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REVIEW ARTICLE

Hydrogen Bonding Effects on Vibrational Dynamics and Photochemistry in Selected Binary Molecular Complexes

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Abstract | This brief review presents an overview and analysis of the experimental studies performed recently in the laboratory of the authors demonstrating the role of hydrogen bonding as a promotional factor for intermolecular vibrational energy relaxation, and as a driving force for the occurrences of specific reaction channels in binary molecular complexes. Both vibrational and electronic spectroscopic methods have been used, and measurements have been performed in the supersonic jet expansion, in cold inert gas matrixes and also in suitable liquids at room temperature. Pure and mixed dimers of two types of aromatic chromophores, 7-azaindole and phenol, have been used as the model molecular systems, which involve O–H···O, O–H···N and N–H···N types of hydrogen bonds. The promotional effect of vibrational relaxation has been demonstrated showing large broadening of either of the infrared X–H stretching fundamentals of the donor groups in the hydrogen-bonded X–H···Y network of the binary complexes or broadening of the fluorescence spectra upon excitations to single vibronic levels of the isolated complexes in the gas phase and making comparisons with the corresponding spectra of the monomers. A similar approach has been adopted to demonstrate the promotion of photodissociation and charge transfer reactions in binary complexes by hydrogen bonding.

Keywords: *Vibrational relaxation, Photodissociation, Charge transfer reactions, Laser-induced fluorescence, Matrix isolation infrared spectroscopy*

1 Introduction

Hydrogen bonding, ever since its discovery as a weak non-covalent attractive interaction, has been recognized to be a crucial binding force to determine the structures, physical and chemical properties of numerous substances, and it acts as a guiding influence in determining the course of many biochemical reactions that involve proton, electron and coupled electron–proton transfers[1–3]. Much efforts have also been devoted therefore in recent years in suggesting a satisfactory definition of hydrogen bonding that fulfils all of its attributes and origin[4–7]. In the present review, we have aimed to give an overview with convincing experimental evidences that hydrogen bonding accelerates intermolecular energy dissipation by promoting intermode vibrational coupling, and it also initiates and favours specific reaction channels. Although many studies have been devoted in the recent past to decipher these attributes of hydrogen bonding, here, within the limited space, only selected findings from studies carried out in our laboratory are presented.

Energy redistribution of an excited molecule by means of intermode vibrational coupling is central to chemical reaction and molecular dynamics, and much attention has been devoted to understand and control this dynamical

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phenomenon with both theoretical and experimental studies[8–12]. Historically the subject was developed in attempts to understand the features of thermal unimolecular reactions[13, 14]. Therefore, experimental investigation of vibrational energy redistribution has remained as a key topic for research in the area of chemical dynamics.

In the present study, the main issue is to show that in a hydrogen-bonded dimeric molecular complex, the dissipation of vibrational energy is accelerated upon vibrational and electronic excitations, and the linkage can also act as a conduit for the coupled electron proton transfer reaction and also in bond breaking HX elimination reaction. The frequencies for hydrogen bond vibrational modes in a molecular adduct are usually very low, and as a result, the vibrational mode densities are rapidly increased with an increase in excitation energy. But we show here that such vibrations not only create passive bath, but the vibrational modes are coupled efficiently with the intramolecular modes of the donor–acceptor moieties to accelerate the energy dissipation. In the past few decades, many studies both in time and frequency domain have been devoted to address this issue, and the measurements have been carried out under different physical conditions like in bulk liquids, in the gas phase with the size-selected molecular clusters and also in the cryogenic environment of argon matrix[15–22].

A very common manifestation of hydrogen bond-induced vibrational dynamics is the very broad and red-shifted appearance of the infrared O–H stretching fundamental of liquid water in contrast to the sharp ro-vibrational transitions associated with all the vibrational fundamentals in the vapour phase at a low pressure[23]. Similar spectral broadening is also observed for liquid alcohols[24]. Similar spectral changes along with large red-shifting of vibrational stretching fundamentals have been observed also in O–H···O and N–H···O hydrogen-bonded dimeric complexes of carboxylic acids and cyclic amides[25–27]. Even under a supersonic jet expansion condition, the vibrational fundamental in the mid-infrared spectrum displays extremely complex features as a manifestation of enhanced vibrational dynamics. Fermi resonance interactions of the spectrally red-shifted O–H stretching fundamentals with the overtones and combinations of the fingerprint modes of the hydrogen-bonded moieties are considered to be responsible for the broad and complicated appearances of the spectra[28]. In addition, anharmonic coupling of very low-frequency intermolecular modes with the Fermi multiplets of $\nu_{O\text{–}H}$ also accelerates the vibrational dynamics and spectral broadening.

