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ARTICLE

Ground-state and excited-state multiple proton transfer via hydrogen-bonded water wire for 3-Hydroxypyridine

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In this work, the multiple proton transfer reactions in the ground and first excited states of 3-hydroxypyridine (3HP) in aqueous solution have been investigated by using density functional theory and time dependent density functional theory methods. The effect of water wire ($\text{H}_2\text{O}\dots\text{H}_2\text{O}\dots\text{H}_2\text{O}$) on the multiple proton transfer has been elucidated for 3HP. We have confirmed that the multiple proton transfer process can take place more easily in the excited state than in the ground state, and zwitterionic cluster 3-pyridone-(H_2O)₃ (3Py-(H_2O)₃) is the optimal proton transfer product. For the case of neutral 3HP-(H_2O)₃ and zwitterionic 3Py-(H_2O)₃ clusters, the intermolecular hydrogen bonds are demonstrated to be significantly strengthened and weakened respectively in the excited state by comparison with those in the ground state, and these have been discussed in detail. Moreover, a conclusive description of the proton transfer cycle has been revealed on the basis of our calculated transition energies and potential energy profiles. This photocycle can reasonably explain why no fluorescence of the 3HP species in the excited state.

Introduction

Intermolecular hydrogen bonding plays a very important role in many chemical complexes and biological macromolecules as well as physical processes.¹⁻¹⁰ The dynamics of hydrogen bonds in the ground and excited states have been increasingly studied with the use of many different experimental and theoretical techniques.¹¹⁻²⁰ Recently, Zhao *et al.* have theoretically investigated that the hydrogen bonding dynamics in the excited state is associated with electronic spectral shifts, tuning effects on photochemistry, and fluorescence quenching, and so forth.¹⁶⁻²² Many interesting mechanisms of hydrogen bond dynamics in the ground and excited states have been preensively proposed and demonstrated. In particular, the intermolecular proton transfer (PT), which is one of the most fundamental reactions in many photochemical processes.²³⁻²⁶ Fang has reported that the triple-proton-transfer reactions can occur in the ground and excited states of 7-hydroxyquinoline in

methanol solution.²⁶ Leutwyler *et al.* pioneered theoretical works to investigate the mechanism of excited-state intermolecular proton/hydrogen transfer reactions for 7-hydroxyquinoline along hydrogen-bonded solvent wires.^{27,28} Simultaneously, they have also demonstrated that the excited state PT reaction stays on the $\pi\pi^*$ state surface, whereas the excited state hydrogen transfer reaction takes place in the $\pi\sigma^*$ state.^{27,28} Moreover, Sobolewski *et al.* have demonstrated for the first time that the excited-state hydrogen transfer is driven by repulsive $\pi\sigma^*$ states,²⁹ and Ashfold *et al.* have further confirmed that the photochemical mechanism of repulsive $\pi\sigma^*$ state by means of a new experimental technique (total kinetic energy release spectroscopy).³⁰ Nowadays, the PT process of many novel biological molecules needs to be sequentially confirmed, which is very useful to insight into the supramolecular structures and photochemical processes.²⁷⁻³²

3-pyridone (3Py) and 3-hydroxypyridine (3HP) have attracted considerable attention, due to a wide range of drugs of different

pharmacological functions.³³⁻³⁸ Furthermore, they have been used as probes to characterize the binding sites in human serum albumin.³⁹⁻⁴⁸ Early in 1955, Metzler and Snell have investigated the equilibrium between zwitterionic (3Py) and neutral (3HP) forms of the 3-hydroxypyridines in dioxane-water and alcohol-water mixtures, and demonstrated the zwitterionic form predominate in neutral aqueous solutions.⁴⁶ After this earlier study, Bridges *et al.* reported the zwitterion (3Py) has fluorescent, but the neutral form (3HP) has no fluorescent in aqueous solution.⁴⁷ It is obvious that the properties have been gradually presented for the 3HP/3Py system in these works.⁴⁶⁻⁴⁸ However, these explorations provide only indirect information on the conversion process of the studied 3HP/3Py system.

