J. Phys. Chem. A **2003,** *107,* 83−90

Excited State Prototropic Activities in 2-Hydroxy 1-Naphthaldehyde

Papia Chowdhury, Subhasis Panja, and Sankar Chakravorti*

Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

Received: June 28, 2002; In Final Form: October 10, 2002

Excited state proton transfer in 2-hydroxy 1-naphthaldehyde (HNL) has been reported on the basis of steady state absorption and emission, time-resolved emission, and semiempirical quantum chemical calculations. The existence of open and closed ring conformers in the ground state gives rise to different emissions upon excitation in hydroxylic and hydrocarbon solvents, respectively. Formation of the ground state HNL ion in open conformer was observed with addition of base. Excitation of the closed conformer leads to intramolecular proton transfer across the preexisting intramolecular hydrogen bond to give excited zwitterion in hydrocarbon solvents. On excitation of the open ring conformer in hydroxylic solvents, emission from the neutral excited state could be observed for the first time apart from the emission of ionic intermolecular proton transfer species. An increase or decrease in pH results in enhancement or a decrease of emission from the ionic conformer with parallel dwindling or intensification of emission of the neutral species. Phosphorescence in both the solvents arises from the open conformer.

Introduction

More than 50 years ago, Förster[1] introduced the concept of excited state intermolecular proton transfer (ESI$_{er}$PT) on the basis of some unusual shifts in fluorescence spectrum of some organic molecules. In 1955, Weller[2] found that methyl salycylate exhibited fluorescence with an unusually large stokes shift, which corresponded to an excited state isomer formation via proton transfer. The classic paper[3] of Weller on excited state intramolecular proton transfer (ESI$_{ra}$PT) of methyl salycilate (MS) spurred intense research on this subject in many laboratories.[4−18] Among them, MS[7−10] and its related compounds such as *o*-hydroxyacetophenone (OHAP)[11−13] and *o*-hydroxybenzaldehyde (OHBA)[14−17] have been well-studied as prototypes of the molecules showing the ESIPT processes. It is a well-known fact that the properties of the molecules experience a change in the excited states with respect to the ground state due to the change in charge density distribution after excitation. When acid and base moieties of the same molecule become stronger acids or bases in the excited state, proton transfer (PT) may occur rapidly in the excited state to form a tautomer; the signature of that process is emission of strongly stokes-shifted fluorescence following absorption of a UV photon. Kasha[18] first showed that an intramolecular PT is facilitated in the excited state in those molecules where there is a hydrogen bond between the H atom of the donor group and the acceptor of that molecule in the ground state. The importance of this H-bond is such that it is convenient to discuss its nature. Transfer of a proton between two groups of an aromatic molecule causes a large electronic and structural rearrangement, which is associated with significant changes in dipole moments, molecular geometry, and quite large (≥ 1000 cm^{-1}) fluorescence shift. The dynamics of such a process could strongly be dependent on the nature of the solvent, namely, with respect to the formation of a hydrogen bond. One of the prime features common to most excited state PTs is their rapidity, on the femtosecond to nanosecond time scale.[19−21] These rapid transfers are commonly attributed to a barrierless process. Also, a number of systems containing more than one H-bond exhibit multiple PTs.[18]

ESIPT has a wide range of applications. These include energy/data storage devices and optical switching,[11,22−24] Raman filters and hard scintillation counters,[25] polymer photostabilizers,[26,27] and triplet quenchers.[28] Other applications center around electroluminescent materials with photochemical stability, resistance to thermal degradation, and low self-absorption and light-emitting diode materials.[28] It has been suggested that ESIPTs have the potential for understanding the binding properties of protein,[29] as well as optical probes for biomolecules.[30,31] Because of all of the interesting and useful applications, different groups throughout the world are working with a wide variety of fluorescing acid−base-containing molecules in order to systematize and control their emissive properties.

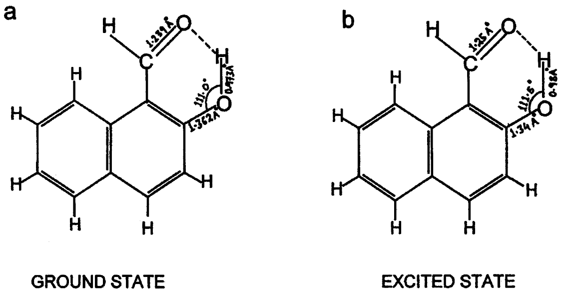
In the present work, we study the emission properties of 2-hydroxy 1-naphthaldehyde (HNL) by steady state and time-resolved emission spectroscopy. HNL is the simplest aromatic molecule with intramolecular hydrogen bonding involving carbonyl groups.[32] The properties of this molecule are interesting in relation to OHBA. Luminescence properties of HNL are rather different from OHBA. HNL shows dual fluorescence, but OHBA shows single fluorescence only in the visible region. So, we hope that a combination of steady state emission spectroscopy with picosecond spectroscopy will provide useful information concerning the structure and dynamics involving the excited states of HNL. In this paper, we first perform quantum semiempirical calculations to see the feasibility of excited state intramolecular proton transfer with respect to the dipole moment change and charge density distribution from the ground to excited state. On the basis of prediction, a detailed investigation of absorption and fluorescence properties of HNL in different environments and in β-cyclodextrin (β-CD) was carried out. We try to identify the species that are responsible

---

* To whom correspondence should be addressed. E-mail: spsc@mahendra.iacs.res.in.

10.1021/jp026404q CCC: $25.00

CHART 1: Optimized Geometry of HNL in the (a) Ground State and (b) Excited State



for different emissions with a view to understand different aspects of ESI$_{ra}$PT.

Experimental

Materials. HNL, purchased from Fluka, was purified by recrystallization followed by vacuum sublimation. *β*-CD (Aldrich) was used as supplied. Methyl cyclohexane (MCH) (Fluka) was purified by nitration and sulfonation, dried over anhydrous sodium sulfate, and distilled at 101 °C. *n*-Heptane and benzene (spectroscopic grade) were used after distillation (dry) and checking of any emission in the required wavelength range. Ethanol (EtOH), acetonitrile (ACN), chloroform ($CHCl_3$), methanol (MeOH), sulfuric acid (H_2SO_4), and triethylamine (TEA) (E Merck, spectroscopic grade) were used as supplied but only after checking the purity fluorimetrically in the wavelength range of interest. For aqueous solution, we used deionized Millipore water.

Absorption and Emission Spectra. The absorption spectra were taken with a Shimadzu UV−vis absorption spectrophotometer model UV-2401PC. The fluorescence and phosphorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer. For emission measurements, the sample concentration was maintained at $\sim 10^{-5}$ M in each case in order to avoid aggregation. The quantum yields were determined by using a secondary standard method with recrystallized *β*-naphthol in MCH ($\phi_f = 0.23$).