Fermi resonance: It originates because of accidental degeneracy of a vibrational fundamental with the combination or overtone of other modes of a polyatomic molecule upon satisfaction of symmetric criterion. In vibrational or vibrationally resolved electronic spectra, Fermi resonance is manifested as band splitting. In addition, there occurs substantial changes in the intensity of the transitions, the weaker band becomes more intense by means of intensity borrowing.

The review has been organized in the following way: first, we have shown that under a matrix isolation condition below 10 K, the spectral appearance of N–H stretching fundamental of 7-azaindole (7-AI) is drastically altered upon formation of N–H···N hydrogen-bonded cyclic dimer, and also the photo-isomerization process involving the hydrogen-bonded network of the dimer. Using *p*-fluorophenol-water (pFP–H_2O) binary complex, it has been shown that in the first excited state, the single O–H···O hydrogen bond very significantly accelerates the vibrational energy dissipation from an excited ring mode. Second, for the occurrence of excited state coupled electron–proton transfer reaction, the effect of a cyclic O–H···N type hydrogen-bonded network between 7-AI and phenol has been shown. Finally, for the promotion of light-induced HX elimination reaction, the effect of intermolecular hydrogen bonding has been discussed using fluorophenols as prototypical systems.

2 N–H···N Hydrogen Bonding: Cyclic Dimer of 7-Azaindole

The doubly hydrogen-bonded cyclic dimer of 7-AI, inset Fig. 1, has long been studied as a convenient prototype to understand the effect of UV radiations on the base pairs of double-stranded nucleic acids[29–31]. The dimer undergoes a tautomeric conversion via double proton exchange along the two intermolecular N–H···N hydrogen bonds upon UV excitation as shown in the inset of Fig. 2. A similar light-induced process in doubly hydrogen-bonded base pairs of nucleic acids can result to tautomeric conversions of the nucleobases, and which can cause mismatching in interstrand base pairing leading to errors in DNA replication. Therefore, to investigate how the characteristics of the N–H bond are altered due to formation of the cyclic networks, the infrared N–H stretching fundamentals of the monomer and dimer of 7-AI have been compared by isolating the species in an argon matrix, and the measured spectra are depicted in Fig. 1.

The top panel (trace *a*) shows the N–H stretching fundamental of 7-AI monomer, which appears as a sharp band at ~3500 cm^{-1}. In contrast, the same transition for the dimer (trace *b*) appears with an extremely complicated structure within the frequency range of 2800–3300 cm^{-1}, and the overall appearance of this feature does not change if the spectrum of the dimer is recorded in CCl_4 solution at room temperature

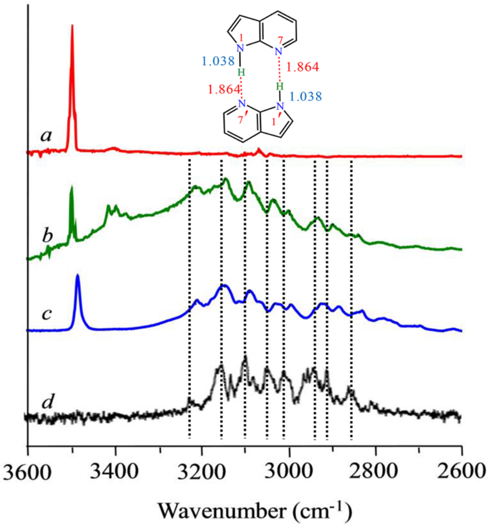

Figure 1: Infrared N–H stretching fundamentals of 7-azaindole monomer (trace a) and doubly hydrogen-bonded cyclic dimer (inset), both measured in an argon matrix (trace b), in CCl_4 solution (trace c) and in a supersonic jet expansion (trace d) as reported in Ref. [32].

