



Multiple hydrogen bonding in excited states of aminopyrazine in methanol solution: Time-dependent density functional theory study



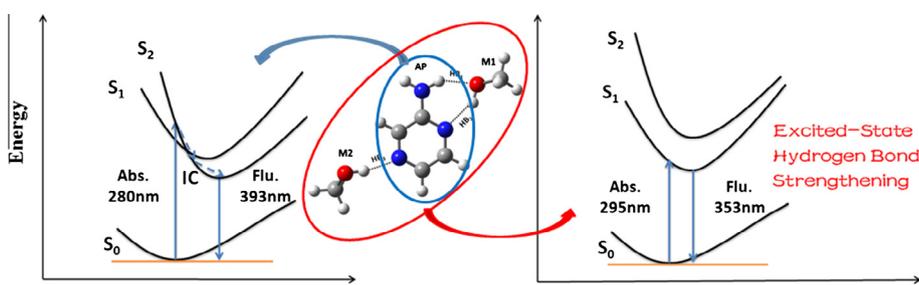
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HIGHLIGHTS

- The excited state dynamics of aminopyrazine in solution is studied by TDDFT method.
- Multiple hydrogen bonding strengthenings in electronic excited states are confirmed.
- Photochemistry is influenced by intermolecular hydrogen bonding strengthening.

GRAPHICAL ABSTRACT



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ABSTRACT

Aminopyrazine (AP) and AP-methanol complexes have been theoretically studied by using density functional theory (DFT) and time-dependent density functional theory (TDDFT). The excited-state hydrogen bonds are discussed in detail. In the ground state the intermolecular multiple hydrogen bonds can be formed between AP molecule and protic solvents. The AP monomer and hydrogen-bonded complex of AP with one methanol are photoexcited initially to the S_2 state, and then transferred to the S_1 state via internal conversion. However the complex of AP with two methanol molecules is directly excited to the S_1 state. From the calculated electronic excited energies and simulated absorption spectra, we find that the intermolecular hydrogen bonds are strengthened in the electronic excited states. The strengthening is confirmed by the optimized excited-state geometries. The photochemical processes in the electronic excited states are significantly influenced by the excited-state hydrogen bond strengthening.

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Introduction

Intermolecular hydrogen bonding, as one of the most important intermolecular interactions, plays a significant role in photophysics and photochemistry [1–3]. This interaction exists widely between hydrogen donor and acceptor molecules and affects the material features and functions in various phases, e.g. the solute–solvent interactions in solution by intermolecular hydrogen bonding and in solid state the organic molecules arranged in a dense packing mode forced by the intermolecular hydrogen bonding [4–8]. The organic molecules that can form intermolecular hydrogen bonding are applied to many photochemical processes, such as fluorescent

sensors, fluorescent recordings and probes for solvation dynamics [9–12].

In solution the solute and solvent molecules can assemble together by intermolecular hydrogen bonding in the ground state. Once the hydrogen-bonded complexes are photoexcited to the electronic excited states, the corresponding photophysical and photochemical reactions would take place. The hydrogen bond strengthening or weakening usually happens in electronic excited states and can facilitate or obstruct the related photoinduced processes, e.g. electron transfer, proton transfer and energy transfer between the hydrogen donor and acceptor. The excited-state dynamics investigation is helpful to understand photochemical phenomenon and provide the specific mechanism explanation [13–16]. In recent years the intermolecular hydrogen bonding in solution has attracted the attentions of many researchers and the

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related experimental and theoretical investigations have been reported extensively [17–20]. Mathies and coworkers have performed femtosecond experiments to study the ultrafast dynamics and simulated Raman spectroscopies to probe the structural changes of chromophore [21–24]. Zhao et al. investigated a series of hydrogen-bonded complexes both in ground and excited states and the relevant photochemistry processes, such as hydrogen bond strengthening, intermolecular proton transfer, charge transfer and fluorescence quenching [3,25–34]. They theoretically demonstrated that the hydrogen bonding of coumarins in solution can be strengthened in excited states rather than cleavage put forward by some researchers in femtosecond experiments [28]. Recently, more and more hydrogen bonding dynamics researches are performed using both experimental and theoretical methods. Liu et al. further explored the hydrogen bonding interaction between coumarin and solvent molecules and reconfirmed the hydrogen bond strengthening in the electronic excited states [35–37]. The hydrogen bond strengthening or weakening mechanism judging from the spectral shifts proposed by Zhao et al. have been extensively employed to explain the photochemical phenomenon in experiments.