Picosecond Measurement. For lifetime measurement, the sample was excited with Rhodamine 6G dye laser (coherent 702-1) pumped by a cw mode-locked Nd:YAG laser (coherent Antares 765). The emission was detected by a Hamamatsu MCD photomultiplier (2809U). The fluorescence decays were deconvoluted using global lifetime analysis software (PTI).

Results and Discussion

Quantum Chemical Calculation. To have some idea about the excited state properties as well as the proton transfer feasibility and mechanism of HNL in excited and ground states, we have calculated the energies of different electronic states, heats of formation (enthalpy), and the dipole moment of HNL using the MOPAC version 5 package with the AM1 Hamiltonian in different states of HNL. Chart 1 depicts the calculated equilibrium geometry of HNL in the ground state as well as in the excited state. In the ground state, the O−H bond length is ∼0.972522 Å but in the optimized excited state the O−H bond length increases to ∼0.980430 Å and the C−O−H angle increases from ∼111 to 111.5°. This structural change of HNL in its excited state indicates the possibility of proton transfer in its excited state. The increase of the dipole moment from ground state to excited state indicates possible redistribution of charge of HNL in its excited state, and this is only possible by intramolecular charge transfer from the acid moiety to the basic moiety of HNL. The dependence of the ground state singlet energy (S_0) on the O−H bond length has a prominent effect. The S_0 energy increases (Figure 1) with the increase of the O−H bond length. So, the ground state proton transfer is no longer possible. The variation of the other two singlet states (S_1 and S_2) has been calculated from CI (6 × 6) calculation and is shown in Figure 1. The first excited singlet state (S_1) shows a minimum value for a particular O−H bond length whereas the second excited singlet state S_2 does not show such a variation. The variation of dipole moment as well as the heat of formation with O−H bond length, where the other parameters remain unaltered, has been calculated and plotted in Figure 2. The increase of the heat of formation with the O−H bond length indicates that some external energy is required for the ESIPT

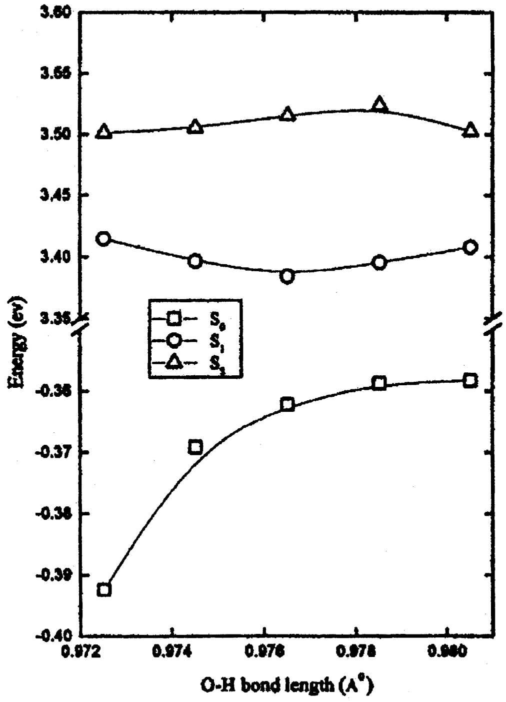


Figure 1. Variation of S_0, S_1, and S_2 energy with O−H bond distance of HNL.

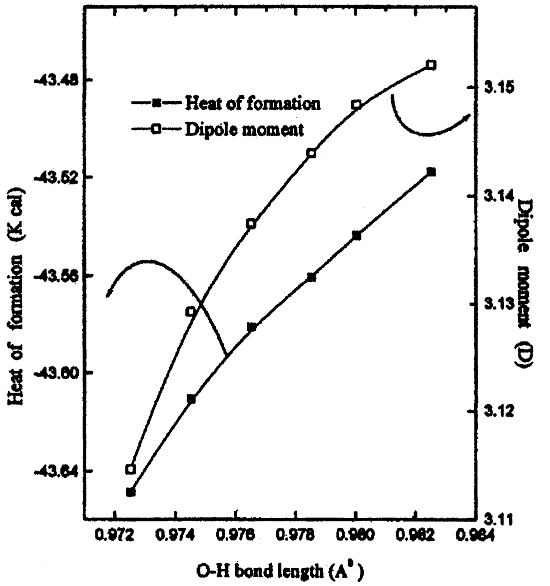


Figure 2. Variation of heat of formation and dipole moment as a function of O−H bond distance keeping the ground state geometry fixed for HNL.

TABLE 1: Absorption and Emission Data of HNL

	absorption data		fluorescence data		
			fluorescence peak		
solvent	abs maxima (nm)	ϵ_{max} at lower energy band (dm^3 mol^{-1} s^{-1})	λ_f^1 (nm)	λ_f^2 (nm)	quantum yield ϕ
MCH	359, 384	8142, 2094		424	0.0078
MCH + TEA	358, 384	7990, 2075		420	0.0092
MCH + H_2SO_4	359, 384	6888, 2080	344		0.0087
n-heptane	359, 384	9629, 2383		425	0.0068
benzene	358, 383.6	8095, 2353		428	0.0071
$CHCl_3$	361	9332	335	434	0.0061
ACN	358	8636	335	433	0.0149
EtoH	359, 407	9029, 1014	350	447	0.0285
EtOH + TEA	396.6	20 800	350	455	0.031
EtOH + H_2SO_4	361.4	10 653	345		0.026
MeOH	359, 407	8477, 661	345	448	0.028
water	358, 410	7415, 276	349	450	0.022
water + TEA	395	11 076	353	445	0.034
water + acid	359	7412	343	444	0.01
water + β-CD	364, 414	7562, 781	341	442	0.031

from the O−H group of the HNL, which is only possible by exciting the molecule. After examination of the computed charge distribution using the Mulliken scheme, it is evinced that there is an increase of charge distribution on the oxygen atom of the C═O group (basic moiety) and a simultaneous decrease in charge on the oxygen atom of the O−H group (acid moiety) in going from the ground to excited state, which indicates a possible proton translocation in the excited state. So, from the quantum chemical calculation, we get a clear idea about the intramolecular relaxation of HNL in its excited state. It is probable that excitation of HNL will achieve a delocalized excited state and then relaxes to the proton transfer configuration by transferring the proton from the acid moiety to the basic moiety. With this piece of information, we move on to the steady state absorption and emission and also time-resolved emission spectroscopy to get the mechanistic details of proton transfer, if any, in the excited state.

Absorption. Absorption spectra of HNL were investigated in different organic polar, nonpolar, and aqueous solutions and in restricted geometries (β-CD) at 298 K. In a dilute solution of HNL (~10^{-5} mol dm^{-3}), the absorption spectrum exhibits a band in the region of 357−361 nm and another at ~318 nm, depending upon the polarity of solvents.

