Calixarene building block bis(2-hydroxyphenyl)methane (2HDPM) and hydrogen-bonded 2HDPM-H$_2$O complex in electronic excited state

Se Wang · Ce Hao · Zhanxian Gao · Jingwen Chen · Jieshan Qiu

Abstract Intramolecular and intermolecular hydrogen bonding in electronic excited states of calixarene building blocks bis(2-hydroxyphenyl)methane (2HDPM) monomer and hydrogen-bonded 2HDPM-H$_2$O complex were studied theoretically using the time-dependent density functional theory (TDDFT). Twenty-four stable conformations (12 pairs of enantiomers) of 2HDPM monomer have been found in the ground state. From the calculation results, the conformations 1a and 1b which both have an intramolecular hydrogen bond are the most stable ones. The infrared spectra of 2HDPM monomer and 2HDPM-H$_2$O complex in ground state and S$_1$ state were calculated. The stretching vibrational absorption band of O$_2$−H$_3$ group in the monomer and complex disappeared in the S$_1$ state. At the same time, a new strong absorption band appeared at the C=O stretching region. From the calculation of bond lengths, it indicates that the O$_2$−H$_3$ bond is significantly lengthened in the S$_1$ state. However, the C$_1$−O$_2$ bond is drastically shortened upon electronic excitation to the S$_1$ state and has the characteristics of C=O band. Furthermore, the intramolecular hydrogen bond O$_2$−H$_3$···O$_4$ of the 2HDPM monomer and the intermolecular hydrogen bonds O$_2$−H$_3$···O$_7$ and O$_7$−H$_9$···O$_4$ of 2HDPM-H$_2$O complex are all shortened and strengthened in the S$_1$ state.

S. Wang · C. Hao (✉) · Z. Gao · J. Chen · J. Qiu
State Key Laboratory of Fine Chemicals, Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China
e-mail: haoce_dlut@126.com

S. Wang
State Key Laboratory of Molecular Reaction Dynamics and Center for Theoretical and Computational Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Introduction

Hydrogen bonding (H-bonding), as a site-specific interaction between hydrogen donor and acceptor, plays a very important role on understanding microscopic structure and function in many organic systems [1–8]. Currently, many experimental and theoretical studies have been performed to investigate the electronic ground-state properties of hydrogen bonds [9–13]. However, little is known about the properties of hydrogen bonds in the electronically excited states. When photoexcited, the hydrogen donor and acceptor molecules undergo reorganization and greatly change because of difference in charge distribution for different electronic states [14–17]. This process is defined as the H-bonding dynamics, which controls the excited-state dynamics of hydrogen-bonded complexes in a significant way [18–20].

H-bonding dynamics always occurs on ultrafast timescales, which are set by vibrational motions of the hydrogen donor and acceptor groups [21, 22]. It is of great importance for the electronic excited-state dynamics of the hydrogen-bonded (H-bonded) complexes. Zhao et al. have first demonstrated that the electronic excited-state H-bonding dynamics can strongly facilitate the ultrafast radiationless deactivation processes, such as fluorescence quenching, internal conversion (IC) and intersystem crossing (ISC), excited-state proton transfer, solute-solvent intermolecular electron transfer and intermolecular photoinduced electron transfer (PET) [4, 18, 22–30]. Femtosecond time-resolved infrared spectroscopic has shown the potential to give a good insight into the H-bonding dynamics. At the same time, Zhao et al. have also demonstrated that the DFT and TDDFT methods can be perfectly used to

describe intramolecular and intermolecular H-bonding in ground and electronically excited states [22–30].

