INTRODUCTION

Intermolecular hydrogen bonding, which is as a site-specific interaction between hydrogen donor and acceptor molecules, is an important type of solute-solvent interactions\textsuperscript{14} and puts a giant impact on the understanding of microscopic structure and function in many organic and biological systems.\textsuperscript{5-15} It is particularly interesting to investigate the nature of the intermolecular hydrogen bonding in solution.\textsuperscript{16-17} For decades, hydrogen bonding in ground state has been extensively studied by many different experimental and theoretical methods.\textsuperscript{18-19} When photoexcited, the solute and solvent molecules which are engaged in the formation of hydrogen bonds undergo reorganization and greatly changing because of difference in charge distribution for the different electronic states.\textsuperscript{1,20} This process is defined as hydrogen-bonding dynamics which plays an important role on the electronically excited-state dynamics of the hydrogen-bonded complexes.\textsuperscript{21-35} However, knowledge about the process of excited-states hydrogen-bonding dynamics is rather limited because of the extremely short time scale involved.
Excited-state hydrogen-bonding dynamics occurs on ultrafast timescales, which is set by vibrational motions of the hydrogen donor and acceptor groups.\textsuperscript{54} Femtosecond time-resolved infrared spectroscopic has shown the potential to give a good insight into the microscopic dynamics of the intermolecular hydrogen bonding and provide information on local structures.\textsuperscript{54-60} However, it is not adequate to use ultrafast spectroscopy only because of the limited spectral resolution for the femtosecond laser pulses.\textsuperscript{36-40} To study the hydrogen-bonding dynamics, it needs to use TDDFT method which has been demonstrated as a reliable tool to calculate the vibrational absorption spectra in electronically excited states.\textsuperscript{51-56} In this work, the TDDFT method has been used to investigate the excited-state hydrogen-bonding dynamics of phenol-(H\(_2\)O)$_n$.

Phenol which is a weak acid (pK\(_a\) 9.9 in water) resulting in a better proton donor than water is the simplest prototype of an aromatic acid. Hydration of phenol has been studied as a natural first step to understand hydrogen bond which represents solute-solvent interaction in aqueous solutions of organic acids. For this reason the interaction between phenol and water is the subject of several experimental\textsuperscript{44-46} and theoretical\textsuperscript{47-50} studies. There are three stable structures for phenol-(H\(_2\)O)$_n$ in ground state: two open structures and one ring structure.\textsuperscript{51} At the same time, the best agreement is established between the calculated and experimentally observed frequencies in the OH stretching region for the ring structure.\textsuperscript{51-56} Therefore, it can be concluded that the ring structure is the most stable.\textsuperscript{51-56} Many experimental and theoretical studies have shown that phenol-(H\(_2\)O)$_{2,5}$ all have a ring form.\textsuperscript{57} In the ring structure, every monomer acts both as a proton donor and a proton acceptor simultaneously. Dimitrova has studied the changes of the vibrational characteristics (vibrational frequencies, infrared intensities and Raman activities) for the hydrogen-bonded phenol-(H\(_2\)O)$_2$ complex by ab initio calculations at different levels of ab initio MO theory.\textsuperscript{51} He found that the most sensitive to the complex is the OH stretching vibration from the phenol side and the frequency of phenolic OH stretching vibration is redshifted due to the intermolecular hydrogen bond.\textsuperscript{51} At the same time, the IR intensity and Raman activity of OH stretching vibration from the phenol side increase upon hydrogen bond.\textsuperscript{51} Watanabe et al. reported the IR spectra of phenol-(H\(_2\)O)$_n$ (n=1-4) by using ionization detected infrared (IDIR) spectroscopy.\textsuperscript{54} They found that the OH stretching vibrational frequency of phenol-(H\(_2\)O)$_2$ is redshifted by 269 cm\(^{-1}\) compared with that of free phenol.\textsuperscript{54} The phenomenon is due to the existence of intermolecular hydrogen bond.\textsuperscript{54} In the ring structure of phenol (H\(_2\)O)$_2$, there are three hydrogen-bonded OH groups and two OH groups free from the ring. Five bands are observed in the OH stretching vibrational region: three bands at 3388, 3505, and 3553 cm\(^{-1}\) with relatively broad bandwidths which can be assigned to the hydrogen-bonded OH stretching vibrations in the hydrogen-bonded ring and two closely separated bands at 3722 and 3725 cm\(^{-1}\) which can be assigned to the OH stretching vibrations free from hydrogen bonds.\textsuperscript{54,56} Lipert et al. studied the excited-state dynamics of phenol-(H\(_2\)O)$_2$ and phenol-(H\(_2\)O)$_3$.\textsuperscript{58} Phenol-(H\(_2\)O)$_2$ was found to have an anomalously short singlet-state lifetime (6±1 ns) compared to those of other phenol-water complex systems.\textsuperscript{58} They interpreted that phenol-(H\(_2\)O)$_2$ lacks the type of hydrogen bonding found in phenol-H\(_2\)O and phenol-(H\(_2\)O)$_3$.\textsuperscript{58}