Recently, Abou-Zied *et al.* have demonstrated that the hydrogen-bonded wire with three water molecules (*i.e.* H₂O...H₂O...H₂O) is a comfortable long bridge to connect the polar centers of 3HP/3Py system.⁴⁹ Moreover, the absorption spectra of 3HP/3Py have been measured in the 1,4-dioxane/water binary mixtures for different water content.⁴⁹ There is an absorption band appeared in the pure 1,4-dioxane solvent, which peak at 278 nm and belongs to 3HP.⁴⁹ Upon increasing the water content, the absorption peak of 3Py (315 nm) starts to emerge and its intensity increases, whereas the intensity of 3HP peak decreases.⁴⁹ That is to say, 3HP in water solution undergo tautomeric interconversion between 3HP and 3Py forms in the ground state through the multiple PT with the hydrogen bond wire of three water molecules (H₂O...H₂O...H₂O). However, the particular ground state PT process of 3HP-(H₂O)₃ is still remains opaque. Whether the multiple PT reaction can happen in the excited state for 3HP-(H₂O)₃? What is the role of water wire for the multiple PT reaction in 3HP-(H₂O)₃? All of these questions have not a complete explanation. Thus, the multiple PT reaction of 3HP-(H₂O)₃ in the ground and excited states have been proposed. A comparative analysis between the ground and excited states, makes us more in-depth understand the interior properties of 3HP/3Py system.

Consequently, in this paper, we focused our attention on the multiple PT reaction via a hydrogen-bonded water wire for 3HP in the ground and excited states. The optimized potential energy curves for the multiple PT in the ground and excited states have been obtained for 3HP-(H₂O)₃ cluster. Moreover, the most reasonable multiple PT product has been found in the ground and excited states, which is zwitterionic cluster 3Py-(H₂O)₃. The change of intermolecular hydrogen bonded lengths and the shift of

corresponding stretching frequencies have also been discussed in detail of 3HP-(H₂O)₃ and 3Py-(H₂O)₃ clusters in the ground and excited states.

Computational details

In our work, the geometry optimizations of the isolated monomers and the hydrogen-bonded clusters considered here were performed for the ground state, using density functional theory (DFT) with Becke's three-parameter hybrid exchange function with the Lee-Yang-Parr gradient-corrected correlation functional (B3-LYP functional).^{50,51} The excited-state electronic structures were obtained using time-dependent density functional theory (TDDFT) with the B3-LYP hybrid functional. The triple- ζ valence quality with one set of polarization functions (TZVP) was chosen as the basis sets throughout.^{52,53} Fine quadrature grids 4 were employed.⁵³ The IR intensities were determined from the gradients of the dipole moment. All the electronic structure calculations were carried out using the TURBOMOLE program suite.⁵⁰⁻⁵⁵

Results and discussion

The ground state multiple proton transfer process

The DFT calculation has been performed for the bare molecules (3HP and 3Py), and shown that the bare molecules are planar in the ground state. One can find that the hydroxyl group and the nitrogen atom in 3HP are the donor and acceptor groups for hydrogen bond formation in aqueous solvent, respectively. For the bare 3Py molecule, it is a zwitterionic molecule, O⁻ and N⁺-H groups of 3Py are also the acceptor and donor groups for hydrogen bond formation. Hence, the bare molecule (3HP or 3Py) and the water solvent are capable of forming complicated hydrogen bonded interactions. As

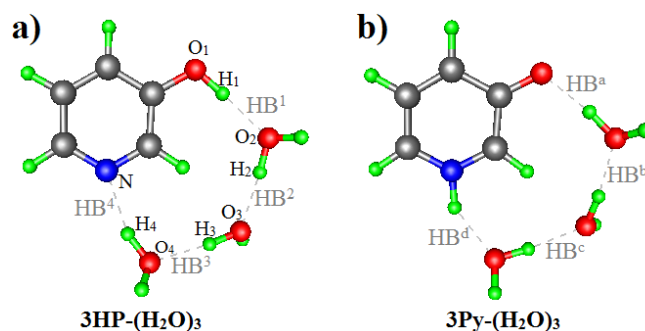


Fig. 1 Most stable geometric structures of 3HP-(H₂O)₃ and 3Py-(H₂O)₃ clusters in the ground state.

mentioned in the introduction section, the hydrogen-bonded wire with three water molecules is comfortable and stable, which is necessary to connect the functional groups of the bare molecule.⁴⁹ Thus, calculated most stable geometric structure of the ground state 3HP-(H₂O)₃ cluster has been presented in Fig. 1a, with numbering each of the hydrogen bond and atoms of intermolecular hydrogen-bonded networks. In 3HP-(H₂O)₃ cluster, the corresponding hydrogen bonds diverge the plane of the 3HP molecule, and all the H₂O molecules resides out of the plane. Obviously, this cluster is complicated spatial structure in the ground state.

