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Solvent dependent excited state spectral properties of 4-hydroxyacridine: Evidence for only water mediated excited state proton transfer process

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ABSTRACT

The possibility of ground and excited state proton transfer reaction across the five member intramolecular hydrogen bonded ring in 4-hydroxyacridine (4-HA) has been investigated spectroscopically and the experimental results have been correlated with quantum chemical calculations. The difference in the emissive behaviour of 4-HA in different types of solvents is due to the presence of different species in the excited state. In non-polar solvents, the species present is non-fluorescing in nature, whereas 4-HA molecule shows normal emission from intramolecularly hydrogen bonded closed conformer in polar aprotic solvents. In polar protic solvents like MeOH, EtOH, etc. (except water), a single broad emission band is attributed to the hydrogen bonded solvated form of 4-HA. However, in case of water, fluorescence from the tautomeric form of 4-HA is observed apart from emission from the solvated form. Emission from the tautomeric form may arise due to double proton transfer via a single water molecule bonded to 4-HA. Evaluation of the potential energy surfaces by quantum chemical calculations using density functional theory (DFT) and time dependent density functional theory (TDDFT), however, points towards the possibility of proton transfer—both intrinsic intramolecular as well as water mediated in the first excited state of 4-HA.

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1. Introduction

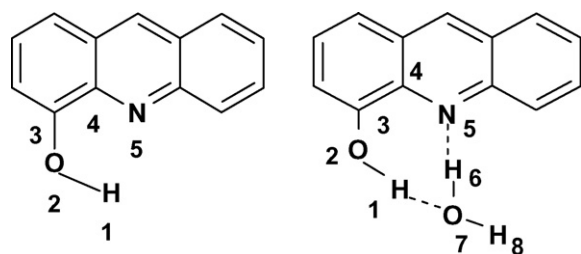
Inter- and intramolecular hydrogen bonding molecular systems have been studied extensively over the past decades due to their interesting photophysical and photochemical properties [1–13]. In particular, proton transfer processes in molecules containing bifunctional groups such as a proton donor and a proton acceptor site have been studied due to their relevance in living systems [7–13]. The types of systems studied for proton transfer reaction can be broadly classified into three categories. The first category comprises of systems with proton donor and acceptor sites within the same molecule having cyclic intramolecular hydrogen bonded (IMHB) ring in the ground state which facilitates proton transfer in the excited state. In this category, apart from the standard systems such as salicylaldehyde, methyl salicylate and their derivatives [8,14–16] a number of other interesting systems such as 7-hydroxy-1-indanone (7HIN) [17,18], 3-hydroxy flavone and its derivatives [4,19–25] hydroxyl naphthyl pyrazoles [26,21] naphthaldehyde derivatives [7,9–13,27], etc. have been studied for excited state intramolecular proton transfer (ESIPT) process. The

second category includes systems where double proton transfer occurs via a concerted process from one functional group to other as was reported in the case of double hydrogen-bonded dimers of 7-azaindole [28–30] or relayed by acyclic bridge of solvent molecules between two different groups such as in 7-hydroxyquinoline (7-HQ) [31–33]. The third category comprises of molecules such as 6-hydroxyquinoline (6-HQ) [34] where the bifunctional groups are far apart from each other and proton transfer is mediated by solvent water. In this case, water serves the purpose well due to its amphiprotic nature.

This work describes a detailed insight into the emissive behaviour of 4-HA. The molecule acridine is one of the several aza-polycyclic aromatic hydrocarbons found in the partial combustion of fossil fuels and tobacco [35]. It is also detected in motor vehicle exhaust emissions, cigarette smoke, shale oil, coal tar and coal liquefaction products [35]. The molecule 4-HA is a substituted product of parent molecule acridine. This compound was chosen for the following reasons—firstly to explore the possibility of proton transfer process in five member hydrogen bonded ring system [4,36–39] which even till date is less studied one compared to six member hydrogen bonded ring systems. A similar type of system with a five member IMHB ring is 7-hydroxy-1-indanone [16–18] in which the tautomer state exists as a metastable state and the spectral properties are different compared to other studied related molecules having six member IMHB ring [11–13]. The five

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Scheme 1. Structure of 4-hydroxyacridine (4-HA) and its single water hydrated cluster with numbering of atoms at the hydrogen bonded site.