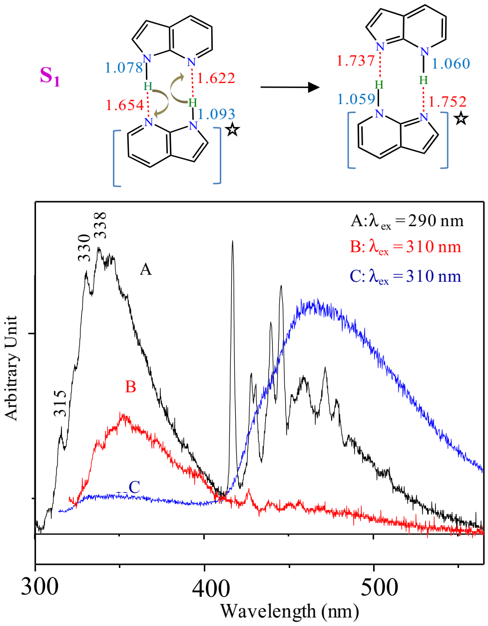

Figure 2: Fluorescence emission spectra of 7-azaindole monomer (trace-A) and dimer (trace-B) measured in an argon matrix. Trace-C depicts the emission spectrum of 7-azaindole dimer in CCl_4 solution measured by exciting the dimer at the same wavelength (310 nm) as that of matrix-isolated dimer. The tautomeric emission is absent in the matrix-isolated spectrum. The narrow bands within 400–500 nm of trace-A are due to phosphorescence emission of 7-azaindole monomer, which is quenched in the case of the dimer due to the hydrogen bond induced shift of the relative energies of the Franck–Condon active singlet (S_1) and nearby isoenergetic triplet states. The light-induced tautomeric conversion of the dimer is also shown.

(trace *c*) or under the cold environment of a supersonic jet expansion (trace *d*) that was measured by Yokoyama et al.[32] using IR–UV double resonance method. A notable attribute of the ν_{N-H} band of the dimer is that the sub-structures and the frequencies remain unchanged in all three media as depicted using dotted vertical lines. Electronic structure calculation predicts that the intensity of the N–H stretching fundamental is largely enhanced in the dimeric network[33]. Therefore, the complex feature of the dimer band has been attributed to extensive Fermi resonance interactions of the intensity enhanced ν_{N-H} transition with many of the overtones and combinations of the lower frequency fundamentals. More than a decade ago, in a time-resolved measurement in CCl_4 solution, Dwyer et al. showed that the lifetime of N–H stretching fundamental of 7-AI is dramatically reduced upon dimerization, from 10 ps for the monomer to 100 fs for dimer[34], and this temporal behaviour is consistent with complementary spectral attributes presented here to show that the vibrational dynamics of the excited N–H stretching band are accelerated upon dimerization. Measurement of fluorescence spectrum of the matrix-isolated dimer also reveals a vital issue that has been discussed again and again concerning the dimensionality of proton exchange at the hydrogen-bonded cyclic interface of the dimer and thereof similar structural motifs upon electronic excitation. In a fluidic medium, such excitation of the dimer results to complete conversion of 7-AI from its normal to tautomeric form, which emits green tautomeric fluorescence in contrast to UV fluorescence of the normal form. For proton exchange to occur, large-amplitude geometry reorganization at the cyclic interface is expected to be essential. However, direct experimental evidence to this respect is rare. A comparison of the fluorescence spectra of the dimer recorded in CCl_4 solution and in matrix isolated condition is presented in Fig. 2.

While in the CCl_4 medium, the dimer emits exclusively the green tautomer fluorescence and the same also occurs in a supersonic jet expansion, the process appears to be completely quenched in the argon (Ar) matrix as it emits only UV fluorescence from the locally excited state. Similar spectral features were observed for the nitrogen (N_2) matrix system[33]. The finding indicates that in the frozen inert gas matrix, tautomerization is inhibited as a result of restrictions of the translational as well as rotational degrees of freedoms of the embedded molecular species. Thus, for inter-moiety proton exchange to occur along the two hydrogen bonds of the centrosymmetric dimer, the large-amplitude vibrations that give rise to the reorganization of the dimer geometry at the interface are essential. Electronic structure calculations predict that the tautomeric form of the dimer, in the excited state, is ~ 7 kcal mol^{-1} more stable[33], and this excess vibrational energy has to be redistributed via excitations of the large-amplitude vibrations in order for tautomerization to occur, which is allowed in a fluidic medium but as said is inhibited in the rigid matrix. It has been demonstrated by Sekiya et al. that the proton exchange process is slowed down upon deuteration of the pyrrolic N–H, which indicates that the process occurs via tunnelling mechanism[35].

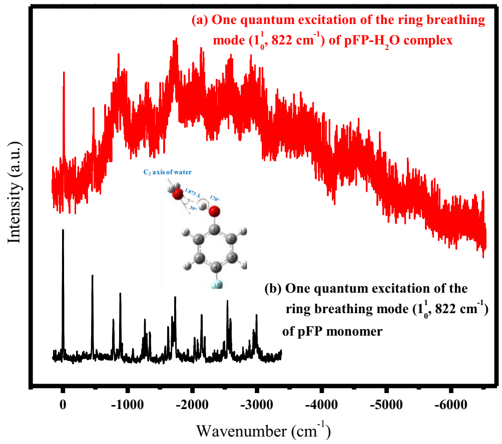

Figure 3: The DF spectrum of the p-fluorophenol–water binary complex (inset) (trace-a) measured upon one quantum excitation of the ring breathing mode (822 cm^{-1}, 1_0^1) of phenolic moiety in the S_1 state. The spectrum measured by exciting to the same level in S_1 of p-fluorophenol monomer is shown in the lower panel. The complete broadening of the spectrum in the former case is the direct manifestation of hydrogen bond-induced vibrational relaxation.