In polar protic and hydroxylic solvents, HNL shows three bands: one at ~318 nm and the other at ~359 nm are strong in nature, and another relatively weak band is observed at ~407 nm region (Figure 3). In all nonpolar and polar hydrocarbon solvents, HNL exhibits two bands: one at ~318 nm and another at the 357−361 nm region (Figure 3). A relatively high molar extinction coefficient ($\epsilon_{max} \sim 8000$) of the first absorption maximum (~358 nm) of HNL in all solvents indicates a character of $S_0 \rightarrow \pi\pi^*$ transition for the first absorption band[33,34] (Table 1).

Comparing absorption spectrum of HNL with that of parent molecule β-naphthol (band at 318 nm, Figure 3), we observe very little similarity between the two. It is interesting to note that in any nonpolar hydrocarbon solvent the HNL spectrum shows one shoulder at ~384 nm. On the other hand, in polar or hydroxyl solvent, this shoulder vanishes producing a more structureless broad band. So, the spectral change and presence of lower energy shoulders in hydrocarbon solvents are due to aldehyde substitutions as well as intramolecular hydrogen bonding between acidic and basic groups of molecule (HNL), which was reported earlier.[34−37] Also, it is important to note here that a red-shifted shoulder in the hydrocarbon solvent and structureless tail possibly account for ground state closed conformeric form I (Scheme 1).[32] The disappearance of the lower energy shoulder in polar or hydroxylic solvent is due to an increase in the solute−solvent interaction causing mainly a loss of structure. It is pertinent to mention here that in ACN solution, HNL shows a lower energy absorption band in the 357−361 nm region and addition of a little amount of alcohol (like EtOH or MeOH) in this solution produces a weak band at ~407 nm region (Figure 4). So, the band at ~407 nm region may be assigned due to ground state intermolecular hydrogen bonding between solute and solvent interaction (Scheme 1).

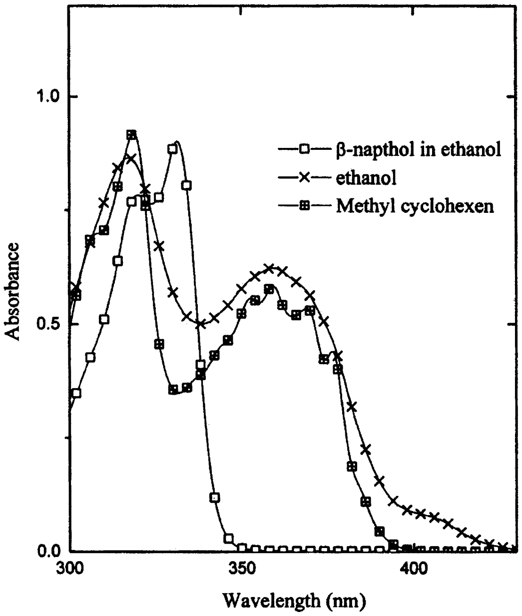
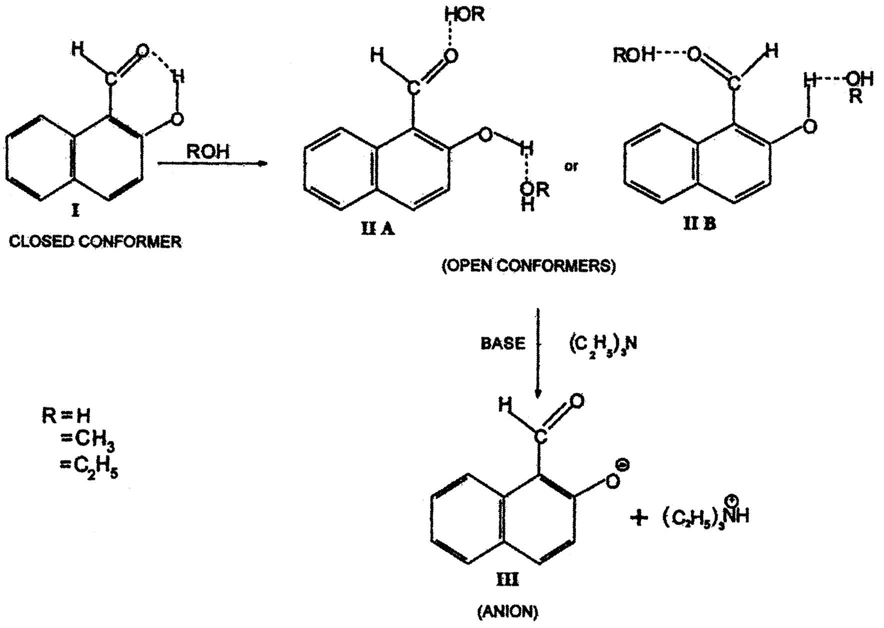


Figure 3. Electronic absorption spectra of HNL in different solvents and electronic absorption spectra of β-naphthol in EtOH; HNL = 5×10^{-5} mol dm^{-3}.

Effect of Acid and Base. Absorption spectra of HNL in water in the presence of TEA are shown in Figure 5. With the increase of pH of the solution by addition of TEA, the intensity of ~407 nm band exhibits a progressive increase as well as a blue shift up to ~395 nm at the expense of the 359 nm band.[38] Hence, this band is due to the transfer of proton to solvent and formation of the anion of HNL[39−41] (Scheme 1). It is pertinent to mention here that for anion formation, a promoter base is necessary. The

SCHEME 1: Ground State Reaction Scheme for HNL in Hydroxylic Solvent



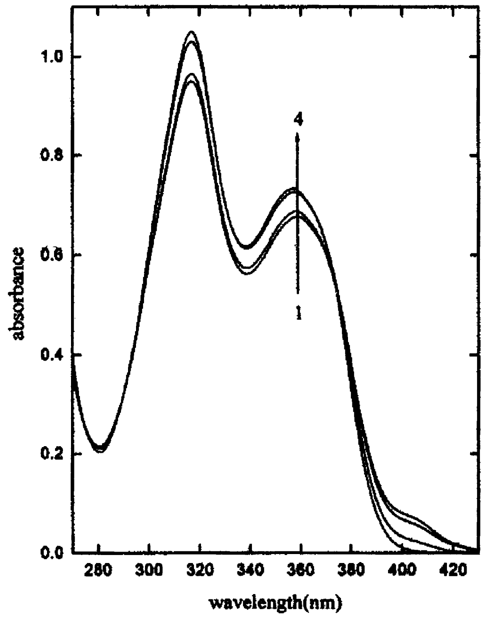


Figure 4. Electronic absorption spectra of HNL in pure ACN and in the presence of EtOH. Range of EtOH (1−4) = 0−7.5 × 10^{-5} mol dm^{-3}.

