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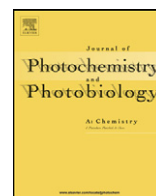


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# Role of the intermolecular and intramolecular hydrogen bonding on the excited-state proton transfer behavior of 3-aminophthalimide (3AP) dimer

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## ARTICLE INFO

### Article history:

Received 28 June 2010

Received in revised form

27 September 2010

Accepted 15 October 2010

Available online 23 October 2010

### Keywords:

Excited state

Hydrogen bonding

Proton transfer

Infrared spectra

## 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 remarkably 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].

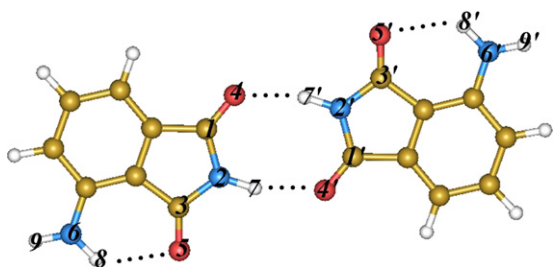
Aminophthalimides, which can form intermolecular hydrogen bonds with solvent molecules and with each other, have some important structural features in common with the nucleic acid bases [36–42]. In our recent works, we have investigated the excited state hydrogen bonding dynamics of 4-aminophthalimide 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<sub>2</sub> complex in ground state.

fore, the IR spectra of the hydrogen-bonded 3AP<sub>2</sub> 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<sub>2</sub> 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- $\zeta$  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

**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 $\rightarrow$ L 96.2%	367 (0.226) H $\rightarrow$ L + 1 48.9% H $\rightarrow$ 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)

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].

## 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  $13^\circ$ . Both the 3AP monomer and dimer are of planar conformations. The dihedral angle of  $C_1-O_4 \cdots H_{7'}-N_{2'}$  is  $0^\circ$ . Fig. 1 shows the optimized geometric structure of the hydrogen-bonded 3AP<sub>2</sub> 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<sub>2</sub> complex is of good symmetry in ground state. The two 3AP molecules of the hydrogen-bonded 3AP<sub>2</sub> 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<sub>2</sub> 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		
$LO_4 \cdots H_{7'}$	1.920	1.814	1.868	1.000		
$LO_{4'} \cdots H_7$	1.920	1.933	1.811	1.954		
$LC_1=O_4$	1.218	1.241	1.229	1.317	1.207	1.226
$LC_{1'}=O_{4'}$	1.218	1.219	1.222	1.222		
$LN_2-H_7$	1.024	1.024	1.032	1.019	1.009	1.009
$LN_{2'}-H_{7'}$	1.024	1.031	1.027	1.795		
$LO_5 \cdots H_8$	2.297	1.984	1.023	2.288	2.299	1.998
$LO_{5'} \cdots H_{8'}$	2.297	2.287	2.301	2.074		
$LC_3=O_5$	1.215	1.241	1.300	1.229	1.216	1.242
$LC_{3'}=O_{5'}$	1.215	1.216	1.214	1.228		
$LN_6-H_8$	1.009	1.027	1.730	1.011	1.009	1.027
$LN_{6'}-H_{8'}$	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		

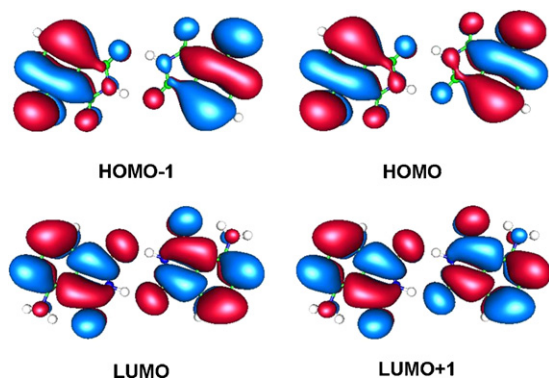


Fig. 2. Frontier molecular orbitals (MOs) of the hydrogen-bonded 3AP<sub>2</sub> complex.

excited states of the 3AP dimer are lower than 3AP monomer correspondingly due to the formation of intermolecular hydrogen bond. Moreover, our calculated electronic excitation energies of the S<sub>1</sub> for both the 3AP monomer and dimer are in good agreement with the experimental results. The orbital transition contributions for the S<sub>1</sub> state of the isolated 3AP and the hydrogen-bonded 3AP<sub>2</sub> complex are also presented in Table 2. It can be seen that four main orbitals are involved in the S<sub>1</sub> state of the hydrogen-bonded 3AP<sub>2</sub> complex: HOMO–1, HOMO, LUMO, LUMO+1.