3 Vibrational Dynamics in *p*-Fluorophenol-Water Dimeric Complex

Microsolvated complexes of phenol and its derivatives are regarded as suitable models to address the solvent effect on light-induced proton as well as H-atom transfer processes that are vital for many issues pertaining to photo-biology and artificial light-harvesting technologies[36–41]. Phenol is the simplest prototype of photoacids. The phenolic residue is abundant in many important molecules in nature (e.g., tyrosine), and it plays vital role for the occurrence of many acid–base, redox reactions as the key steps of natural processes, viz. photosynthesis (e.g., water splitting in PS II), antioxidant activities, and plant signaling etc.,[42–47]. Due to the presence of a polar O–H group, it can interact with its neighboring molecules via different types of hydrogen bonding interactions like O–H···*X*, O–H···π, etc., where *X* is an electronegative atom or group belonging to other molecules[48]. The key issue that has been highlighted here is the promotional effect of a single O–H···O hydrogen bond on the vibrational dynamics in phenolic complexes, and the data presented here are obtained from dispersed fluorescence (DF) spectroscopy measured upon excitation to a single vibronic level of a dimeric complex between phenol and water[49].

Dispersed fluorescence (DF): In this type of spectral acquisition, the sample molecule is excited to a specific vibronic level of the S_1 state, and the fluorescence emission from this level is detected after dispersing through a monochromator. The bands in DF spectrum correspond to the vibrational levels in the ground electronic state (S_0) and the intensity patterns are primarily determined by the Franck–Condon factors of the vibrational level in S_n with corresponding levels in S_0. Valuable information about the excited state molecular geometry and intermode coupling are obtained by analyzing the DF spectra.

The DF spectral method has been used extensively to demonstrate the phenomenon of vibrational energy redistribution upon excitation to a single vibronic level in the excited state of a molecule[50, 51]. For the pFP–H_2O binary complex, the spectrum recorded upon one quantum excitation of the ring breathing mode (822 cm^{-1}) of pFP moiety in a cold supersonic jet expansion is presented in Fig. 3 (upper trace) and the lower trace corresponds to the spectrum recorded by exciting the same mode of the monomer. It is seen that the contrast is remarkable. In the case of the complex, the spectrum is broad, shows only a few structures over the broad background and the resonance fluorescence band is negligibly small indicating occurrence of irreversible vibrational relaxation from the excited (1_0^1) vibronic level of the complex, and the broad red-shifted bands are due to emission from many of the relaxed levels. In contrast, the DF spectrum of the monomer shows only narrow band features, and there is an intense resonance fluorescence band of 1_0^1 type transition at the excitation wavelength, and the vibronic band features are of a regular DF spectrum and show no indication of vibrational relaxation. Similar regular behaviour in the DF spectra has been observed for excitations with up to ~ 1000 cm^{-1} of vibronic energy in the S_1 state of the monomer[52]. Thus, the single hydrogen bond of the complex obviously has an enormous effect on the dynamics of the vibrational energy relaxation. The large density of states and strong intermode coupling have attributed to

