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전자 여기상태에서 phenol-$(H_2O)_2$ 크러스터의 수소결합 동력학: DFT/TDDFT 연구

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Hydrogen Bonding Dynamics of Phenol-$(H_2O)_2$ Cluster in the Electronic Excited State: a DFT/TDDFT Study

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요 약. Phenol-$(H_2O)_2$ 착물의 여기상태 수소 결합 동력학을 시간 의존 밀도 함수 이론(TDDFT) 법으로 연구하였다. 수소-결합된 착물에 대한 바닥 상태 및 다른 전자 여기 상태들 (S_1와 T_1)에서의 기하학적 구조와 IR 스펙트라를 밀도 함수 이론(DFT)와 TDDFT 방법을 사용하여 계산하였다. 페놀과 두 물분자 간에 3개의 수소 결합으로 구성된 고리가 형성되었다. 세 개의 수소 결합에서 분자간 수소결합 O_1-H_2···O_3-H은 S_1 그리고 T_1 상태에서 더 강해졌지만, 수소결합 O_5-H_6···O_1-H은 S_1과 T_1상태에서 약해졌다. 이러한 결과들은 다른 전자 상태에서 수소 결합과 hydrogen-bonding groups의 결합 길이의 변화를 이론적으로 모니터링하여 얻었다. 수소 결합 O_1-H_2···O_3-H가 S_1와 T_1 상태 모두에서 강화된다는 것은 O-H(phenol)의 계산된 신축 진동 모드가 광 여기에 의해 적색-이동한다는 것으로부터 확인 되었다. 전자 여기 상태에서 수소 결합이 강해지고 약해지는 행동은 phenol-$(H_2O)_n$의 다른 고리 구조에 존재할 수 있다.

주제어: 수소결합, 여기 상태, 전자 스펙트럼, 진동 스펙트럼

ABSTRACT. The time-dependent density functional theory (TDDFT) method has been carried out to investigate the excited-state hydrogen-bonding dynamics of phenol-$(H_2O)_2$ complex. The geometric structures and infrared (IR) spectra in ground state and different electronically excited states (S_1 and T_1) of the hydrogen-bonded complex have been calculated using the density functional theory (DFT) and TDDFT method. A ring of three hydrogen bonds is formed between phenol and two water molecules. We have demonstrated that the intermolecular hydrogen bond O_1-H_2···O_3-H of the three hydrogen bonds is strengthened in S_1 and T_1 states. In contrast, the hydrogen bond O_5-H_6···O_1-H is weakened in S_1 and T_1 states. These results are obtained by theoretically monitoring the changes of the bond lengths of the hydrogen bonds and hydrogen-bonding groups in different electronic states. The hydrogen bond O_1-H_2···O_3-H strengthening in both the S_1 and T_1 states is confirmed by the calculated stretching vibrational mode of O-H (phenol) being red-shifted upon photoexcitation. The hydrogen bond strengthening and weakening behavior in electronically excited states may exist in other ring structures of phenol-$(H_2O)_n$.

Keywords: Hydrogen bond, Excited state, Electronic spectra, Vibrational spectra

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[1-4] and puts a giant impact on the understanding of microscopic structure and function in many organic and biological systems.[5-15] It is particularly interesting to investigate the nature of the intermolecular hydrogen bonding in solution.[16-17] For decades, hydrogen bonding in ground state has been extensively studied by many different experimental and theoretical methods.[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.[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.[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.[5-6] 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.[5-6,20] However, it is not adequate to use ultrafast spectroscopy only because of the limited spectral resolution for the femtosecond laser pulses.[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.[5,41-43] In this work, the TDDFT method has been used to investigate the excited-state hydrogen-bonding dynamics of phenol-$(H_2O)_2$.