However, up to now, the detailed information of the hydrogen bonds between phenol and two water molecules was still not clear. In order to give a clear picture of the hydrogen bonding in the different electronically excited states of phenol-(H\(_2\)O)$_n$ complex, we are motivated to theoretically study the excited-state hydrogen-bonding dynamics of the hydrogen-bonded complex. In this article, we have employed the DFT and TDDFT method for calculations of minimum geometries, corresponding energies and vibrational frequencies of the phenol-(H\(_2\)O)$_2$ complex in ground state and different excited states. Electronic excitation energies and corresponding oscillator strengths have also been calculated.

**THEORETICAL AND COMPUTATIONAL METHODS**

The geometric optimization of the hydrogen-bonded phenol-(H\(_2\)O)$_2$ in ground state was performed using DFT method with Becke’s three-parameter hybrid exchange function with Lee-Yang-Parr gradient-corrected correlation functional (B3LYP).\textsuperscript{59} The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as basis set throughout. The excited-state electronic structures were calculated using TDDFT method with the B3LYP functional and the TZVP basis set. Fine quadrature grids 4 were also employed. Harmonic vibrational frequencies in the ground state and the electronically excited state were determined by diagonalization of the Hessian.\textsuperscript{60} The excited-state Hessian was obtained by numerical differentiation of analytical gradients using central differences and default displacements of 0.02 bohr. The infrared intensities were determined from the gradients of

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the dipole moment. The configuration interaction singles (CIS) method with basis set TZVP was also introduced to investigate the excited states of the hydrogen-bonded complex. All the electronic structure calculations were carried out using the TURBOMOLE program suite.

**RESULTS AND DISCUSSION**

**Geometric Conformations**

It has been determined that there are three stable structures for the complex of phenol with two water molecules: two open structures and one ring structure. Many calculations and experiments have shown that the most stable structure is the ring form in which every monomer acts both as a proton donor and acceptor. Therefore, only the ring structure was discussed here. The structures of the hydrogen-bonded phenol-(H$_2$O)$_2$ complex in ground state and different excited states were obtained with DFT and TDDFT method. Fig. 1 shows the optimized conformations of the complex in different electronic states. All the structures shown here are the lowest-energy conformers. The optimized ground-state conformation of phenol-(H$_2$O)$_2$ shows that all three hydrogen bonds reside out of the phenol plane, which is similar to many previous theoretical calculation results. It can be clearly seen that in the excited states (S$_1$ and T$_1$) three hydrogen bonds also reside out of the phenol plane. The bond length of free O-H in a phenol monomer is calculated to be 0.964Å in the ground state, while the bond length of O$_2$-H$_2$ in the hydrogen bond O$_1$-H$_2$···O$_2$-H is lengthened to 0.983Å of the phenol-(H$_2$O)$_2$ complex. The bond length of the hydrogen-bonded OH group is slightly lengthened due to the formation of the intermolecular hydrogen bond O$_1$-H$_2$···O$_3$-H. Moreover, the lengths of the hydrogen bonds H-O$_1$···H$_5$O$_3$ and H-O$_5$···H$_2$O$_1$ and H-O$_3$···H$_2$O$_1$ are calculated to be 1.994Å and 1.896Å and 1.808Å in ground state, respectively. Herein, the lengths show that the order of the strength of three hydrogen bonds in ground state is to be H-O$_1$···H$_5$O$_3$ < H-O$_5$···H$_2$O$_1$ < H-O$_3$···H$_2$O$_1$. Although the hydrogen bonding lengths are different in T$_1$ state and S$_0$ state, one can find that the direction of O-H bond of water molecules in T$_1$ state is almost the same as that in the ground state. It should be noted that the structural conformation in S$_1$ state is markedly different from the ground-state conformation. In S$_1$ state, the water molecule H-O$_1$-H$_2$ rotates a large angle, resulting in the hydrogen bond H-O$_1$···H$_6$O$_3$ being lengthened from 1.994 Å in S$_0$ state to 2.219 Å in S$_1$ state.