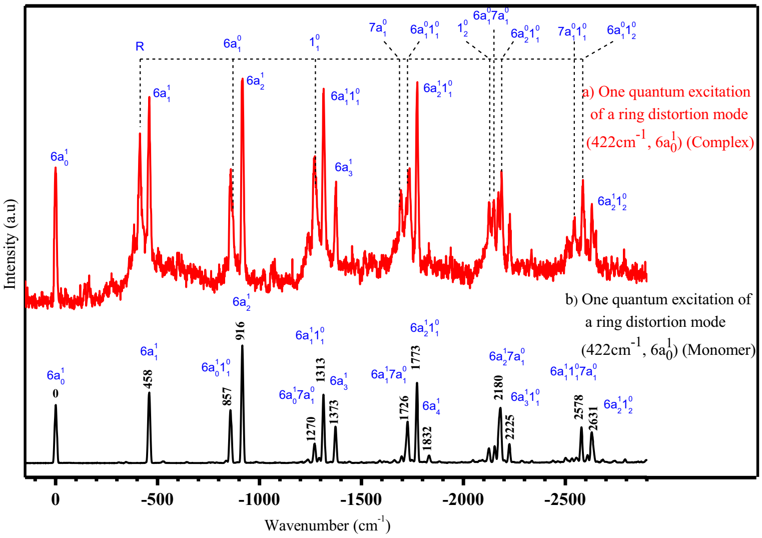

Figure 4: The DF spectrum (trace-a) of the p-fluorophenol–water binary complex measured upon one quantum excitation of a ring distortion mode (422 cm^{-1}, $6a^1_0$) in the S_1 state of phenolic moiety. The spectrum measured by exciting to the same level in S_1 of p-fluorophenol monomer is shown in the lower panel (trace-b). In the top panel, the additional intense band, labeled by R, is an indication of opening up of additional emission channel induced by hydrogen bonding. The emission occurs from a level in S_1 which is not accessible for direct excitation.

the early onset of vibrational relaxation in the case of the complex. To depict the occurrence of hydrogen bond induced vibrational relaxation in the ground electronic state, Ebata et al. had used a multi-resonance time-resolved infrared spectroscopic method[53]. The authors suggested that the energy threshold for initiation of vibrational relaxation in the case of the parent phenol-water complex has a similar value as compared to that observed for pFP–H_2O binary complex in the excited state[53].

It has been suggested that the hydrogen bond promotes coupling between the vibronic level directly excited and some of the background levels that are Franck–Condon inactive[49]. Restricted vibrational relaxations are observed when such coupling involves only a limited number of background levels. This phenomenon is revealed in the DF spectrum when a ring distortion mode, with frequency as small as 422 cm^{-1}, of pFP moiety of the complex under discussion, was excited. The DF spectra of both the binary complex and pFP monomer are shown in Fig. 4, and clearly the spectrum in the former case is more complex, which shows a number of new features that are absent in the spectrum of the monomer, and the most intense one is labeled with R, and the band appears as combination all through the spectrum. The emission spectral bands, in the case of pFP monomer, are only from the excited vibronic level. Whereas, in the case of the complex, the hydrogen bond promotes level mixing of the Franck–Condon level with a number of background levels that are not accessible for direct excitation from the ground electronic state of the complex.

A direct manifestation of intermode vibrational coupling is the appearance of Fermi resonance bands in the measured spectra. In present context, the aim is to demonstrate appearance of Fermi resonance transitions involving hydrogen bond modes. Although, the hydrogen bond stretching frequency of the same binary complex in the excited state is ~155 cm^{-1}, and no other band is expected to appear in the same frequency region of the fluorescence excitation (FE)spectrum, which is equivalent to electronic absorption spectrum, the measured spectrum displays two adjacent features at 155 and 161 cm^{-1}[149]. On the other hand, the DF spectra recorded upon excitations at these two vibronic levels of the complex are found to look identical[49], and which is possible only if the two levels have similar vibrational character as a result of Fermi resonance interaction. Further analysis reveals that the doublet band of the FE spectrum is due to Fermi resonance interaction of the hydrogen bond stretching fundamental with a low-frequency overtone of the out of plane bending vibration of the two *para* substituted groups of the aromatic ring.

Fluorescence excitation (FE): In this technique, total emission or a segment of the emission of sample is probed while scanning the excitation wavelength over the sample's absorption spectral range. In FE spectrum, the vibrational band structures indicate allowed vibronic transitions corresponding to the $S_1 \leftarrow S_0$, i.e., the vibrational levels in the S_1 state. Analysis of FE spectrum of a molecule provides information about the excited state nonradiative dynamics.

4 Hydrogen Bonding Promotes Photochemical Reactivity by Lowering Energy Barrier

Although fluorine is the highest electronegative element in the periodic table, a covalently bound F-atom in an organic molecule is known as a weak hydrogen bond acceptor. However, conclusive experimental evidence has been provided recently showing that intermolecular hydrogen bonding involving F as acceptors promotes HF elimination reaction in electronically excited hydrogen-bonded dimeric complexes of 2- and 3-fluorophenols (2- and 3-FP) in the gas phase. The reaction has been probed using the method of resonant two-photon ionization mass spectrometry[54].

