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Time-dependent density functional theory study on electronic excited states of the hydrogen-bonded solute–solvent phenol–(H₂O)_n (n=3–5) clusters

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ABSTRACT

The solute–solvent interactions of hydrogen-bonded phenol–(H₂O)_n (n=3–5) clusters in electronic excited states were investigated by means of the time-dependent density functional theory (TDDFT) method. The geometric structures and IR spectra in ground state, S₁ state, and T₁ state of the clusters, were calculated using the density functional theory (DFT) and TDDFT methods. Only the ring form isomer, the most stable one of the cluster, was considered in this study. Four, five and six intermolecular hydrogen bonds were formed in phenol–(H₂O)₃, phenol–(H₂O)₄, and phenol–(H₂O)₅ clusters, respectively. Based on the analysis of IR spectra, it is revealed that the “window region” between unshifted and shifted absorption bands in both S₁ and T₁ state becomes broader compared with that in ground state for the corresponding clusters. Furthermore, two interesting phenomenon were observed: (1) with the anticlockwise order of the ring formed by the intermolecular hydrogen bonds in the H-bonded phenol–(H₂O)_n (n=3–5) clusters, the strengths of the intermolecular hydrogen bonds decrease in all the S₀, S₁ and T₁ states; (2) upon electronic excitation, the smaller the distance between phenol and water is, the larger the change of intermolecular hydrogen bonds strength is. Moreover, the intermolecular hydrogen bond (phenolic OH is the H donor) is strengthened in excited state compared with that in ground state. But the intermolecular hydrogen bond (phenolic OH is the H acceptor) is weakened in excited state.

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1. Introduction

Intermolecular hydrogen bonding, which is an important type of solute–solvent interactions, puts a giant impact on the physical, chemical, and biological processes [1–15]. One molecule is surrounded by other molecules in clusters, which is considered as a good model for solute–solvent systems [16–36]. The hydrogen-bonded (H-bonded) phenol–(H₂O)_n clusters are prototypes for the investigation of H-bonded systems and solvent–solute interactions, since phenol is the simplest aromatic acid and the study on phenol–(H₂O)_n clusters is of great interest and very important for understanding the molecular interactions in organic acids [20–23,28–32]. Furthermore, phenol is one of the most abundant pollutants in industrial wastewaters and becomes a big threat to the aquatic life because of its high toxicity. The degradation of phenol in aqueous environment can be carried out by direct ultraviolet (UV) radiation or hydrogen peroxide (H₂O₂) or the combination of UV with H₂O₂ [37,38]. The solute–solvent interactions between phenol

and water molecules in electronic excited states are of great importance for the studies of photodegradation process and mechanism of phenol in aqueous environment.

In recent years, there have been various studies on structures and vibrations of H-bonded phenol–(H₂O)_n clusters in their ground state [16–18,20–23,25,27,28–32]. Lipert and Colson [18] firstly investigated the clusters of phenol with water by using mass-selected multiphoton ionization. In addition, many experimental and theoretical studies have reported that phenol–(H₂O)_n (n=2–5) clusters have a ring structure, where every monomer acts both as a proton donor and a proton acceptor [16,17,20,21,25,27,29,32]. For phenol–(H₂O)_n (n=2–4), the ring structure is more stable [16,17,20,21,25,27,29,32]. Phenol–(H₂O)₅ with many isomers is very complicated. However, ab initio calculations have shown that the ring structure is also the most stable isomer for phenol–(H₂O)₅ [17,25]. Furthermore, the OH stretching vibrations of phenol–(H₂O)_n (n=1–5) in ground state have also been investigated by many studies [16,17,21,27,28,32]. The stretching vibration of phenolic OH of phenol–H₂O cluster in the ground state was first observed by Hartland et al. [28]. Stanley and Castleman [29,30] reported the assignment of intermolecular hydrogen bonding vibrations of phenol–(H₂O)_n (n=1–4) in the

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ground state by using ion-dip spectroscopy. Ebata et al. [23,31] used ionization detected infrared (IDIR) spectroscopy to observe the OH stretching vibrations of phenol-(H₂O)_n cluster in the ground state. The Mikami group obtained the IR spectra of phenol-(H₂O)_n ($n \leq 4$) by experimental methods [22,23]. Watanabe and Iwata [17] calculated the infrared spectra of phenol-(H₂O)_n ($n \leq 4$) with ab initio molecular orbital methods. Some results have revealed that stretching vibration of the phenolic hydroxyl group in phenol-(H₂O)_n clusters shifts toward the lower energy compared with that of the free phenol because of the intermolecular hydrogen bonds [16,17]. The most sensitive to the clusters is the OH stretching vibration from the phenol side. Moreover, the spectral patterns of the H-bonded phenol-(H₂O)_n ($n=2-5$) clusters are very characteristic. The frequencies of the symmetric stretching vibration of the waters and the OH stretching vibration of phenol side are reduced with increasing n [16,22]. However, the antisymmetric stretching bands of waters are almost unchanged [16,22]. Therefore, the “window region”, which is named by Mikami between shifted and unshifted absorption bands becomes wider with increasing n [16,22]. In a word, tremendous effort has been spent studying the ground state properties of the intermolecular hydrogen bonding in phenol-(H₂O)_n ($n=3-5$) clusters. In contrast, knowledge about the hydrogen bonding of clusters in the electronic excited states is rather limited because of the extremely short time scale involved. Although Ebata et al. [32] have investigated OH stretching vibrations of phenol-(H₂O)₁ and phenol-(H₂O)₃ in the S₁ state by experimental methods. The detailed information about the changes of the hydrogen bonding of phenol-(H₂O)_n ($n=3-5$) clusters in different electronic excited states has not been given until now.