Now, we have the purpose to study the assistant effect of the water wire (H₂O...H₂O...H₂O) on the ground state multiple PT reaction of 3HP-(H₂O)₃ system. In order to compare, the ground state optimized energy profile along the O₁-H₁ bond of 3HP monomer has been calculated and displayed in Fig. 2a. The energy of 3HP monomer is increased continuously due to the lengthening of O₁-H₁ bond. Through the observation of molecular structure in Fig. 1a, for better studying the PT mechanism of 3HP-(H₂O)₃ cluster, we design the three different types of PT paths. Three types of possible PT processes have been presented in Scheme 1. In our design, the water wire is regarded as a whole due to their functions are the same (both proton donor and acceptor groups). The stepwise mechanism is distinctly divided into two types (Type 1 and Type 2), when one proton is moving, the others are also transfers via the intermolecular hydrogen bonded interactions. Type 3 is a concerted mechanism, the two protons begin to move simultaneously. The three types of potential energy curves are calculated and scanned by increasing the bond length with a step of 0.1 Å in Fig. 2b. It is noted that each point in the energy profile is sufficiently optimized. It can be clearly seen that the multiple PT process successfully occurs via the three different types of reaction channels in the ground state. The multiple PT reaction with Type 2 mechanism is the smallest barrier process in the ground state, the other two potential energy curves have higher barriers for the PT reaction. Therefore, the ground state multiple PT reaction along the hydrogen bond O₄-H₄...N is the most possible reaction channel. In addition, it is interesting to make a comparison between Fig. 2b (Type 1) and Fig. 2a. One can clearly see that the water cluster can directly induce the whole multiple PT process in the ground state. The energy barriers for the PT reaction become visibly reduced because of the effect of the water cluster, and water wire is the PT channel.

Optimized energy profile for the ground state of 3HP-(H₂O)₃ along the hydrogen bond HB^d (O₄-H₄...N) by fixing the O₄-H₄ bond

length in different values has been rearranged, which is recorded in Fig. 2c. At the same time, some key points of optimized geometric conformations have been revealed. For this multiple PT process, we can divide it into two parts for analyzing PT mechanism. It was seen as the first stage, when the O₄-H₄ bond length is between 1.0 and 1.6 Å. The lengthening of O₄-H₄ bond would lead the transfer of H₄ to

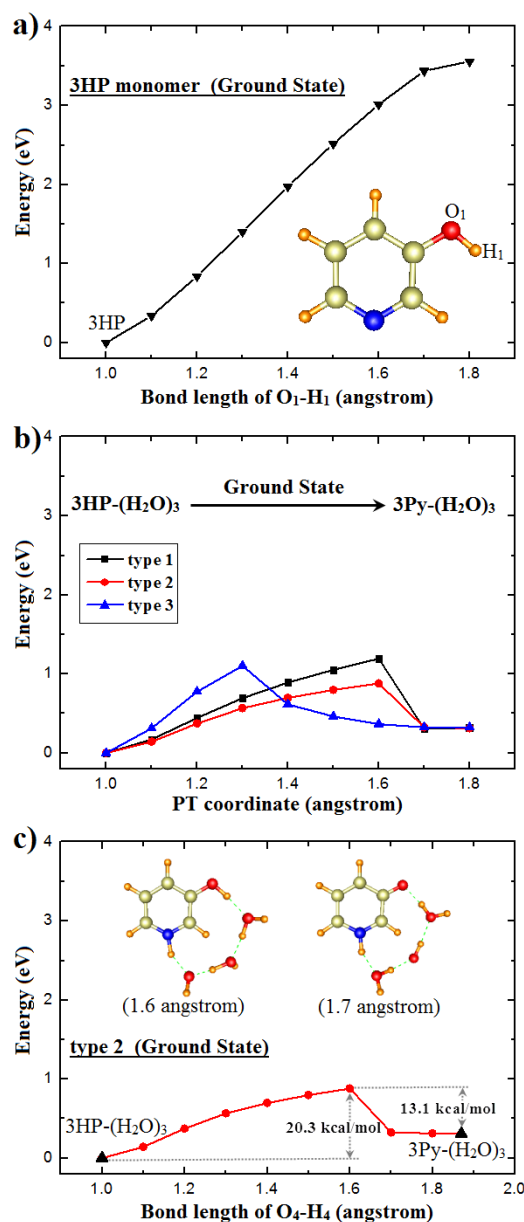
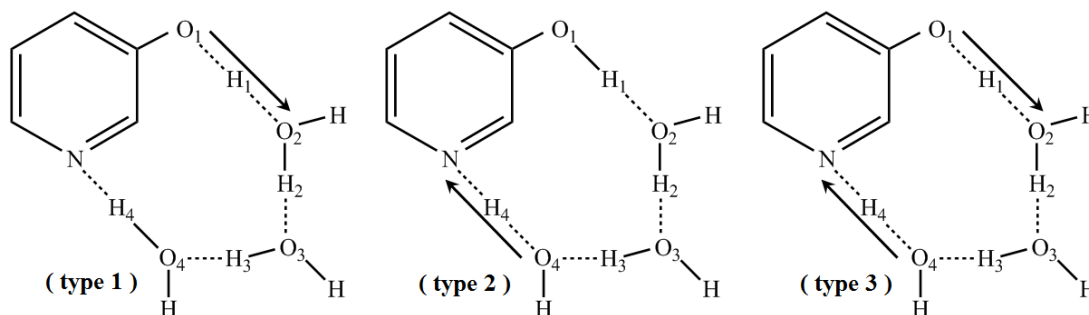