The simplest photochemistry that occurs upon the lowest $\pi\pi^*$ excitation of phenol in the vapour phase is the dissociation of the O–H bond. The proposed dynamical mechanism for occurrence of this reaction is an interplay between S_1, the lowest $\pi\pi^*$ (bound) and S_2, which is $\pi\sigma^*$ in nature (dissociative), and the detailed features of the reaction have been analyzed in recent years both by experimental and theoretical approaches[55–60]. The dynamics of photo-fragmentation of 2-, 3- and 4-chlorophenol monomers have been investigated recently by Ashfold and co-workers, and it has been observed that the S_1 state lifetime of the *syn* conformer of 2-chlorophenol (2-CP) is much shorter, of the order of subpicosecond, in comparison to those of 3-, and 4-chlorophenols (3- and 4-CP)[61]. However, no such lifetime shortening occurs in the case of 2-FP as reported by Pino et al. by measuring the S_1 state lifetimes directly using picosecond pump–probe spectroscopy[62]. As an explanation it was suggested that in the case of 2-CP, intramolecular O–H⋯Cl hydrogen bonding is the main promoting factor for breaking of the C–Cl bond and results to lifetime shortening[54]. The intramolecular O–H⋯F hydrogen bonding in 2-FP being weaker and C–F bond energy is larger compared to that of C–Cl bond, its S_1 dynamics is similar to that of parent phenol[63]. In the case of fluorophenols, it was proposed earlier by performing mass spectrometric analysis that upon resonant two-photon ionization, 2-FP monomer undergoes HF elimination reaction to a little extent but the same does not occur at all in the case of 3-FP monomer[54]. On the other hand, a resonant 2-photon (266 nm) ionization mass spectrometric analysis with the hydrogen-bonded dimer of 2-FP reveals that the HF loss tendency is so large that the mass spectrum shows only HF loss fragment ion mass peak ($m/z = 204$ amu) and no intact dimer cation survives, as shown in Fig. 5a. On the other hand, for 3-FP, the mass ion peak corresponding to HF loss from the monomer is absent (Fig. 5b) and the predominant photochemical channel is CO loss as happened from parent phenol cation. But the HF loss channel is opened up for 3-FP dimer, and the mass spectrum (inset) shows both the intact dimer cation as well as HF loss fragment ion signals.

Resonant two-photon ionization: In this technique, the sample molecules are irradiated by a laser with tunable wavelength range where the wavelength of the laser light is adjusted in such a way that the molecules are excited to an intermediate electronic state by absorbing one photon and absorption of a second photon leads to ionization. The rate of ionization is enhanced by several orders of magnitude due to excitation to the electronic states resonant with the incident light energy.

Electronic structure theory calculation predicts that HF loss from the dimer is a barrierless process in the S_1 state but there is a small barrier (~ 0.1 eV) in the case of the monomer[54]. The same reaction in the cationic ground state is a high barrier process, which is nearly 3.15 eV for 2-FP monomer and 2.8 eV for the dimer. Thus, we suggest that the reaction takes place only in the S_1 state. The calculation at the same level predicts that for 3-FP monomer, CO loss is more favourable compared to HF loss[54]. However, in the hydrogen-bonded dimer, HF loss in the S_1 state is still a high barrier process, although, the process is energetically favourable in the cationic ground state and as a result, both intact dimer and HF loss signals are observed in the mass spectrum.

5 Coupled Electron–Proton Transfer Reaction in 7-Azaindole-Phenol Binary Complex

Coupled electron–proton transfer reaction is a variant of H-atom transfer reaction, which can also take place as a proton-coupled electron transfer (PCET) reaction. The differences among the processes are the reaction sequences and types of molecular orbitals involved in the electron transfer step. It has been demonstrated that such reaction occurs very efficiently in a binary complex of phenol with 7-AI in a nonpolar liquid upon electronic excitation[64]. As a result of such reaction, the fluorescence signal of excited 7-AI is quenched. The study also revealed that although anisole is a more effective electron donor, it cannot quench the 7-AI fluorescence at all. In the ground state, the binary complex between phenol and 7-AI assumes a planar cyclic structure, where phenol acts both as hydrogen bond donor as well as acceptor. Such hydrogen bonding network has been suggested to be the main factor for the occurrence of the coupled reaction as similar network cannot be formed in the case of the complex between anisole and 7-AI.

The complex formation was carried out by mixing 7-AI and phenol in different concentration ratios in methylcyclohexane (MCH)

