E. Merck and hexane, pentane, and methylcyclohexane of BDH were further purified by fractional distillation. Freshly prepared and deoxygenated solutions of concentrations 10^{-4}—10^{-5} M were used for recording all the spectra except in the cases of $T \leftarrow S_0$ absorptions where more concentrated solutions (*ca.* 10^{-3} M) were used.

Apparatus: The room temperature (300 K) solution and vapor phase (*ca.* 10^{-2} Torr†) emission spectra and low temperature (77 K) emission, excitation and polarization spectra were recorded on a Perkin Elmer Model MPF 44A fluorescence spectrophotometer. The vapor phase absorption spectra with 10 cm quartz cell at 300 K and 760 Torr and the solution spectra at 300 K and 77 K with a 1 cm quartz cell were obtained with a Shimadzu 210A UV-VIS Absorption spectrophotometer. Photoselection technique was employed for the measurement of the degree of polarization, which was corrected following Azumi and McGlynn.[25] The phosphorescence lifetimes were determined by using Molectron UV-1000 N_2-Laser as the excitation source in conjunction with an EC storage Oscilloscope.

Results

Absorption Characteristics. Figure 1 shows the absorption spectrum of acetophenone in the vapor phase and in protic as well as aprotic solvents at room temperature (300 K). Appreciable solvatochromic effects, such as the hypso- and bathochromic shifts, respec-

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† 1 Torr = 133.322 Pa.

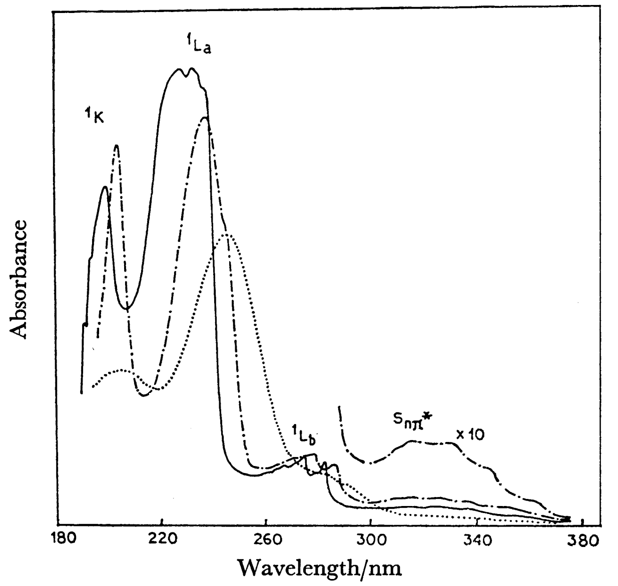

Fig. 1. Singlet-singlet absorption spectra of acetophenone in the vapor phase (——), 3-MP (—·—), and 1% HCl (······) at 300 K.

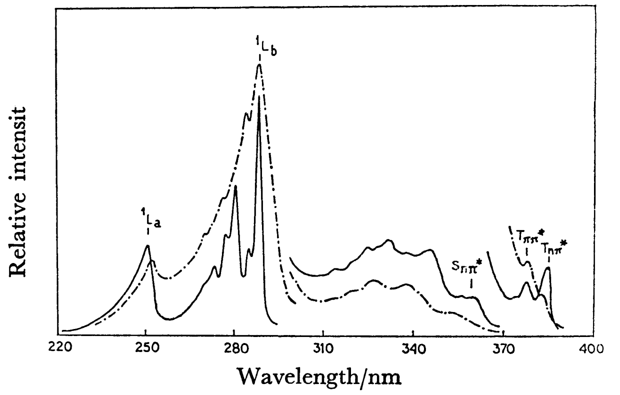

Fig. 2. Phosphorescence excitation spectra of acetophenone in 3-MP (——) and ethanol (—·—) at 77 K.

tively, of the n-π^* and π-π^* bands and noticeable hypochromic effect on both types of bands are evident from a comparison of the spectra. Although in moderately polar and H-bonding media (*e.g.*, ethanol) the higher energy π-π^* bands (^1L_a and ^1K) are relatively less affected, in highly polar and acidic media (*e.g.*, 1% HCl), the red-shifts and hypochromic effect on these bands are substantial but the n-π^* bands are completely obliterated. The results demonstrate the effects of intermolecular H-bonding on the various $\pi^*\leftarrow$n and $\pi^*\leftarrow\pi$ electronic transitions of acetophenone in protic media.