Phenol which is a weak acid (pKa 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[44-46] and theoretical[47-50] studies. There are three stable structures for phenol-$(H_2O)_2$ in ground state: two open structures and one ring structure.[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.[51-56] Therefore, it can be concluded that the ring structure is the most stable.[51-56] Many experimental and theoretical studies have shown that phenol-$(H_2O)_{2\text{-}5}$ all have a ring form.[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-$(H_2O)_2$ complex by ab initio calculations at different levels of ab initio MO theory.[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 red-shifted due to the intermolecular hydrogen bond.[51] At the same time, the IR intensity and Raman activity of OH stretching vibration from the phenol side increase upon hydrogen bond.[51] Watanabe et al. reported the IR spectra of phenol-$(H_2O)_n$ (n=1-4) by using ionization detected infrared (IDIR) spectroscopy.[54] They found that the OH stretching vibrational frequency of phenol-$(H_2O)_2$ is red-shifted by 269 cm^{-1} compared with that of free phenol.[54] The phenomenon is due to the existence of intermolecular hydrogen bond.[54] In the ring structure of phenol $(H_2O)_2$, 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.[54,56] Lipert *et al*. studied the excited-state dynamics of phenol-$(H_2O)_2$ and phenol-$(H_2O)_3$.[58] Phenol-$(H_2O)_2$ was found to have an anomalously short singlet-state lifetime (6±1 ns) compared to those of other phenol-water complex systems.[58] They interpreted that phenol-$(H_2O)_2$ lacks the type of hydrogen bonding found in phenol-H_2O and phenol-$(H_2O)_3$.[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-$(H_2O)_2$ 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-$(H_2O)_2$ 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-$(H_2O)_2$ 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).[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.[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

the dipole moment.[61] 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-$(H_2O)_2$ 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-$(H_2O)_2$ 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_1-H_2 in the hydrogen bond O_1-H_2···O_3-H is lengthened to 0.983Å of the phenol-$(H_2O)_2$ 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_6-O_5 and H-O_5···H_4-O_3 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_6-O_5 < H-O_5···H_4-O_3 < 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_5-H_6 rotates a large angle, resulting in the hydrogen bond H-O_1···H_6-O_5 being lengthened from 1.994 Å in S_0 state to 2.219 Å in S_1 state.

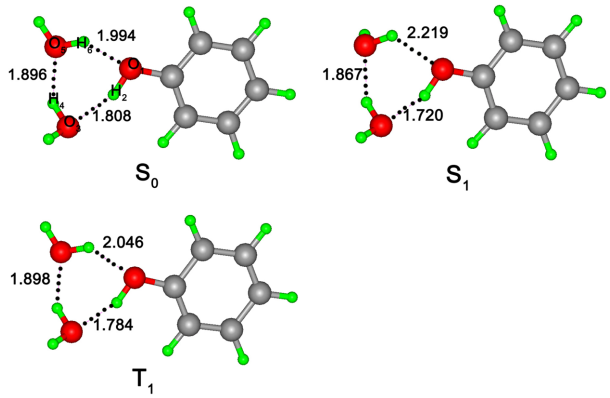

***Fig.* 1.** Geometric structures of phenol-$(H_2O)_2$ in different electronic states.

Nature of Low-Lying Excited States

To understand the nature of the electronically excited states for the hydrogen-bonded phenol-$(H_2O)_2$ 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_2O are also investigated here for comparison. One can find that the absorption peak of the S_1 state for phenol-$(H_2O)_2$ 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-$(H_2O)_2$ (compared with phenol monomer) is smaller than that of phenol-H_2O. These phenomena may be due to the combined action of the ring of three hydrogen bonds in phenol-$(H_2O)_2$ complex, whereas there is only one hydrogen bond exiting in phenol-H_2O 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-$(H_2O)_2$ complex are shown in *Fig.* 2. From the TDDFT calculations, the S_1 state of the hydrogen-bonded phenol-$(H_2O)_2$ 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 π and π^* character, respectively. So the S_1 state of phenol-$(H_2O)_2$ has the π-π^* 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

***Table* 1.** Calculated electronic excitation energies (nm) and corresponding oscillator strengths (in parentheses) of phenol-$(H_2O)_2$, phenol-H_2O as well as isolated phenol (R: redshift). (a) singlet electronic excited states; (b) triplet electronic excited states. The orbital transition contributions for the singlet and triplet electronic excited states are also listed (H, HOMO; L, LUMO)