Excited-state hydrogen bonding dynamics occurs on ultrafast timescale, which is set by vibrational motions of the hydrogen donor and acceptor groups [33–38]. It is difficult to measure the excited-state hydrogen bonding by time-resolved techniques. To study the hydrogen bonding dynamics, it needs to use time-dependent density functional theory (TDDFT) method, which has been demonstrated as a reliable tool to calculate the vibrational absorption spectra in electronically excited states [39–48]. Zhao and coworkers have made a significant contribution in the excited-state hydrogen bonding research field. They demonstrated for the first time that the intermolecular hydrogen bonds can be strengthened or weakened in the electronic excited states upon photoexcitation and the excited-state hydrogen bond strengthening and weakening behaviors play a key role on tuning many photophysical processes and photochemical reactions [1,13,33,35]. In this study, we employed the density functional theory (DFT) and TDDFT methods to investigate the properties of the intermolecular hydrogen bonds of phenol-(H₂O)_n ($n=3-5$) clusters in different electronic states (S₀, S₁, and T₁). The minimum geometries, electronic excitation energies, vibrational frequencies, and lengths of hydrogen bonds and hydrogen bonding groups of H-bonded phenol-(H₂O)_n ($n=3-5$) clusters in ground and excited states have been investigated. Furthermore, we provided the details of the changes of hydrogen bonds in the ring in S₀, S₁, and T₁ states. The results revealed that the changes of the solvation of phenol with water in different electronic excited states involve two points as follows: (1) with the order of the hydrogen bonds of the ring in the clusters, the change of hydrogen bonding strength has regularity in the electronic states (S₀, S₁, and T₁). (2) Upon electronic excitation, with the change of the distance between the phenol and water molecule, the change of hydrogen bonding strength shows regularity.

2. Computational details

In this study, the geometric optimizations of the H-bonded phenol-(H₂O)_n ($n=3-5$) clusters in the ground state were performed using DFT method with Becke's three-parameter

hybrid exchange function with Lee–Yang–Parr gradient-corrected correlation functional (B3LYP hybrid functional) [49]. The triple- ζ valence quality with one set of polarization functions (TZVP) was chosen as basis set throughout [50]. The stable structures of all the clusters in the electronic excited state were calculated using the TDDFT method with the B3LYP hybrid functional and the TZVP basis set [35,49–51]. Fine quadrature grids 4 were also employed [52]. Harmonic vibrational frequencies in the ground state and the electronically excited states were determined by diagonalization of the Hessian [53]. The infrared intensities were determined from the gradients of the dipole moment [54–56]. For comparison, the configuration interaction singles (CIS) method with bases set TZVP was also introduced to investigate the electronic excitation energies of the clusters. All the electronic structure calculations were carried out using the TURBOMOLE program suite.

3. Results and discussion

3.1. Ground-state geometric conformations

The optimized geometric structures of the H-bonded phenol-(H₂O)_n ($n=3-5$) clusters are shown in Fig. 1. Many experimental and theoretical studies indicated that the most stable structure of the H-bonded phenol-(H₂O)_n ($n=3-5$) clusters in ground state is the ring form [16,17,20,21,25,27,29,32]. Therefore, only the ring structures of the clusters are considered in this study. Fig. 1 shows that the OH of phenol and waters in the clusters can form a ring, where every monomer can act both as a proton donor and a proton acceptor. Four, five, and six intermolecular hydrogen bonds are formed in phenol-(H₂O)₃, phenol-(H₂O)₄ and phenol-(H₂O)₅ clusters, respectively. Furthermore, for phenol-(H₂O)₄ cluster, two ring structure isomers, which are the most stable ones are found. The results are similar to those reported by Watanabe et al. [16]. The major difference of the two isomers of phenol-(H₂O)₄ is the orientation of the O–H bonds of waters. The H-bonded OH of phenol in phenol-(H₂O)_n ($n=3-5$) clusters is slightly lengthened compared to that of the free phenol due to the formation of the intermolecular hydrogen bond O–H ... O–H. The bond lengths of the intermolecular hydrogen bonds of the phenol-(H₂O)_n ($n=3-5$) clusters are shown in Tables 2–4. One can find that in the ground state the order of the intermolecular hydrogen bonds length for phenol-(H₂O)₃ is as follows: O₁–H₂ ... O₃–H < O₃–H₄ ... O₅–H < O₅–H₆ ... O₇–H < O₇–H₈ ... O₁–H. That is to say the order of the strength of the intermolecular hydrogen bonds for phenol-(H₂O)₃ in the ground state is O₁–H₂ ... O₃–H > O₃–H₄ ... O₅–H > O₅–H₆ ... O₇–H > O₇–H₈ ... O₁–H. The orders of the strength of the intermolecular hydrogen bonds for phenol-(H₂O)₄ (a), phenol-(H₂O)₄ (b), and phenol-(H₂O)₅ are the same to that of phenol-(H₂O)₃. Therefore, it is demonstrated that the intermolecular hydrogen bond formed by H atom (from OH of phenol) and O atom (from OH of water) is the strongest, but the intermolecular hydrogen bond formed by O atom (from OH of phenol) and H atom (from OH of water) is the weakest for all the H-bonded phenol-(H₂O)_n ($n=3-5$) clusters in the ground state. This is due to that phenol, a weak acid, is a better proton donor than water. Moreover, it could be proposed that in the ground state with the anticlockwise order of the ring formed by the intermolecular hydrogen bonds in the H-bonded phenol-(H₂O)_n ($n=3-5$) clusters, the strengths of the intermolecular hydrogen bonds decrease.