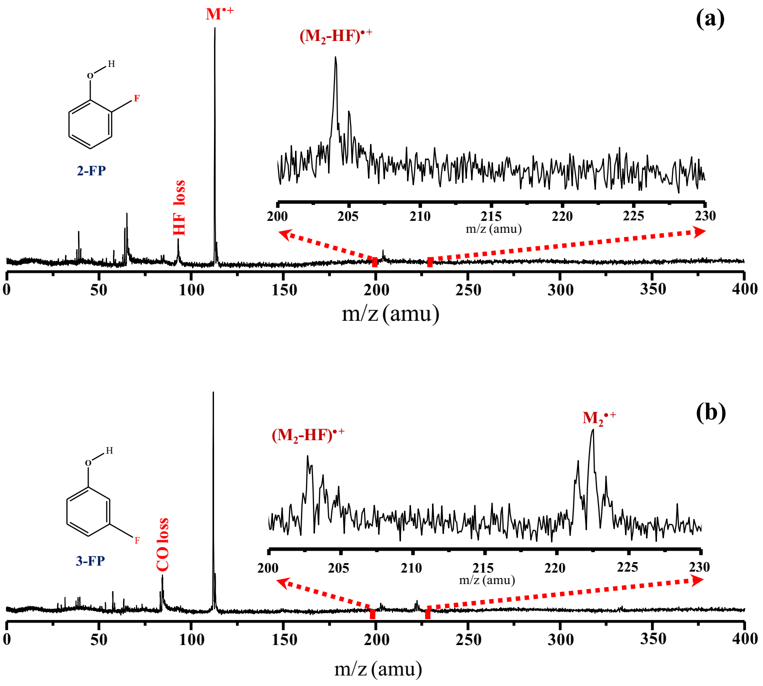

Figure 5: Time-of-flight (TOF) mass spectra recorded upon photoionization (266 nm) of 2- and 3-fluorophenols (shown in the insets) (**a**, **b**, respectively) under supersonic jet expansion condition at laser energy of 32 μJ pulse^{-1} in each case. The supersonic jet expansion was carried out using argon backing pressure of 0.5 atm to promote cluster formation. The expanded views of the dimer mass regions are displayed in the insets.

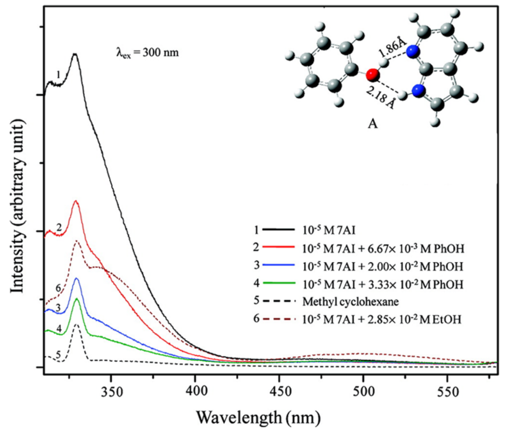

Figure 6: The quenching of the fluorescence of 7-azaindole monomer upon mixing with phenol at different concentrations in methylcyclohexane solutions at room temperature. Trace-1 for pure 7-azaindole solution in absence of phenol. Traces 2, 3 and 4 indicate occurrence of fluorescence quenching with increasing concentration of phenol in the solutions. Trace-5 is for pure solvent indicating there is no fluorescence impurity. Trace-6 indicates that instead of phenol if ethanol is added, tautomerization is promoted. The observed quenching is interpreted in terms of PCET reaction.

solution. Phenol preferentially forms 1:1 complex with 7-AI, and calculation predicts that a cyclic doubly hydrogen-bonded geometry is the most suitable for this complex where each moiety simultaneously acts as hydrogen bond donor as well as acceptor (inset, Fig. 6).

The identity of the 1:1 nature of the binary complex was established analyzing the changes in intensity of the complex band in the UV–visible absorption spectra in terms of Benesi–Hildebrand plot[64]. In the absorption spectrum, the band for the complex appears with a redshift of a few nanometers with respect to that of 7-AI monomer. In the fluorescence spectra, the 7-AI monomer fluorescence is largely quenched in the presence of phenol as shown in Fig. 6. Mechanistically the quenching has been proposed to be due to a coupled electron–proton transfer, where phenol is the donor for both the proton and electron. Furthermore, phenol being a weak acid, it is expected that it would act as a catalyst for the conversion of 7-AI from normal to tautomeric form. However, the observed quenching indicates that electron–proton transfer involving the hydrogen-bonded network between pyridinic N and phenolic O–H (N···O–H) is preferred over the competing tautomerization process.