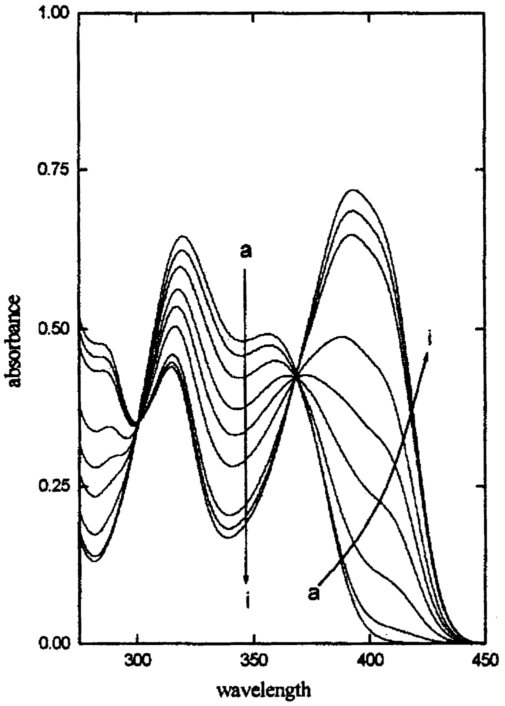


Figure 5. Electronic absorption spectra of HNL in water and in the presence of acid (H_2SO_4) and base (TEA) as a function of pH; (a) with addition of acid pH 2.6; (b−i) with addition of base pH 6, 6.4, 7, 8.3, 9, 10.7, 11.6, and 12.7.

presence of an isosbestic point in the ground state indicates equilibrium between the closed conformer and the anion of HNL.[42]

It is observed that the weak red absorption band of HNL (~407 nm) disappeared by the gradual addition of dilute H_2SO_4 (pH 2.6) (Figure 5). The progressive quenching (Figure 5) and disappearance of the red absorption band ($n\pi^*$ band) are due to the rupture of intermolecular hydrogen bonding between solute and solvent. The hydroxyl group proton of the compound is certainly responsible for this mechanism.[43]

*Effect of **β**-CD.* The absorption spectra of HNL in constrained β-CD cavity were studied. As β-CD concentration is increased, the absorption maximum is red-shifted accompanied by two distinct isosbestic points at 364 and 330 nm (Figure 6). This observation confirms that in aqueous solution of β-CD a caged species of HNL with 1:1 stoichiometry is formed.[35] A slight increase in absorbance is presumably due to the detergent effect of β-CD and is attributed to the additional dissolution of HNL absorbed on the surface of the walls of the container.[44,45]

Emission. HNL exhibits one large Stokes-shifted fluorescence band in all hydrocarbon solvents and distinct dual fluorescence bands in almost all polar and hydroxylic solvents having a bathochromic shift of fluorescence maximum with increasing solvent polarity (Figure 7a) at room temperature. HNL shows a single large Stokes-shifted band at ~424 nm in MCH. The band position and shape are found to be independent of excitation wavelength (λ_{exe}) in almost all solvents and independent of concentration in the range of 10^{-4}−10^{-5} mol dm^{-3}. The fluorescence excitation spectrum in MCH monitoring at

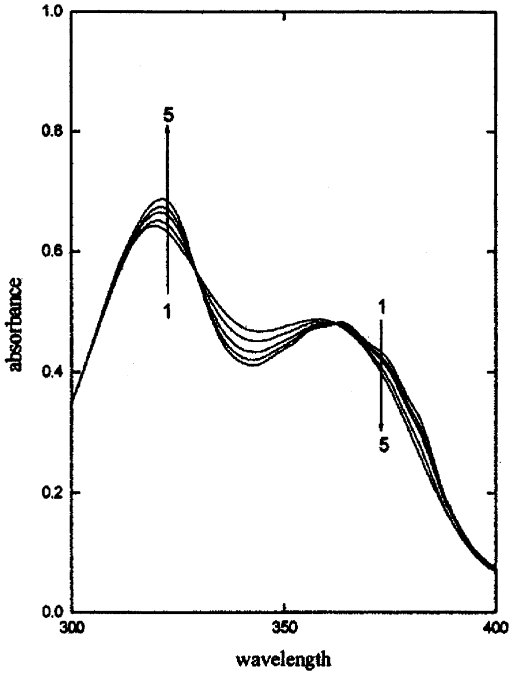


Figure 6. Electronic absorption spectra of HNL with different concentrations of β-CD in aqueous solution: (1) without β-CD (pure water), (2) 9.1 mM, (3) 6.06 mM, (4) 2.6 mM, and (5) 1.3mM β-CD.

424 nm exhibits a single band at ~380 nm, which agrees reasonably well with the absorption spectra showing that the Stokes-shifted fluorescence originates from the main absorbing species in the ground state (Figure 7a). The main species existing in nonpolar solvents is considered to be the intramolecularly hydrogen-bonded species (closed conformer). In analogy with the fluorescence of MS[3] and OHBA,[13] the large Stokes-shifted lower energy band (5800 cm^{-1}) may be considered to originate from the excited state proton transfer (ESIPT)[16] form of HNL but the characters of this species will be discussed later.

The fluorescence spectrum of HNL in EtOH shows two distinct fluorescence bands, one higher energy band at ~345 nm and a large Stokes-shifted intense lower energy band at ~448 nm. The fluorescence lifetime in EtOH was measured to be 84 ps monitoring at 450 nm (Figure 7b). The lifetime in other solvents is below the measuring limit of the instrument. The excitation spectrum of HNL in EtOH is not similar to that obtained in MCH, and it is rather complicated. The fluorescence excitation spectrum in EtOH obtained by monitoring the emissions at 448 and 345 nm clearly reflects the absorption spectrum. This observation evidently indicates that there are two fluorescing species, one with the emission maximum at shorter wavelength and the other with the emission maxium at longer wavelength (Scheme 1). So in the ground state, there are two main absorbing species, one is the intramolecularly hydrogen-bonded closed conformer (I) and another is the intermolecularly hydrogen-bonded open conformer (II)(Scheme 1). The natures of these species will be discussed in a later section. A similar result was obtained in MeOH. In polar solvents, HNL shows an increase in emission intensity of a lower energy band with a slight red shift. Hydroxy derivatives of aromatic compounds are generally acidic in the excited singlet state relative to the ground state[46] so there is a tendency for intermolecular proton transfer to solvent. Because in water the proton activity is high, an intermolecular translocation of proton is observed. This is reflected in the increase of rate of excited state proton transfer in polar solvents. Comparing fluorescence spectrum of HNL with β-naphthol, we conclude that the higher energy band of HNL is due to normal fluorescence of β-naphthol. This spectrum is fitted to the higher energy band in polar solvent with a small solvent shift.