3.2. Nature of low-lying excited states

To understand the nature of the electronically excited states for the H-bonded phenol-(H₂O)_n ($n=3-5$) clusters, electronic excitation energies and their corresponding oscillator strengths

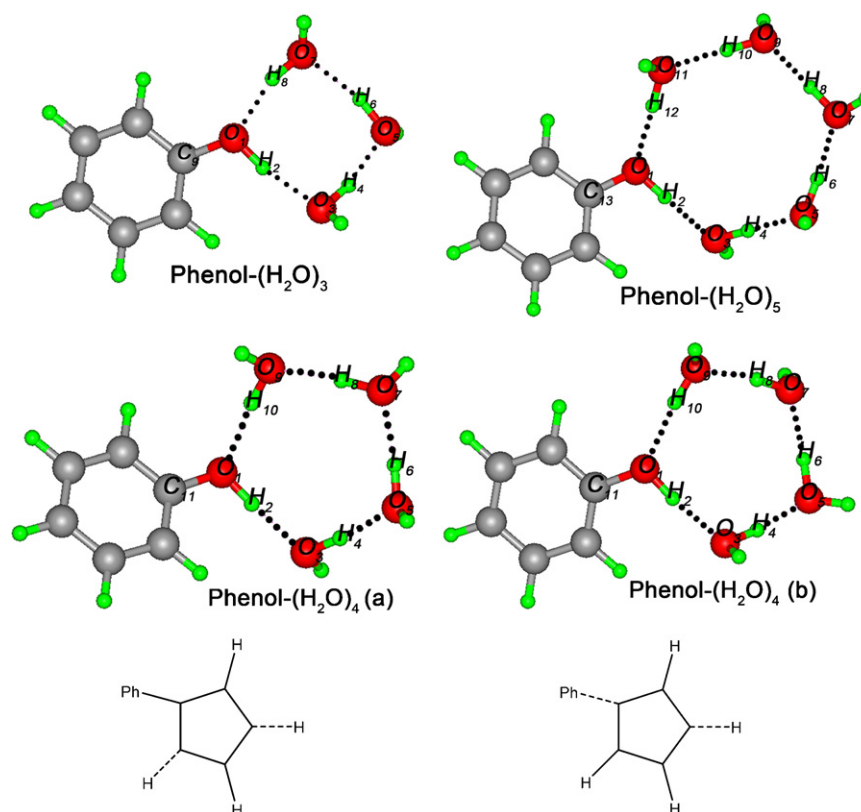


Fig. 1. Optimized geometric structures of H-bonded phenol-(H₂O)_n ($n=3-5$) clusters.

Table 1

The calculated electronic excitation energies (nm) and corresponding oscillator strengths for the H-bonded phenol-(H₂O)_n ($n=3-5$) clusters and the isolated phenol monomer.

	Phenol-(H ₂ O) ₃		Phenol-(H ₂ O) ₄ (a)		Phenol-(H ₂ O) ₄ (b)		Phenol-(H ₂ O) ₅		Phenol	
	TDDFT	CIS	TDDFT	CIS	TDDFT	CIS	TDDFT	CIS	TDDFT	CIS
S ₁	243 (0.030) H→L 79.8%	240 (0.029) H→L 72.8%	244 (0.030) H→L 81.0%	241 (0.030) H→L 74.2%	243 (0.031) H→L 80.0%	240 (0.030) H→L 73.0%	244 (0.031) H→L 81.1%	241 (0.031) H→L 74.4%	243 (0.034) H→L 80.4%	239 (0.033) H→L 73.3%
S ₂	216 (0.019)	216 (0.010)	216 (0.019)	215 (0.007)	219 (0.004)	219 (0.003)	217 (0.009)	217 (0.003)	209 (0.034)	208 (0.000)
S ₃	210 (0.040)	202 (0.050)	210 (0.031)	203 (0.040)	210 (0.050)	202 (0.051)	211 (0.041)	204 (0.042)	208 (0.000)	201 (0.034)
S ₄	191 (0.006)	191 (0.002)	195 (0.003)	194 (0.002)	197 (0.001)	197 (0.000)	198 (0.001)	197 (0.002)	184 (0.001)	184 (0.001)
S ₅	188 (0.018)	188 (0.005)	188 (0.089)	187 (0.029)	190 (0.003)	190 (0.001)	189 (0.007)	189 (0.001)	179 (0.368)	179 (0.001)
S ₆	184 (0.001)	184 (0.001)	185 (0.002)	185 (0.001)	186 (0.001)	186 (0.000)	189 (0.052)	188 (0.019)	179 (0.625)	171 (0.473)
T ₁	330 (0.028)	303 (0.058)	330 (0.029)	303 (0.061)	330 (0.028)	303 (0.058)	330 (0.030)	303 (0.062)	330 (0.029)	303 (0.063)
T ₂	295 (0.550)	291 (0.495)	296 (0.539)	293 (0.484)	295 (0.548)	292 (0.493)	297 (0.537)	293 (0.482)	296 (0.550)	292 (0.488)
T ₃	269 (0.992)	265 (0.993)	269 (0.991)	266 (0.984)	269 (0.985)	266 (0.981)	270 (0.983)	266 (0.986)	269 (0.981)	265 (0.987)
T ₄	230 (0.423)	229 (0.398)	230 (0.432)	229 (0.406)	230 (0.425)	228 (0.400)	230 (0.434)	228 (0.408)	229 (0.427)	227 (0.402)
T ₅	217 (0.001)	217 (0.001)	216 (0.002)	216 (0.002)	220 (0.000)	220 (0.000)	218 (0.001)	218 (0.001)	214 (0.000)	213 (0.000)
T ₆	192 (0.002)	192 (0.002)	195 (0.004)	195 (0.004)	198 (0.001)	198 (0.001)	198 (0.003)	198 (0.003)	187 (0.001)	187 (0.001)