Flexible molecules calixarenes (CAs), which are cyclic oligomers, are built with phenol molecules connected via the *ortho* positions by methylene groups. CAs have OH groups H-bonded with each other, resulting in forming H-bonded network. CAs have a cavity and are recognized as molecular receptors [31, 32]. They can form complexes with cations, anions and neutral molecules [31, 32]. The common CAs compounds are C4A, C6A and C8A. In addition, CAs are flexible compounds with complicated conformations. It is extremely difficult to investigate conformations, properties and functions of CAs and their derivatives. Therefore, the building block bis(2-hydroxyphenyl)methane (2HDPM) that make up CAs need to be studied. There are many conformational isomers exiting in the 2HDPM molecule in the ground state [33–35]. Some studies show that the most stable conformation possesses a single intramolecular $O-H \cdots O$ hydrogen bond between the two OH groups [33–35]. The second stable one has two equivalent $O-H \cdots \pi$ hydrogen bonds and C_2 symmetry [33–35]. In addition, the vibrational spectra of 2HDPM in the ground state has also been analyzed via computational and experimental methods [33, 34]. Pillsbury et al. has used laser-induced fluorescence, single-vibronic level fluorescence (SVLF), UV hole burning, and fluorescence dip infrared (FDIR) spectroscopy to characterize the ground-state and first excited-state vibronic spectroscopy of 2HDPM molecule [34]. However, the study about the 2HDPM molecule in the solvent water in different electronic states is so scarce. Therefore, it calls for more detailed theoretical calculations.

In the present study, we investigated the properties of hydrogen bonds in the isolated 2HDPM monomer and H-bonded 2HDPM-H_2O complex in the ground state and S_1 state employing the DFT and TDDFT methods, respectively. The stable conformations of the monomer and H-bonded complex in the ground state have been calculated. The excited-state geometric optimizations for the monomer and H-bonded complex have been performed. We have also calculated the ground-state and excited-state infrared spectra at the $O-H$ stretching vibrational region of the monomer and the H-bonded complex.

Computational details

The geometric optimizations of the isolated 2HDPM monomer as well as the hydrogen-bonded 2HDPM-H_2O complex in the ground state were calculated using density functional theory (DFT) with Becke's three-parameter hybrid exchange function with Lee-Yang-Parr gradient-correlated correlation functional (B3LYP hybrid functional) [36]. The triple-ζ valence quality with one set of polarization functions

(TZVP) was chosen as basis sets throughout [37]. The excited-state calculation was performed using the time-dependent density functional theory (TDDFT) method with the B3LYP hybrid functional and TZVP basis set [36–38]. Fine quadrature grids 4 were also employed [39]. Harmonic vibrational frequencies in the ground state and excited state were determined by diagonalization of the Hessian [40]. The excited-state Hessian was obtained by numerical differentiation of analytical gradients using central differences and default displacements of 0.02 Bohr [41]. The infrared intensities were determined from the gradients of the dipole moment [42]. All the calculated vibrational frequencies are scaled by a factor of 0.95 to correct the anharmonicity effects in this work [40–45]. All the computations were performed using the TUBOMOLE program suite [38].

Results and discussion

The calculated stable conformations of the isolated 2HDPM monomer in the ground state are shown in Fig. 1. There are 24 stable conformations found via our calculations in the ground state. Among these conformations, 1a, 5a, 2a, 6b, 12b, 10b, 8a are consistent with the seven stable conformations reported by Katsyuba et al. [33] In Fig. 1 the isomers in the right column are enantiomers of those in the left column. The calculated results indicate that the most stable conformation is 1a and 1b. One intramolecular hydrogen bond is formed between the hydroxyl groups of 1a (1b). The second stable conformation is 5a and 5b. They possess two equivalent $O-H \cdots \pi$ hydrogen bonds and are C_2 symmetry, which are in agreement with the results of Pillsbury et al. [34]. Except for 1a and 1b, other conformations can be divided into three types: propeller-like structure (2a to 5b), gable structure (6a to 8b) and T-shaped structure (9a to 12b).

In this paper, we focus our attention on the most stable conformation 1a (1b is its enantiomer). The geometric optimizations of the H-bonded 2HDPM-H_2O complex and the isolated 2HDPM monomer in the ground state are shown in Fig. 2. The intramolecular hydrogen bond $O_2-H_3 \cdots O_4$ is formed between the two OH groups of the isolated 2HDMP monomer [4]. However, with adding one water molecule to the monomer, the intramolecular hydrogen bond disappears. In contrast, two intermolecular hydrogen bonds $O_2-H_3 \cdots O_7$ and $O_7-H_9 \cdots O_4$ are formed between the OH groups of phenol and water. Furthermore, one phenol rotates, resulting in a structure of 2HDPM similar to that of 2HDPM 11b.