Fig. 2 Calculated potential energy curves. (a) The calculated energy profile of 3HP monomer along the O₁-H₁ bond in the ground state. (b) Calculated potential energy curves along the proton transfer coordinate with different mechanisms in the ground state. (c) Optimization ground state proton-transfer profile for 3HP-(H₂O)₃ cluster along the O₄-H₄ bond.



Scheme 1 Three types of the proton transfer reaction mechanism.

the nitrogen atom in 3HP, but it almost does not influence the rest of two water molecules. The second stage, the range of the O_4-H_4 bond length is 1.6-1.7 Å. This range will appear sequentially multiple PT, and induce the rest of two water molecules to complete the whole process of the ground state PT. Moreover, as shown, there is a single barrier (20.3 kcal/mol) in the multiple PT reaction. From our theoretical calculation, it has one of the most stable structure for $3Py-(H_2O)_3$ in the ground state, when the O_4-H_4 bond length is 1.87 Å. In order to facilitate our understanding, the detailed geometric structure of the ground state $3Py-(H_2O)_3$ cluster has been shown in Fig. 1b. The optimized energy profile can illustrate that the $3HP-(H_2O)_3$ cluster is more stable than the $3Py-(H_2O)_3$ cluster, which is in accordance with the previous works using ab initio methods.⁴⁹ The thermodynamic equilibrium is beneficial to the reverse ground state PT reaction, whereas the potential barrier of the reverse reaction is computed to be 13.1 kcal/mol, the reverse PT reaction may occur but not very easily. It is distinct that the ground state $3HP-(H_2O)_3$ and $3Py-(H_2O)_3$ clusters can coexist in aqueous solvent.

Absorption spectra and frontier molecular orbitals

The electronic excitation energies and corresponding oscillator strengths of the 3HP and 3Py monomers as well as two hydrogen bonded clusters are demonstrated in Table 1. It can be clearly found that the absorption maxima for four systems are located in higher energy levels than the first excited (S_1) state. The calculated maximum absorption peaks of isolated 3HP and 3Py are located at 280 and 328 nm due to electronic excitation to the S_1 state, respectively. Similarly, the calculated absorption peaks are 278 and 329 nm of $3HP-(H_2O)_3$ and $3Py-(H_2O)_3$ clusters in the S_1 state. It is clear that, our calculation results are in good agreement with the spectral results recorded in the experiment.⁴⁹ According to our calculated electronic excitation energies, moreover, we can expect that the 3HP and 3Py moiety can be electronically excited to the S_1

state upon photoexcitation, while the H_2O wire in $3HP-(H_2O)_3$ and $3Py-(H_2O)_3$ will remain in the ground state. Through the above analysis, in the present work, we only consider the characteristics and mechanisms of hydrogen bonded $3HP-(H_2O)_3$ and $3Py-(H_2O)_3$ clusters in the S_1 state.

Table 1 The excited energy (nm) and corresponding oscillator strengths (in the parenthesis) of two monomers and $3HP-(H_2O)_3$ and $3Py-(H_2O)_3$ clusters in different electronic state.

	3HP	3Py	3HP-(H ₂ O) ₃	3Py-(H ₂ O) ₃
S_1	280 (0.003)	328 (0.090)	278 (0.066)	329 (0.082)
Exp. ⁴⁹			278	315
S_2	261 (0.052)	320 (0.001)	260 (0.003)	320 (0.008)
S_3	254 (0.000)	243 (0.000)	234 (0.000)	244 (0.000)
S_4	215 (0.075)	237 (0.145)	231 (0.005)	237 (0.145)
S_5	206 (0.000)	229 (0.000)	229 (0.002)	228 (0.000)
S_6	205 (0.008)	211 (0.009)	226 (0.001)	210 (0.003)
S_7	187 (0.236)	204 (0.000)	224 (0.089)	204 (0.000)