of the low-lying excited states are calculated using the TDDFT method and are listed in Table 1. The phenol monomer is also investigated for comparison. The electronic excitation energies and their corresponding oscillator strengths of phenol-(H₂O)_n ($n=3-5$) clusters and the monomer phenol in S₁ state are almost the same to each other, which can be due to the total impact of the intermolecular hydrogen bonds forming a ring in phenol-(H₂O)_n ($n=3-5$) clusters. It is similar for the case in T₁ state. Moreover, one can see that the electronic excitation energies of

phenol-(H₂O)_n ($n=3-5$) clusters from S₂ state to S₆ state are a little redshifted compared with those of monomer phenol due to the formation of intermolecular hydrogen bonds. The impact of intermolecular hydrogen bonds of phenol-(H₂O)_n ($n=3-5$) clusters on the electronic excitation energies in electronic excited triplet states is almost the same to that in electronic excited singlet states. Furthermore, to demonstrate the reliability of the TDDFT results, we have also investigated all of the clusters using the CIS method, and the results are also shown in Table 1. It can

Table 2

Calculated lengths (Å) of hydrogen bonds and H-bonded groups of phenol-(H₂O)₃ in S₀, S₁, and T₁ states.

Phenol-(H ₂ O) ₃	S ₀	S ₁	T ₁
C ₉ —O ₁	1.370	1.345	1.360
O ₁ —H ₂	0.991	1.007	0.996
H ₂ ... O ₃	1.713	1.626	1.688
O ₃ —H ₄	0.988	0.990	0.988
H ₄ ... O ₅	1.742	1.722	1.740
O ₅ —H ₆	0.985	0.983	0.984
H ₆ ... O ₇	1.769	1.779	1.776
O ₇ —H ₈	0.980	0.974	0.978
H ₈ ... O ₁	1.826	1.939	1.861

Table 3

Calculated lengths (Å) of hydrogen bonds and H-bonded groups of phenol-(H₂O)₄ (a) and phenol-(H₂O)₄ (b) in S₀, S₁, and T₁ states.

	Phenol-(H ₂ O) ₄ (a)			Phenol-(H ₂ O) ₄ (b)		
	S ₀	S ₁	T ₁	S ₀	S ₁	T ₁
C ₁₁ —O ₁	1.369	1.342	1.358	1.369	1.345	1.360
O ₁ —H ₂	0.994	1.013	1.000	0.993	1.011	0.998
H ₂ ... O ₃	1.680	1.584	1.649	1.684	1.593	1.660
O ₃ —H ₄	0.991	0.995	0.992	0.989	0.992	0.989
H ₄ ... O ₅	1.701	1.669	1.695	1.719	1.695	1.716
O ₅ —H ₆	0.989	0.989	0.988	0.988	0.988	0.988
H ₆ ... O ₇	1.720	1.714	1.722	1.726	1.719	1.727
O ₇ —H ₈	0.986	0.985	0.986	0.986	0.984	0.985
H ₈ ... O ₉	1.741	1.753	1.747	1.742	1.755	1.750
O ₉ —H ₁₀	0.982	0.974	0.980	0.982	0.976	0.980
H ₁₀ ... O ₁	1.803	1.930	1.835	1.778	1.875	1.800

Table 4

Calculated lengths (Å) of hydrogen bonds and H-bonded groups of phenol-(H₂O)₅ in S₀, S₁, and T₁ states.