Molecular orbitals (MOs) analysis can directly provide insight into the nature of the excited states [4]. Figure 3 depicts the frontier MOs of the isolated 2HDPM monomer and the H-bonded 2HDPM-H_2O complex. The TDDFT calculation results have shown that the S_1 states of the isolated 2HDPM monomer and the H-bonded 2HDPM-
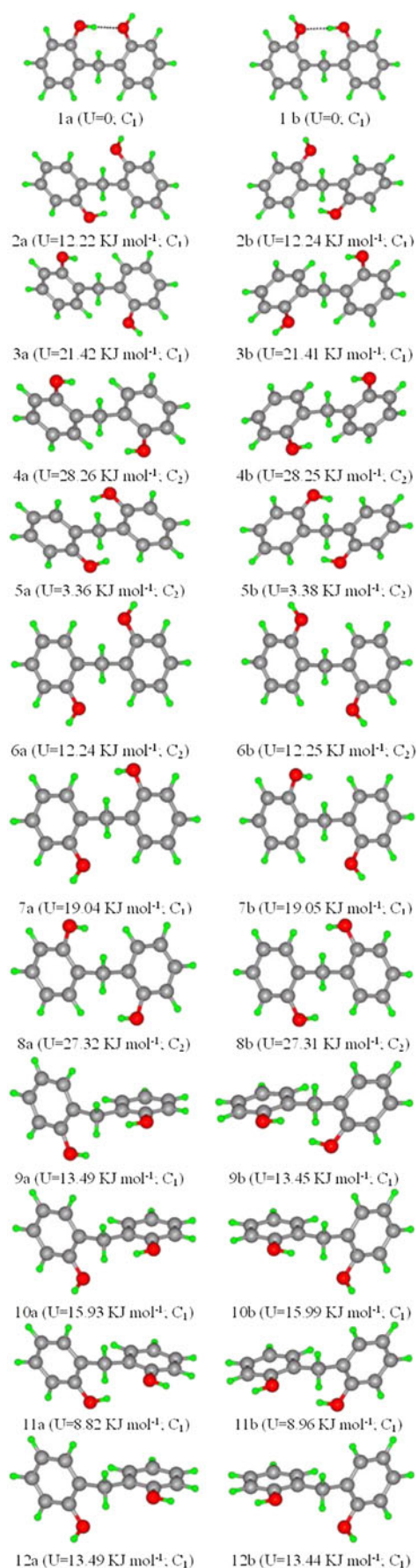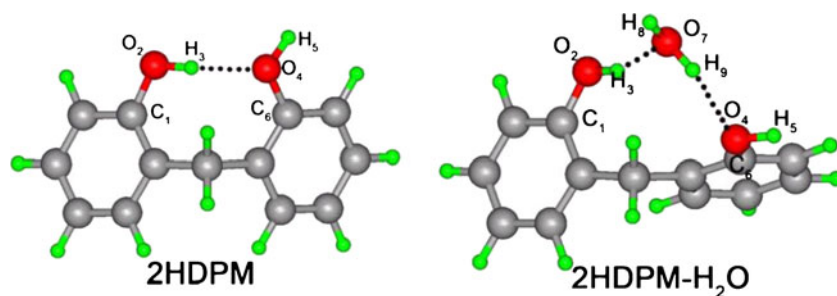
H_2O complex are both mainly contributed by the orbital transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) (97.4 % and 99.2 %). Therefore, we only show the HOMO and LUMO in this paper. It can be clearly seen that for the isolated 2HDPM monomer the electron densities of HOMO are localized in one phenol moiety (H donor), whereas most of the LUMO are localized in the other phenol moiety (H acceptor). In addition, the oscillator strength (0.001) of the S_1 state is very low. Therefore, the S_1 state of 2HDPM monomer is the intramolecular charge transfer (ICT) state, which is similar to brominated diphenyl ether 181 [46]. At the same time, one can find that the electron densities in the OH group (the H donor) are deduced from HOMO to LUMO. Therefore, the intramolecular hydrogen bond may be influenced by the electronic excitation. For the H-bonded 2HDPM-H_2O complex, it is clear that from HOMO to LUMO the electron densities are transited from one phenol moiety (H donor) to the other phenol moiety (H acceptor). Similar to monomer, the S_1 state with very low oscillator strength (0.001) of H-bonded 2HDPM-H_2O complex is ICT state [4]. Furthermore, from HOMO to LUMO the electron densities in the OH group (the H donor) are deduced. Therefore, the intermolecular hydrogen bond may be strongly influenced by charge redistribution in S_1 state. Both the transitions from HOMO to LUMO of monomer and H-bonded complex are of $\pi\pi^*$ character.

