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Role of the intermolecular and intramolecular hydrogen bonding on the excited-state proton transfer behavior of 3-aminophthalimide (3AP) dimer

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ABSTRACT

In this work, both the intermolecular and intramolecular hydrogen bonding of 3-aminophthalimide (3AP) dimer complex in the electronically excited state have been investigated theoretically using the time-dependent density functional theory (TDDFT) method. The calculated infrared spectrum of the hydrogen-bonded 3AP dimer complex for the S_1 state shows that the C=O and H–N bonds involved in the intramolecular hydrogen bond $C_3{=}O_5\cdots H_8{-}N_6$ and intermolecular hydrogen bond $C_1{=}O_4\cdots H_{7'}{-}N_{2'}$ which are markedly red-shifted compared with those predicted for the ground state. The calculated length of the two hydrogen bonds $C_3{=}O_5\cdots H_8{-}N_6$ and $C_1{=}O_4\cdots H_{7'}{-}N_{2'}$ are significantly shorter in S_1 state than in the ground state. However, the bond lengths of the intramolecular hydrogen bond $C_{3'}{=}O_5\cdots H_{8'}{-}N_{6'}$ and intermolecular hydrogen bond $C_{1'}{=}O_{4'}\cdots H_7{-}N_2$ nearly unchanged upon electronic excitation to the S_1 state. Thus, the intramolecular hydrogen bond $C_3{=}O_5\cdots H_8{-}N_6$ and intermolecular hydrogen bond $C_1{=}O_4\cdots H_{7'}{-}N_{2'}$ of the hydrogen-bonded 3AP dimer complex are stronger in the electronically excited state than in the ground state. Moreover, it has been demonstrated that the excited-state proton transfer reaction is facilitated by the electronic excited-state hydrogen bond strengthening.

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1. Introduction

It is well-known that hydrogen bonds play a critical role for structure and function of molecules [1–6]. Both intra- and intermolecular hydrogen bonding have a significant effect on chemical behavior, especially on the excited state properties [7–12]. For instance, the photophysics and photochemistry of chromophores in hydrogen bonding surroundings can be remarkablely tuned by the intermolecular hydrogen bonding in electronic excited states [13–29]. Zhao and co-workers has been demonstrated that the hydrogen bond strengthening behavior in electronic excited states can significantly facilitate the internal conversion, photoinduced electron transfer, proton transfer reactions, etc [30–35].

Aminophthalimides, which can form intermolecular hydrogen bonds with solvent molecules and with each other, have some important structural features in common with the nucleic acid bases [36–42]. In our recent works, we have investigated the excited state hydrogen bonding dynamics of 4-aminophthalimide in hydrogen-donating water solvent by theoretical computation [43]. We have demonstrated that the intermolecular hydrogen bonds are significantly strengthened in the electronically excited state in 4AP systems. Further more, the hydrogen-bonded 3-aminophthalimide dimer ($3AP_2$) complex is also aroused our great interest in there intra- and intermolecular hydrogen bond. Chen and Topp used infrared spectroscopy under jet-cooled condition in both the ground and excited states to determine the structural geometry of the hydrogen-bonded $3AP_2$ complex [44]. They testified the $3AP_2$ is favored a structure that is doubly hydrogen bonded *via* the 4, 7 positions (see Fig. 1). Moreover, they inferred that maybe the hydrogen bond of $3AP_2$ undergo proton transfer in the excited state by analysis the infrared spectrum of the hydrogen-bonded $3AP_2$ complex. Chen and Topp have demonstrated for the first time that excited state proton transfer reaction is facilitated by the electronic excited state hydrogen bond strengthening [44]. Thus, the intra- and intermolecular hydrogen bonding of the hydrogen-bonded $3AP_2$ complex may be strengthened and strong enough to induce the proton transfer reaction in the excited state. Whether or not the hydrogen-bonded $3AP_2$ complex undergoes proton transfer reaction in the excited state? What about the details of the proton transfer reaction? In view of this, we are motivated to theoretically study the excited state property of the hydrogen-bonded $3AP_2$ complex, based on the experimental results.

In the present work, we have investigated the hydrogen-bonded $3AP_2$ complex using the time-dependent density functional theory (TDDFT) method for the calculations of the excited state minimum geometries, electronic excitation energies. The TDDFT method has been demonstrated to be a reliable tool for the calculation of the infrared spectra in the electronically excited state [45–50]. There-

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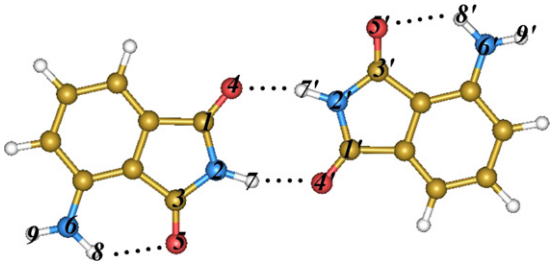

Fig. 1. Optimized geometric structure of the hydrogen-bonded $3AP_2$ complex in ground state.

fore, the IR spectra of the hydrogen-bonded $3AP_2$ complex in different electronic states are also calculated by the TDDFT method. We focused our attention on the transient changes of intra- and intermolecular hydrogen bonds in the early time of electronic excitation. In particular, the role of this transient changes on excited state proton transfer of the hydrogen-bonded $3AP_2$ complex was analyzed in detail. In this work, we theoretically demonstrated that the intermolecular hydrogen bond $C_1{=}O_4\cdots H_{7'}{-}N_{2'}$ and intramolecular hydrogen bond $C_3{=}O_5\cdots H_8{-}N_6$ of the hydrogen-bonded 3AP dimer complex are dramatically strengthened in electronically excited state yet the other intermolecular hydrogen bond $C_{1'}{=}O_{4'}\cdots H_7{-}N_2$ and intramolecular hydrogen bond $C_{3'}{=}O_{5'}\cdots H_{8'}{-}N_{6'}$ are almost unchanged upon photoexcitation. Meanwhile, the strengthened intra- and intermolecular hydrogen bond are liable to take excited-state single proton transfer reaction. Herein, the excited-state proton transfer process should be tightly associated with the intra- and intermolecular hydrogen bond strengthening in the electronic excited state.