Phenol-(H ₂ O) ₅	S ₀	S ₁	T ₁
C ₁₃ —O ₁	1.368	1.341	1.358
O ₁ —H ₂	0.994	1.014	1.000
H ₂ ... O ₃	1.671	1.575	1.644
O ₃ —H ₄	0.991	0.996	0.992
H ₄ ... O ₅	1.695	1.660	1.690
O ₅ —H ₆	0.988	0.989	0.988
H ₆ ... O ₇	1.718	1.705	1.718
O ₇ —H ₈	0.988	0.988	0.987
H ₈ ... O ₉	1.719	1.723	1.722
O ₉ —H ₁₀	0.986	0.985	0.985
H ₁₀ ... O ₁₁	1.736	1.752	1.743
O ₁₁ —H ₁₂	0.982	0.974	0.980
H ₁₂ ... O ₁	1.784	1.930	1.813

be seen that the CIS method gives slightly higher electronic excitation energies than the TDDFT method. The results are similar to these reported by Zhao et al. [35].

As we know, molecular orbitals (MOs) analysis can directly provide insight into the nature of the excited states. Fig. 2 depicts the MOs of the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters. Herein, the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) orbital are shown, since the S₁ state of the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters is associated with the two orbitals. One can find that the electron density distribution of HOMO orbitals (LUMO orbitals) of the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters is almost the same. Furthermore, it can be clearly seen that the electron densities of both the orbitals are localized in the phenol moiety. Thus, the S₁ state of the H-bonded phenol-(H₂O)_n (*n*=3–5)

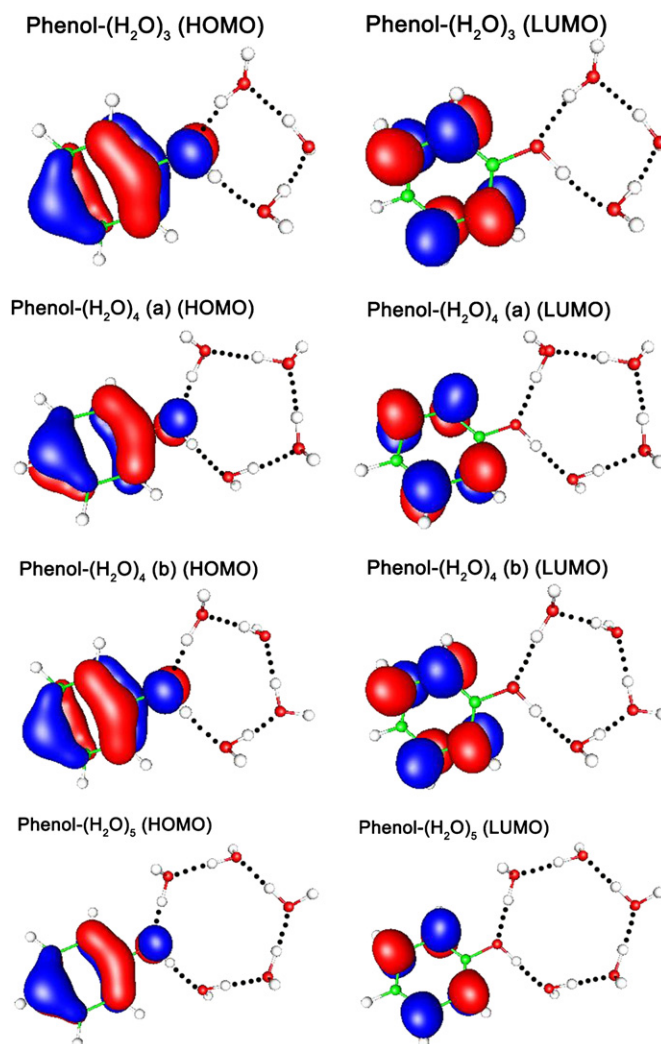


Fig. 2. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters.

clusters is a locally excited (LE) state. One can also find that in addition to the π - π^* electronic excitation of the benzene ring moiety, the electron in the hydroxyl group is also electronically excited. Upon electron excitation, the electron density of phenolic hydroxyl group is drastically reduced. And the phenolic O–H bond is predicted to be shortened in S₁ state. Thus, the hydrogen bond formed by H atom (from OH of phenol) and O atom (from water molecule) will be influenced by the charge redistribution in the S₁ state.

3.3. Infrared spectra of ground and excited states

The excited-state geometric optimizations for the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters have also been performed using the TDDFT method. Furthermore, the infrared spectra in the ground state S₀ and excited states S₁ and T₁, are also calculated. It has been demonstrated that the TDDFT method is a reliable tool to calculate the electronic excited-state IR spectra [39–48]. Their computational results are in good agreement with the corresponding experimental results. It should be noted that the calculation of the infrared spectra in electronically excited states is very difficult and time consuming. The changes of the intermolecular hydrogen bonding interactions in different electronic states can be monitored by the spectral shift of the stretching vibrational mode of the O–H group. Thus, the calculated

stretching vibrational frequencies of the O–H group in different electronic states are labeled in Figs. 3–6. The dash dot line (3620 cm^{-1}) indicates the stretching vibrational frequency of

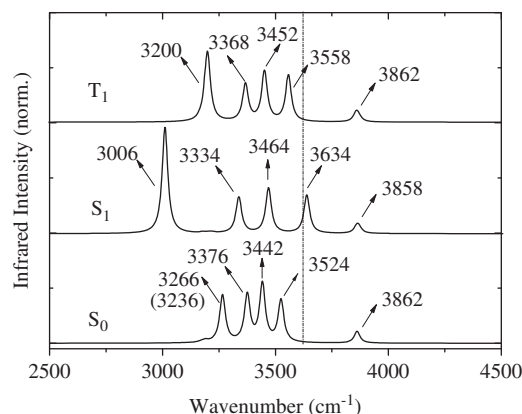


Fig. 3. Calculated infrared spectra of the hydrogen-bonded phenol-(H₂O)₃ complex in different electronic states at the region of O–H stretching vibration. The dash dot line (3620 cm^{-1}) indicates the stretching vibration frequency of O–H bond of the isolated phenol in ground state. The corresponding value by experiment is in parentheses [16].