To depict the nature of the low-lying electronically excited states, the frontier molecular orbitals (MOs) of the hydrogen-bonded 3AP dimer are shown in Fig. 2. Herein, we only show the HOMO–1, HOMO, LUMO, and LUMO+1 orbitals, since the S<sub>1</sub> state of the hydrogen-bonded 3AP dimer is associated with these orbitals. It can be clearly seen that the electron densities of all the orbitals are localized in the whole molecule, so the tentative conclusion that one 3AP molecule reverts to the ground state and the other molecule in the excited state [44]. The two 3AP molecules of the hydrogen-bonded 3AP dimer are all involved in excitation. In addition, one can find that the HOMO–1, HOMO and LUMO, LUMO+1 orbitals are the  $\pi$  and  $\pi^*$  character, respectively. Therefore, it is evident that the S<sub>1</sub> state is the  $\pi\pi^*$  feature. Moreover, it is distinct that the transitions from HOMO–1 to LUMO and from HOMO to LUMO+1 involve the intramolecular charge redistribution from the amino group to the carbonyl group moiety. Thus, the strength of the intra- and intermolecular hydrogen bond may be changed in the S<sub>1</sub> state.

The geometric structures of the 3AP monomer and dimer in the excited state are optimized using the TDDFT method. The details of the geometrical parameters for the 3AP monomer and dimer both in the ground state and excited state are shown in Table 1. It can be clearly seen that the symmetrical structure of the hydrogen-bonded 3AP<sub>2</sub> complex disappeared in the electronic excited state. We can find that the length of intramolecular hydrogen bond C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub> between O<sub>5</sub> and H<sub>8</sub> atoms is obviously shortened from 2.297 Å in ground state to 1.984 Å in excited state. At the same time, the bond lengths of both the C<sub>3</sub>=O<sub>5</sub> and H<sub>8</sub>–N<sub>6</sub> groups are slightly increased during the hydrogen-bonded complexes are excited to the S<sub>1</sub> state. Moreover, the length of the intermolecular hydrogen bond C<sub>1</sub>=O<sub>4</sub>...H<sub>7</sub>–N<sub>2</sub> between O<sub>4</sub> and H<sub>7</sub> is also shortened from 1.920 to 1.814 Å due to the electronic excitation to the S<sub>1</sub> state of the hydrogen-bonded 3AP<sub>2</sub> complex. Meanwhile, the bond lengths of both the C<sub>1</sub>=O<sub>4</sub> and H<sub>7</sub>–N<sub>2</sub> groups are also slightly increased in the S<sub>1</sub> state. However, the length of the other intramolecular hydrogen bond C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub> and intermolecular hydrogen bond C<sub>1</sub>=O<sub>4</sub>...H<sub>7</sub>–N<sub>2</sub> are almost unchanged in the electronic excited state upon photoexcitation. The calculated results testify that the intramolecular hydrogen bond C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub> and

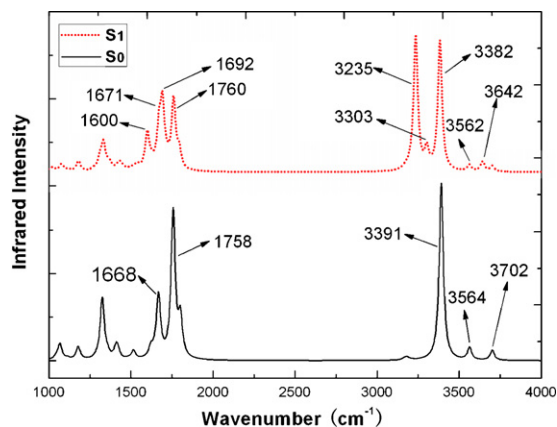


Fig. 3. Calculated vibrational absorption spectra of the 3AP dimer in different electronic states. Ground-state assignments: 1668 (intra C=O stretch); 1757 (inter C=O stretch); 3391 (imide donor NH); 3563 (amide donor NH); 3702 (amino free NH).

intermolecular hydrogen bond C<sub>1</sub>=O<sub>4</sub>...H<sub>7</sub>–N<sub>2</sub> are considerably strengthened in electronic excited state while the other intermolecular hydrogen bond C<sub>1</sub>=O<sub>4</sub>...H<sub>7</sub>–N<sub>2</sub> and intramolecular hydrogen bond C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub> of the hydrogen-bonded 3AP<sub>2</sub> complex are almost unchanged in the electronically excited state.

