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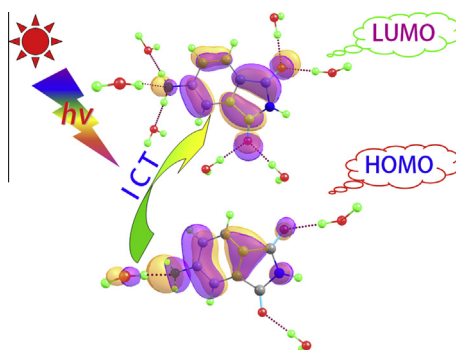
Modulation of the 4-aminophthalimide spectral properties by hydrogen bonds in water

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HIGHLIGHTS

- Geometric structures of clusters 4AP-(H₂O)_n (n = 1–7) in states S₀ and S₁ were optimized.
- In S₁ state, A-type hydrogen bond is weakened whereas B- and C-type hydrogen bonds are strengthened.
- Weakening of A causes blueshifts of absorption and infrared spectra.
- Strengthening of B and C leads to redshifts of electronic and infrared spectra.

GRAPHICAL ABSTRACT



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ABSTRACT

TD-DFT and DFT calculations have been performed to examine the relationship between the spectral shifts of 4-aminophthalimide (4AP) and the formation of hydrogen bonds in water solution. The computations of the S₀ state are at the IEFPDM-B3LYP/6-311++G(d, p) level and the S₁ state at the TD-IEFPDM-B3LYP/6-311++G(d, p) level. The eleven structures of the hydrogen-bonded 4AP clusters formed with different number water molecules in both S₀ and S₁ states were optimized. The absorption, fluorescence and infrared spectra were calculated. The results of the hydrogen bond energy and length reveals that the hydrogen bonds formed by the nitrogen atom of the amine group with water molecule (A type) are significantly weakened from states S₀ to S₁. In contrast, the hydrogen bonds formed by the oxygen atoms of the two carbonyl groups (B type) with water molecules and those formed by the two hydrogen atoms of the amine group (C type) with water molecules are remarkably strengthened. Comparing with the 4AP monomer spectra, the weakening for the hydrogen bond of A type could be responsible for the blueshifts of the electronic absorption spectra and the stretching vibrational spectra of the two N–H groups in 4AP from states S₀ to S₁. The significant redshifts of the electronic spectra and the S₀–S₁ downshifts of the stretching vibrational modes of the two N–H groups and the two carbonyl groups in 4AP could be attributed to the strengthening of hydrogen bonds for B and C types.

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Introduction

It is well-known that coexistence of an electron donor (e.g., amine group) and an electron acceptor (usually carbonyl group) in an aromatic ring would lead to significant changes in the

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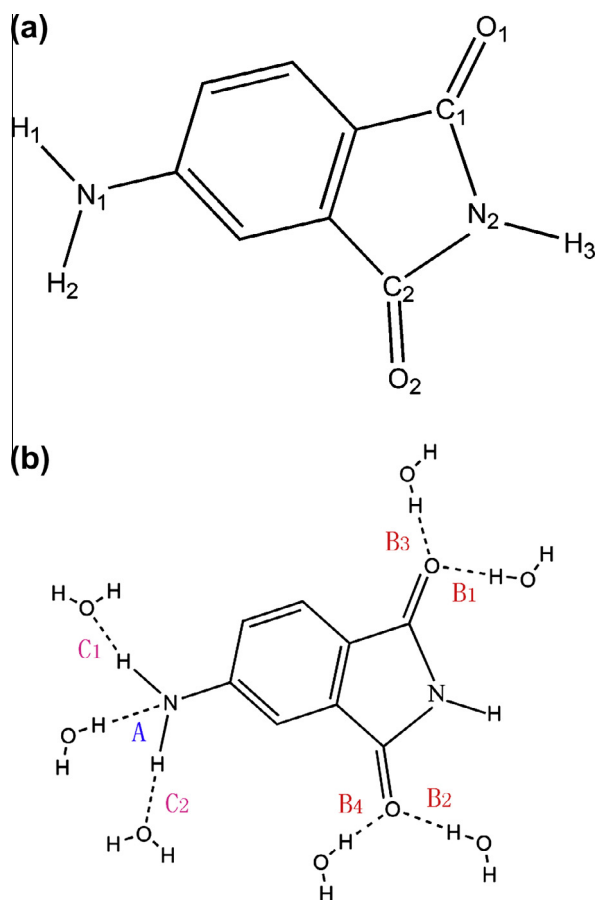
electron density distribution upon electronic excitation of such a molecule [1–3]. 4-aminophthalimide (4AP) is a probe molecule that contains both an electron donor (the amine group) and two electron acceptors (the two carbonyl groups of the five-numbered ring), as shown in Scheme 1a. The molecule has been extensively studied in different environments including water [3–8], alcohols [9] and other systems [10]. In the previous investigation, it was found that the bathochromic shifts of the emission spectra of 4AP in protic solvents are much greater than those observed in aprotic ones. The greatest one was observed in water. It could indicate that there would be strong hydrogen bond interactions between 4AP and water molecules [6]. Using infrared spectroscopy technique, Topp and coworkers [7] determined the structural geometries of the hydrogen-bonded clusters formed by 4AP molecule with one and two water molecules. They found that the water molecule could be attached by proton donation to one of the two $>C=O$ groups in cluster $4AP-(H_2O)_1$. Two different conformers $4AP-(H_2O)_1$ -A and $4AP-(H_2O)_1$ -B were determined. When two water molecules were hydrogen-bonded to one 4AP molecule to form cluster $4AP-(H_2O)_2$, a water bridge was formed between the NH_2 group and the adjacent $>C=O$ group [7].

