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Role of intramolecular hydrogen bonding in the excited-state intramolecular double proton transfer (ESIDPT) of calix[4]arene: A TDDFT study

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Abstract: The time-dependent density functional theory (TDDFT) method was performed to investigate the excited-state intramolecular double proton transfer (ESIDPT) reaction of calix[4]arene (C4A) and the role of the intramolecular hydrogen bonds in the ESIDPT process. The geometries of C4A in the ground state and excited states (S_1, S_2 and T_1) were optimized. Four intramolecular hydrogen bonds formed in the C4A are strengthened or weakened in the S_2 and T_1 states compared to those in the ground state. Interestingly, upon excitation to the S_1 state of C4A, two protons H1 and H2 transfer along the two intramolecular hydrogen bonds O1-H1$\cdots$O2 and O2-H2$\cdots$O3, while the other two protons do not transfer. The ESIDPT reaction breaks the primary symmetry of C4A in the ground state. The potential energy curves of proton transfer demonstrate that the ESIDPT process follows the stepwise mechanism but not the concerted mechanism. Findings indicate that intramolecular hydrogen bonding is critical to the ESIDPT reactions in intramolecular hydrogen-bonded systems.

Keywords: Intramolecular hydrogen bond; ESIDPT; Calix[4]arene; Excited state; TDDFT

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1 Introduction

Hydrogen bonding is one of the most important concepts in the disciplines of physics, chemistry, and biology [1, 2]. Hydrogen bonding includes intermolecular hydrogen bonds and intramolecular hydrogen bonds, which often play a remarkable role in conformational preference, and photochemical and photophysical processes [3–5]. For example, Zhao *et al.* investigated intramolecular hydrogen bonding in both singlet and triplet excited states of aminofluorenones, and their findings indicated that the intramolecular hydrogen bond can facilitate an intersystem crossing (ISC) process and inhibit the occurrence of twisted intramolecular charge transfer (TICT) [6].

Proton transfer reactions in the excited state attract a lot of attention in physical, chemical, and biological systems [7–13]. Due to molecular structure, proton transfer can be intermolecular as well as intramolecular. Excited-state intramolecular proton transfer (ESIPT) reactions in hydrogen-bonded systems have been studied experimentally and theoretically [14–17]. A large number of organic molecules which undergo ESIPT have been identified, such as 4'-N,N-diethylamino-3-hydroxyflavone (DEAHF) [18], 2,5-bis(2-benzoxazolyl)-4-methoxyphenol (BBMP) [19], and 2-(2'-hydroxyphenyl)benzazole (HBO) [20]. Specifically, [2,2'-bipyridyl]-3,3'-diol ($BP(OH)_2$) [21, 22], a diaminobipyridine based C_3-symmetrical disk molecule (TAB) [23], and a subgroup molecule (DAC) [23] show interesting excited-state intramolecular double proton transfers (ESIDPT).

The calixarenes are particularly attractive as a basic skeleton for new supramolecular systems due to their well-defined molecular framework [24–28]. The calix[4]arene (C4A) has four conformers [25, 29–32]. Previous studies have demonstrated that the cone conformer is the most stable [29, 32]. Four intramolecular hydrogen bonds O-H$\cdots$O are formed in the cone conformers of C4A, which allows C4A to act as host for a wide range of guests. Thus, C4A is an excellent model in which to study intramolecular

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hydrogen bonding in the excited state [32–35]. However, little information is available on electronic excited-state intramolecular hydrogen bonding due to the extremely short timescales involved. The ESIPT reaction may take place in the excited state of C4A.

Recently, it has been reported that excited-state double proton transfer (ESDPT) in 2-aminopyridine (2AP)/acid systems is facilitated by electronic excited-state hydrogen bond strengthening and employs the stepwise mechanism [36]. However, the mechanism of the ESIPT process and the role of intramolecular hydrogen bonding in the ESIPT process of C4A are still unknown. This study is concentrated on the cone conformer and the geometric conformations of C4A in the ground state and the excited state using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, respectively. The TDDFT method has been confirmed as a very useful and reliable tool to study the excited states of large molecules [37–44]. This study probes the excited-state geometries of C4A and the changes in excited-state intramolecular hydrogen bonding. How many protons transfer in the excited state? We focus our attention on the mechanism of the ESIPT reaction and the role of intramolecular hydrogen bonding in the ESIPT reaction.

