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Uncooperative Effect of Hydrogen Bond on Water Dimer

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The water dimer demonstrates a completely different protype in water systems, it prefers not forming larger clusters instead existing in vapor phase stably, which contracts the viewpoint of the cooperative effect of hydrogen bond (O–H···O). It is well accepted that the cooperative effect is beneficial to forming more hydrogen bonds (O–H···O), leading to stronger H-bond (H···O) and increase in the O–H bond length with contraction of intermolecular distance. Herein, the high-precision *ab initio* methods of calculations applied on water dimer shows that the O–H bond length decreases and H-bond (H···O) becomes weaker with decreasing H-bond length and O···O distance, which can be considered as the uncooperative effect of hydrogen bond (O–H···O). It is ascribed to the exchange repulsion of electrons, which results in decrease of the O–H bond length and prevents the decrease in the O···O distance connected with the increasing scale of water clusters. Our findings highlight the uncooperative effect of hydrogen bond attributed to exchange repulsion of electrons as the mechanism for stabilizing water dimer in vapor phase, and open a new perspective for studies of hydrogen-bonded systems.

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As one of important issues worthy of paying attention and recognized in public views, peculiar and complicated water has been studied by many researchers.[1–4] Compared with most of the other properties, the phase diagram of water is extremely special and complex.[5] It has been reported that the phases of water involve the arrangement of molecules and hydrogen bonds, ice as well as liquid water were acquainted as the hexagonal and tetrahedral hydrogen-bonded systems respectively.[6,7] However, the water dimer exists in the supposed simple vapor phase stably, it does not prefer forming large clusters[8] instead serving a completely different protype in water systems.[9] It has been revealed that the water dimer cannot be the original model of bulk water and should be separated from other clusters. Although it can be observed experimentally,[10,11] it has never been explained, which captures our attention.

Cooperative effect of hydrogen bond, proved to exist in water systems widely,[12–14] is known to play a critical role in the structures dominating the phases.[15–17] It was recognized that the existence of hydrogen bond between water monomers is beneficial to forming more hydrogen bonds (O–H···O), accumulating the water monomers, and strengthening H-bond (H···O) initially.[18–20] The subsequent researches have suggested a more intuitive conformation change reflected by the cooperative effect, the O–H bond length increases with simultaneous decreases of H-bond length and O···O distance between any pairs of water molecules for water clusters and bulk water,[13,21,22] contributing to the structural formation of liquid water and ice.[13] In addition, the widely applied methods of density functional theory (DFT) and force field[23,24] can account for the structures and properties in liquid and solid phases of water.[25,26] Nevertheless, the influence of forming more hydrogen bonds and increasing scale of water clusters of cooperative effect is not exerted on the water dimer, it reminds that the cooperative effect does not originate from water dimer,[27] and a more precise approach applied on the special water dimer is needed.

To explore the nature of water dimer's stable existence in vapor phase, we investigate the water dimer from the structural perspective with the *ab initio* wave function theory and other diverse methods, especially the properties with the compression of water dimer. Surprisingly, the results obtained with the *ab initio* methods reject those with other methods or even with generally admired DFT calculations. The O–H bond length decreases with the simultaneous decreases of H-bond distance and O···O distance instead of its increase as reported in previous studies. It is also opposite with the conformational change when the scale of water clusters increases.[13,28] Moreover, the bond energy of H-bond is smaller, indicating the weaker

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H-bond. The decreasing O–H bond length and the weaker H-bond can be seen as the uncooperative effect on water dimer. Most importantly, we find that the uncooperative effect of hydrogen bond (O–H···O) on the water dimer results from exchange repulsion of electrons, which tends to prevent the decrease of O···O distance accompanied with the increasing scale of water clusters, leading to the stable existence of water dimer.