The phosphorescence excitation spectra of acetophenone (Fig. 2) in glassy polar ethanol and nonpolar 3-MP at 77 K provide further data attributable to the effect of solute-solvent H-bonding interaction (Table 1). An appreciable blue shift (*ca.* 464 cm^{-1}) and marked diminution and blurring out of vibrational structure of the ^{1}n-$\pi^*\leftarrow S_0$ bands in the excitation spectra are observed in going from 3-MP to ethanol. The ^{1}n-$\pi^*\leftarrow S_0$ excitation spectra show a significant lowering (*ca.* 100 cm^{-1}) of the excited state carbonyl stretching frequency of the molecule in ethanol as compared to that in 3-MP glass (Table 2). With increase in the polarity of the medium (*e.g.*, from ethanol to predominantly ethanol–water mixture), further obliteration of the ^{1}n-$\pi^*\leftarrow S_0$ bands takes place. In highly polar and acidic media (1% HCl) these bands are no longer observable in the phosphorescence excitation spectra. The ^1L_a band also shows a similar solvent dependent intensity variation.

TABLE 1. RELATIVE POSITIONS (cm^{-1}) OF THE n-π^* AND π-π^* SINGLET AND TRIPLET STATES OF ACETOPHENONE MEASURED FROM THE ABSORPTION SPECTRA[a)]

Electronic energy levels	300 K			77 K	
	Vapor	3-MP	Ethanol	3-MP	Ethanol
^1L_a	42997	42092	41395	39875 (39892)	39740 (39749) (39358)[b)]
^1L_b	35387	34954	34712	34687 (34675)	34615 (34532) (34500)[b)]
^{1}n-π^*	27886	27692	31736	27769 (27776)	28003 (28240) (28481)[b)]
$^3\pi$-π^*	26946	26517	26510	26377 (26383)	26308 (26377) (26363)[b)]
^{3}n-π^*	25899	26000	—	25832 (25933)	25966 (26034) (26075)[b)]

a) Values in parentheses are obtained from the phosphorescence excitation spectra at 77 K. b) Data in ethanol-water mixture.

Both the vapor and solution phase $T\leftarrow S_0$ absorption spectra of acetophenone (Fig. 3) display two weak but distinct bands. The spectral positions of these bands under different environmental conditions are given in Table 1. From a consideration of the relative changes in absorbance and the solvatochromic shifts exhibited by the bands on passing from the vapor phase to hydrocarbon and to polar solvents, the respective assignments of these bands to $^3\pi$-$\pi^*\leftarrow S_0$ and ^{3}n-$\pi^*\leftarrow S_0$ transitions have been made (Fig. 3). The bands can be clearly discerned in the phosphorescence excitation spectra of acetophenone in polar as well as in nonpolar media at 77 K (Fig. 2). In glassy hydrocarbon (3-MP), the lower energy band (25933 cm^{-1}) has an eminent overlap with the phosphorescence band origin (25815 cm^{-1}), the higher energy one appearing at 26383 cm^{-1}, *i.e.* 450 cm^{-1} towards the higher frequency side of the former. The assignment of these bands to ^{3}n-$\pi^*\rightarrow S_0$ and $^3\pi$-$\pi^*\leftarrow S_0$, respectively on the basis of their characteristic solvatochromic shifts and hypochromic effects are analogous to and conform with those made in the case of absorption.