To depict the transient change of the hydrogen bond in the early time of electronic excitation, the infrared spectra of the ground-state and S<sub>1</sub> state for the hydrogen bonded 3AP<sub>2</sub> complexes are calculated using the DFT and TDDFT method. Fig. 3 shows the calculated results. The calculated vibrational absorption spectra are in good agreement with the experimental results recorded in the ground-state infrared spectra of jet-cooled for 3AP<sub>2</sub> in the 3100–3700 cm<sup>–1</sup> region [44]. As shown in the IR spectrum got by Chen et al., there are three broad absorption frequencies between 3100 and 3700 cm<sup>–1</sup> in the ground state: 3218 (imide donor NH), 3426 (amino internal donor NH to O=C<) and 3553 (amino free NH), while the situation in the excited state is more complex and not easy to identify all the frequencies to the corresponding bond: one weak band near 3000 cm<sup>–1</sup>, a very strong band at 3193 cm<sup>–1</sup>, and three weaker bands at 3422, 3479 and 3552 cm<sup>–1</sup>. The wave number 1668 cm<sup>–1</sup> is the donor C=O stretching band of the intramolecular hydrogen bonds C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub> and C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub>. Upon electronic excitation, the C<sub>3</sub>=O<sub>5</sub> stretching band is drastically red-shifted to 1600 cm<sup>–1</sup> yet the C<sub>3</sub>=O<sub>5</sub> stretching band is nearly unchanged. At the same time, the amine donor N<sub>6</sub>–H<sub>8</sub> group stretching band of the intramolecular hydrogen bonds C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub> is markedly red-shifted by 261 cm<sup>–1</sup> from 3564 cm<sup>–1</sup> in ground state to 3303 cm<sup>–1</sup> in S<sub>1</sub> state, and the stretching band of N<sub>6</sub>–H<sub>8</sub> group is slightly shifted from ground state to excited state. Moreover, the C<sub>1</sub>=O<sub>4</sub> and N<sub>2</sub>–H<sub>7</sub> stretching band of the intermolecular hydrogen bond C<sub>1</sub>=O<sub>4</sub>...H<sub>7</sub>–N<sub>2</sub> are also drastically red-shifted yet the C<sub>1</sub>=O<sub>4</sub> and H<sub>7</sub>–N<sub>2</sub> stretching band of the intermolecular hydrogen bond C<sub>1</sub>=O<sub>4</sub>...H<sub>7</sub>–N<sub>2</sub> are almost unchanged upon electronic excitation to the S<sub>1</sub> state of the hydrogen-bonded 3AP<sub>2</sub> complex. From the calculated results of the IR spectrum, the behavior of the intramolecular hydrogen bond C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub> and intermolecular hydrogen bond C<sub>1</sub>=O<sub>4</sub>...H<sub>7</sub>–N<sub>2</sub> strengthened while the other intermolecular hydrogen bond C<sub>1</sub>=O<sub>4</sub>...H<sub>7</sub>–N<sub>2</sub> and intramolecular hydrogen bond C<sub>3</sub>=O<sub>5</sub>...H<sub>8</sub>–N<sub>6</sub> of the hydrogen-bonded 3AP dimer unchanged in electronically excited state can be strongly supported.