Results and Discussion. The study was carried out with different methods: (1) coupled-cluster singles and doubles with perturbative triple excitations [CCSD(T)][29] and explicitly corrected coupled-cluster singles and doubles with perturbative triples method [CCSD(T)-F12][30] of *ab initio* methods, (2) DFT,[31] (3) tight-binding density function theory (DFTB)[32] with various dispersion, (4) methods of force field[33] containing SPC, SPCE, TIP3P and TIP4P water models [see Part 15 in the Supporting Information (SI) for details]. The stable structure optimized with CCSD(T) is shown in Fig. 1(a), and it conforms to the previous researches.[34,35] As it can be seen in Fig. 1(b), the O–H bond lengths of the water dimer calculated with the CCSD(T) and CCSD(T)-F12 methods keeps decreasing with the decreasing O···O distance and H-bond length. However, results obtained with the DFT methods demonstrate that the O–H bond length increases and most of the ΔO–H bond lengths are above zero. The different trends of the O–H bond length in the DFT methods are caused by the negligence of Coulomb repulsion of electrons with spin in opposite direction. Though Pauli repulsion of electrons with spin in the same direction has been considered in the DFT methods, electrons cannot occupy the same position because of Coulomb repulsion. On the contrary, the CCSD(T) method excites electrons from occupied orbitals to unoccupied orbitals, and more excited states reduce the probability of the same position occupied by electrons with opposite spin.[29] Obviously, such considerations are not capable to be implemented in classical simulations. This result is also clearly different from the previous compression results of water that the increasing O–H bond length keeps cooperative with the decreasing H-bond length and O···O distance, which is related to the increasing scale of water clusters[13,20,21] (see Part 16 of the SI for details).

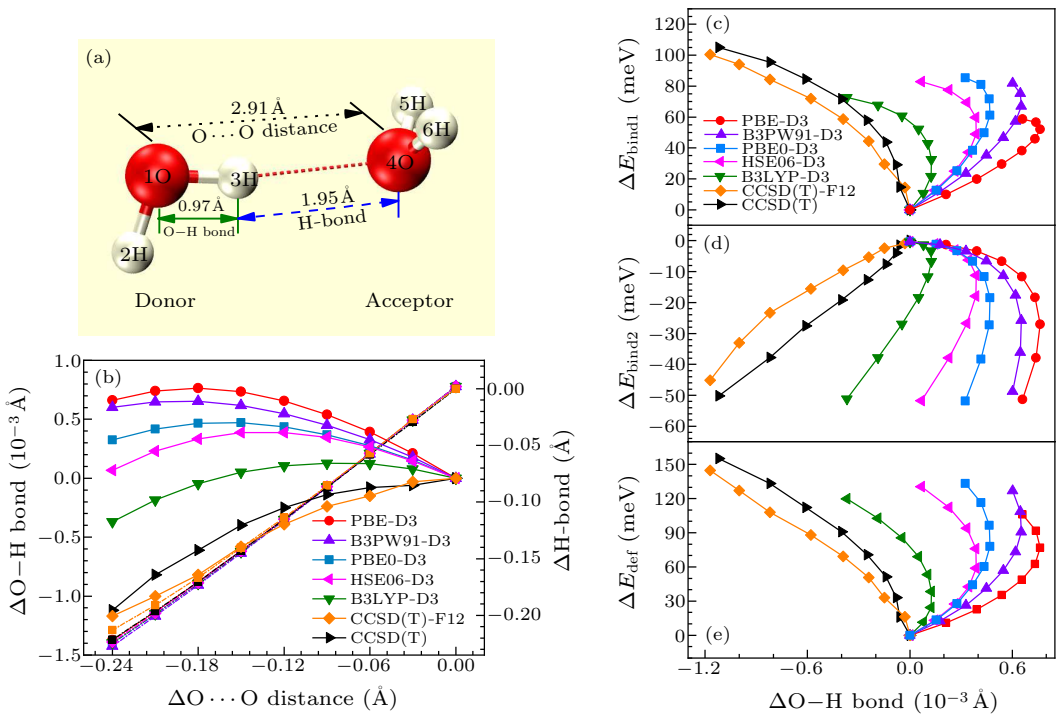

Fig. 1. The structural parameters in the water dimer, the O–H distance and binding energies of O–H bond during the compression. (a) The stable structure of the water dimer optimized with the CCSD(T) method. (b) The O–H bond length (solid line) and the H-bond length (dotted line) in the water dimer scanned with the PEB0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3 methods of DFT as well as the *ab initio* CCSD(T) and CCSD(T)-F12 methods. (c) The binding energies without monomers' deformation energies of the O–H bond in the water dimer calculated with the PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods as well as the CCSD(T)-F12 method. (d) The binding energies with monomers' deformation energies of the O–H bond in the water dimer calculated with the PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods as well as the CCSD(T)-F12 method. (e) The deformation energies of monomers binding O–H bond in the water dimer calculated with the PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods as well as the CCSD(T)-F12 method.