2 Computational methods

The ground-state and electronic excited-state geometry optimizations of C4A were performed by the DFT and TDDFT methods, respectively [45–49]. In our DFT and TDDFT calculations, the B3-LYP (Becke's three-parameter hybrid exchange function with Lee-Yang-Parr gradient-corrected correlation) functional and the TZVP (triple-ζ valence quality with one set of polarization functions) basis set were used [50, 51]. Fine quadrature grids 4 were also employed [52]. Harmonic vibrational frequencies in the ground state were determined by diagonalization of the Hessian [53]. The infrared intensities were determined from the gradients of the dipole moment [54]. All the electronic structure calculations were carried out using the TURBOMOLE program suite [55–58].

3 Results and discussion

3.1 Ground-state geometric conformations

Fig. 1 shows the optimized geometric conformations of C4A in the ground state. C4A consists of methylene linked

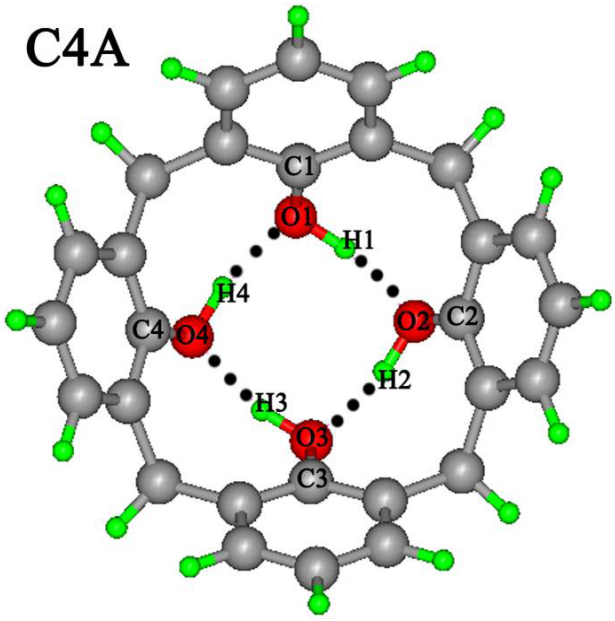


Figure 1: Optimized geometric conformations of calix[4]arene (C4A) in the ground state.

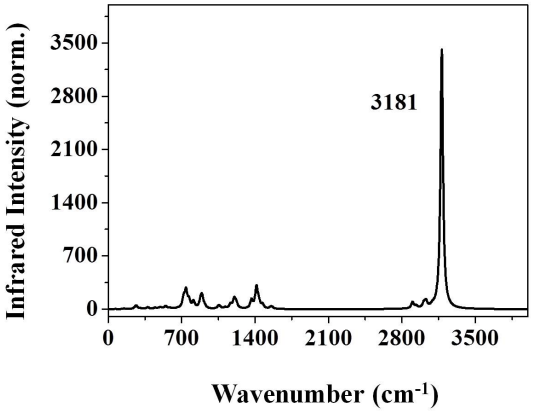


Figure 2: Calculated infrared spectra of calix[4]arene (C4A) in the ground state.

by four phenol molecules with a cavity. There are four intramolecular hydrogen bonds forming a ring in the C4A molecule. The structural parameters of C4A in the ground state are labeled in Table 1. For the C4A molecule, these parameters are almost the same, including the lengths of intramolecular hydrogen bonds, the lengths of C-O bonds, and the angles of intramolecular hydrogen bonds (*e.g.* $\angle$O1-H1$\cdots$O2). Thus, the four intramolecular hydrogen bonds are equal. The infrared vibrational spectrum of C4A in the ground state is calculated (Fig. 2). It can be seen that the calculated H-bonded OH stretching vibra-