Emission Characteristics. *a) Phosphorescence Spectra*: Figure 4 shows the phosphorescence and the phosphorescence polarization (PP) spectra of acetophenone in glassy polar, EPA (ether, isopentane, and ethanol

TABLE 2. OBSERVED VALUES OF PHOSPHORESCENCE BAND ORIGIN, FUNDAMENTAL FREQUENCIES, MEAN PHOSPHORESCENCE LIFETIME (τ_p) AND QUANTUM YIELD RATIO (Φ_P/Φ_F) OF ACETOPHENONE

	300 K		77 K	
	Vapor	Isopentane	3-MP	Ethanol
Phosphorescence band origin/cm^{-1}	25670 25786a)	25668	25815	26007
Fundamental frequency/cm^{-1}	1701	1709	45, 260, 1143, 1346*, 1710	95, 208, 1170, 1240*, 1666
τ_p/ms	2.2	2.4	2.5	5.0 1.2b) × 10^3
Φ_P/Φ_F	—	—	—	500 400c) 125d)

a) Ref. 6. b) Lifetime in acidic media. c) Value in ethanol-water mixture. d) Value in 1% HCl. * C=O stretching frequencies obtained from ^{1}n-π*←S$_0$ phosphorescence excitation spectra at 77 K. Φ_P/Φ_F values are considered to be qualitative.

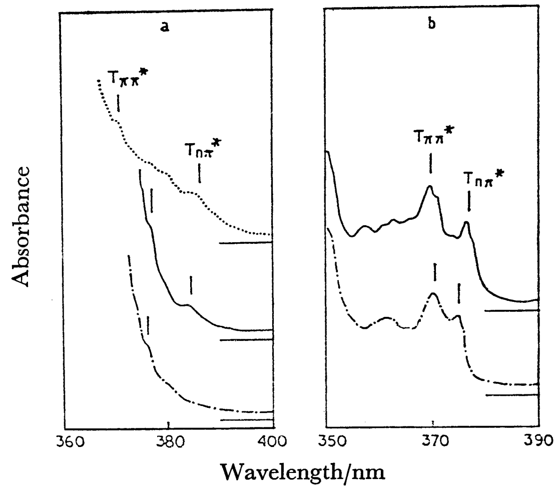

Fig. 3. Singlet-Triplet absorption spectra of acetophenone (a) in the vapor phase (······), 3-MP (——) and ethanol (—·—) at 300 K. (b) In 3-MP (——) and ethanol (—·—) at 77 K.

5:5:2) and nonpolar (3-MP) media under identical conditions. Despite the close resemblance of the two spectra, distinct changes in phosphorescence spectra brought about by the protic solvent are apparent:

(1) The sharp and structured phosphorescence spectrum observed in 3-MP at 77 K appears broadened in EPA glass.

(2) A substantial blue shift (*ca.* 190 cm^{-1}) of the phosphorescence band origin and lowering of carbonyl stretching frequency ($\nu_{C=O}$) occurs with the change of solvent from nonpolar to polar.

(3) A significant diminution in phosphorescence intensity of acetophenone takes place in polar media in comparison with that in glassy hydrocarbon matrices.

(4) Whereas the phosphorescence intensity on the smaller wavelength side of the 0-0 band in glassy hydrocarbon matrices falls steeply, in glassy polar media the band origin is accompanied by a short tail which extends to the higher frequency region beyond the band maximum (384.5 nm). In fact, the phosphorescence spectrum of acetophenone recorded with an expanded scale and higher resolution (Fig. 5) reveals a weak partially resolved blue shoulder at *ca.* 381 nm.