**Nature of Low-Lying Excited States**

To understand the nature of the electronically excited states for the hydrogen-bonded phenol-(H$_2$O)$_2$ complex, electronic excitation energies and corresponding oscillator strengths of the low-lying excited states are calculated using the TDDFT method. At the same time, the CIS method is also used for comparison. The results are shown in the Table 1. The isolated phenol monomer and hydrogen-bonded phenol-H$_2$O are also investigated here for comparison. One can find that the absorption peak of the S$_1$ state for phenol-(H$_2$O)$_2$ is the same as that of phenol and the absorption peaks of other excited states are slightly red-shifted compared with those of the monomer phenol. At the same time, the red-shift of the absorption peaks of phenol-(H$_2$O)$_2$ (compared with phenol monomer) is smaller than that of phenol-H$_2$O. These phenomena may be due to the combined action of the ring of three hydrogen bonds in phenol-(H$_2$O)$_2$ complex, whereas there is only one hydrogen bond exiting in phenol-H$_2$O complex.

As we know, the molecular orbitals (MOs) analysis can directly provide insight into the nature of the excited states. The frontier molecular orbitals of the hydrogen-bonded phenol-(H$_2$O)$_2$ complex are shown in Fig. 2. From the TDDFT calculations, the S$_1$ state of the hydrogen-bonded phenol-(H$_2$O)$_2$ is mainly contributed by the orbital transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). It is obvious that the HOMO and LUMO orbitals are the $\pi$ and $\pi^*$ character, respectively. So the S$_1$ state of phenol-(H$_2$O)$_2$ has the $\pi$-$\pi^*$ feature. In addition, the electron densities of both the HOMO and LUMO are entirely localized on the phenol moiety. This indicates that only the phenol moiety has been electronically excited in the S$_1$ state, while the two water molecules should be located in their electronic ground states. Thus, the S$_1$ state of the hydrogen-bonded
phenol-(H2O)2 complex should be assigned as locally excited (LE) state on phenol molecule. Further observation indicates that the electron density of the O-H group of phenol is decreased from HOMO to LUMO, which can induce the O-H bond of phenol be weakened when photoexcited to the S1 state. The result is similar to the analysis of the geometric conformation of hydrogen-bonded phenol-(H2O)2 complex in S1 state.