Pyridine derivatives are the interesting subjects to many researchers because of their fundamental photochemistry properties, especially the solute–solvent interactions by intermolecular hydrogen bonding. Those derivatives based on aminopyrazine have been paid much attention by spectroscopic experiments as well as theoretical calculations [38–40]. 2-Aminopyridine is one of the most popular compounds in aminopyrazine family and it has been extensively investigated [41–45]. In previous work we have considered the intermolecular hydrogen bonds in 2AP dimer and discussed the mechanism of double proton transfer reaction using spectroscopic measurements as well as theoretical calculations [46]. The 3AP dimer has been studied in terms of the intermolecular and intramolecular hydrogen bonds in excited states using quantum chemistry methods [47]. Aminopyrazine (AP) has three nitrogen atoms as hydrogen donor and acceptor in the pyrazine ring and amino moiety, which are responsible for the formation of multiple intermolecular hydrogen bonds in and out of the pyrazine plane with protic solvents. Yamada et al. investigated the vibrational spectra of three pyrazine derivatives including AP in solution and discussed various solvation effects on the vibrational modes of amino group [48]. However they did not discuss the excited-state dynamics and the detailed photochemical properties of the intermolecular hydrogen-bonded complexes. The photochemical processes of AP in solution are greatly influenced by the intermolecular hydrogen bond. It is significant to understand the hydrogen bond dynamics in the electronic excited states of AP in solution and identify the solvent effect on the photochemical behaviors.

In the present work, the multiple hydrogen bonding between AP and methanol solvent is considered in both ground and electronic excited states, respectively. Two methanol molecules can be easily assembled with AP by the intermolecular hydrogen bonds in different positions. The DFT and TDDFT methods are employed to study the hydrogen-bonded systems, which have been demonstrated useful and reliable tools to investigate the photochemistry of organic molecular materials. We focus on the influence of the intermolecular hydrogen bonding on the photoexcitation processes of the investigated systems. The hydrogen bond strengthening is detected from the simulated steady absorption spectra and confirmed by comparing the optimized geometries in the ground and excited states.

Theoretical methods

In the present work, the electronic structure calculations are performed using Gaussian 09 program suite [49]. The density

functional theory and time-dependent density functional theory are employed to study the structural and electronic properties of isolated AP and hydrogen-bonded complexes. The ground and electronic excited states of investigated systems are optimized using DFT and TDDFT methods, respectively. Becke's three parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP functional) is employed in both the DFT and TDDFT calculations [50–52]. The 6-311++G** is chosen as basis set in the calculations. The local minima are confirmed by the absence of an imaginary mode in vibrational analysis calculations. The TDDFT method has been demonstrated reliable to investigate the excited-state dynamics of organic complexes [32–37,53].

Results and discussion

There are three nitrogen atoms in the AP molecule which act as hydrogen donor as well as acceptor. Thus multiple hydrogen bonds exist between AP and protic solvents in solution. Three hydrogen bonds between AP and protic methanols are considered since they are relatively stable in both ground and excited states. In this work four systems are calculated to understand the excited-state hydrogen bonding dynamics: the isolated AP, complex of AP with one methanol (AP-M1 and AP-M2) and complex of AP with two methanol (AP-2M). The structures of isolated AP and AP-2M complexes are shown in Fig. 1. The hydrogen bonds in AP-M1 are numbered as HB₁ and HB₂, which denote the interaction of N–H bond in AP with O atom in methanol and N atom in AP with O–H in M1, respectively. HB₃ is defined as the intermolecular interaction between AP and M2. The relevant atoms and bonds are described in Fig. 1. There are also other hydrogen bonds, the one of N₁–H with O atom in methanol in the opposite side of HB₁, which is similar to HB₁. The hydrogen bonding of O–H in methanol perpendicular to the conjugated AP plane is too weak to be considered, which is easily cleaved in the electronic excited states.

The intermolecular hydrogen bonds in the ground states are formed between AP and methanol. The systems with the local minimized ground state geometries are photoexcited to the electronic excited states. Table 1 lists the calculated low-lying electronic excitation energies, fluorescence wavelengths and corresponding oscillator strengths of AP monomer, AP-M1, AP-M2 and AP-2M complexes. By comparing the oscillator strengths of these systems we find that AP, AP-M1 and AP-M2 are initially excited to the S₂ state with relatively large oscillator strengths. While the complex AP-2M is initially excited to the S₁ state with the largest oscillator strength. The excitation wavelengths are 280, 290, 284 and 295 nm for AP, AP-M1, AP-M2 and AP-2M, respectively. The excited energies to the S₂ states of AP-M1 and AP-M2 are obviously red-shifted in comparison with the corresponding value of isolated AP, and the shift of 10 nm and 4 nm are observed in the hydrogen-bonded complexes, respectively. We find that the intermolecular hydrogen bonding induces the shift of excited energy. The hydrogen bond strengthening is evaluated from the red shift of excited energy. The complex of AP-2M is excited to the S₁ state with the excited energy of 295 nm which is significantly lower than that of 280 nm for AP monomer. The calculated fluorescence wavelengths in the S₁ states of investigated systems are also shown in Table 1. The fluorescence wavelengths from the S₁ state of AP monomer and three hydrogen-bonded complexes are 393, 386, 369 and 353 nm, respectively. The fluorescence is blue-shifted for the hydrogen-bonded complexes.

The absorption spectra of four investigated systems are calculated by using time-dependent DFT method, as shown in Fig. 2. The calculations are at the B3LYP/6-311++G** level of theory. The absorption peaks of the four systems appear in two regions, the

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