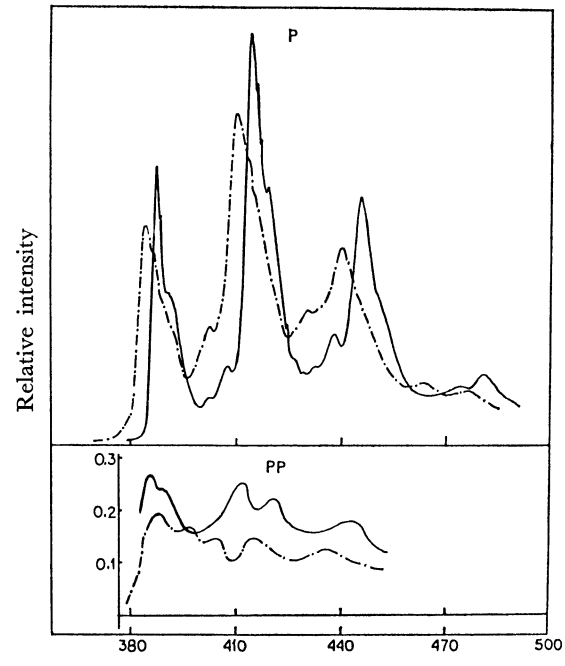

Fig. 4. Phosphorescence (P) and phosphorescence polarization (PP) spectra (with 250 nm excitation) of acetophenone in 3-MP (——) and EPA (—·—) at 77 K.

The phosphorescence polarization (PP) curves of acetophenone in glassy hydrocarbon (3-MP) and polar (EPA) media show that in both cases the phosphorescence is strongly positively polarized with respect to ^1L_a excitation, indicating a predominantly in-plane polarization of the phosphorescence emission (Fig. 4). The sharp fall in the value of the degree of polarization (*P*) in the 3-MP curve around the immediate vicinity of the phosphorescence band origin indicates the presence of some low frequency nontotally symmetric vibronic band in the phosphorescence spectrum. An important distinction between the PP curves in 3-MP and EPA glass is that the *P* value is predominantly more positive in aprotic medium than in protic medium. The PP curve in EPA also shows markedly less positive value at 381 nm. A further decrement of the polarization is observed in more polar EWA (ether, water, and ethanol 5:1:4) glass at 77 K.

The phosphorescence decay curves for acetophenone show that while the nature of the decay is nearly exponential in the case of vapor and in hydrocarbon solutions, it is markedly nonexponential (in fact, biexponential) in rigid polar media like ethanol and water at 77 K (Fig. 6). The initial and final slopes of a first order plot from the decay curves of acetophenone in ethanol glass correspond to lifetimes (τ_p) of *ca.* 5 and 70 ms, respectively. The shorter lived component of the phosphorescence emission is, however, found to be contributing mostly (*ca.* 90% of the total intensity) to the phosphorescence intensity. In ethanol–water mixture at 77 K the τ_p values corresponding to the short and long lived components are 6 and 100 ms, respectively, in agreement with the earlier findings.[5)]

As the polarity of the solvent is increased there occurs an enhancement in the intensity of the longer lived component of the dual phosphorescence emission until in strongly acidic media it overwhelms the shorter lived one. In this case the phosphorescence lifetime becomes of the order of seconds. This result is similar to that reported by Lamola.[3)]

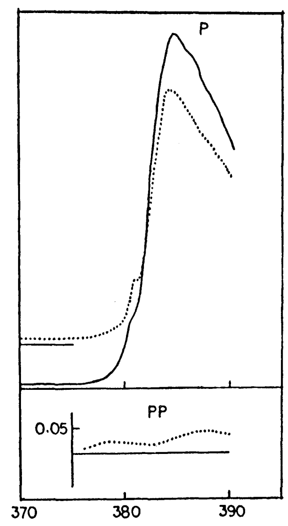

Fig. 5. Part of the phosphorescence (P) spectra (recorded on expanded scale) of acetophenone showing the phosphorescence band origins and the blue shoulder in ethanol (——), EWA (······) glasses at 77 K and the corresponding phosphorescence polarization (PP) spectrum in EWA.