member ring in 7HIN imparts a strain to the hydrogen bonded site and hence, the hydrogen bond is weak in nature [16–18]. Therefore, 7HIN easily forms anion in protic solvents and in some polar aprotic solvents whereas other ESIPT systems with the six member IMHB do not form such anions under the same experimental condition [9,11–13]. Secondly, the photophysical study of 4-HA could be interesting as it is used in analytical chemistry as a good chelating agent. The cyclopalladated complex of 4-HA is known to have anticancer activity [40]. Metal complexes are known to serve as the intercalators for DNA [40]. Lastly, our interest is to investigate whether the change of chromophore from the basic quinoline unit to acridine unit can influence the photophysics. The molecule 4-HA has never been studied earlier for proton transfer reaction, though its naphthalene counterparts, 8-hydroxyquinoline (8-HQ) [36,37] and 8-mercaptoquinoline (8-MQ) [38,39] are well-studied compounds. We are interested to study the photophysics of 4-HA by a thorough analysis of ground and excited state properties in various solvents at different temperature and pH of the medium using absorption and emission spectroscopy. Furthermore, the structural calculations have been performed for the ground and excited states at DFT and TDDFT levels of theory. In particular, the potential energy curves (PECs) for intrinsic intramolecular proton transfer in the ground and excited states have been calculated along the proton transfer coordinate O_2-H_1 distance (Scheme 1) and PECs for water assisted proton transfer are calculated by simultaneous variation of O_2-H_1 and N_5-H_6 distance (Scheme 1) at the proton translocation site to correlate the theoretical findings with the experimental results. Presence of IMHB has been confirmed by analysis of the IR spectrum in solid as well as in solution phase.

2. Materials and methods

2.1. Materials

The molecule 4-hydroxyacridine (Scheme 1) and Aerosol OT (AOT) were purchased from Aldrich Chemicals and used as supplied. The solvents methylcyclohexane (MCH), heptane (HEP), cyclohexane (CYC), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), acetonitrile (ACN), isopropanol (Iso-prop), ethanol (EtOH) and methanol (MeOH) were purchased from Spectrochem and the purity of solvents have been checked in the wavelength range used for spectroscopic study. Triple distilled water was used for the preparation of aqueous solutions. Sulphuric acid (H_2SO_4), hydrochloric acid (HCl), acetic acid and triethylamine (TEA) from E-Merck were used as supplied. Analytical grade sodium hydroxide (NaOH) was used.

2.2. Steady state measurements

The absorption and emission spectra of 4-HA in solvents of varying polarity have been taken by Hitachi UV-Vis (Model U-3501) spectrophotometer and PerkinElmer (Model LS-50B) fluorimeter,

respectively. In all measurements, the sample concentration has been maintained within the range 10^{-4} – 10^{-5} mol/dm³ in order to avoid aggregation and reabsorption effects. IR spectrum of the molecule in KBr pellets and in different solvents is measured by a PerkinElmer spectrophotometer (PerkinElmer Spectrum RXI FT-IR system serial no. 54350).

2.3. Time-resolved measurements

The fluorescence lifetime of the molecule has been measured by a picosecond time correlated single photon counting (TCSPC) set-up [41]. A picosecond diode laser is used as exciting light source (IBH, UK, NanoLED-07, s/n 03931, 408 nm). The fluorescence signal was detected in magic angle (54.7°) polarization using Hamamatsu MCP PMT (3809U). The typical system response of the laser system was 75 ps. The decays were analyzed using IBH DAS-6 decay analysis software.

2.4. Computational procedures

The computed ground state geometry of the neutral species (N-form), open form (O-form) and its monohydrate complex (SN-form in scheme 2 and 3) have been computed at DFT levels with B3LYP functional and 6-311++G** basis set using Gaussian 03 software [42]. For the calculation of excited states information, TDDFT method has been used with the same functional and basis set. Possibility of ground state intramolecular proton transfer (GSIPT) was explored by constructing the PEC with the variation of O_2-H_1 distance (Scheme 1). At different OH bond distances the geometry has been optimized to get the ground state potential energy curve. The excited state surface can be generated by different methods [43–46]. In general, similar to the ground state calculation the excited state optimization can be performed at different OH distances using CIS method [46]. However, information regarding ESIPT mechanism can be obtained by constructing the Franck–Condon curves by adding the TDDFT/6-311++G** vertical excitation energies to the corresponding GSIPT curves. Such methods are successfully implemented to evaluate the PECs for the ESIPT reaction in several studied systems [43–45]. The possibility of water assisted proton transfer in the monohydrate complex of 4-HA monomer was also studied for both the ground and excited states following the same procedure. Here, both O_2-H_1 and N_5-H_6 (Scheme 1) distances are simultaneously varied to construct the potential energy curves.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of 4-HA (Fig. 1) were measured in various types of solvents and the absorption band maxima are presented in Table 1. As seen in Fig. 1, the absorption spectra exhibit two bands in all solvents—one at ~ 285 nm and another broad band at ~ 385 nm. The spikes observed at ~ 340 and ~ 360 nm arise from the parent chromophore unit of acridine. Such types of spikes have been observed in the absorption spectra of some nitrogen containing polycyclic compounds studied earlier [47,48]. As we move from non-polar solvents to the polar ones, the band smoothens out indicating greater solute solvent interaction as was observed for numerous systems with IMHB in the ground state [9,12,13].

Addition of H_2SO_4 or acetic acid to methanolic solution of 4-HA leads to emergence of a new band at ~ 435 nm (Fig. 2a). Addition of TEA or NaOH results in generation of a band at ~ 450 nm (Fig. 2b). The same result was observed for the variation of pH in ACN solution as well as in water solution. The species formed on addition

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