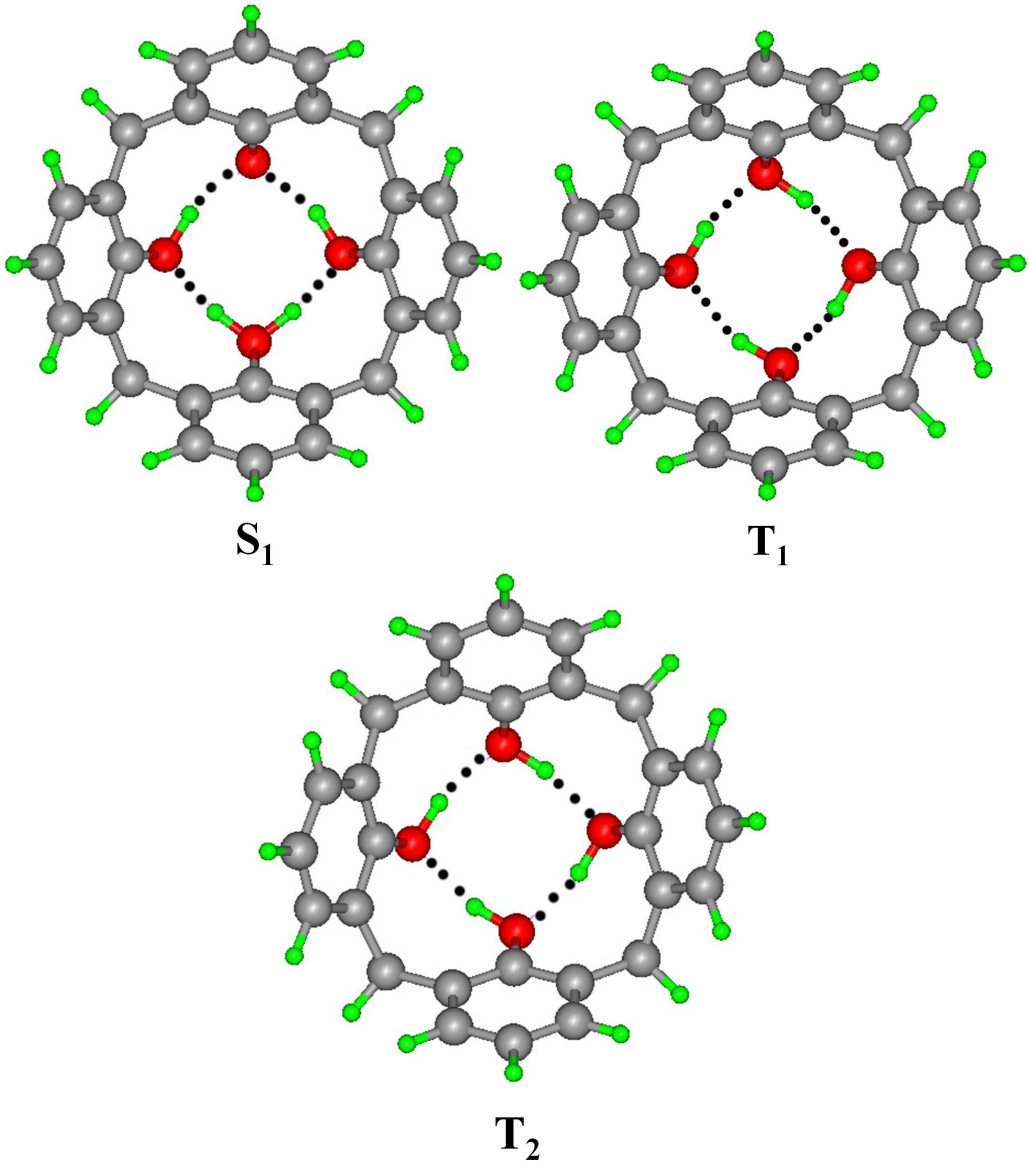


Figure 3: Optimized geometric conformations of calix[4]arene (C4A) in the excited states.

tional frequency in the ground state is 3181 cm^{-1}. The corresponding experimental datum is 3158 cm^{-1} [33].

3.2 Excited-state geometric conformations and the excited-state intramolecular double proton transfer reaction

Optimized geometric conformations of C4A in the S_1, S_2 and T_1 states are shown in Fig. 3. It is noted that the ESIDPT process occurs for the C4A molecule in the S_1 state. Interestingly, upon excitation to the S_1 state, both the protons H1 and H2 of the C4A molecule transfer along the intramolecular hydrogen bonds O1-H1$\cdots$O2 and O2-H2$\cdots$O3, respectively, while the protons H3 and H4 do not transfer. Furthermore, with the ESIDPT reaction proceeding in the S_1 state, the symmetry of C4A (C_{4v} in the ground state) is broken.