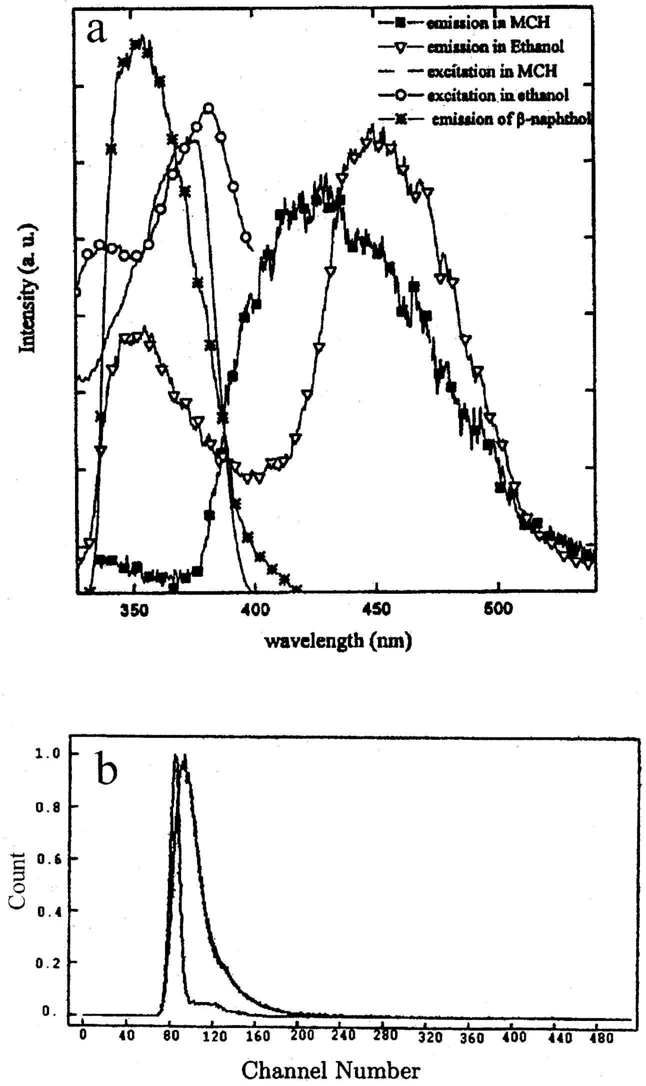
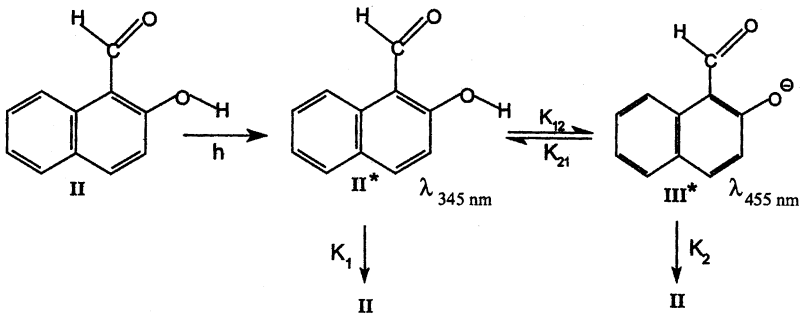


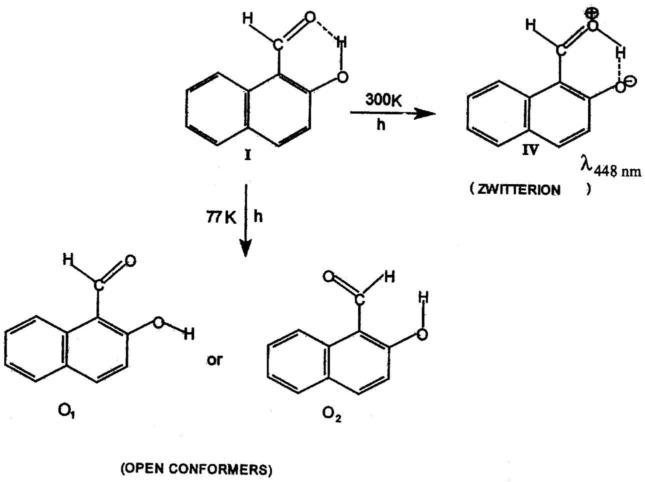
Figure 7. (a) Fluorescence emission spectra and fluorescence excitation spectra of HNL in different solvents; fluorescence emission spectra of β-naphthol in EtOH at room temperature. (b) Typical decay profile of HNL (emission wavelength monitored at 450 nm) in EtOH. The gray solid curve represents the best computer fit of the experimental points to a single exponential decay; excitation wavelength is 310 nm; the lamp profile is denoted by the dark solid line.

Effect of Acid and Base. The spectral behavior of HNL in EtOH by varying pH value with addition of electron donor as base (TEA) is depicted in Figure 8a. In aqueous EtOH with addition of TEA, a high intensity emission peak is observed at ~455 nm with a decrease in intensity of the higher energy emission peak. The electron-donating alkyl group is present in polar solvents (MeOH, EtOH) and is able to release an electron toward the oxygen atom of the hydroxyl group (due to +I effect); that is, when the dipole moment of the probe molecule is larger in more polar environments, they act as strong proton acceptors, particularly in the excited state. This indicates that HNL has been deprotonated to its anion in various polar solvents (Scheme 2). The intensity of the lower energy band seems to increase with a small red shift with addition of base. Excitation spectra corresponding to 455 nm emission show bands at 350 nm and at 400 nm in base medium, which agree well with the respective absorption bands of the closed conformer and the

SCHEME 2: Photochemical Scheme for HNL



SCHEME 3: Excited State Reaction Scheme of HNL at Room Temperature and at 77 K



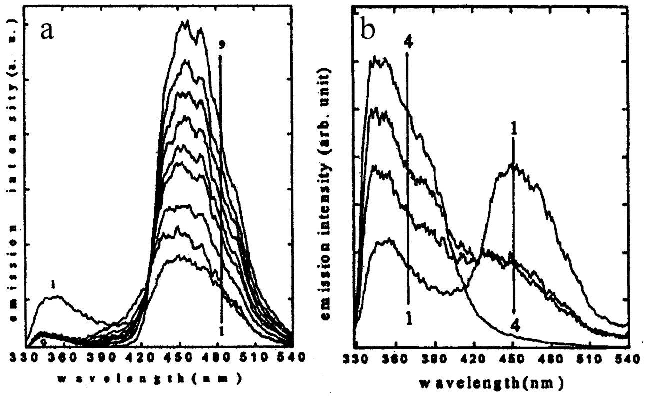


Figure 8. (a) Fluorescence emission spectra of HNL in EtOH with the presence of base (TEA) as a function of pH; (1) without base (EtOH); (2−9) with increasing pH as addition of base. (b) Fluorescence emission spectra of HNL in EtOH with the presence of acid (H_2SO_4); (1) without acid (EtOH); (2−4) with increasing acid concentration.

