

**Supporting Information for**  
**Sequential Flipping: A Donor-Acceptor Exchange Mechanism in**  
**Water Trimer**

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Part 1. The stable structures of water trimer.

Part 2. The transition state structures for all mentioned processes.

Part 3. The BSSE effect on water trimer.

Part 4. The tunneling probability and isotope effect.

## Part 1. The stable structures of water trimer.

The definition of the conformation of the water trimer should be determined. The positions of the free hydrogens are denoted “u” or “d” when they lie above the plane of the ring (up) and below the plane of the ring (down), respectively. The stable structures of water trimers are called uuu (ddd) and udd (uud), in which the udd structure is the global minimum while the uuu structure is the local minimum. The following are the coordinates and electronic energies of the stable structures obtained at MP2/aug-cc-pVTZ level. The unit of coordinates is Å.

uuu (ddd)

-229.011733 Hartree

O	-0.79065400	1.40065700	-0.06648600
H	0.16587300	1.23084600	-0.00153600
H	-0.96488900	2.13029300	0.53323300
O	-0.81760200	-1.38499600	-0.06632900
H	-1.36346000	-1.90101500	0.53212600
H	-1.14882200	-0.47170600	-0.00148900
O	1.60824700	-0.01556800	-0.06633100
H	2.32817600	-0.22990800	0.53212300
H	0.98319200	-0.75925300	-0.00128700

udd (uud)

-229.012934 Hartree

O	-1.32170000	-0.91582100	-0.09299800
H	-1.21817900	0.05089600	-0.02256300
H	-1.99262000	-1.14930100	0.55372800
O	1.45885400	-0.67636600	-0.08340900
H	1.99924400	-1.12211300	0.57403500
H	0.58137200	-1.09540600	-0.02774900
O	-0.13618500	1.59734200	0.10899700
H	-0.03077600	2.24631400	-0.59181800
H	0.65320500	1.02837400	0.05365500

## Part 2. The transition state structures for all mentioned processes.

The initial structure of all processes is the global minimum point (udd or uud). The following are the coordinates of The transition state (TS) structures for all mentioned processes obtained at MP2/aug-cc-pVTZ level. The unit of coordinates is Å.

The TS structure for single flipping process

O	0.06854200	1.60824500	0.10374500
H	-0.67555800	0.98139300	0.03928800
H	-0.07198800	2.23765300	-0.60861200
O	1.33345600	-0.86187400	-0.00702900
H	2.27354900	-1.05312900	0.00737800
H	1.24501200	0.10700400	0.01666600
O	-1.43739900	-0.74258800	-0.09790600
H	-1.92910400	-1.14677400	0.62213000
H	-0.55870700	-1.15641100	-0.06732600

The TS structure for bifurcation process

O	1.16274300	-1.22042900	-0.00165500
H	0.56229300	-1.35173200	-0.74572400
H	0.58633100	-1.41811800	0.74604900
O	0.50236900	1.51400900	-0.08202500
H	0.93157400	2.13804200	0.50884000
H	1.00724100	0.68468200	-0.00200200
O	-1.59737600	-0.34812400	0.03052000
H	-2.51742500	-0.11064200	-0.10948900
H	-1.11189900	0.49411600	0.02760000

The TS structure for sequential flipping process

O	0.82263900	-1.39375400	0.07159800
H	1.02506300	-0.87789700	-0.71790600
H	1.14544300	-2.27944100	-0.11818000
O	0.82260400	1.39377300	-0.07159800
H	1.14538900	2.27946700	0.11817700
H	1.02504600	0.87792200	0.71790600
O	-1.87167800	-0.00002100	0.00000000
H	-1.26472100	-0.73683400	0.13750400
H	-1.26473500	0.73680300	-0.13750200

The TS structure for proton transfer process

O	-1.18566900	-0.68056600	-0.10530900
H	-0.82113000	0.47391100	0.01392400
H	-1.66680300	-0.97670800	0.67365200
O	1.18567000	-0.68056300	-0.10530900
H	1.66680500	-0.97670400	0.67365200
H	0.00000100	-0.95182900	-0.04524000
O	-0.00000200	1.36376200	0.12541800
H	-0.00000200	1.93635600	-0.64831600
H	0.82112900	0.47391300	0.01392400

### Part 3. The BSSE effect on water trimer.

In addition, we tested the effect of BSSE correction on the energy and structure of water trimer. As shown in Table S1, the BSSE correction values of the energies for the transition state structure and the stable structure offset each other. Therefore, the BSSE correction values on the energy barrier of the hydrogen bond network rearrangement process is so small as to be approximately negligible in the discussion of the manuscript.