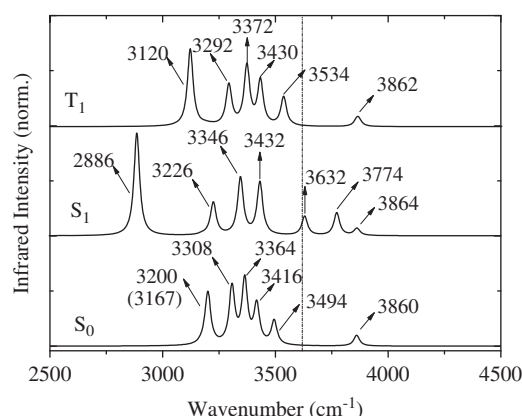


Fig. 4. Calculated infrared spectra of the hydrogen-bonded phenol-(H₂O)₄ (a) complex in different electronic states at the region of O–H stretching vibration. The dash dot line (3620 cm^{-1}) indicates the stretching vibration frequency of O–H bond of the isolated phenol in ground state. The corresponding value by experiment is in parentheses [16].

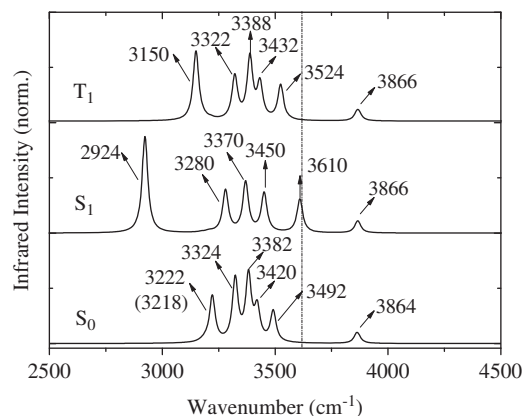


Fig. 5. Calculated infrared spectra of the hydrogen-bonded phenol-(H₂O)₄ (b) complex in different electronic states at the region of O–H stretching vibration. The dash dot line (3620 cm^{-1}) indicates the stretching vibration frequency of O–H bond of the isolated phenol in ground state. The corresponding value by experiment is in parentheses [16].

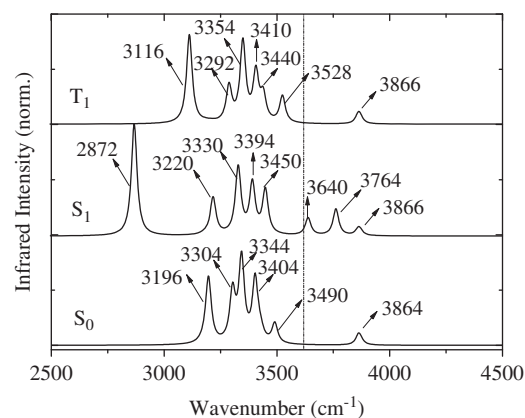


Fig. 6. Calculated infrared spectra of the hydrogen-bonded phenol-(H₂O)₅ complex in different electronic states at the region of O–H stretching vibration. The dash dot line indicates the stretching vibration frequency of O–H bond of the isolated phenol in ground state.

O–H bond of the isolated phenol monomer in ground state for comparison. For all the clusters, the bands belonging to the former group are assigned to the phenolic OH stretching vibration and the water symmetric stretching bands and the bands in the latter group are assigned to the antisymmetric stretching bands of the waters. It can be seen that the calculated phenolic OH stretching vibrational frequencies in the ground state for the H-bonded phenol-(H₂O)_{3,4} clusters are in good agreement with the corresponding experimental values. For the H-bonded phenol-(H₂O)₃ cluster in ground state, the calculated stretching vibrational frequency of the O₁–H₂ bond is downshifted to 3266 cm^{-1} compared with that of isolated phenol monomer (3620 cm^{-1}) due to the formation of the intermolecular hydrogen bond O₁–H₂ ... O₃–H. Upon electronic excitation, the O–H stretching vibrational band continues to downshift by 260 and 66 cm^{-1} to the S₁ state and T₁ state from 3266 cm^{-1} in the ground state, respectively. It can be concluded that the hydrogen bond O₁–H₂ ... O₃–H should be strengthened in the S₁ and T₁ states. Furthermore, it is demonstrated that the order of the strength of the hydrogen bond O₁–H₂ ... O₃–H in different electronic states should be: S₁ state > T₁ state > S₀ state. For the H-bonded phenol-(H₂O)₄ cluster, the calculated infrared spectral feature of isomer (a) and (b) is very similar. The formation of intermolecular hydrogen bond O₁–H₂ ... O₃–H between phenol and water induces a strong redshift of 400 cm^{-1} for the O–H stretching band from the free O–H stretching vibrational frequency of 3620 cm^{-1} for isolated phenol. Then, the stretching vibrational mode of O₁–H₂ is further redshifted by 314 and 20 cm^{-1} to 2886 and 3120 cm^{-1} in S₁ state and T₁ state compared with that in ground state, respectively. Therefore, the order of the strength of the hydrogen bond O₁–H₂ ... O₃–H of phenol-(H₂O)₄ (a) in different electronic states should be S₁ state > T₁ state > S₀ state. At the same time, the characteristics of the infrared spectra of phenol-(H₂O)₄ (b) and phenol-(H₂O)₅ are similar to those of phenol-(H₂O)₄ (a) and phenol-(H₂O)₃. Furthermore, it can be clearly seen that for phenol-(H₂O)_n ($n=3-5$) the symmetric stretching bands of the waters and the OH stretching vibration of phenol side are redshifted with increasing n , and the frequencies of the antisymmetric stretching bands of the waters are not hardly changed. The “window region” named by Mikami [22] appears between unshifted and shifted absorption bands and becomes wider for the larger clusters. In the electronically excited state, the “window region” becomes narrow compared with that in the ground state for the H-bonded phenol-(H₂O)_n ($n=3-5$) clusters.