We also calculate the binding energies of the O–H bond with the *ab initio* CCSD(T), CCSD(T)-F12 and DFT methods. As shown in Figs. 1(c)–1(e), the binding energies of the O–H bond without and with monomers' deformation energies, as well as the deformation energies of monomers, are displayed, respectively. Without the deformation energies of monomers, the shorter the O–H bond length compared with the stable point is, the greater the released energies of bonded monomers calculated with CCSD(T) and CCSD(T)-F12 methods [see Fig. 1(c)] are. This indicates that more energies are needed to break the O–H bond and the bond energies of O–H bond are larger than the value 5.61 eV for the stable structure.[36] However, the relationship between the O–H bond length and the corresponding binding energies calculated with the DFT methods does not fit the linear relation obtained with the *ab initio* CCSD(T) and CCSD(T)-F12 methods. It reflects the inaccurate trend of the O–H bond during the compression with the DFT methods. The similar results are also obtained in the binding energies of the O–H bond with the deformation energies considered [see Fig. 1(d)], and there are less released energies compared with 5.43 eV for the stable structure [see Fig. 1(d) and Part 7 of the SI for details]. More clearly shown by Fig. 1(e), the deformation energies of *ab initio* methods become larger with further compression on the water dimer, while there is not an obvious connection between deformation energies and structures obtained with the DFT methods. All these consequences reveal that the DFT methods are improper for treating compression especially the water dimer.

Furthermore, we calculate the binding energies of H-bond without monomers' deformation energies using the CCSD(T) and CCSD(T)-F12 methods. In contrast to the binding energies of the O–H bond, the value of −0.20 eV for H-bond in the stable structure is relatively smaller, which is consistent with the previous research.[37] As shown in Fig. 2(a), compared with the stable structure, there are less bond energies of H-bond with compression of water dimer. The weaker H-bond shows the uncooperative effect, which hinders to form more hydrogen bonds and to accumulate water monomers.