**Table S1.** The effect of BSSE correction on the energy and structure of water trimer.

MP2/aug-cc-pVTZ		Stable Structure		Transition State Structure (SF)	
		without BSSE	with BSSE	without BSSE	with BSSE
Energy (Hartree)		-229.013	-229.011	-229.003	-229.001
Distance (Å)	O <sup>1</sup> -O <sup>4</sup>	2.791	2.810	2.791	2.810
	O <sup>4</sup> -O <sup>7</sup>	2.784	2.805	3.034	3.060
	O <sup>1</sup> -O <sup>7</sup>	2.786	2.807	3.034	3.060
	O <sup>1</sup> -H <sup>2</sup>	0.975	0.974	0.965	0.964
	O <sup>1</sup> -H <sup>3</sup>	0.961	0.961	0.962	0.962
	O <sup>4</sup> -H <sup>5</sup>	0.961	0.961	0.962	0.962
	O <sup>4</sup> -H <sup>6</sup>	0.974	0.973	0.965	0.964
	O <sup>7</sup> -H <sup>8</sup>	0.961	0.961	0.964	0.964
	O <sup>7</sup> -H <sup>9</sup>	0.970	0.974	0.964	0.964

## Part 4. The tunneling probability and isotope effect.

It can be known that the PT process is mainly the motion of H atoms along the O-H axis, while the SF process is mainly the motion of H atoms perpendicular to the O-H axis. This difference of quantum tunneling effect in SF and PT processes can be understood as a difference of quantum tunneling effect of H atoms in the two directions, as reported in the past.<sup>1</sup> To further explore the contribution of the two processes for different H atoms, we further discussed the effect of different D-atom substitution types on the two pathways. The quantum tunneling effect can be quantified using a reaction path described by IRC and the reduced mass corresponding to the frequency. Specifically, we calculated the tunneling probabilities ( $P_{\text{tunneling}}$ ) for each reaction path according to the Wenzel-Kramers-Brillouin (WKB) approximation, as follows:<sup>2-4</sup>

$$P_{\text{tunneling}} = \text{Exp} \left[ -\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(V(x) - E)} dx \right] \#(3)$$

where  $V(x)$  are one-dimensional PESs obtained and  $\hbar$  is reduced Planck constant.  $x_1$  and  $x_2$  represent the intersection points at different energies.

**Table S2.** The vibration frequency ( $\nu$ ) of the transition state and the corresponding reduced mass, as well as the tunneling probability ( $P_{\text{tunneling}}$ ) at the zero-point energy (ZPE) in sequential flipping (SF) and proton transfer (PT) processes based on the substitution of different atoms by deuterium (D).

D-substituted atom	SF (ZPE = 0.067 eV)			PT (ZPE = 0.166 eV)		
	$\nu$ (cm <sup>-1</sup> )	Red. mass (a.u.)	$P_{\text{tunneling}}$	$\nu$ (cm <sup>-1</sup> )	Red. mass (a.u.)	$P_{\text{tunneling}}$
No atoms	-139.08	1.062	$6.31 \times 10^{-71}$	-1810.56	1.026	$4.61 \times 10^{-47}$
2	-122.79	1.376	$1.22 \times 10^{-80}$	-1637.85	1.187	$1.45 \times 10^{-50}$
6	-122.79	1.376	$1.22 \times 10^{-80}$	-1633.36	1.193	$1.12 \times 10^{-50}$
8	-137.54	1.085	$1.12 \times 10^{-71}$	-1637.85	1.187	$1.45 \times 10^{-50}$
9	-137.54	1.085	$1.12 \times 10^{-71}$	-1809.36	1.027	$4.47 \times 10^{-47}$
2, 6, 8	-110.45	1.729	$2.79 \times 10^{-90}$	-1298.42	2.053	$2.98 \times 10^{-66}$
2, 6, 8, 9	-109.71	1.751	$7.54 \times 10^{-91}$	-1296.80	2.061	$2.22 \times 10^{-66}$
All H atoms	-100.65	2.160	$7.71 \times 10^{-101}$	-1292.85	2.081	$1.06 \times 10^{-66}$

As can be seen in Table S1, when the H atom is replaced by D, the frequency of the TS decreases and the mass corresponding to the reaction increases, leading to a decrease in the  $P_{\text{tunneling}}$ . This effect is more pronounced when the substituted atom is the main participant in the reaction process. It can be seen that atoms 2, 6, 8 and 9 are all involved in the SF process, where atoms 2 and 6 are equivalent and atoms 8 and 9 are equivalent. For the PT process, the three hydrogen atoms 2, 6 and 8 in the hydrogen bonding network of the water ring plane have similar effects. Specifically, atoms 2 and 8 are equivalent but have a slight difference for atom 6, which is due to the difference in the states in which the three H atoms are in the water trimer. Depending

on the number of terminal hydrogens on the same side of the O-O-O plane in the initial Structure, water molecules H<sup>3</sup>-O<sup>1</sup>-H<sup>2</sup> and H<sup>8</sup>-O<sup>7</sup>-H<sup>9</sup> is referred to as the “majority” and water molecule H<sup>5</sup>-O<sup>4</sup>-H<sup>6</sup> is referred to as the “minority”. The isotope effect amplifies the difference in vibration of water molecules in different states, which can also explain three small red-shifts (from 1152, 1572 and 1586 to 1155, 1574 and 1593 cm<sup>-1</sup>) caused by the SF process in Fig. 2(a).

Based on the TST, the tunneling splitting of the reaction can be roughly inferred from the tunneling probability at the zero-point vibrational energy as well as the vibrational frequency.<sup>5,6</sup> From Table 2, it can be inferred that the tunneling splitting of the SF process will be much smaller than that of the PT process ( $1.9 \times 10^{-5}$  cm<sup>-1</sup> by large curvature tunneling effects and  $8.2 \times 10^{-8}$  cm<sup>-1</sup> by small curvature tunneling effects),<sup>6</sup> which means that it is under the experimentally observed limit of about 1 MHz ( $3 \times 10^{-5}$  cm<sup>-1</sup>).

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