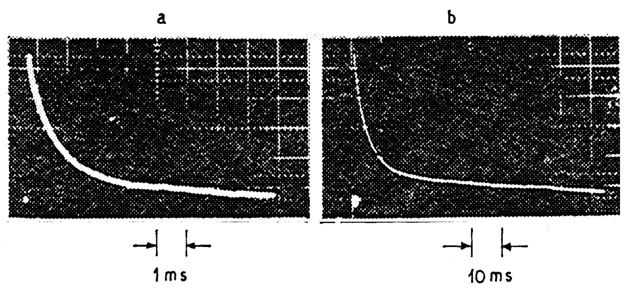

Fig. 6. Phosphorescence decay curves of acetophenone (a) in the vapor phase at 300 K (b) in ethanol at 77 K.

Thus, the predominantly in-plane polarization of the phosphorescence emission, the short lifetime, the solvent shifts and the vibronic structure of the phosphorescence emission provide the conclusive evidence for the n-π^* character of the lowest triplet state of acetophenone in its vapor phase and in nonpolar as well as moderately polar media (*e.g.*, EPA, ethanol) at 77 K. The $T \leftarrow S_0$ absorption spectra of the compound strongly confirm the n-π^* nature of its lowest triplet state in these media.

b) Fluorescence Spectra: In addition to its characteristic strong ^{3}n-$\pi^* \rightarrow S_0$ phosphorescence emission, acetophenone in rigid protic media at 77 K exhibits a very weak $^1\pi$-$\pi^* \rightarrow S_0$ fluorescence with ^1L_a and ^1L_b excitation (Fig. 7). Increase in the polarity or H-bond forming capacity (*e.g.*, ethanol+water, 1% HCl) of the media results in a progressive enhancement of such fluorescence but a gradual decrease in the phosphorescence intensity in the same order. The measured Φ_P/Φ_F values of acetophenone in these polar media are given in Table 2. The data when combined with the reported value of $\Phi_P(\approx 0.6)$ for acetophenone[4)] yield an approximate Φ_F value of 1.2×10^{-3} for this molecule in ethanol. Under these conditions, no emission attributable to the ^{1}n-$\pi^* \rightarrow S_0$ fluorescence could be detected.

Discussion

Occurrence of the phenomena, *viz.*, blue-shifts of the n-π^* bands, hypochromic effect on the n-π^* and π-π^* (^1L_a) bands, significant lowering of ν_{CO}, fluorescence activation and dual phosphorescence emission from acetophenone in protic media and the progressive enhancement of each with increasing solvent H-bond

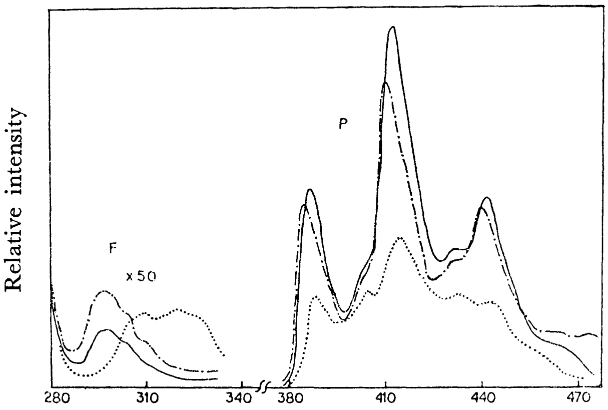

Fig. 7. Fluorescence (F) and phosphorescence (P) spectra of acetophenone in 3-MP (——), predominantly ethanol–water mixture (—·—), and in 1% HCl (······) at 77 K (Note the broken wavelength scale.).

donor capacity, indicates a close interrelation with intermolecular H-bonding. It might be related to changes in the electronic configuration of the acetophenone molecules caused by solute-solvent interaction, in view of the importance of the electronic structure associated with the carbonyl group, particularly the nonbonding (n) orbital on the oxygen atom, in determining the photophysical behavior of the aromatic ketones and the possible involvement of the oxygen electrons in intermolecular H-bond formation.