As we know, the frontier molecular orbitals (MOs) can give the most intuitive explanation of the charge transfer changes.^{1,16,22} From our TDDFT calculations, upon electronic excitation to the S_1 state of the hydrogen bonded $3HP-(H_2O)_3$ and $3Py-(H_2O)_3$ clusters corresponds to the orbital transition from HOMO to LUMO. Therefore, only the HOMO and LUMO orbitals are exhibited in the Fig. 3. By comparing the HOMO and LUMO, the character of $\pi\pi^*$ transfer can be clearly found. And there is more electronic density distribution located around the nitrogen of 3HP and 3Py moiety, and barely electronic density located around the oxygen atom. These results are more conducive to the occurrence of the PT reaction in the S_1 state. Furthermore, in Fig. 3, it should be noted that the electron densities of both the HOMO and LUMO are strictly

localized on the 3HP and 3Py moiety. So it has been vividly demonstrated that the hydrogen-bonded wire ($\text{H}_2\text{O} \cdot \cdot \text{H}_2\text{O} \cdot \cdot \text{H}_2\text{O}$) always stays in its electronic ground state. The distinct observation can just demonstrate the inference of our theoretical electronic excitation energies.

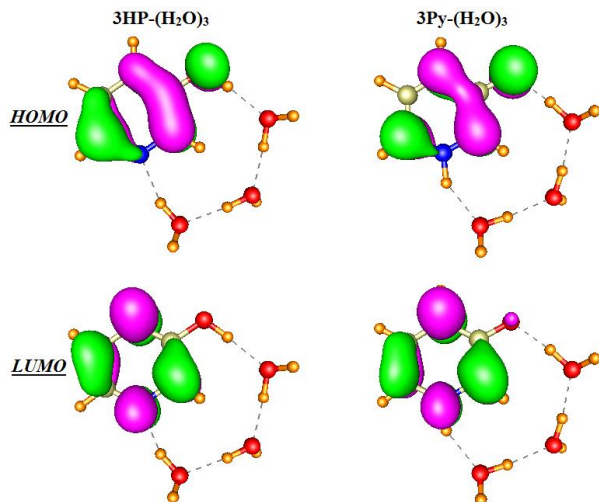


Fig. 3 Frontier molecular orbitals of the hydrogen-bonded 3HP-(H_2O)₃ and 3Py-(H_2O)₃ clusters.

The excited state multiple proton transfer reaction

The excited state multiple PT reaction of 3HP-(H_2O)₃ cluster has been investigated thoroughly. The optimized energy profile along the $\text{O}_1\text{-H}_1$ bond of 3HP monomer in the excited state has been calculated and shown in Fig. 4a. As shown, there is a single barrier (13.1 kcal/mol) in the optimized energy profile of 3HP monomer. Two stable geometric structures have been found in the excited state and their energy is the same, when the $\text{O}_1\text{-H}_1$ bond length is 0.97 and 1.59 Å. For the geometric structure of 1.59 Å, we can see that the hydrogen H_1 already separated from the phenolic group. We assume that there is a reasonable hydrogen transfer path for the hydrogen H_1 , it will be successful transfer. For our better understanding, three types of possible transfer processes have been calculated and presented in Fig. 4b. Our results indicate that the Type 1 is the hydrogen transfer reaction, whereas the Type 2 and 3 paths are the PT process of 3HP-(H_2O)₃ cluster. Furthermore, it is obvious that the multiple PT reaction along the hydrogen bond $\text{O}_4\text{-H}_4 \dots \text{N}$ (Type 2) is the most possible reaction channel in the excited state, which is in accordance with the mechanism of the ground state. There is a competition between hydrogen-transfer and optimized PT reactions in Fig. 4b. The excited state

hydrogen transfer reaction takes place along the Type 1 path, the first hypervalent H_3O radical is temporarily formed and continuous hydrogen transfer reactions happen along a hydrogen-bonded water wire. Whereas, the Type 2 path belongs to the optimized PT reaction, the covalent OH bond is temporarily generated and then complete proton conduction