3.4. Change of intermolecular hydrogen bonds in excited states

The optimized geometric conformations of the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters in S₁ state and T₁ state are shown in Fig. 7. The structures of these clusters in the S₀, S₁, and T₁ states are similar except that the lengths of hydrogen bonds change in different electronic states. Calculated lengths of hydrogen bonds and H-bonded groups of phenol-(H₂O)_n (*n*=3–5) clusters in S₀ and S₁ and T₁ states are shown in Tables 2–4. For all the clusters, the phenolic OH bond is lengthened and the intermolecular hydrogen bond O₁–H₂ ... O₃–H is shortened in electronically excited states (S₁ and T₁ state). That is to say the phenolic OH bond is weakened and the intermolecular hydrogen bond O₁–H₂ ... O₃–H is strengthened in electronically excited states, which is in accordance with the result of IR spectra. The orders of the hydrogen bonding strength of phenol-(H₂O)₃ in S₁ and T₁ states are O₁–H₂ ... O₃–H > O₃–H₄ ... O₅–H > O₅–H₆ ... O₇–H > O₇–H₈ ... O₁–H, which is similar to that in ground state. This phenomenon also exists in the H-bonded phenol-(H₂O)₄ (a), phenol-(H₂O)₄ (b) and phenol-(H₂O)₅ clusters. In other words, the change of hydrogen bonding strength has regularity in all the electronic states. The hydrogen bond, which is formed between H atom (from OH of phenol) and O atom (from water), is the shortest and the strongest, whereas the hydrogen bond, which

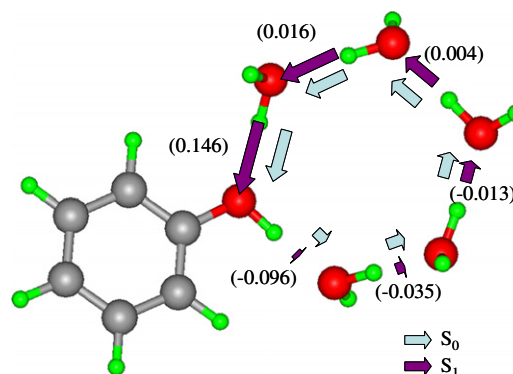


Fig. 8. The trends of the changes of hydrogen bonding strength in the H-bonded ring in S₀ and S₁ states. The blue arrows represent the relative lengths of the hydrogen bonds in S₀ state. The purple arrows represent the relative lengths of the hydrogen bonds in S₁ state. In parentheses are the ΔL ($\Delta L = L_{S1} - L_{S0}$). L_{S0} and L_{S1} are the lengths of intermolecular hydrogen bonds in S₀ and S₁ states, respectively (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

is formed between H atom (from water) and O atom (from OH of phenol), is the longest and the weakest in the S₀ and S₁ and T₁ states. Moreover, we find a very interesting phenomenon. And the H-bonded phenol-(H₂O)₅ cluster is taken for example, which is shown in Fig. 8. The blue arrows represent the relative lengths of the intermolecular hydrogen bonds in the S₀ state and the purple arrows represent the relative lengths of the intermolecular hydrogen bonds in the S₁ state. As seen in Fig. 8, one can find that in the ring the orders of the hydrogen bonding length in S₀ and S₁ states are: O₁–H₂ ... O₃–H < O₃–H₄ ... O₅–H < O₅–H₆ ... O₇–H < O₇–H₈ ... O₉–H < O₉–H₁₀ ... O₁₁–H < O₁₁–H₁₂ ... O₁–H. From the values in parentheses of Fig. 8, it can be concluded that the change of the strength of intermolecular hydrogen bonds near to the solute phenol in different electronic states is very remarkable. However, the strength change of intermolecular hydrogen bonds far to the solute phenol molecule in different electronic states is insignificant. In other words, upon electronic excitation, with the change of the distance between the phenol and water molecule, the change of strength of hydrogen bonds has regularity. At the same time, the intermolecular hydrogen bond (phenolic hydroxyl group is the H donor) is strengthened in the S₁ state; however, the intermolecular hydrogen bond (phenolic hydroxyl group is the H acceptor) is weakened in the S₁ state. The cases of other clusters are similar to phenol-(H₂O)₅. Furthermore, the change of intermolecular hydrogen bond strength in the T₁ state (compared with S₀ state) is smaller than that in the S₁ state (compared with S₀ state), though the change trend of intermolecular hydrogen bond strength is the same in the S₁ and T₁ state.