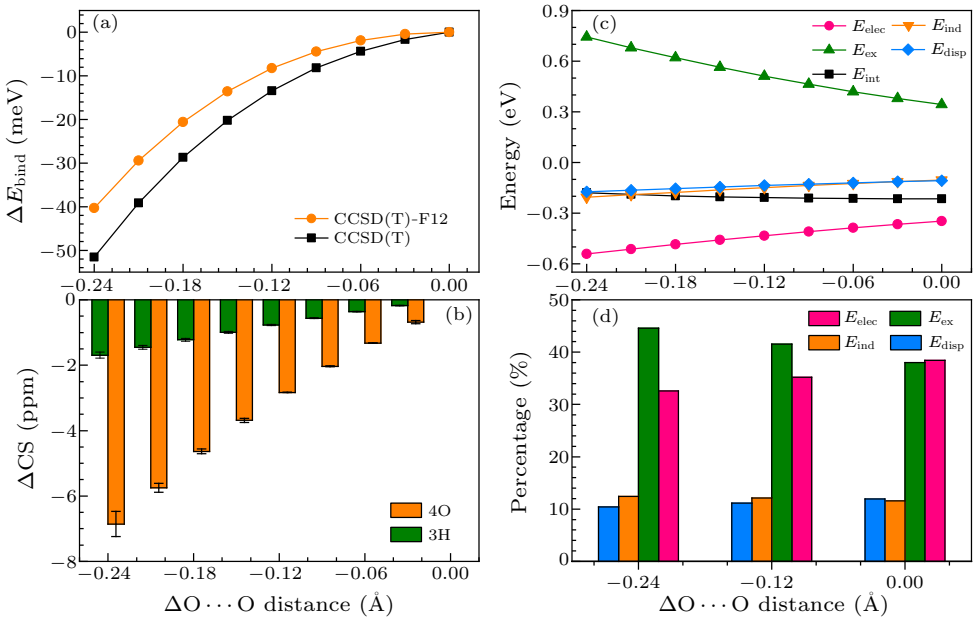

Fig. 2. The related experimental properties and energy decomposition as well as the corresponding percentage of the four terms in the total interaction during the compression of the water dimer. (a) The binding energies of H-bond during compression of water dimer. (b) The NMR chemical shift of the O and H atoms connecting H-bond in water dimer scanned with the CCSD(T) method during the compression. The error bar respects the difference between the data of water dimer scanned with the CCSD(T) method and the CCSD(T)-F12 method. (c) The energy decomposition containing four parts $E_{\rm elec}$, $E_{\rm ex}$, $E_{\rm orb}$ and $E_{\rm disp}$ in Psi4 of the water dimer calculated with the CCSD(T) method. (d) The percentage of the four parts $E_{\rm elec}$, $E_{\rm ex}$, $E_{\rm orb}$ and $E_{\rm disp}$ in the energy decomposition corresponding to the structures of the water dimer at O···O distances of 0 Å, −0.12 Å and −0.24 Å, corresponding O···O distances of 2.91 Å, 2.79 Å and 2.67 Å.

For observation of experiment in the future, the nuclear magnetic resonance (NMR) chemical shift of the O and H atoms connecting H-bond is calculated with the CCSD(T) and CCSD(T)-F12 methods, as shown in Fig. 2(b). We can conclude that the chemical shift of the O and H atoms connecting the H-bond is decreasing under the compression, while the data of other atoms are almost unchanged compared with

the stable structure (see Part 10 of the SI for details). This indicates that the H-bond becomes weaker because the formation of H-bond between free molecules would lead to the increase in the chemical shift.[38] For the fact that the variation of chemical shift shows the change of the electron density and the NMR reflects the shielding effect of electron density around H nuclei to external magnetic field, it points out a redistribution of the electron density upon H-bond formation.[39,40] The decrement of the NMR chemical shift shows the increment of the shielding effect and the electron density. In our work, the value of the O and H atoms in the H-bond calculated with the CCSD(T) and CCSD(T)-F12 methods decreases. This reveals the more delocalized electron density and less electronegative O atom as well as the weaker ability of the O atom to attract electrons, leading to the decreasing bond energies of H-bond with compression of water dimer.

Table 1. The percentage (%) of the four terms ($E_{\rm elec}$, $E_{\rm ex}$, $E_{\rm ind}$, $E_{\rm disp}$) in the energy composition for three points (in the beginning, middle and last) of the water dimer's scanning at different O···O distances.

ΔO···O distance	$E_{\rm elec}$	$E_{\rm ex}$	$E_{\rm ind}$	$E_{\rm disp}$
0 Å	38.36	38.09	11.63	11.91
−0.12 Å	35.11	41.58	12.19	11.11
−0.24 Å	32.40	44.67	12.58	10.35

To explain the uncooperative effect of hydrogen bond with compression of water dimer, we perform the symmetry-adapted perturbation theory (SAPT) calculation based on the quantum mechanics. The SAPT decomposes the interaction of two water monomers into four components: electrostatic interaction, exchange repulsion, induction, and dispersion simply and clearly [see Fig. 2(c) and Part 9 of the SI for details]. The decreasing O–H bond length can be explained by the exchange repulsion term in the energy decomposition, the $E_{\rm ex}$ increases with compression, and the percentage is the largest among the four terms, showing that the $E_{\rm ex}$ dominates the interaction between the water monomers [see Fig. 2(d)]. Considering that the exchange repulsion between water monomers mainly arises from the overlap of electrons' wavefunction, the physical basis of it can be seen as a pure quantum effect,[41] which leads to the decrease in the O–H bond length as well as the weaker H-bond (H···O). What's more, the exchange repulsion of electrons prevents the decrease in the O···O distance related to the increasing scale of water clusters and formation of more hydrogen bonds, resulting in the stable existence of water dimer in vapor phase.