anion (vide supra). The effect of acid on HNL in nonpolar and polar protic solvents shows some interesting results. As the acid concentration is increased in EtOH solution, the intensity of the higher energy band increases relative to that of the lower energy band. the intensity of the higher energy band is weak at neutral solution. A further increase in acid concentration shows total disappearance of the lower energy band with an intense higher energy band at ∼345 nm (Figure 8b). In nonpolar solvent also, the lower energy emission band (∼424 nm) completely disappears with the addition of acid (H_2SO_4). These results indicate the existence of more than one ground state conformer of neutral HNL, and these conformers have different absorption spectra.

Our results can most plausibly be explained by postulating the existence of three distinct excited state species. The first of these is neutral HNL (II of Scheme 2), which is responsible for the emission band at ∼345 nm; emitting further to the red is the zwitterion (IV of Scheme 3), formed by intramolecular proton transfer; and the phenolate anion (III of Scheme 2), resulting from excited state proton transfer to the solvent. A panoply of evidence[47−49] favors the assignments that the excited phenolate anion is responsible for an emission band with a maximum at ∼455 nm, while the zwitterion fluorescence maximum is at ∼448 nm. Both the zwitterion and the phenolate anion are capable of considerable resonance stabilization by delocalization of their formal charges. It is therefore expected that their fluorescence will exhibit unusually large Stokes shifts. The neutral molecule on the other hand can undergo no stabilization, and its fluorescence should exhibit a more normal Stokes shift. Such effects are commonly observed in molecules such as 2-naphthol,[47] methyl salicylate,[48] and salicylamide,[49] etc., which undergo excited state proton transfer reactions. So, the change in large Stokes-shifted fluorescence intensity could be attributed to fluorescence of the zwitterionic form due to excited state proton transfer[50] (Scheme 3) and formation of anion due to intermolecular reaction with solvent (Scheme 2). By adding base, the intermolecular hydrogen bond is ruptured due to creation of anion and this decreases the normal fluorescence intensity.[51]

Comparing the emission spectrum of β-naphthol with that of HNL, the peak at ∼455 nm of HNL may be assigned due to the fluorescence from the phenolate anion and the 345 nm peak may be assigned due to the fluorescence from neutral HNL, and these two peaks arise from II* and III* according to Scheme 2. The higher energy emission band of HNL may well be assigned as the fluorescence of pure neutral form II*. Analysis of the variation in peak intensity for both of the species as a function of pH indicates that the change occurs solely as a consequence of the change in the ground state absorption. We could not observe any spectral change in nonpolar solvents with addition of base. This confirms that the intramolecular hydrogen bond is much stronger in HNL in the excited state, and an open conformer of HNL cannot be formed even in the presence of base in these solvents.

A fluorescence emission spectrum of HNL as a function of aqueous β-CD concentration was recorded. For maximum concentration of β-CD in aqueous solution, the intensity of the lower energy band of HNL increases with a slight blue shift of fluorescence maxima. On decreasing concentration of β-CD, fluorescence spectra are shifted toward red and finally they overlap the spectra of HNL in aqueous solution. This blue shift of fluorescence spectra is produced due to the lower polarity of the β-CD cavity.[44] When a probe molecule enters into the cavity, it gets a less polar environment, which shows lower stabilization of the zwitterionic form in the fluorescence spectrum.

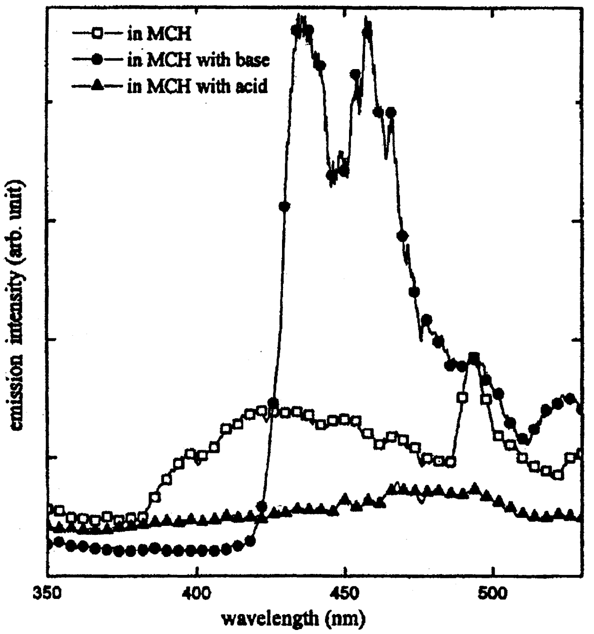


Figure 9. Emission spectra of HNL in MCH glass in the presence of TEA and H_2SO_4 at 77 K.

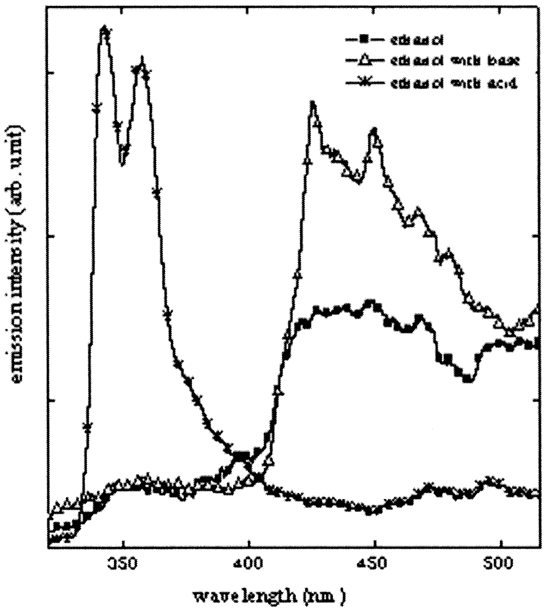


Figure 10. Emission spectra of HNL in EtOH glass in the presence of TEA and H_2SO_4 at 77 K.