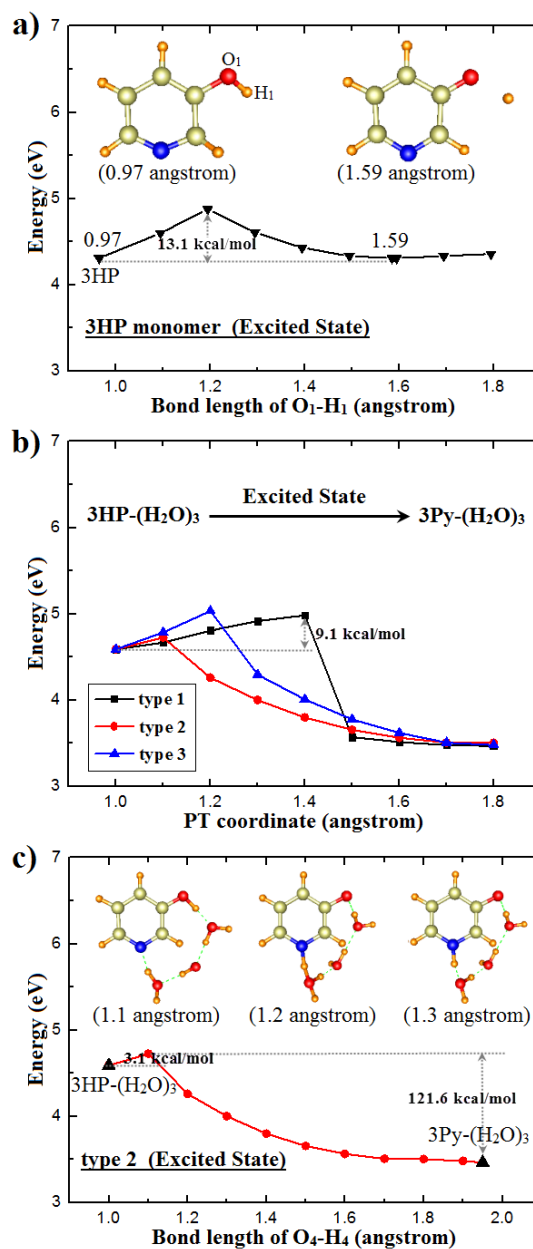


Fig. 4 (a) The calculated energy profile for S_1 state of 3HP monomer. (b) Calculated potential energy curves along the transfer coordinate with different mechanisms in the S_1 state. (c) Optimization proton-transfer profile for 3HP-(H_2O)₃ cluster along the $\text{O}_4\text{-H}_4$ bond in the S_1 state.

appears. We can find that optimized PT takes place more easily than hydrogen transfer for 3HP-(H₂O)₃ in Fig. 4b. Compare Fig. 4a and Fig. 4b (Type 1), the hydrogen transfer energy barrier has been markedly reduced due to the interaction between 3HP and water wire, and three molecules of water act as a “bridge” which assists the hydrogen transfer from the oxygen to nitrogen atoms of 3HP. Moreover, the hydrogen transfer mechanism is in very good agreement with Leutwyler’s works.^{27,28}

In Fig. 4c, we chose the O₄-H₄ bond distances as the potential energy reaction coordinate, and the remaining coordinates were optimized at each step of the reaction. Meanwhile, some key points of optimized geometric structures in this process have been listed in Fig. 4c. One can see that this process has the greatest barrier (3.1 kcal/mol) for frontward excited state potential energy curve, when the O₄-H₄ bond length is 1.1 Å. The excited state multiple PT reaction cannot happen due to the change of the O₄-H₄ bond is only slightly elongated. While the range of the O₄-H₄ bond length is 1.1–1.2 Å, the multiple PT can occur during this section due to continue to extend the O₄-H₄ bond. Nonetheless, the O₄-H₄ bond length is 1.2 Å, the attraction between O₄ and H₄ atoms still exists, so the O₄-H₄ bond doesn't disconnect. Namely, the O₄-H₄ bond is partially broken, H₄-N bond is partially formed. We continue to increase the length of the O₄-H₄ bond, the O₄-H₄ bond will be separated, the excited state multiple PT process is drastically finished. The most stable geometric structure (3Py-(H₂O)₃) has been found in the potential energy curve, when the O₄-H₄ bond length is 1.95 Å. For the excited state multiple PT reaction, the thermodynamic equilibrium in strongly favor of the frontward reaction, due to the quite low energy of excited 3Py-(H₂O)₃ in Fig. 4c. Hence, the excited state multiple PT reaction of 3HP-(H₂O)₃ cluster through a very small barrier would occur favorably. In addition, there is a very big energy barrier (121.6 kcal/mol) on the reverse pathway in the excited state. Therefore, the reverse process from 3Py-(H₂O)₃ to 3HP-(H₂O)₃ can hardly take place.

From our discussions above, the multiple PT reaction of 3HP-(H₂O)₃ cluster can take place successfully via the formation/breaking of covalent bonds in the ground and excited states. The stepwise mechanism (Type 2) of the multiple PT reaction for 3HP-(H₂O)₃ cluster is confirmed in the ground and excited states. We have demonstrated that the proton motion along the intermolecular hydrogen bond O₄-H₄...N takes place first, then the rest of protons transfer along the intermolecular hydrogen bond begins to continuously occur. Furthermore, the excited state PT reaction is

more likely to proceed, because of it is a smaller barrier to be crossed by comparison with those in the ground state and beneficial thermodynamic equilibrium.