The excited-state geometric optimizations for the isolated 2HDPM monomer and the H-bonded 2HDPM-H_2O complex have been performed using the TDDFT method. Furthermore, the infrared spectra both in the ground state and S_1 state are also calculated. It should be noted that the calculation of the infrared spectra in electronically excited states is difficult and very time consuming [4]. The changes of the intermolecular H-bonding interactions in different states can be monitored by the spectral shift of the stretching vibrational mode of the O−H group [28, 47].

The calculated IR spectra for the isolated 2HDPM monomer in different electronic states are shown in Fig. 4. One can find that the calculated O−H stretching vibrational frequencies in the ground state are in good agreement with the experimental values [33]. Upon excitation, the stretching vibrational mode of the O_4-H_5 group is redshifted by 119 cm^{-1} from 3623 cm^{-1} in the ground state to 3504 cm^{-1} in the S_1 state. It should be noted that the stretching vibrational absorption band of the O_2-H_3 group disappeared in the S_1 state. This indicates the O_2-H_3 group is significantly lengthened upon excitation to the S_1 state [4]. Therefore, one cannot find the O_2-H_3 stretching

vibrational band in the S$_1$ state due to that the O$_2$−H$_3$
stretching vibrational strength becomes so weak [4]. At the
same time, a new vibrational absorption band appeared at
1970 cm^{-1}. This indicates that C$_1$−O$_2$ bond has some char-
acteristics of the C=O group. So the C$_1$−O$_2$ bond should be
markedly shortened in the S$_1$ state of the isolated 2HDPM
monomer. It is similar to the behavior of the O−H group of
the dihydrogen-bonded phenol-BTMA complex in the S$_1$
state of the Zhao et al. study [20]. These changes of the O−
H bond and C−O bond show that the intramolecular

hydrogen bond O$_2$−H$_3$···O$_4$ should be strengthened in the
electronically excited states [4, 20].