The hypsochromic shift of $\pi^*\leftarrow$n transition bands of carbonyls in H-bonding media has now been established.[26,27] It is known by infrared and Raman studies[22,28,29] that the ν_{CO} of carbonyls decreases with increasing H-bonding. Our experimental results are in line with these findings.

Intermolecular H-bonding interaction between the proton acceptor carbonyls and the donor protic molecules affects the electronic configuration of the carbonyl group in several ways. It increases the polarity of the carbonyl group (in the direction C^+–O^-) by increasing the π electron charge on the carbonyl oxygen atom[28,30,31]. As a consequence, the C–O bond strength decreases leading to an increased C–O bond length and smaller ν_{CO}. Since the n electrons on the carbonyl are primarily involved in intermolecular H-bond formation, such solute-solvent interaction is expected to have a pronounced effect on the n orbital of the oxygen atom. The work of Hollas *et al.*[32] indicates that the s character of the n orbital and its extent of delocalization are important in determining the $\pi^*\leftarrow$n transition intensity in aromatic aldehydes and ketones. The marked diminution in the intensity of n-π^* bands of acetophenone observed in going from hydrocarbon to hydroxylic solvents suggests an appreciable decrease in the s character of the sp^2 hybridized[28,33,34] n orbital of the carbonyl oxygen atom.

In aromatic aldehydes and ketones, because of the presence of closely spaced n-π^* and π-π^* electronic states (the n-π^* states being the lower-lying one), the spin-orbit and vibronic interactions between n-π^* and π-π^* excited states are generally very strong. The radiationless deactivation processes, such as internal conversion (IC) and intersystem crossing (ISC) between the pertinent excited states, are very fast and efficient in these types of molecules. This largely accounts for their nonfluorescent nature. The occurrence of π-π^* fluorescence from acetophenone in protic media and the progressive enhancement of such emission with increasing H-bond donor capacity of the solvent thus imply a considerable decrease in the efficiency of ISC or IC, or of both in such media.

The rate or the efficiency of IC between the n-π^* and π-π^* states is dependent to a significant extent on the vibrational overlap integral between the states concerned. Since the magnitude of vibrational overlap integral between n-π^* and π-π^* states decreases as a result of decrease in the charge density of the nonbonding electrons following H-bond formation,[34,35] it is expected that the efficiency of IC between the $^1\pi$-π^* and ^{1}n-π^* states of acetophenone would decrease in protic media.

The magnitude of spin-orbit coupling between the $^1\pi$-π^* and ^{3}n-π^* states of aromatic aldehyde and ketone molecules is largely governed by factors such as the partial π electron density (C_ν^2) and Slater charge (Z_ν) on the carbonyl oxygen atom and the form (hybridization and extent of delocalization) of the n orbital on this atom.[36] It follows that while the π electron density on the carbonyl oxygen atom increases a little, the hybridization factor (γ) undergoes a significant decrement upon H-bond formation. The analysis of Del Bene[37] shows that the increase of π electron charge on the heteroatom due to H-bonding leads to the lowering of the effective nuclear charge (Z_ν) of the atom. Because of the dependence of the spin-orbit interaction matrix element, $|\beta|^2$ (Eq. 8, Ref. 36), on the higher power of Z and the fact that both γ and Z values decrease as a result of H-bonding, it seems that there is an overall decrease in the value of $|\beta|^2$, despite a small increment in the value of C_ν^2. Accordingly, the spin-orbit coupling between the $^1\pi$-π^* and ^{3}n-π^* states of acetophenone should decrease in H-bonding media, and so should the ISC rate between them. It is conceivable, therefore, that because of the decreased efficiencies or rates of $^1\pi$-$\pi^* \rightsquigarrow {}^1$n-$\pi^*$ IC and $^1\pi$-$\pi^* \rightsquigarrow {}^3$n-$\pi^*$ ISC, the $^1\pi$-$\pi^*\rightarrow S_0$ radiative process may become to some extent competitive with these radiationless processes such that some π-π^* fluorescence could be emitted from acetophenone molecules in protic media.