Emission and Excitation Spectra at 77 K. The emission spectrum of HNL in hydrocarbon solvent (Figure 9) consists of a superposed Stokes-shifted fluorescence and phosphorescence spectrum, as was observed in the case of OHBA.[13] HNL shows a Stokes-shifted fluorescence in ~420 nm region in MCH at 77 K. Contrary to the room temperature fluorescence, an increase in λ_{exe} results in an increase in the low-temperature emission intensity, keeping the peak position unchanged. The Stokes-shifted fluorescence is considered to arise from the species, which is responsible for room temperature fluorescence[13] in nonpolar solvents. In the presence of a strong base like TEA, an intense red-shifted fluorescence with two peaks is observed. Because the peaks are so close to each other, these could be due to some vibronic effect. On addition of acid (H_2SO_4) to the solution, the fluorescence peak disappears. The phosphorescence peak is observed at ~500 nm. In the case of a polar solvent like EtOH at 77 K, two fluorescence peaks are observed similar to the room temperature fluorescence. Like a nonpolar solvent, the spectrum of HNL in a polar solvent consists of phosphorescence (Figure 10). The intensity of fluorescence is decreased, and the intensity of phosphorescence is increased in EtOH more than in MCH. It is observed that as the temperature is raised the phosphorescence intensity gradually decreases, which is due to phosphorescence quenching, and only fluorescence is observed at room temperature. The presence of phosphorescence in the fluorescence spectrum seems to be due to the presence of an intersystem crossing (ISC) in the proton transfer process of HNL. So, the HNL spectrum is characteristic of a $^3\pi\pi^*$ aromatic carbonyl of the benzaldehyde type. This type of spectrum is usually found for benzaldehydes, which are intermolecularly hydrogen-bonded.[52,53] As was suggested by Nagaoka et al.,[13,16,54] the phosphorescence is likely to be due to the open conformer II (Scheme 1). Both the conformers IIa and IIb (Scheme 1) could give rise to the phosphorescence in these solvents. The phosphorescence lifetime was determined to be 25 ms in MCH and 72 ms in EtOH.

Excitation spectra for HNL in both solvents for phosphorescence are similar to those of room temperature absorption spectra, indicating that the main species existing in polar and nonpolar solvents are intermolecularly hydrogen-bonded open conformers. The phosphorescence spectra of HNL in MCH could be characterized by a progression of C=O stretching modes, which is characteristic of a $^3n\pi^*$ aromatic carbonyl of a benzaldehyde type of molecule. The short lifetime in MCH than EtOH confirms this assignment. A benzaldehyde type of molecule without intramolecular hydrogen bonding (i.e., open conformers, Scheme 3) is likely to be produced under irradiation.[52,53] Experimental evidence explains this phenomenon of HNL by suggesting that the phosphorescence should be obtained from the open conformer that is formed due to the rotation of carbonyl group. So, there are two suggested structural forms of open conformers of OHBA.[13] Going by similar arguments for HNL, it may be put forward that phosphorescence arises from open conformers, which are due to the rotation of the carbonyl group (O_1 and O_2, Scheme 3). In nonpolar solvents, phosphorescence is weak but in the presence of TEA intense phosphorescence is observed. This indicates that the intramolecular hydrogen bond of HNL is stronger in a nonpolar solvent and the rupture of the intramolecular hydrogen bond is necessary for phosphorescence. The promoter base plays a definite role for breaking of the intramolecular bond of HNL. As the strength of the hydrogen bond depends on the substitution of the >C=O group, the interaction with the base hydrogen bond is broken, the carbonyl group rotates easily to form an open conformer, and phosphorescence is observed even in nonpolar solvents. In polar solvents, phosphorescence intensities do not increase because the open conformers exist before irradiation.

In EtOH, glass matrix molecules take ionic forms. EtOH is a hydrogen-bonding solvent, and it breaks the intramolecular hydrogen bond of the closed conformer to form an open conformer and anion. The strength of the intermolecular hydrogen-bonding capacity increases from EtOH to EtOH glass. Because of this capability in HNL, with EtOH glass, the intermolecular hydrogen bonding increases at a lower temperature than room temperature resulting in fluorescence and phosphorescence at 77 K.

Conclusion

The quantum chemical calculations on HNL reveal that the charge density distribution and stretching of the O−H bond in the excited state points that HNL is a good candidate for intramolecular transfer of the proton in the excited state. The absorption spectra of HNL in different solvents point to the presence of an intramolecularly hydrogen-bonded closed conformer in the form of 384 nm band in a nonpolar hydrocarbon solvent, whereas a 407 nm band arises in protic and hydroxylic solvent due to intermolecular hydrogen bonding between solute and solvent. The addition of base causes a considerable increase in intensity of the 407 nm band marked by the formation of the HNL ion. The addition of acid quenches this band due to the rupture of the intermolecular hydrogen bond. In β-CD, a 1:1 inclusion complex is formed as evinced by two isosbestic points.

A large Stokes-shifted fluorescence at 424 nm in hydrocarbon solvent has been identified to be due to a possible excited state proton transfer, and an excitation spectrum confirms the appearance of this band due to excitation of the ground state closed conformer. In hydroxylic solvents, the two bands at ∼345 and ∼448 nm of HNL were analyzed and found to be due to an intermolecularly hydrogen-bonded open conformer and intramolecularly hydrogen-bonded closed conformer, respectively. In basic alcoholic medium, the lower energy band intensifies with a red shift (band at ∼455 nm) with a decrease in the 345 nm band. The excitation spectrum of the 455 nm band corresponds to bands due to a closed conformer and the anion. In acidic medium, the higher energy band gets pronounced with simultaneous disappearance of the lower energy band. The foregoing results evince a possible existence of the excited state species: one due to neutral HNL (∼345 nm), the second due to a zwitterionic intramolecular proton transfer (closed conformer ∼448 nm), and the third due to the formation of phenolate anion (open conformer) in intermolecular proton transfer (∼455 nm). The effect of β-CD shows less stabilization of the zwitterionic form.

In MCH rigid glass, HNL shows Stokes-shifted fluorescence and phosphorescence in one envelope at 77 K. The acid quenches the fluorescence to show phosphorescence at ∼500 nm. The phosphorescence in MCH glass has been assigned to arise from the open conformer formed due to rotation of the carbonyl group as evinced from the addition of promoter base. The phosphorescence intensity is increased in EtOH due to an increase in intermolecular hydrogen bonding. In ethanolic glass also, fluorescence and phosphorescence arise from a room temperature intermolecular hydrogen-bonded open conformer.

Acknowledgment. We thank Prof. K. Bhattacharya, Department of Physical Chemistry, I.A.C.S., Kolkata, for kindly allowing us to use the picosecond lifetime measurement instrument.