A cyclic mechanism of 3HP-(H₂O)₃ and 3Py-(H₂O)₃ clusters

To better analyse two hydrogen-bonded clusters in the ground and the excited states, intermolecular hydrogen bonds have been reconsidered. The hydrogen bond lengths in both the ground and excited states for the hydrogen-bonded 3HP-(H₂O)₃ and 3Py-(H₂O)₃ clusters are computed and listed in Table 2. We can see an interesting changes about the ground state hydrogen-bonded lengths for 3HP-(H₂O)₃ and 3Py-(H₂O)₃ clusters. The intermolecular hydrogen-bonded distances (HB¹, HB²) are longer than corresponding hydrogen-bonded (HB^a, HB^b), whereas the HB³ and HB⁴ bond lengths are shorter in comparison with the hydrogen-bonded (HB^c, HB^d). We can deduce that the change is beneficial to the frontward and reverse multiple PT reactions in the ground state. At the same time, it is very satisfying to compare between our results and Abou-Zied’s calculations in the ground state.⁴⁹ One can see that the results obtained by these two different theoretical methods are accordant well with each other. This reveals the reliability of our calculation methods for the 3HP-(H₂O)₃ and 3Py-(H₂O)₃ systems. From Table 2, it can be noted that four intermolecular hydrogen bond lengths of 3HP-(H₂O)₃ cluster were shortened upon electronic excitation to the excited state. On the contrary, the four intermolecular hydrogen bond lengths are remarkably lengthened in excited state by comparison with those in ground state for 3Py-(H₂O)₃ cluster. Moreover, a remarkable phenomenon that the four hydrogen bond lengths of 3HP-(H₂O)₃ are shorter than the hydrogen bond lengths of 3Py-(H₂O)₃ in the excited state. This characteristic can effectively facilitate the releasing of the proton from the phenolic group of 3HP moiety to the hydrogen-bonded water wire and conducive to the frontward multiple PT in the excited state. The mechanism is in conformity to our works of the excited state

Table 2 Calculated hydrogen bonded lengths (Å) of the 3HP-(H₂O)₃ and 3Py-(H₂O)₃ clusters in different electronic state.

	3HP-(H ₂ O) ₃				3Py-(H ₂ O) ₃			
	HB ¹	HB ²	HB ³	HB ⁴	HB ^a	HB ^b	HB ^c	HB ^d
S ₀	1.772	1.780	1.767	1.832	1.658	1.730	1.782	1.873
S ₁	1.613	1.710	1.757	1.831	1.863	1.816	1.794	1.947

Table 3 The calculated stretching frequencies of hydrogen atom donor groups for the hydrogen-bonded wire in different electronic state, and the downshifts due to the corresponding hydrogen bond ($\Delta \omega$).

mode	3HP-(H ₂ O) ₃				3Py-(H ₂ O) ₃			
	O ₁ -H ₁	O ₂ -H ₂	O ₃ -H ₃	O ₄ -H ₄	H ₁ -O ₂	H ₂ -O ₃	H ₃ -O ₄	H ₄ -N
S ₀ - ω (cm ⁻¹)	3360	3460	3402	3258	3021	3323	3431	3285
S ₁ - ω (cm ⁻¹)	3270	3412	3310	2964	3472	3520	3564	3520
$\Delta \omega$ (cm ⁻¹)	90(HB ¹)	48(HB ²)	92(HB ³)	294(HB ⁴)	451(HB ^a)	197(HB ^b)	133(HB ^c)	235(HB ^d)
Type	red shift				blue shift			

multiple PT.

As we all know, it is especially difficult to determine the binding energies of the orbicular hydrogen bonds for 3HP-(H₂O)₃ and 3Py-(H₂O)₃ systems simultaneously. The formation of hydrogen bond would lead a downshift of the stretching mode of the hydrogen atom in the two clusters.¹ Hence, the binding energies of the corresponding hydrogen bonds can be distinctly reflected by monitoring the changes of the stretching vibrational mode for the donor groups in different electronic states.¹⁶⁻²² Herein, the corresponding information have been calculated and sketched in Table 3. For 3HP-(H₂O)₃ cluster, hydrogen bond (HB⁴) strength is largest for both the ground and excited states. Hence, the proton H₄ transfer will occur firstly because of a low barrier suggested by the strong hydrogen bonded interaction, which is in keeping with our finding. Moreover, the markedly red-shifted has been found in the excited state for each hydrogen bond in comparison to that in the ground state, so the intermolecular hydrogen bonds are strengthened for 3HP-(H₂O)₃ cluster. For the same reason, the PT will take place firstly in hydrogen bond (HB^a) due to the hydrogen bond (HB^a) strength largest in 3Py-(H₂O)₃ cluster. We can confirm the hydrogen bonds are weakened in the excited state through blue-shifting phenomena.