As shown in Fig. 3 and Table 1, the geometric conformations of C4A in the S_2 and T_1 states are not changed much compared with the ground state. For the C4A molecule in the S_2 state, the intramolecular hydrogen bonds O1-H1$\cdots$O2 and O3-H3$\cdots$O4 are longer by 0.075 Å and 0.207 Å than in the ground state, respectively. At the same time, the intramolecular hydrogen bonds O2-H2$\cdots$O3 and O4-H4$\cdots$O1 are shorter by 0.101 Å and 0.018 Å than in the ground state, respectively. In other words, when photoexcited to the S_2 state, the four in-

Table 1: Calculated lengths (Å) and angles (°) of intramolecular hydrogen bonds and intramolecular hydrogen-bonded groups of calix[4]arene (C4A) in the ground state and excited states.

	ground state	excited state		
	S_0	S_1	S_2	T_1
C1-O1	1.381	1.265	1.389	1.381
C2-O2	1.381	1.394	1.347	1.381
C3-O3	1.381	1.488	1.409	1.383
C4-O4	1.381	1.394	1.353	1.374
O1-H1	0.987	1.722	0.979	0.986
(O1···H1)				
H1···O2	1.701	0.982	1.776	1.700
(H1-O2)				
O2-H2	0.987	1.586	1.010	0.986
(O2···H2)				
H2···O3	1.701	1.015	1.600	1.715
(H2-O3)				
O3-H3	0.987	1.014	0.973	0.983
H3···O4	1.702	1.588	1.909	1.771
O4-H4	0.987	0.982	0.993	0.987
H4···O1	1.702	1.726	1.684	1.738
O1-H1···O2	163.5	158.6	158.7	164.0
(O1···H1-O2)				
O2-H2···O3	163.6	167.9	165.6	163.5
(O2···H2-O3)				
O3-H3···O4	163.6	167.8	152.6	162.6
O4-H4···O1	163.6	158.4	161.4	160.9