(a)	phenol-$(H_2O)_2$		phenol-H_2O		phenol	
	TDDFT	CIS	TDDFT	CIS	TDDFT	CIS
S_1	243 (0.031) H→L,79.8% H-1→L+1,14.1%	240 (0.030) H→L,72.8% H-1→L+1,18.9%	256 (0.000) R H→L,99.6%	256 (0.000) R H→L,99.6%	243 (0.034) H→L,80.4% H-1→L+1,19.1%	239 (0.033) H→L,73.3% H-1→L+1,25.9%
S_2	218 (0.024) R H→L+1,57.4% H→L+2,40.1%	218 (0.016) R H-1→L+1,18.9% H→L+2,53.4% H→L+1,45.2%	247 (0.039) R H→L+1,82.7% H-1→L+2,16.9%	242 (0.039) R H→L+1,75.5% H-1→L+2,23.6%	209 (0.034) H→L+1,67.5% H-1→L,31.2%	208 (0.000) H→L+2,98.7%
S_3	210 (0.040) R	202 (0.050)	213 (0.000) R	213 (0.000) R	208 (0.000)	201 (0.034)
S_4	189 (0.001) R	189 (0.002) R	211 (0.052) R	203 (0.052) R	184 (0.001)	184 (0.001)
S_5	188 (0.030) R	188 (0.009) R	188 (0.001) R	188 (0.001) R	179 (0.368)	179 (0.001)
S_6	184 (0.006) R	184 (0.002) R	181 (0.320) R	176 (0.018) R	179 (0.625)	171 (0.473)
S_7	180 (0.343) R	171 (0.412) R	180 (0.653) R	172 (0.397) R	179 (0.001)	166 (0.964)
S_8	180 (0.666) R	168 (0.502) R	176 (0.017) R	168 (0.000) R	166 (0.000)	166 (0.000)
S_9	168 (0.002) R	167 (0.564) R	168 (0.000) R	167 (1.004) R	163 (0.000)	163 (0.000)
S_{10}	166 (0.002) R	165 (0.015) R	166 (0.000) R	166 (0.000) R	161 (0.005)	161 (0.005)
S_{11}	164 (0.003) R	164 (0.004) R	164 (0.004) R	164 (0.004) R	157 (0.004)	157 (0.004)
S_{12}	163 (0.005) R	163 (0.016) R	160 (0.004) R	160 (0.003) R	154 (0.000)	154 (0.000)
(b)	phenol-$(H_2O)_2$		phenol-H_2O		phenol	
	TDDFT	CIS	TDDFT	CIS	TDDFT	CIS
T_1	330 (0.029) H→L+1,41.2% H-1→L,37.4% H→L+2,17.3%	303 (0.060) H→L+1,46.3% H-1→L,30.1% H→L+2,19.1%	305 (0.096) H→L+2,60.8% H-1→L+1,34.9%	305 (0.096) R H→L+2,66.3% H-1→L+1,25.6%	330 (0.029) H→L+1,57.9% H-1→L,37.7%	303 (0.063) H→L+1,63.2% H-1→L,30.2%
T_2	295 (0.549) H→L, 97%	292 (0.494) H→L,96.3%	299 (0.450) R H→L+1,97.4%	299 (0.450) R H→L+1,92.9%	296 (0.550) H→L,96.7%	292 (0.488) H→L,94.0%
T_3	269 (1.145)	266 (1.018) R	267 (1.001) R	267 (1.001) R	269 (1.140)	265 (1.013)
T_4	230 (0.422) R	229 (0.397) R	257 (0.000) R	257 (0.000) R	229 (0.427)	227 (0.402)
T_5	219 (0.001) R	219 (0.001) R	227 (0.420) R	227 (0.420) R	214 (0.000)	213 (0.000)
T_6	190 (0.002) R	190 (0.002) R	213 (0.000) R	213 (0.000) R	187 (0.001)	187 (0.001)
T_7	189 (0.000) R	189 (0.001) R	191 (0.001) R	191 (0.001) R	180 (0.001)	180 (0.001)
T_8	186 (0.002) R	186 (0.002) R	177 (0.025) R	177 (0.025) R	178 (0.020)	176 (0.021)
T_9	178 (0.021) R	176 (0.022) R	176 (0.002) R	176 (0.002) R	171 (0.001)	169 (0.001)
T_{10}	172 (0.001) R	170 (0.046) R	170 (0.000) R	170 (0.000) R	168 (0.000)	168 (0.000)
T_{11}	170 (0.048) R	170 (0.000) R	170 (0.001) R	170 (0.001) R	168 (0.006)	167 (0.004)
T_{12}	170 (0.000) R	170 (0.001) R	170 (0.003) R	170 (0.003) R	164 (0.000)	164 (0.000)