References and Notes

(1) Förster, T. *Naturwissenschaften* **1949**, *36*, 186.
(2) Weller, A. *Naturwissenschaften* **1955**, *42*, 175.
(3) Weller, A. *Z. Electrochem*. **1956**, *60*, 1144.
(4) Van Benthem, M. H.; Gillispie, G. D. *J. Phys. Chem.* **1984**, *88*, 2954.
(5) Ghiggino, K. P.; Scully, A. D.; Leaver, H. I. *J. Phys. Chem.* **1986**, *90*, 5089.
(6) Kosower, E. M.; Huppert, D. *Annu. Rev. Phys. Chem.* **1986**, *37*, 127.
(7) Law, K.-Y.; Shoham, J. *J. Phys. Chem.* **1995**, *99*, 12103.
(8) Goodman, J.; Brus, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 7472.
(9) Herek, J. L.; Pedersen, S.; Banares, L.; Zewail, A. H. *J. Chem. Phys.* **1992**, *97*, 9046.
(10) Acuña, A. U.; Toribio, F.; Amat-Guerri, F.; Catalan, J. *J. Photochem.* **1985**, *30*, 339.
(11) Nishiya, T.; Yamauchi, S.; Hirota, N.; Baba, M.; Hanazaki, I. *J. Phys. Chem.* **1986**, *90*, 5730.
(12) Peteanu, L. A.; Mathies, R. A. *J. Phys. Chem.* **1992**, *96*, 6910.
(13) Nagaoka, S.; Hirota, N.; Sumitani, M.; Yoshihara, K. *J. Am. Chem. Soc.* **1983**, *105*, 4220.
(14) Morgan, M. A.; Orton, E.; Pimentel, G. C. *J. Phys. Chem.* **1990**, *94*, 7927.
(15) Nagaoka, S.; Nagashima, U.; Ohta, N.; Fujita, M.; Takemura, T. *J. Phys. Chem.* **1988**, *92*, 166.
(16) Nagaoka, S.; Hirota, N.; Sumitani, M.; Yoshihara, K.; Lipczynska-Kochany, E.; Iwamura, H. *J. Am. Chem. Soc.* **1984**, *106*, 6913.
(17) Catalan, J.; Tribio, F.; Acuña, A. U. *J. Phys. Chem.* **1982**, *86*, 303.
(18) Kasha, M. *J. Chem. Soc., Faraday Trans. II* **1986**, *82*, 2379.
(19) Mosquera, M.; Penedo, J. C.; Rodriguez, M. C. R.; Rodriguez-Prieto, F. *J. Phys. Chem.* **1996**, *100*, 5398.
(20) Chudoba, C.; Riedle, E.; Pfeiffer, M.; Elsaesser, T. *Chem. Phys. Lett.* **1996**, *263*, 622.
(21) Cho, D. W.; Kim, Y. H.; Yoon, M.; Jeoung, S. C.; Kim, D. *Chem. Phys. Lett.* **1994**, *226*, 275.
(22) Chou, P. T.; McMorrow, D.; Aartsma, T. J.; Kasha, M. *J. Phys. Chem.* **1984**, *88*, 4596.
(23) Kasha, M. *In Molecular Electronic Devices*; Carter, F. L., Siatkowski, R. E., Wohljen, H., Eds.; Elsevier Science Publishers: New York, 1988; p 107.
(24) Kuldová, K.; Corval, A.; Trommsdorff, H. P.; Lehn, J. M. *J. Phys. Chem. A* **1997**, *101*, 6850.
(25) Martinez, M. L.; Cooper, W. C.; Chou, P. T. *Chem. Phys. Lett.* **1992**, *193*, 151.
(26) Heller, H. J.; Blattmann, H. R. *Pure Appl. Chem.* **1973**, *36*, 141.
(27) Werner, T.; Woessner, G.; Kramer, H. E. A. *In Photodegradation and Photostabolization of Coating*; Pappas, S. P., Winslow, F. H., Eds.; American Chemical Society: Washington, DC, 1981; Vol. 151, p 1.
(28) Tarkka, R. M.; Zhang, X.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1996**, *118*, 9438.
(29) Sytnik, A.; Del Valle, J. C. *J. Phys. Chem.* **1995**, *99*, 13028.
(30) Sytnik, A.; Gormin, D.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91*, 11968.
(31) Sytnik, A.; Litvinyuk, I. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 12959.
(32) Salman, S, R. *Spectrochim. Acta* **1986**, *42A*, 409.
(33) Seliskar, C, J. *J. Mol. Spectrosc.* **1974**, *53*, 140.
(34) Bergmann, E. D.; Hirshberg, Y.; Pinchass, S. *J. Chem. Soc.* **1950**, 2351.
(35) Bangal, P, R.; Chakravorti, S. *J. Phys. Chem. A* **1999**, *103*, 8585.
(36) Woolfe, G. J.; Thistlethwaite, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 3849.
(37) Oki, M.; Hirota, M.; Hirofuji, S. *Spectrochim. Acta* **1966**, *22*, 1537.
(38) Melchior, N. C. *Spectrochim. Acta* **1949**, *71*, 3647.
(39) Elsaesser, T.; Schmetzer, B. *Chem. Phys. Lett.* **1987**, *140*, 293.
(40) Potter, C, A, S.; Brown, R, G. *Chem. Phys. Lett.* **1988**, *153*, 7.
(41) Guha, P.; Mandal, A.; Mukherjee, S. *J. Lumin.* **1999**, *185*, 79.
(42) Durmis, J.; Karvas, M.; Manaseck, Z. *Collect. Czech. Chem. Commun.* **1978**, *38*, 215.
(43) Weller, A. *Z. Electrochem.* **1965**, *60*, 113.
(44) Bortulos, P.; Monti, S. *J. Phys. Chem.* **1987**, *91*, 5046.
(45) Yorozu, T.; Hoshino, M.; Imamura, M. *J. Phys. Chem.* **1982**, *86*, 4426.
(46) Cramer, L. E.; Spears, K. G. *J. Am. Chem. Soc.* **1978**, *100*, 221.
(47) Stryr, L. *J. Am. Chem. Soc.* **1966**, *88*, 5708.
(48) Beens, H.; Grellman, K. H.; Gurr, H.; Weller, A. H. *Discuss. Faraday. Soc.* **1965**, *39*, 183.
(49) Woolfe, G. J.; Thistlethwaite, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 6917.
(50) Smith, K, K.; Kaufmann, K, J. *J. Phys. Chem.* **1981**, *85*, 2895.
(51) Weller, A. *Program React. Kinet.* **1961**, *1*, 188.
(52) Duben, A, J.; Goodman, L.; Koyanagi, M. *Excited State*; Lim, E. C., Ed.; Academic Press: New York, 1974; p 295.
(53) Lim, E. C. *Excited State*; Lim, E. C., Ed.; Academic Press: New York, 1977; p 305.
(54) Hoshimoto, E.; Yamauchi, S.; Hirota, N.; Nagaoka, J. *J. Phys. Chem.* **1991**, *95*, 10229.