Consequently, the four hydrogen bonds are strengthened mechanism in the excited state than in the ground state for 3HP-(H₂O)₃ cluster, which can be sufficiently explained the PT process occurs more easily in the excited state than in the ground state. To the best of our knowledge, we theoretically investigate the mechanism of hydrogen-bond strengthening in accordance with Zhao's works.¹⁶⁻²² In addition, we can confirm the hydrogen bonds are weakened in the excited state by comparison with those in ground state for 3Py-(H₂O)₃ cluster. For zwitterionic cluster 3Py-(H₂O)₃, the O⁻ group is more acidic and the ring nitrogen more basic in the excited state than in the ground state, due to electronic charge migrates from the exocyclic conjugated atom to the atoms of the rings via intermolecular hydrogen bonded interactions. The change

of acid-base property for the functional groups will directly lead to the hydrogen bonded weakening.^{26,56} This structural feature, which has been noticed in the previous exploration, agrees with Mason's mechanism.^{27,28,56}

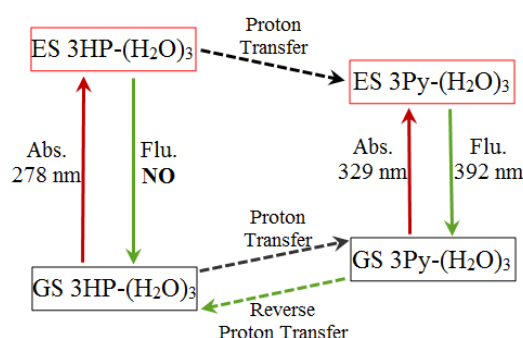


Fig. 5 The schematic view of the equilibrium between 3HP-(H₂O)₃ and 3Py-(H₂O)₃ both in ground state (GS) and first excited state (ES).

At last, on the basis of the data and analysis above, Fig. 5 gives the schematic view of the equilibrium between 3HP-(H₂O)₃ and 3Py-(H₂O)₃ both in the ground and first excited states, together with previous experimental findings.⁴⁷ Upon photoexcitation to a Franck-Condon S₁ excited state of 3HP-(H₂O)₃ cluster, the protons tunnel through a very small barrier on the way to the product, zwitterionic cluster 3Py-(H₂O)₃. Subsequently, zwitterionic cluster emit fluorescence, giving back to the ground-state 3Py-(H₂O)₃. Finally, the reverse PT reaction in the ground state from 3Py-(H₂O)₃ to 3HP-(H₂O)₃ closing the cycle. The calculated absorption and fluorescence values are in good agreement with the experimental results.⁴⁷ Our calculation results can sufficiently explain why no fluorescence of the neutral species in experimental emission spectra, whereas the zwitterionic species has fluorescent.⁴⁷

Conclusions

This paper is devoted to a study of the multiple PT reaction in the ground and first excited states of 3HP in aqueous solution using the DFT/TDDFT methods. First, the multiple PT motion in the ground and excited states can be triggered by the surrounding water network ($\text{H}_2\text{O}\dots\text{H}_2\text{O}\dots\text{H}_2\text{O}$). The water wire can drastically lower the energy barrier for the PT reaction, and provide a nice channel of the PT reaction. Second, the multiple PT reaction of $3\text{HP}-(\text{H}_2\text{O})_3$ cluster can take place successfully via the stepwise mechanism (Type 2) in the ground and excited states. Moreover, the PT process takes place more easily in the excited state in comparison to that in the ground state. Third, we demonstrated that intermolecular hydrogen bonds of $3\text{HP}-(\text{H}_2\text{O})_3$ cluster are strengthened in the excited state than in ground state, whereas the hydrogen bonds interactions of $3\text{Py}-(\text{H}_2\text{O})_3$ cluster are weakened in the excited state by comparison with those in ground state.

A complicated cycle process between $3\text{HP}-(\text{H}_2\text{O})_3$ and $3\text{Py}-(\text{H}_2\text{O})_3$ in the ground and first excited states has been presented. The result well explains that the fluorescence is forbidden of the excited state 3HP in the experiment.

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Notes and references

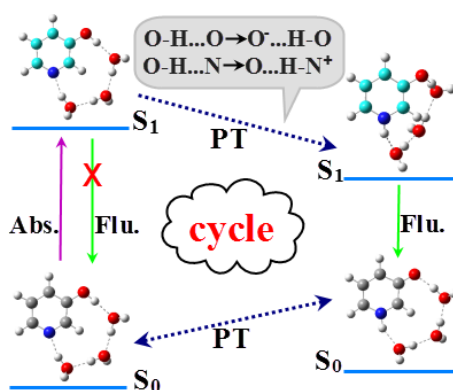
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Graphical Abstract



The multiple proton transfer reactions of 3-hydroxypyridine-(H_2O)₃ have been demonstrated, and a perfect proton transfer cycle has been revealed in the ground and excited states.