Figure 5 shows the calculated IR spectra of the H-bonded
2HDPM-H$_2$O complex in different electronic states. The
calculated stretching vibrational frequency of the H-
bonded O−H group of water molecule is downshifted from
3616 cm^{-1} in ground state to 2823 cm^{-1} in S$_1$ state. There-
fore, the intermolecular hydrogen bond O$_7$−H$_9$···O$_4$ should
be strengthened in the electronically excited states [4]. Fur-
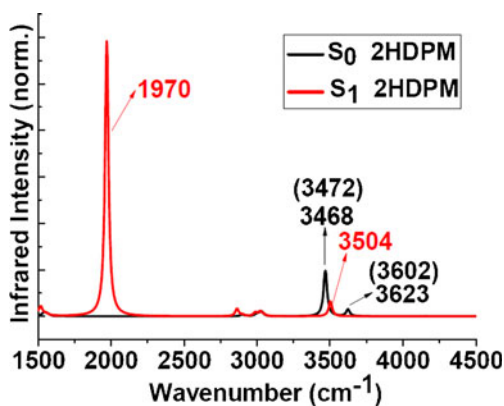thermore, the stretching vibrational absorption band of the
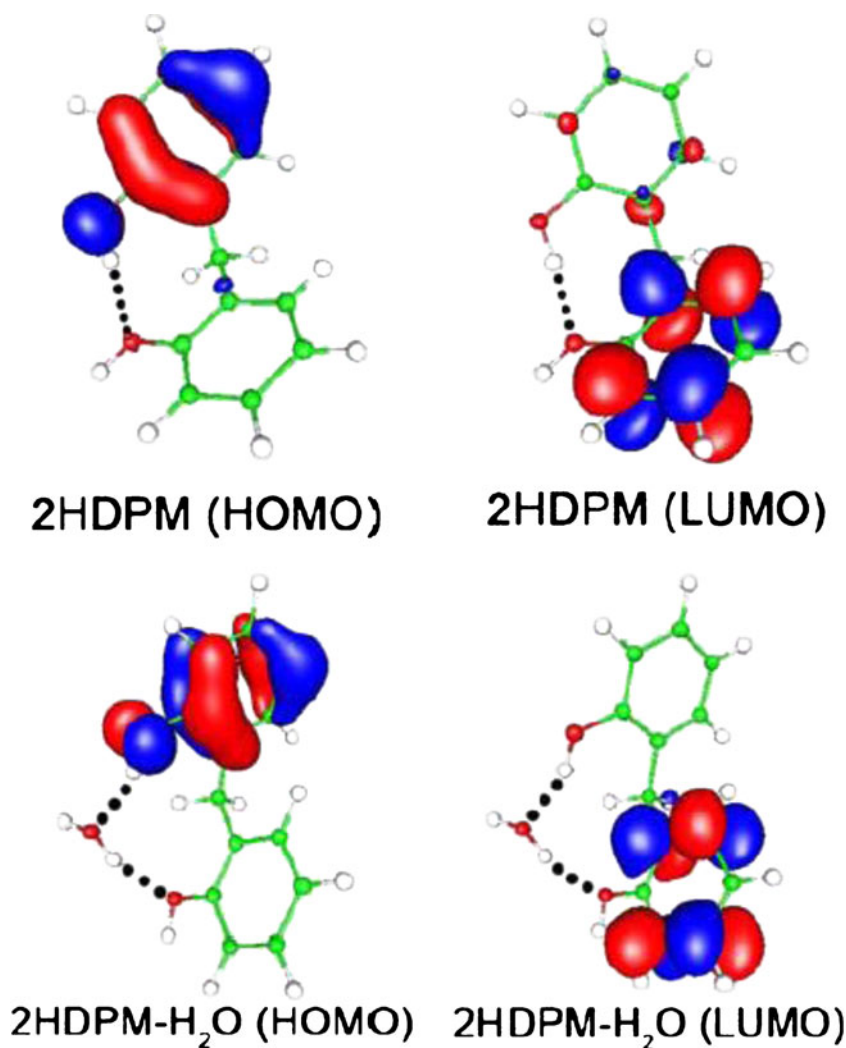
Fig. 4 Calculated infrared spectra of the isolated 2HDPM monomer in different electronic states. The corresponding experimental results are in parentheses (ref. [33])

Table 1 Calculated lengths (Å) of hydrogen bonds and hydrogen-bonded groups of the isolated 2HDPM monomer and its hydrogen-bonded 2HDPM-H_2O complex in the S_1 state

	2HDPM		2HDPM-H_2O	
	S_0	S_1	S_0	S_1
C_1-O_2	1.364	1.289	1.358	1.287
O_2-H_3	0.972	1.066	0.976	1.079
$H_3 \cdots O_4$	1.874	1.390	–	–
O_4-H_5	0.964	0.968	0.965	0.969
O_4-C_6	1.385	1.437	1.392	1.430
$H_3 \cdots O_7$	–	–	1.887	1.376
$H_9 \cdots O_4$	–	–	1.936	1.561
O_7-H_8	–	–	0.963	0.963
O_7-H_9	–	–	0.972	1.009

O_2-H_3 group disappeared in the S_1 state. It is similar to the behavior of O_2-H_3 group of the isolated 2HDPM monomer. It could be proposed that the O_2-H_3 group is significantly lengthened upon excitation to the S_1 state. At the same time, a new vibrational absorption band appeared at 1906 cm^{-1}. This indicates that C_1-O_2 bond has some characteristics of the C=O group. So the intermolecular hydrogen bond $O_2-H_3 \cdots O_7$ should also be strengthened in the electronically excited states [4].

Table 1 lists all the bond lengths associated with the formation of intramolecular and intermolecular hydrogen bonds in the isolated 2HDPM monomer and the H-bonded 2HDPM-H_2O complex. For the isolated 2HDPM monomer, it can be seen that the C_1-O_2 bond is significantly shortened from 1.364 to 1.289 Å upon electronic excitation to the S_1 state. Therefore, the C_1-O_2 bond in the S_1 state has some characteristics of C=O bond, which is consistent with the result of IR calculations [4]. Furthermore, the O_2-H_3 bond is markedly lengthened by 0.094 Å in the S_1 state compared to that in the ground state. Thus, the O_2-H_3 bond in the S_1 state becomes so weak that its stretching vibrational absorption band cannot be found in the calculated infrared spectra.
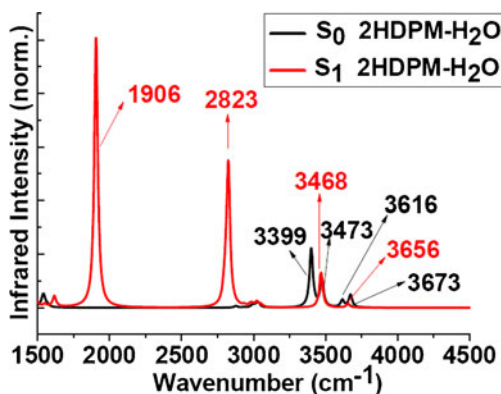