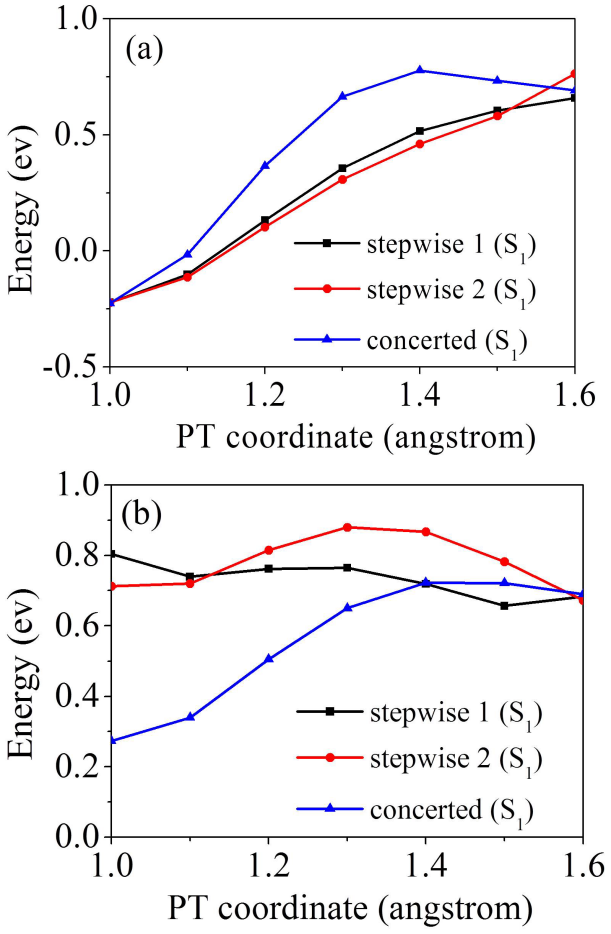


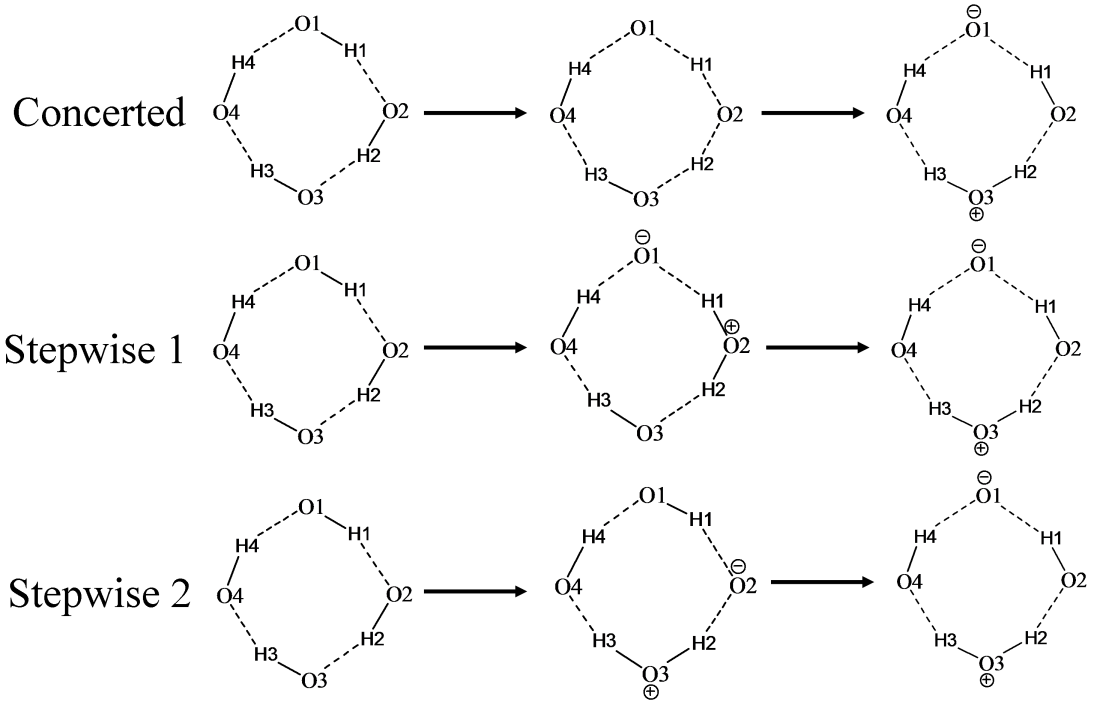
Figure 4: Calculated potential energy curves of Calix[4]arene (C4A) along the proton transfer (PT) coordinate with different mechanisms. (a) represents transfer of the first proton. (b) represents transfer of the second proton.

tramolecular hydrogen bonds are weakened and strengthened in turn in comparison with the ground state. In the T_1 state, the intramolecular hydrogen bond O1-H1···O2 is shortened by 0.001 Å compared with the ground state, and the intramolecular hydrogen bonds O2-H2···O3, O3-H3···O4 and O4-H4···O1 are lengthened by 0.014 Å, 0.069 Å and 0.036 Å, respectively.

3.3 Excited-state intramolecular double proton transfer reaction mechanism

In the S_1 state of C4A, the protons H1 and H2 transfer along the intramolecular hydrogen bonds O1-H1···O2 and O2-H2···O3, respectively. The fundamental question is the ESIDPT reaction mechanism. Three types of possible ESIDPT process for C4A are shown in Scheme 1. In the concerted mechanism, proton H1 transfers along the intramolecular hydrogen bond O1-H1···O2, and proton H2 transfers along O2-H2···O3. The two protons move concertedly. The stepwise 1 mechanism has proton H1 transferring along the intramolecular hydrogen bond O1-H1···O2. After the proton H1 arrives, proton H2 starts to transfer along the intramolecular hydrogen bond O2-H2···O3. The stepwise 2 mechanism has the sequence opposite to the stepwise 1 mechanism. However, the exact mechanism still needs to be investigated.

The potential energy curves are very helpful for investigating the proton transfer reaction mechanism. Fig. 4a presents three calculated potential energy curves in the S_1 state along the proton transfer coordinates of C4A. The first corresponds to the stepwise 1 mechanism, where the proton H1 transfers along the intramolecular hydrogen bond O1-H1···O2. The excited-state potential energy curves are calculated and scanned by increasing the length of the O1–H1 bond with a step of 0.1 Å. The second curve belongs to the stepwise 2 mechanism, in which proton H2 transfers along the intramolecular hydrogen bond O2-H2···O3. The



Scheme 1: Three types of the excited-state intramolecular double proton transfer (ESIDPT) reaction mechanism of calix[4]arene (C4A).