In summary, different from ice as well as liquid water known as the hexagonal and tetrahedral hydrogen-bonded systems respectively, the water dimer acts a quite special role in water systems, without forming large clusters and existing in vapor phase stably. It shows the uncooperative effect of hydrogen bond (O–H···O) that the O–H bond length decreases and the H-bond (H···O) becomes weaker with decreasing H-bond length and O···O distance, which can be attributed to the exchange repulsion of electrons. More importantly, as the exchange repulsion of electrons between water monomers tends to prevent the decrease of O···O distance, which is accompanied with the increasing scale of water clusters,[13,22] the mechanism of water dimer's stable existence in vapor phase is uncovered.

In addition, our findings also reflect the limitations of DFT methods compared with *ab initio* methods and refresh the traditional perspective of hydrogen bond by investigating the unusual water dimer. It is of great significance for related study of water phase and electronic quantum effect of hydrogen-bonded systems in the future.

Author Contributions. D. Li performed the theoretical simulations, Z. Wang initiated the work. Z. Wang and Y. Gao supervised the work. D. Li, Z. Zhang, W. Jiang and Y. Zhu discussed the results. D. Li, Y. Gao and Z. Wang wrote the article.

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Supporting Information: The Uncooperative Effect of Hydrogen Bond on Water Dimer

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Part 1. Methods.

Part 2. The coordinate system for water dimer optimized with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

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Part 6. The bond angles of O-H⋯O in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

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Part 1. Methods.

Development of methods applied on compression of water dimer

Similar with researches of other molecular systems, the studies of water are limited by computing resources and the methods of high-precision ab initio wave function theory (WFT) can't be applied, leading the FF and DFT methods were used and developed widely[1-3]. The TIP4P and modified TIPS models using the FF methods are applied to the experiments of compression of water[4] besides comparation of potential functions[5-6]. Nevertheless, the FF methods are based on the empirical parameters and were assumed that a set of equations in the form of classical motion exits[7], they are not suitable for the calculation of compression. Although the ab initio WFT methods were not widely used with the improvement of computing cost, DFT methods of first-principles which were developed mainly for their application in complex systems containing large-scale molecules as well as solid-state physics[8-9] were put into researches of water widespreadly[10-12], they can't deal with the questions related to water perfectly as well especially the compression–the DFT methods are based on Hartree-Fock equation, considering electronic correlation and Pauli repulsion of the electrons with spin in the same direction, they are derived from Hartree equation, but neglect the Coulomb repulsion of opposite spin orientated electrons[13]. The DFT methods have been used in many researches about water: (1) change of the conformation and radial distribution function[2], (2) charge distribution and deformation[10], (3) orbital calculation[11], (4) the compression of water[14-15]. But there is still the same trouble with development of DFT, and it can be clearly seen that neither FF nor DFT methods can serve as the

benchmark of theoretical researches for water[16]. Fortunately, compared with former methods, the coupled-cluster singles and doubles with perturbative triple excitations CCSD(T) method of high-precision ab initio is the winner–it is based on the post Hartree-Fock corrected the electronic correlation energy, considering the Coulomb repulsion of electrons with spin in opposite direction. And multinomial configuration interaction of electron excitation is also included. Therefore, we are convinced that theorical methods can be responsible for the unsolved matter of water dimer, and CCSD(T) method can be applied in the compression.

Exchange repulsion, Pauli repulsion, Coulomb repulsion and classical Coulomb force

The wave function of electrons in the methods of density function theory fit the equation as follows[24]:

$$E = \sum_{k=1}^{n} \int \varphi_k^*(q_1)\, \boldsymbol{h}(\overrightarrow{r_1})\varphi_k(q_1)dq_1 + \sum_{k\neq k'=1}^{n} \int \varphi_k^*(q_1)\varphi_k'^*(q_2)dq_2 \frac{1}{r_{12}}$$

$$\varphi_k(q_1)\varphi_{k'}(q_2)dq_1dq_2 - \sum_{k\neq k'=1}^{n} \int \varphi_k^*(q_1)\varphi_k'^*(q_2)\frac{1}{r_{12}}\varphi_k'(q_1)\varphi_k(q_2)dq_1dq_2$$

Where the first term of the equation denotes the kinetic energies of all electrons and the potential energy produced by the attractive interaction between nucleus and electrons, while the second terms indicates the electrostatic repulsion energy. To describe the wave function theory of electrons more accurately, a further correction is shown in the third term exchange repulsion, considering the electrons with spins in the same direction are impossible to occupy the same space resulting from Pauli repulsion, which is also contained in post-Hartree-Fock.