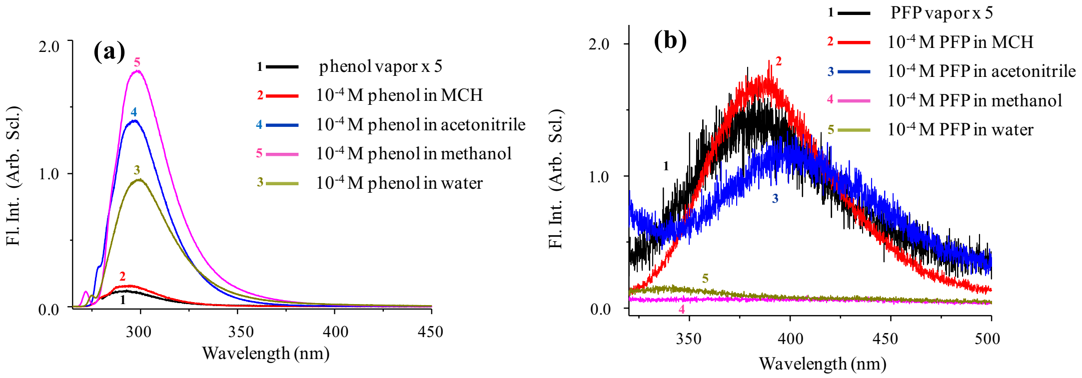

Figure 7: Solvent effects on fluorescence spectra of (**a**) phenol and (**b**) PFP. In each solution, the concentration of the solute is same, 10^{-4} M. In the former case, protic solvents enhance the intensity of the fluorescence, but the behaviour in the latter case is completely opposite.

6 Perfluoro Effect on Emitting Behaviour of Phenol in Protic Solvents

Perfluoro effect refers to a significant change in electronic absorption spectral appearance and photophysical behaviour of an aromatic compound occurring as a result of complete or nearly complete replacement of hydrogen atoms of the molecule by fluorine. The notable manifestations of perfluoro effect, from the viewpoint of electronic structure, is appearance of many low-lying $\pi\sigma^*$ states, and in many cases one or more of such states are energetically below the lowest $\pi\pi^*$ states, where the latter are responsible for near UV absorption bands of small aromatic molecules. Direct electronic transitions from the ground state to these low-lying $\pi\sigma^*$ states are not Franck–Condon allowed, but due to strong coupling with the nearly isoenergetic $\pi\pi^*$ states, the electronic spectra are significantly distorted, and in many cases the sharp vibrational structures associated with the electronic transitions are lost and the spectra appear as a broad feature. The other notable effect is the much red-shifted emission spectra because the emission occurs from the low-lying $\pi\sigma^*$ states. In the context of the present review, an interesting feature that has been observed is the effect of the hydrogen bonding protic solvents on the emission spectral characteristics of such perfluorophenols as stated briefly in the following paragraph.

The protic solvents are known to have a remarkable effect on the fluorescence spectral properties of phenol[65]. While the fluorescence quantum yield of phenol in the vapour phase is very small with a lifetime as short as 2 ns[66], the fluorescence yield is increased by about two orders of magnitude in the hydrogen-bonded liquid methanol. The common explanation that is given is that the shifting of the electronic energy levels by solvation process blocks the non-radiative internal conversion process which is very efficient for phenol in the vapour phase and also in non-protic liquids. Completely opposite behaviour is noted in the case of perfluorophenols. Upon hydrogen bonding with the protic solvent molecules, some of the dark $\pi\sigma^*$ states of perfluorophenols are lit up with appreciable intensity and the new bands appear in the electronic absorption spectra but those are absent in the spectra of the vapour phase. Electronic structure theory calculations for size-specific clusters with water show that intensities of a number of $\pi\sigma^*$ states are enhanced with increase in cluster size, pentafluorophenol–$(H_2O)_n$, i.e., with increase in the value of n[65]. In contrast, the emission behaviour is totally opposite, and in protic solutions the fluorescence is completely quenched as shown below (Fig. 7). In the case of parent phenol, conical intersection of the lowest $\pi\sigma^*$ state (dissociative along O–H stretching coordinate) with the ground state is a major factor to determine its non-radiative electronic relaxation behaviour. As perfluorophenols have many such states, their relative positions and their interactions with the ground state by the protic liquids determine the emission behaviour.

7 Summary and Outlook

The large volume of literature accumulated over the past decades on hydrogen bonding has dealt with, nearly exclusively, the roles of this ubiquitous non-covalent specific interaction on different issues pertaining to structure and physical properties of molecules, clusters, crystals, and liquids.

On the other hand, although limited in number, there are reports demonstrating conclusive evidences that this interaction plays a vital role in chemical dynamics. Only a handful of illustrations have been cited here, covering key issues of chemical dynamics, viz. vibrational relaxation, bond dissociation, and charge transfer. In every case, hydrogen bonding plays active role either by augmenting coupling of the molecular bond vibrational modes with the bath modes produced by low-frequency hydrogen bond vibrations or providing suitable orientations for occurrences of reactions involving H atoms. There are numerous examples in the literature showing that molecular complexes and materials with tailor-made designs involving hydrogen-bonded networks have been used to channelize photo-induced hydrogen or coupled electron proton transfer reactions in artificial light-harvesting systems. Much scope is there to explore fundamental issues of such reactions with size-specific molecular complexes, and research activities in this direction are expected in the coming days.

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