We have got two tautomers of hydrogen-bonded 3AP<sub>2</sub> complex in electronic excited state by TD-B3LYP method. Fig. 4 shows the optimized geometric structure of the two tautomers. The structures we optimized have been compared with the exper-



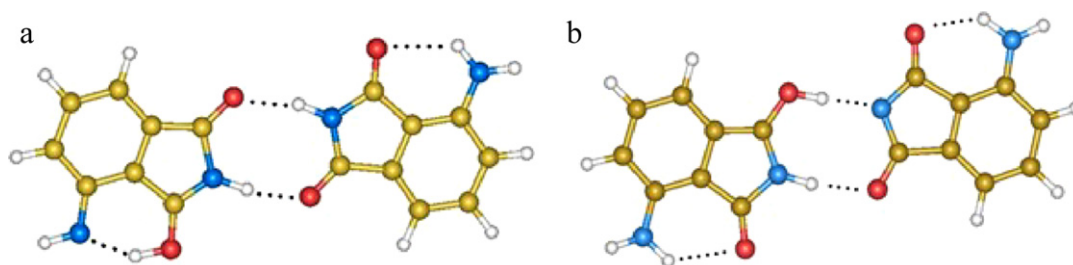


Fig. 4. Optimized geometric structures of the two tautomers of 3AP dimer.

imental results got by Chen and Topp [44]. Tautomer a and b are refer to the intramolecular single proton transfer and intermolecular single proton transfer, respectively. The excited state single proton transfer behavior in hydrogen-bonded 3AP<sub>2</sub> complex is quite different from the phenomenon of excited state double proton transfer in other dual hydrogen-bonded dimer such as 7-Azaindole dimer [56–59]. From the above discussion, hydrogen-bonded 3AP<sub>2</sub> complex is of good symmetry in ground state but the symmetrical structure disappeared in the electronic excited state upon photoexcitation. One intramolecular hydrogen bond and one intermolecular hydrogen bond are strengthened while the other intramolecular hydrogen bond and one intermolecular hydrogen bond are almost unchanged in electronic excited state. The single proton transfer in the excited state becomes a barrierless process since the excited-state strengthening of the intramolecular hydrogen bond  $C_3=O_5 \cdots H_8-N_6$  and intermolecular hydrogen bond  $C_1=O_4 \cdots H_7-N_2$ . However, due to the other intermolecular hydrogen bond  $C_1'=O_4' \cdots H_7'-N_2'$  and intramolecular hydrogen bond  $C_3'=O_5' \cdots H_8'-N_6'$  of the hydrogen-bonded 3AP<sub>2</sub> complex unchanged in electronically excited state, when the first proton is transfer, the second proton is difficult to transfer in the excited state. The single proton transfer is significantly associated with that the one set of inter- and intramolecular hydrogen bonding is strengthened and another is not. Therefore, the intra- and intermolecular hydrogen bonding in the electronic excited state plays a very important role on the excited-state single proton transfer. The excited-state single proton transfer should be facilitated by the hydrogen bond strengthening in excited states.

#### 4. Conclusion

In summary, the electronic excited state properties of hydrogen-bonded 3AP<sub>2</sub> complex were investigated by TDDFT method. According to the optimized geometry of the hydrogen-bonded 3AP<sub>2</sub> complex, two intermolecular hydrogen bonds  $C_1=O_4 \cdots H_7-N_2$ ,  $C_1'=O_4' \cdots H_7'-N_2'$  and two intramolecular hydrogen bonds  $C_3=O_5 \cdots H_8-N_6$ ,  $C_3'=O_5' \cdots H_8'-N_6'$  exist in the hydrogen-bonded 3AP<sub>2</sub> complex. Analysis of the hydrogen bond lengths revealed that the intramolecular hydrogen bond  $C_3=O_5 \cdots H_8-N_6$  and intermolecular hydrogen bond  $C_1=O_4 \cdots H_7-N_2$  are sharply shortened in electronic excited state. The IR spectra of the ground state and excited state of the hydrogen-bonded 3AP<sub>2</sub> complex were also calculated. The calculated stretching vibrational modes of the C=O and H–N of the intramolecular hydrogen bond  $C_3=O_5 \cdots H_8-N_6$  and intermolecular hydrogen bond  $C_1=O_4 \cdots H_7-N_2$  are markedly red-shifted upon photoexcitation. We were demonstrated that the intramolecular hydrogen bond  $C_3=O_5 \cdots H_8-N_6$  and intermolecular hydrogen bond  $C_1=O_4 \cdots H_7-N_2$  are significantly strengthened in the electronically excited state. Moreover, the hydrogen-bonded 3AP<sub>2</sub> complex takes proton transfer reaction through the two strengthened hydrogen bond. It can be concluded that the excited state proton transfer reaction is facilitated by the electronic excited state hydrogen bond strengthening.

#### Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 20773018) and the Key Laboratory of Industrial Ecology and Environmental Engineering, China Ministry of Education.

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