The ^1L_a state of aromatic aldehydes and ketones (*e.g.*, benzaldehyde and acetophenone) which provides the dipole allowed character and in-plane polarization to the lowest triplet state through spin-orbit coupling[1] is known[38] to possess considerable intramolecular charge transfer character. The marked diminution in the ^1L_a band intensity of acetophenone in protic media indicates that the intramolecular charge transfer character of the associated singlet-singlet $\pi^*\leftarrow\pi$ transition is perhaps inhibited as a result of solute-solvent H-bonding interaction. The significant lowering of the P values of phosphorescence emission from acetophenone molecules in H-bonding media, compared to those observed in nonhydrogen bonding media, could be related, at least partly, to the diminished spin-orbit coupling between $^1\pi$-π^* $(^1L)_a$ and ^{3}n-π^* state due to H-bonding. This may be interpreted as evidence in favor of the supposition that the spin-orbit coupling should decrease in H-bonding media.

The simultaneous emission of phosphorescence from both the triplet states (^{3}n-π^* and $^3\pi$-π^*) of acetophenone in protic media suggests that the solvent induced decrease in the efficiency of $^3\pi$-$\pi^* \rightsquigarrow {}^3$n-$\pi^*$ IC process could be at the basis of such phenomenon.

According to Avouris *et al.*,[39] the rate constant of the IC process between two states is given by

$$K_{if}^{IC} = 2\pi/\hbar V_{if}^2 \rho_f(E_i), \tag{1}$$

where $\rho_f(E_i)$ is the density of closely spaced state 'f' (final) nearly degenerate with the initial state 'i' and V_{if} is the interaction matrix element for the IC process. V_{if} is dependent on the electronic factor β_{el}^{IC} and vibrational overlap integral.

Intermolecular H-bonding can bring about a diminution in the overlap integral through the decrease of nonbonding charge density. It can be shown that the magnitude of V_{lf} in the triplet manifold would also decrease as a result of intermolecular H-bond formation. We see from Eq. 1 that the density of states, $\rho_f(E_1)$ could also be an important factor contributing to the radiationless transition between the two triplet states. Because of the smaller energy gap between the T_2 (π-π^*)—T_1 (n-π^*) states of acetophenone in protic solvents, the level densities of T_1 near the T_2 origin are expected to be small. Consequently, internal conversion from the low-lying vibrational levels of T_2 to T_1 would be less efficient. As a result of the combined effect of a decrease in both these factors, it is possible that the $T_2 \rightsquigarrow T_1$ IC rate would become sufficiently slow so as to make the $^3\pi$-$\pi^*\rightarrow S_0$ radiative process to some extent competent with the IC process, leading to the observation of dual phosphorescence emission in the case of acetophenone. Several authors previously observed dual phosphorescence emission from other aromatic ketones, *e.g.*, *p*-benzoquinone,[40] indanone,[41] and related molecules in rigid polar media, and attributed the phenomenon to severely prohibited internal conversion from the $^3\pi$-π^* state to a lower lying ^{3}n-π^* state of these molecules.

Thus, the profound influence of the H-bonding solvents on the luminescence spectral properties of acetophenone is seen to arise primarily from the electronic effect of the intermolecular H-bonding interaction. When polarity or H-bond donor capacity of the solvent increases, the ISC and IC processes become progressively less efficient and a trend of progressive enhancement of the π-π^* fluorescence and $^3\pi$-$\pi^*\rightarrow S_0$ phosphorescence is observed. In strongly acidic media protonation of the carbonyl lone pair electrons occurs; the conjugation of the oxygen electrons across the carbonyl group and the intramolecular charge transfer character of the $^1L_a\leftarrow S_0$ transition are strongly affected. In this situation, as the n electrons on the carbonyl oxygen atom no longer remain nonbonding, the $\pi^*\leftarrow$n electronic transition loses its significance and the luminescence characteristics exhibited by the protonated species become more or less normal π-π^* type.

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