Different with the equation above obtained by solving Schrodinger equation with Hartree-Fock method, the post-Hartree-Fock method takes the Coulomb repulsion of electrons with opposite spin into account by exciting electrons, as the electron has negative charge, electrons are impossible to occupy the same space because of Coulomb repulsion[13].

The Coulomb repulsion of electrons with opposite spin is quite different from classical Coulomb force，as the Coulomb force can be seen an effect on macroscopic objects, changing the position and geometry[17-18], while the Coulomb repulsion of electrons with opposite spin considered in the post-Hartree-Fock describe the position and probability of electrons' appearance, and it is a question of quantum mechanics.

The wave function of CCSD(T) method which is included in post-Hartree-Fock methods is as follows[19]:

$$\psi = e^T\varphi_0$$

$$T = T_1 + T_2 + T_3 + \cdots = \sum_i T_i$$

where

$$T_1 = \sum_i^{occ} \sum_a^{vir} t_i^a T_i^a$$

$$T_2 = \sum_{i<j}^{occ} \sum_{a<b}^{vir} t_{ij}^{ab} T_{ij}^{ab}$$

$$T_3 = \sum_{i<j<k}^{occ} \sum_{a<b<c}^{vir} t_{ijk}^{abc} T_{ijk}^{abc}$$

T_i^a indicates an electron is excited from occupied orbital φ_i into virtual orbitals φ_a. T_{ij}^{ab} denotes an electron is excited from occupied orbital φ_i and φ_j into virtual orbitals φ_a and φ_b respectively. e^T and the total wave function satisfies

$$\psi = \left[1 + T_1 + \left(\frac{1}{2!}T_1^2 + T_2\right) + \left(\frac{1}{3!}T_1^3 + T_1T_2 + T_3\right) + \left(\frac{1}{4!}T_1^4 + \frac{1}{2}T_2T_1^2 + \frac{1}{2}T_2^2 + T_3T_1 + T_4\right) + \cdots\right]\varphi_0$$

The methods and details of calculation in our work

The structures of the water dimer were scanned with high-precision first-principles methods including coupled-cluster singles and doubles methods with perturbative triple excitations (CCSD(T)), and PEB0-D3, B3PW91-D3, HSE06-D3, PBE-D3, B3LYP-D3 methods of density functional theory (DFT) with aug-cc-pVTZ basis set in Gaussian 09[20] respectively and explicitly-corrected coupled-cluster singles and doubles with perturbative triples method CCSD(T)-F12 and VTZ-F12 basis set in Molpro 2012[21].

The comparison of the results about the bond length, optimized energy, variation of the bond angles is provided, which proves all the accuracy of results.

The binding energies were calculated by $E_{int}=E_{AB}-E_A-E_B+E_{bsse}$. What's needed to be illustrated further is that there are four parts in the calculation of the binding energies. (1) The binding energies of O-H bond with deformation energies of monomers. Where the E_{AB} represents the energies of optimized water dimer in the scanning, the E_A and E_B indicate the optimized energies of monomers OH^- and H_3O^+, the E_{bsse} represents the basis set superposition error which is needed to be considered that when the monomers bonded to the compound, the primary function of the monomers will overlap in the compound which will increase the total interaction. (2) The binding energies of O-H bond without deformation energies of monomers. Where the E_{AB}

represents the energies of optimized water dimer in the scanning and the E_{bsse} represents the basis set superposition error, different with the former, the E_A and E_B indicate the energies of monomers OH- and H_3O+ in structures of the scanning. (3) The deformation energies of monomers obtained with $E_{def} = E_{AS} + E_{BS} - E_{AO} - E_{BO}$ Where the E_{AS} and E_{BS} represent the energies of monomers OH^- and H_3O^+ in structures of the scanning while E_{AO} and E_{BO} represent the optimized energies of the monomers[22].

For the NMR chemical shift of water dimer scanned with CCSD(T), CCSD(T)-F12 methods and aug-cc-pVTZ, VTZ-F12 basis set, the data of the O and H atoms in the hydrogen bond O-H ··O was calculated in the CFOUR 2010[23-24] with CCSD(T) method and dzp basis set. For the light elements O and H atoms in the water dimer, the results are accurate and reliable.