### Calculated Vibrational Spectra

To depict the transient change of intermolecular hydrogen bond in the early time of electronic excitation, the infrared spectra of the ground-state and S1 state for the phenol-(H2O)2 complex are calculated using the DFT and TDDFT method. For comparison, the infrared spectra of phenol monomer in different electronic states are also calculated. The change of the intermolecular hydrogen bond O-H...O2-H in different states can be monitored by the spectral shift of the stretching vibrational mode of the O-H bond in the IR spectra. The calculated IR spectra of hydrogen-bonded phenol-(H2O)2 and phenol monomer in different electronic states are
shown in Fig. 3 and Fig. 4, respectively. There are four vibrational bands for the hydrogen-bonded phenol-(H\(_2\)O)\(_2\) complex in S\(_0\) state and S\(_1\) state and T\(_1\) state. In ground state, the band at 3276 cm\(^{-1}\) can be assigned to the phenolic OH stretching vibration, and the bands at 3401 cm\(^{-1}\) and 3468 cm\(^{-1}\) can be assigned to the symmetric stretching vibration of the water molecules. The frequency of the antisymmetric stretching vibration of waters is 3677 cm\(^{-1}\). For the isolated phenol monomer in ground state, the calculated stretching vibrational frequency of the O-H bond for the phenol-(H\(_2\)O)\(_2\) complex in ground state is downshifted by 344 cm\(^{-1}\) to 3276 cm\(^{-1}\) due to the formation of the intermolecular hydrogen bond O\(_1\)-H\(_2\)···O\(_3\)-H. Moreover, one can see that the stretching vibrational mode of the O-H group of the phenol monomer is red-shifted by 103 cm\(^{-1}\) in the S\(_1\) state compared with that in ground state. So the electronic excitation of the phenol monomer can also induce the O-H stretching vibrational mode shift to the red, which means that the O-H bond is lengthened upon electronic excitation on the phenol. The O\(_1\)-H\(_2\) bond stretching vibrational frequency of hydrogen-bonded phenol-(H\(_2\)O)\(_2\) complex in the S\(_1\) state is downshifted by 433 cm\(^{-1}\) compared with that of isolated phenol in the S\(_1\) state. That is to say, the O-H stretching mode has a larger redshift which is induced by the intermolecular hydrogen bond O\(_1\)-H\(_2\)···O\(_3\)-H between phenol and two water molecules in the S\(_1\) state (433 cm\(^{-1}\)) than in the ground state (344 cm\(^{-1}\)). Similarly, the spectral redshift of the O-H stretching vibrational frequency of phenol-(H\(_2\)O)\(_2\) in T\(_1\) state compared with that of phenol monomer in T\(_1\) state is 374 cm\(^{-1}\) (from 3593 to 3219 cm\(^{-1}\)) which is larger than that in the ground state. Since the stretching mode can undergo a shift to lower frequency for stronger hydrogen-bonding interaction, the larger redshift of the O-H stretching vibrational mode in both S\(_1\) state and T\(_1\) states evidently suggests that the intermolecular hydrogen bond O\(_1\)-H\(_2\)···O\(_3\)-H should be strengthened in S\(_1\) state and T\(_1\) state. Moreover, the order of the spectral redshift of the O\(_1\)-H\(_2\) bond stretching mode in S\(_1\) and T\(_1\) state is as follows: S\(_1\)>T\(_1\). Therefore, the strength of the hydrogen bond O\(_1\)-H\(_2\)···O\(_3\)-H in different states can be predicted as follows: S\(_1\)>T\(_1\)>S\(_0\).

Excited-State Hydrogen Bond Strengthening and Weakening
The calculated hydrogen bond lengths and the bond
lengths of hydrogen-bonded groups for the hydrogen-bonded phenol-(H2O)2 complex in the ground state and excited states are listed in Table 2. It can be seen that the length of the hydrogen bond O1-H2···O3-H is shortened by 0.088 Å from S0 state to S1 state, and is also shortened by 0.024 Å in T1 state. At the same time, the hydrogen-bonded O1-H2 is lengthened from 0.983 Å in ground state to 0.995 Å in S1 state and 0.987 Å in T1 state, respectively. So the hydrogen bond O1-H2···O3-H is strengthened in S1 state and T1 state when compared to that in ground state. In addition, similar to the analysis of the calculated vibrational absorption spectra, the order of strength of hydrogen bond strengthening and weakening behavior in electronically excited states of hydrogen bond network in phenol-(H2O)2 are reported for the first time. The hydrogen bond strengthening and weakening behavior in electronically excited states may exist in other ring structures of phenol-(H2O)n.

CONCLUSIONS

In the present work, we have studied the excited-state hydrogen-bonding dynamics of phenol-(H2O)2 using the TDDFT method. The geometric structures of hydrogen-bonded phenol-(H2O)2 complex in the ground state and S1 state and T1 state have been calculated. Meanwhile, the electronic excitation energies as well as corresponding oscillator strengths of phenol-(H2O)2 and phenol-H2O and phenol monomer have been calculated. Based on our calculated results, we have concluded that the S1 state of the hydrogen-bonded phenol-(H2O)2 complex is LE state on phenol moiety, while the two water molecules are located in their electronic ground state. Moreover, electronic spectra can be red-shifted due to the intermolecular hydrogen bonds. Also, the IR spectra of phenol-(H2O)2 complex in different electronic states have been calculated. From the analysis of IR spectra and hydrogen bond lengths and the lengths of hydrogen-bonded groups, we have demonstrated that the order of hydrogen bond strength O1-H2···O3-H in different states is S1>T1>S0. Furthermore, the hydrogen bond O2-H6···O1-H is weakened in both the S1 and T1 states while O2-H6···O3-H is strengthened in S1 state but a little weakened in T1 state. The hydrogen bond strengthening and weakening behavior in electronically excited states of hydrogen bond network in phenol-(H2O)2 are reported for the first time. The hydrogen bond strengthening and weakening behavior in electronically excited states may exist in other ring structures of phenol-(H2O)n.

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