4. Conclusion

In this study, the excited-state hydrogen-bonding dynamics of phenol-(H₂O)_n (*n*=3–5) clusters were investigated using the TDDFT method. The geometric structures of the clusters in the ground state, S₁ state, and T₁ state were calculated. Moreover, the IR spectra of all the clusters in different electronic states were calculated. Four, five, and six hydrogen bonds were formed in phenol-(H₂O)₃, phenol-(H₂O)₄, and phenol-(H₂O)₅ clusters, respectively. Based on the computational results, it can be concluded that the S₁ state of the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters are LE states on phenol moiety. The water molecules are located in their electronic ground state. The frequency of phenolic OH stretching vibration of the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters is reduced compared with that of the isolated phenol

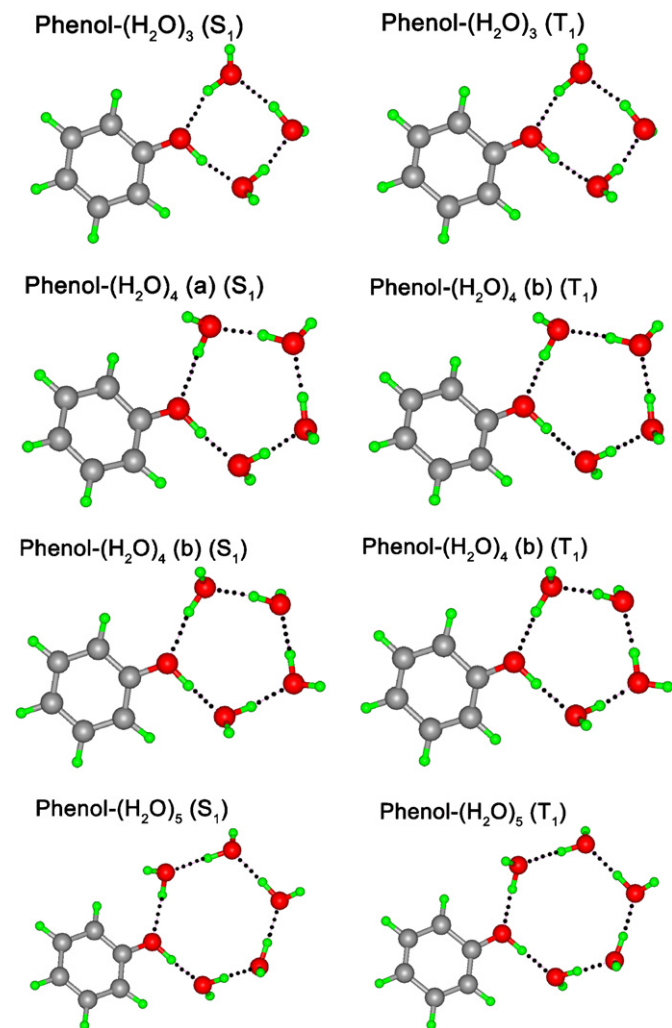


Fig. 7. The optimized geometric conformations of the H-bonded phenol-(H₂O)_n (*n*=3–5) clusters in S₁ state and T₁ state.

monomer due to the intermolecular hydrogen bond $O_1-H_2 \cdots O_3-H$. The OH stretching vibration of phenol side and the symmetric stretching bands of waters in the H-bonded phenol- $(H_2O)_n$ ($n=3-5$) clusters are redshifted with increasing n . However, the antisymmetric stretching bands of waters are almost unchanged. The “window region” between unshifted and shifted absorption bands becomes wider for the larger clusters. Furthermore, in the S_1 state, the “window region” becomes narrow compared with that in the ground state for the corresponding clusters. Moreover, with the order of the hydrogen bonds in the ring of the clusters, the change of hydrogen bonding strength has regularity in all the electronic states. That is with the anticlockwise order of the ring in the H-bonded phenol- $(H_2O)_n$ ($n=3-5$) clusters, the strength of intermolecular hydrogen bonds decreases in S_0 , S_1 , and T_1 states. Upon electronic excitation, with the change of the distance between the phenol solute and water solvent, the strength change of hydrogen bonds displayed regularity. That is to say, upon electronic excitation, the smaller the distance between phenol and water is, the larger the change of intermolecular hydrogen bonds strength is. Moreover, the intermolecular hydrogen bond (phenolic hydroxyl group is the H donor) is strengthened in electronically excited state. In contrast, the intermolecular hydrogen bond (phenolic hydroxyl group is the H acceptor) is weakened in electronically excited state. The study on the H-bonded solute-solvent phenol- $(H_2O)_n$ ($n=3-5$) clusters in electronic excited states is of great importance for understanding the molecular interactions in organic acids, the photodegradation process, and mechanism of phenol in water solution.

Acknowledgments

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