2. Theoretical methods

The ground state geometric optimizations of the 3AP monomer and the hydrogen-bonded dimer were performed using the density functional theory (DFT) with Becke's three-parameter hybrid exchange function with Lee–Yang–Parr gradient-corrected correlation (B3LYP) functional [51]. The time-dependent density functional theory (TDDFT) method with B3LYP functional was used to investigate the excited state electronic structures [51–53]. The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as basis sets [52]. At the same time, fine quadrature grids 4 were employed. Harmonic vibrational frequencies in the ground state and the excited state were determined by diagonalization of the Hessian [54]. The excited-state Hessian was obtained by numerical differentiation of analytical gradients using central differences and default displacements of 0.02 Bohr [55]. The infrared intensities were determined from the gradients of the dipole moment. All the quantum chemistry calculations were carried out using the TURBOMOLE program suite [51–55].

Table 2
Calculated electronic excitation energies (nm) and corresponding oscillator strengths of 3AP monomer and dimer.

	3AP	3AP dimer
S_1	361 (0.097) H → L 96.2%	367 (0.226) H → L+1 48.9% H − 1 → L 47.6%
Exp.	376	383
S_2	320 (0.001)	364 (0.000)
S_3	280 (0.004)	348 (0.001)
S_4	272 (0.000)	347 (0.000)

3. Results and discussion

Structures of 3AP monomer and dimer in ground state are calculated using B3LYP density functional theory with the TZVP basis set. The optimized conformation of isolated 3AP shows that only the two hydrogen atoms of the amino are not on the plane of the 3AP molecule. The dihedral angle between the plane of 3AP molecule and N_6–H group is 13°. Both the 3AP monomer and dimer are of planar conformations. The dihedral angle of $C_1{-}O_4\cdots H_{7'}{-}N_{2'}$ is 0°. Fig. 1 shows the optimized geometric structure of the hydrogen-bonded $3AP_2$ complex. Some important atoms are also labeled in Fig. 1. One can find that two intermolecular hydrogen bonds $C_1{=}O_4\cdots H_{7'}{-}N_{2'}$ and $C_{1'}{=}O_{4'}\cdots H_7{-}N_2$, and two intramolecular hydrogen bonds $C_3{=}O_5\cdots H_8{-}N_6$ and $C_{3'}{=}O_{5'}\cdots H_{8'}{-}N_{6'}$ can be formed between the two 3AP molecules. Some geometrical parameters of 3AP monomer and dimer are listed in Table 1. From the listed bond lengths and bond angles, it can be clearly seen that the hydrogen-bonded $3AP_2$ complex is of good symmetry in ground state. The two 3AP molecules of the hydrogen-bonded $3AP_2$ are completely the same in the ground state.

The electronic excitation energies and corresponding oscillator strengths of the 3AP monomer and dimer are calculated using the TDDFT method and presented in Table 2. One can note that the S_1 state has the largest oscillator strength for both the isolated 3AP and the hydrogen-bonded $3AP_2$ complex. Hence, the absorption maxima located in the S_1 state. The S_1 absorption peak is calculated to be at 361, 367 nm for the 3AP monomer and dimer, respectively. The slightly redshift is induced by the intermolecular hydrogen bonding interaction. Meanwhile, the electronic excitation energies for all the

Table 1
Summary of the geometrical parameters of 3AP dimer in ground and S_1 excited state. The bond distances and the bond angles are in angstrom and degree, respectively.

	Dimer				Monomer	
	S_0	S_1			S_0	S_1
		Normal	Tautomer a	Tautomer b		
$L_{O_4\cdots H_{7'}}$	1.920	1.814	1.868	1.000		
$L_{O_{4'}\cdots H_7}$	1.920	1.933	1.811	1.954		
$L_{C_1=O_4}$	1.218	1.241	1.229	1.317	1.207	1.226
$L_{C_{1'}=O_{4'}}$	1.218	1.219	1.222	1.222		
$L_{N_2-H_7}$	1.024	1.024	1.032	1.019	1.009	1.009
$L_{N_{2'}-H_{7'}}$	1.024	1.031	1.027	1.795		
$L_{O_5\cdots H_8}$	2.297	1.984	1.023	2.288	2.299	1.998
$L_{O_{5'}\cdots H_{8'}}$	2.297	2.287	2.301	2.074		
$L_{C_3=O_5}$	1.215	1.241	1.300	1.229	1.216	1.242
$L_{C_{3'}=O_{5'}}$	1.215	1.216	1.214	1.228		
$L_{N_6-H_8}$	1.009	1.027	1.730	1.011	1.009	1.027
$L_{N_{6'}-H_{8'}}$	1.009	1.009	1.009	1.023		
$\delta_{C_1-O_4\cdots H_{7'}-N_{2'}}$	−0.0	0.7	−0.3	146.2		
$\delta_{C_{1'}-O_{4'}\cdots H_7-N_2}$	0.2	0.4	0.1	−3.7		

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