phenol-$(H_2O)_2$ 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 S_1 state. The result is similar to the analysis of the geometric conformation of hydrogen-bonded phenol-$(H_2O)_2$ complex in S_1 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 S_1 state and T_1 state for the phenol-$(H_2O)_2$ 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_1-H_2···O_3-H in different states can be monitored by the spectral shift of the stretching vibrational mode of the O_1-H_2 bond in the IR spectra. The calculated IR spectra of hydrogen-bonded phenol-$(H_2O)_2$ and phenol monomer in different electronic states are

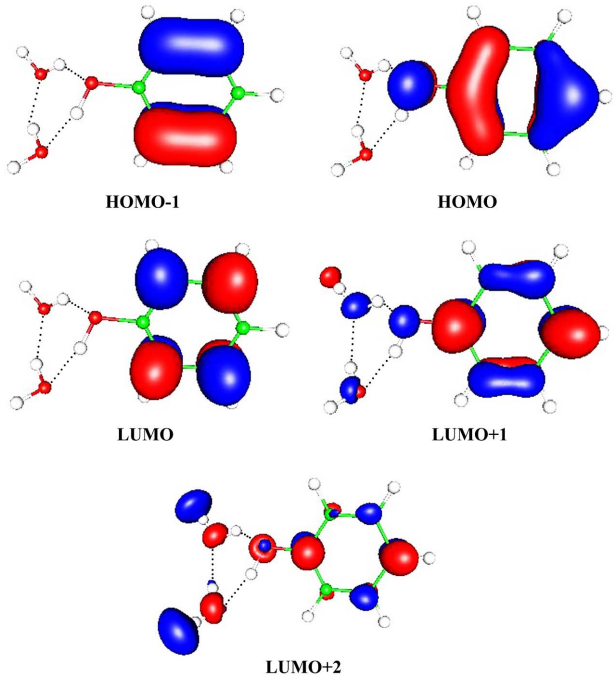

***Fig.* 2.** Frontier molecular orbitals (MOs) of the hydrogen-bonded phenol-$(H_2O)_2$ complex.

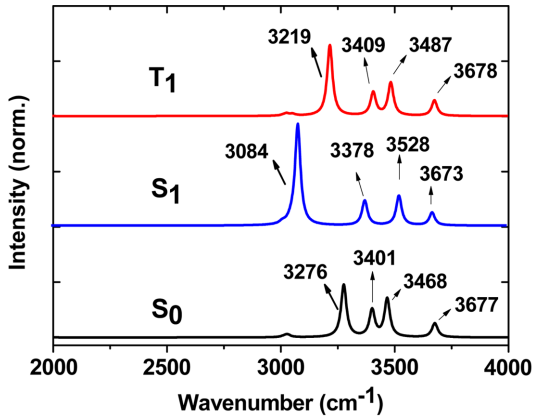

***Fig.* 3.** Calculated vibrational absorption spectra of phenol-$(H_2O)_2$ in different electronic states.

shown in *Fig.* 3 and *Fig.* 4, respectively. There are four vibrational bands for the hydrogen-bonded phenol-$(H_2O)_2$ 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 mode of the O-H group is 3620 cm^{-1}. However the calculated stretching vibrational frequency of the O_1-H_2 bond for the phenol-$(H_2O)_2$ com-