Theoretical calculations, especially those using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods [8,11–29], have been proved to be efficient and reliable in the determinations of the geometric structures, electronic and infrared spectra as well as the hydrogen bond energies of hydrogen-bonded systems in both ground and excited states. Furthermore, it has been demonstrated by TD-DFT calculations that many photophysical processes and photochemical reactions, such as photoinduced electron transfer (PET) [11–13], intramolec-

ular charge transfer (ICT) [8,11–29] and metal-to-ligand charge transfer (MLCT) [17] are significantly modulated by the excited-state hydrogen bonding dynamics. Especially, based on the DFT and TD-DFT calculations, Zhao and Han [23] had pointed out that excited-state hydrogen bond strengthening could lower the excitation energy of a related excited state and induce an electronic spectral redshift. In contrast, an excited-state hydrogen bond weakening could heighten the excitation energy of a related excited state and induce an electronic spectral blueshift. The relationship between electronic spectral shifts and the electronic excited-state hydrogen bonding changes had been confirmed by other groups in their investigations of hydrogen-bonded systems [16,26–29].

Based on the structures given by Topp and coworkers [7], Hao and coworkers [8] investigated the excited-state hydrogen-bonding dynamics of 4AP in water with TD-DFT method. They found that the intermolecular hydrogen bonds $C=O \cdots H-O$ and $N-H \cdots O-H$ formed in the water bridge of cluster $4AP-(H_2O)_2$ are significantly strengthened in the electronically excited state. However, as demonstrated by Krystkowiak et al. [30,31] and Ramogowda [18], two water molecules could be hydrogen-bonded with one carbonyl group simultaneously. Similar conformations are also adopted by Ding et al. [19], Han et al. [21] and others [26,29], who used methanol as the hydrogen bond donating solvent. Therefore, as shown in Scheme 1b, seven water molecules are hydrogen-bonded to a 4AP molecule to form clusters in the present work at most. The hydrogen bonds between the 4AP molecule and water could be classified into three types, which refer to the hydrogen bonds formed by the nitrogen atom of the 4AP amine group and water (A type), the hydrogen bonds formed by the oxygen atoms of the 4AP two carbonyl groups and water (B type), and those formed by the two hydrogen atoms of the 4AP amine group and water (C type). As to how the hydrogen bonds of different types change upon photoexcitation of 4AP and how they influence the spectral properties of 4AP molecule, Maciejewski and coworkers [32] have demonstrated that 4AP molecule can form three relatively strong hydrogen bonds with trimethylamine (TMA) and triethylamine (TEA), which leads to the formation of S_0 -complexes between the solute and solvent molecules. Upon excitation and deactivation of 4AP molecule, only the two hydrogen bonds formed with the amine group of 4AP (C type) significantly increase their energies from 3780 (3605) cm^{-1} to 5360 (5085) cm^{-1} whereas the one formed with the imide group of 4AP ($H_3 \cdots N$) slightly decreases its energy from 4970 cm^{-1} to 4690 cm^{-1} . Furthermore, compared with that of 4AP monomer, the S_0-S_1 transition energies of the two singly hydrogen-bonded complexes formed by 4AP with TMA through the amine group are red-shifted by 1440 and 1330 cm^{-1} where as that of the complex formed through the imide group is blue-shifted by 280 cm^{-1} . This once again confirms the significant strengthening of the two C-type hydrogen bonds and the slight weakening of hydrogen bond $H_3 \cdots N$ formed with the imide group of 4AP, according to the relationship between hydrogen bond strength change and absorption spectra shifts clarified by Han and Zhao [23,25]. Moreover, Maciejewski and coworkers have also demonstrated that the changes of the time-resolved emission spectra of 4AP in SDS micelles should be due to the significant strengthening of hydrogen bonds formed between the two carbonyl groups of 4AP and water molecules (B type) present in the micelles after excitation [33].

Water, whose Kamlet–Taft parameters are $\alpha = 1.17$ and $\beta = 0.47$ [34], is capable of forming both types of hydrogen bonds with probe molecule such as 4AP. In such hydrogen-bonded systems, the fundamental condition for a correct description of the spectral properties of the probe is an accurate determination of the respective contributions of the probe–solvent non-specific and specific hydrogen bond interactions. This information can be obtained from



Scheme 1. (a) Chemical structure of 4-aminophthalimide (4AP) and (b) illustration of hydrogen bonds A, B₁, B₂, B₃, B₄, C₁ and C₂ formed by 4AP with water molecules.

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