The energy decomposition based on symmetry adapted perturbation theory (SAPT)[25] of the water dimer scanned with CCSD(T) was implemented in the Psi4[26-27], the interaction energies of the water monomers are given by $E_{int}=E_{elstat}+E_{ex}+E_{ind}+E_{disp}$, it divided the interaction energy of the water monomers into four parts: the electrostatic term, the exchange repulsion term, the induction term and the dispersion term and the sum of the electrostatic term, the exchange repulsion term is related to the variation of the conformation of water dimer closely.

Electrostatic interaction includes Coulombic multipole-multipole-type interactions as well as the interpenetration of charge clouds. Exchange repulsion is a repulsive force that arises from monomer wavefunction overlap and the fermionic anti-symmetry requirements of the dimer wavefunction. Induction includes polarization from each monomer's response to the other's electric field as well as charge transfer. Dispersion is resulting from the dynamic correction between the electrons on one monomer with those on another.

Part 2. The coordinate system for water dimer optimized with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

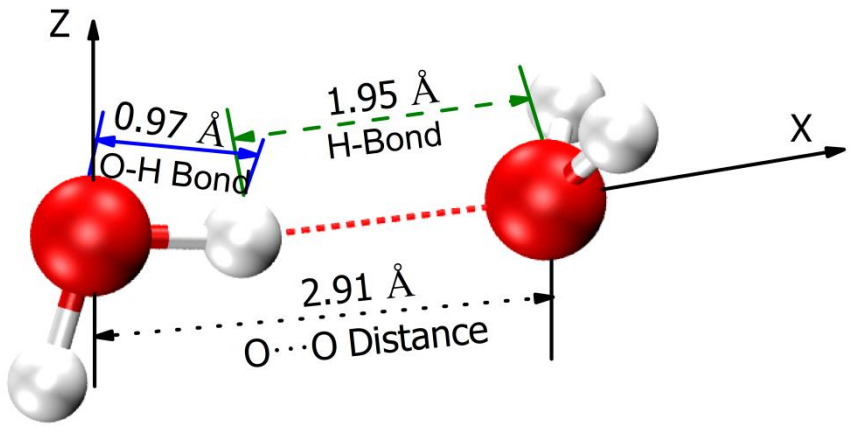

FIG. S1. The stable structure of water dimer optimized with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09[20] and Molpro 2012[21]. It is similar with the former research[28].

TABLE S1. The coordinate of the stable structure of water dimer optimized with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09.

Coordinate	X	Y	Z
O	0.000000000	-0.00000000	-0.00000000
H	-0.33144933	-0.00186772	-0.90179726
H	0.96302640	-0.00015063	-0.09524652
O	2.91369253	-0.00000000	-0.00000000
H	3.22432397	0.76251322	0.49831101
H	3.22411594	-0.76026949	0.50185420

TABLE S2. The coordinate of the stable structure of water dimer optimized with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

Coordinate	X	Y	Z
O	0.000000000	0.00000000	0.00000000
H	-0.32742945	0.31865670	0.84183516
H	0.96097170	0.03124514	0.08298045
O	2.91307524	-0.00000000	0.00000000
H	3.23657529	-0.88190074	-0.19474926
H	3.23763260	0.54530444	-0.71946544

Part 3. The bond length of O-H bond in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

TABLE S3. The bond length of O-H bond in the scan of water dimer with PBE0-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance (Å)	O-H Distance (Å)	ΔO ··O Distance (Å)	ΔO-H Distance (Å)
2.88434	0.96748	0	0
2.85434	0.96764	-0.03	0.00154
2.82434	0.96776	-0.06	0.000276
2.79434	0.96785	-0.09	0.000368
2.76434	0.96792	-0.12	0.000436
2.73434	0.96796	-0.15	0.000470
2.70434	0.96795	-0.18	0.000466
2.67434	0.96790	-0.21	0.000417
2.64434	0.96781	-0.24	0.000326
2.61434	0.96768	-0.27	0.000196
2.58494	0.96755	-0.30	0.000067