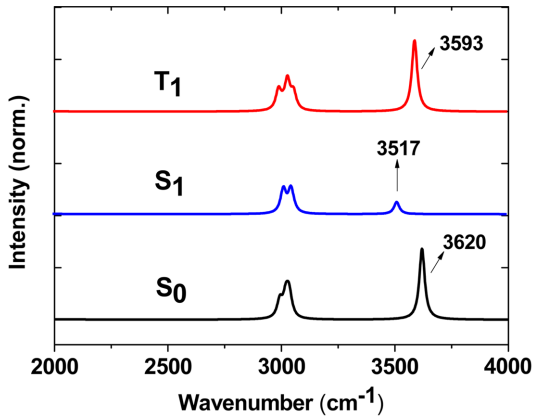

***Fig.* 4.** Calculated vibrational absorption spectra of phenol monomer in different electronic states.

plex 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-$(H_2O)_2$ 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-$(H_2O)_2$ 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 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 follow: 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 follow: S_1>T_1>S_0.

Excited-State Hydrogen Bond Strengthening and Weakening

The calculated hydrogen bond lengths and the bond

***Table* 2.** Calculated lengths of hydrogen bonds (in Å) and hydrogen bonding groups for phenol-$(H_2O)_2$ in different electronic states

	$L_{O1\text{-}H2}$	$L_{O3\text{-}H4}$	$L_{O5\text{-}H6}$	$L_{O3\cdots H2}$	$L_{O5\cdots H4}$	$L_{O1\cdots H6}$
S_0	0.983	0.977	0.973	1.808	1.896	1.994
S_1	0.995	0.979	0.969	1.720	1.867	2.219
T_1	0.987	0.977	0.972	1.784	1.898	2.046

lengths of hydrogen-bonded groups for the hydrogen-bonded phenol-$(H_2O)_2$ complex in the ground state and excited states are listed in *Table* 2. It can be seen that the length of the hydrogen bond O_1-H_2···O_3-H is shortened by 0.088 Å from S_0 state to S_1 state, and is also shortened by 0.024 Å in T_1 state. At the same time, the hydrogen-bonded O_1-H_2 is lengthened from 0.983 Å in ground state to 0.995 Å in S_1 state and 0.987 Å in T_1 state, respectively. So the hydrogen bond O_1-H_2···O_3-H is strengthened in S_1 state and T_1 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 O_1-H_2···O_3-H in different states is S_1>T_1>S_0. Furthermore, the hydrogen bond O_5-H_6···O_1-H is lengthened from 1.994 Å in ground state to 2.219 Å in S_1 state and 2.046 Å in T_1 state, respectively. At the same time, the bond O_5-H_6 is shortened from 0.973 Å in S_0 state to 0.969 Å in S_1 state and 0.972 Å in T_1 state, respectively. While the hydrogen bond O_3-H_4···O_5-H is shortened in S_1 state but is a little lengthened in T_1 state compared to that in the ground state. Therefore, the hydrogen bond O_5-H_6···O_1-H is weakened in both S_1 and T_1 states, while the hydrogen bond O_3-H_4···O_5-H is strengthened in S_1 state but a little weakened in T_1 state.

CONCLUSIONS

In the present work, we have studied the excited-state hydrogen-bonding dynamics of phenol-$(H_2O)_2$ using the TDDFT method. The geometric structures of hydrogen-bonded phenol-$(H_2O)_2$ complex in the ground state and S_1 state and T_1 state have been calculated. Meanwhile, the electronic excitation energies as well as corresponding oscillator strengths of phenol-$(H_2O)_2$ and phenol-H_2O and phenol monomer have been calculated. Based on our calculated results, we have concluded that the S_1 state of the hydrogen-bonded phenol-$(H_2O)_2$ 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-$(H_2O)_2$ 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 O_1-H_2···O_3-H in different states is S_1>T_1>S_0. Furthermore, the hydrogen bond O_5-H_6···O_1-H is weakened in both the S_1 and T_1 states while O_3-H_4···O_5-H is strengthened in S_1 state but a little weakened in T_1 state. The hydrogen bond strengthening and weakening behavior in electronically excited states of hydrogen bond network in phenol-$(H_2O)_2$ 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-$(H_2O)_n$.

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