Fig. 5 Calculated infrared spectra of the hydrogen-bonded 2HDPM-H_2O complex in different electronic states

Following the lengthening of the O_2-H_3 bond in the S_1 state, the intramolecular hydrogen bond $O_2-H_3 \cdots O_4$ is significantly shortened from 1.874 Å in the ground state to 1.390 Å in the S_1 state. This means that hydrogen bond $O_2-H_3 \cdots O_4$ becomes strengthened markedly in the S_1 state compared to that in the ground state. Similarly, for the H-bonded 2HDPM-H_2O complex, the O_2-H_3 bond is drastically lengthened to 1.079 Å in the S_1 state from 0.976 Å in the ground state. The intermolecular hydrogen bond $O_2-H_3 \cdots O_7$ is significantly shortened from 1.887 Å in the ground state to 1.376 Å in the S_1 state. That is to say the $O_2-H_3 \cdots O_7$ becomes strengthened in the S_1 state compared to that in the ground state. Furthermore, the intermolecular hydrogen bond $O_7-H_9 \cdots O_4$ is also shortened and strengthened in the S_1 state [4].

Conclusions

In this study, the electronic excited state properties of hydrogen bonds in the isolated 2HDPM monomer and H-bonded 2HDPM-H_2O complex are investigated by TDDFT method. Twenty-four stable conformations (12 pairs of enantiomers) of the isolated 2HDPM monomer have been obtained in the ground state. From the calculation results, the conformations 1a and 1b which both have an intramolecular hydrogen bond are the most stable. Thus, only conformation 1a is considered in the present work (1b is the enantiomer). In the optimized conformations of the isolated 2HDPM monomer and the H-bonded 2HDPM-H_2O complex, one intramolecular hydrogen bond ($O_2-H_3 \cdots O_4$) and two intermolecular hydrogen bonds ($O_2-H_3 \cdots O_4$ and $O_7-H_9 \cdots O_4$) can be formed, respectively. The TDDFT calculation results have shown that the S_1 states of the isolated 2HDPM monomer and the H-bonded 2HDPM-H_2O complex are both mainly contributed by the orbital transition

from HOMO to LUMO and are both ICT states. From the infrared spectra of 2HDPM monomer and the H-bonded 2HDPM-H_2O complex in the ground state and S_1 state, the stretching vibrational absorption band of O_2-H_3 of both the monomer and H-bonded complex disappeared in the S_1 state. At the same time, a new strong absorption band appears at 1970 cm^{-1} and 1906 cm^{-1} for the monomer and H-bonded complex, respectively, which is assigned to C_1-O_2 bond. From our calculated lengths of the O_2-H_3 and C_1-O_2 of both the monomer and the H-bonded complex in the different electronic states, we find that the O_2-H_3 bond is significantly lengthened and C_1-O_2 bond is drastically shortened in the S_1 state. Therefore, the vibrational absorption band of the O_2-H_3 bond cannot be found in the IR spectra in the S_1 state and C_1-O_2 bond has some characteristics of the C=O bond in the S_1 state. Furthermore, it has been found that the calculated $H_3 \cdots O_4$, $H_3 \cdots O_7$, and $H_9 \cdots O_7$ distances are markedly shortened in the S_1 state. It is demonstrated that the intramolecular hydrogen bond $O_2-H_3 \cdots O_4$ of the 2HDPM monomer and the intermolecular hydrogen bonds $O_2-H_3 \cdots O_7$ and $O_7-H_9 \cdots O_4$ of the H-bonded 2HDPM-H_2O complex are all strengthened in the S_1 state.

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