potential energy curves in the excited state are calculated and scanned by increasing the length of the O2-H2 bond with a step of 0.1 Å. The third type is in accordance with the concerted mechanism, where protons H1 and H2 begin to move simultaneously. In this case, it is proposed that the rate of proton H1 transfer is approximately equal to that of proton H2. Hence, the lengths of both the O1-H1 and O2-H2 bonds are synchronously tuned with a step of 0.1 Å. It can be seen that the barrier of the potential energy curve with the concerted mechanism is the highest of the three potential energy curves. Furthermore, the potential energy curve with the concerted mechanism is higher than the other two potential energy curves with stepwise mechanisms. Therefore, it is demonstrated that the concerted mechanism is impossible for C4A. In addition, due to the two protons H1 and H2 being equal in the molecular structure, the difference between the barriers of the potential energy curves with the stepwise 2 mechanism and stepwise 1 mechanism is not so obvious. Hence, it is demonstrated that the stepwise 1 and 2 mechanisms are both possible for the ESIDPT reaction of C4A.

To further confirm the stepwise mechanism and exclude the concerted mechanism, Fig. 4b shows and additional three potential energy curves in the S_1 state along the proton transfer coordinate for C4A. Of the three potential energy curves, the first (stepwise 1 mechanism) denotes that the proton H2 transfers along the hydrogen bond O2-H2$\cdots$O3 after the proton H1 has arrived. The second curve (stepwise 2 mechanism) denotes that the proton H1 transfers along the hydrogen bond O1-H1$\cdots$O2 after the proton H2 has arrived. The third curve (concerted mechanism) denotes that the proton H1 transfers when the proton H2 is located in the intermediate site of the hydrogen bond O2-H2$\cdots$O3. One can clearly note that the barrier of the third potential energy curve is always the highest among the three possibilities. Hence, the concerted mechanism is excluded and the stepwise mechanism for the ESDPT process is confirmed again. Additionally, the barriers of the potential energy curves with the stepwise mechanisms in Fig. 4a are higher than those of corresponding potential energy curves in Fig. 4b. It is demonstrated that a proton (H2 or H1) is easier to transfer after the other proton (H1 or H2) has arrived. In other words, the transfer of one proton, before which no protons has transferred, occurs with more difficulty.

3.4 The role of intramolecular hydrogen bonding in the excited-state intramolecular double proton transfer

An interesting question is put forward: for the C4A molecule in the S_1 state, why do only the two protons H1 and H2 transfer along the intramolecular hydrogen bonds

rather than all of the protons? For the C4A molecule in the S_1 state, the distance between H1 and O2/H2 and O3 is drastically shortened by 0.719 Å/0.686 Å in comparison with the ground state, which may be caused by the proton transfer reaction. However, the intramolecular hydrogen bonds O3-H3···O4 and O4-H4···O1 are shortened by only 0.114 Å in the former case and even lengthened by 0.024 Å in the latter in the S_1 state, which may not induce the proton to transfer. In the S_2 state of C4A, the intramolecular hydrogen bonds O1-H1···O2 and O3-H3···O4 are lengthened and O2-H2···O3 and O4-H4···O1 are only shortened by 0.101 Å and 0.018 Å compared to the ground state, which may not induce the protons to transfer. The case study for C4A in the T_1 state is similar to the S_2 state. Hence, it is demonstrated that the changes of intramolecular hydrogen bonds in the excited state play a crucial role in the ESIDPT reaction. The ESIDPT reaction can be facilitated by the strengthening of the excited-state intramolecular hydrogen bonds.

4 Conclusion

The intramolecular hydrogen bonds in C4A are strengthened or weakened in the S_2 and T_1 states compared to those in the ground state. Upon excitation to the S_1 state of C4A, the two protons H1 and H2 transfer along the two intramolecular hydrogen bonds O1-H1···O2 and O2-H2···O3, while the other two protons do not transfer. The ESIDPT reaction breaks the primary symmetry of C4A in the ground state. The potential energy curves of proton transfer were calculated to investigate the ESIDPT mechanism. It is demonstrated that for C4A, the concerted mechanism is excluded. The stepwise 1 mechanism (H1 transfers first) and stepwise 2 mechanism (H2 transfers first) are both possible due to the equivalence of protons H1 and H2 in the molecular structure. In addition, some intramolecular hydrogen bonds are strengthened remarkably in the S_1 state and strong enough to lead to proton transfer, which could directly influence the molecular structures and reactivity. The ESIDPT reaction could directly influence the molecular structures and reactivity. The important role of intramolecular hydrogen bonding in the ESIDPT reactions may exist in other intramolecular hydrogen-bonded systems.

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