TABLE S4. The bond length of O-H bond in the scan of water dimer with PBE-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	O-H Distance (Å)	ΔO ··O Distance (Å)	ΔO-H Distance (Å)
2.89236	0.98053	0	0
2.86236	0.980804	-0.03	0.000212
2.83236	0.980986	-0.06	0.000393
2.80236	0.981132	-0.09	0.000539
2.77236	0.981249	-0.12	0.000656
2.74236	0.981327	-0.15	0.000734
2.71236	0.981357	-0.18	0.000764
2.68236	0.981333	-0.21	0.000740
2.65236	0.981254	-0.24	0.000661
2.62236	0.981117	-0.27	0.000524
2.59236	0.980918	-0.30	0.000325

TABLE S5. The bond length of O-H bond in the scan of water dimer with B3PW91-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	O-H Distance (Å)	ΔO ··O Distance (Å)	ΔO-H Distance (Å)
2.90831	0.968456	0	0
2.87831	0.968633	-0.03	0.000178
2.84831	0.968784	-0.06	0.000328
2.81831	0.968905	-0.09	0.000449
2.78831	0.969004	-0.12	0.000548
2.75831	0.969075	-0.15	0.000619
2.72831	0.96911	-0.18	0.000654
2.69831	0.969103	-0.21	0.000647
2.66831	0.969057	-0.24	0.000602
2.63831	0.968971	-0.27	0.000515
2.60831	0.968846	-0.30	0.000390

TABLE S6. The bond length of O-H bond in the scan of water dimer with B3LYP-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	O-H Distance (Å)	ΔO ··O Distance (Å)	ΔO-H Distance (Å)
2.90919	0.969566	0	0
2.87919	0.969645	-0.03	0.000079
2.84919	0.969691	-0.06	0.000124
2.81919	0.969694	-0.09	0.000127
2.78919	0.969673	-0.12	0.000106
2.75919	0.969618	-0.15	0.000052
2.72919	0.969521	-0.18	-0.0000456
2.69919	0.96938	-0.21	-0.000186
2.66919	0.969198	-0.24	-0.000368
2.63919	0.96899	-0.27	-0.000576
2.60919	0.96872	-0.30	-0.00085

TABLE S7. The bond length of O-H bond in the scan of water dimer with HSE06-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	O-H Distance (Å)	ΔO ··O Distance (Å)	ΔO-H Distance (Å)
2.87668	0.967911	0	0
2.84668	0.968058	-0.03	0.000147
2.81668	0.968176	-0.06	0.000265
2.78668	0.968257	-0.09	0.000346
2.75668	0.9683	-0.12	0.000388
2.72668	0.96829	-0.15	0.000387
2.69668	0.968245	-0.18	0.000334
2.66668	0.96814	-0.21	0.000229
2.63668	0.96798	-0.24	0.000068
2.60668	0.96777	-0.27	-0.000143
2.57668	0.96752	-0.30	-0.000391

TABLE S8. The bond length of O-H bond in the scan of water dimer with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	O-H Distance (Å)	ΔO ··O Distance (Å)	ΔO-H Distance (Å)
2.91369	0.96773	0	0
2.88369	0.96767	-0.03	-0.00006
2.85369	0.96765	-0.06	-0.00008
2.82369	0.96759	-0.09	-0.00014
2.79369	0.96748	-0.12	-0.00025
2.76369	0.96733	-0.15	-0.0004
2.73369	0.96712	-0.18	-0.00061
2.70369	0.96691	-0.21	-0.00082
2.67369	0.96661	-0.24	-0.00112

TABLE S9. The bond length of O-H bond in the scan of water dimer with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

O ··O Distance(Å)	O-H Distance (Å)	ΔO ··O Distance (Å)	ΔO-H Distance (Å)
2.91308	0.96505	0	0
2.88308	0.96502	-0.03	-0.00003
2.85308	0.96490	-0.06	-0.00015
2.82308	0.96481	-0.09	-0.00024
2.79308	0.96466	-0.12	-0.00039
2.76908	0.96447	-0.15	-0.00058
2.73308	0.96423	-0.18	-0.00082
2.70308	0.96405	-0.21	-0.001
2.67908	0.96388	-0.24	-0.00117
2.64308	0.96365	-0.27	-0.0014
2.61308	0.96335	-0.30	-0.0017

Part 4. The bond length of H-bond in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

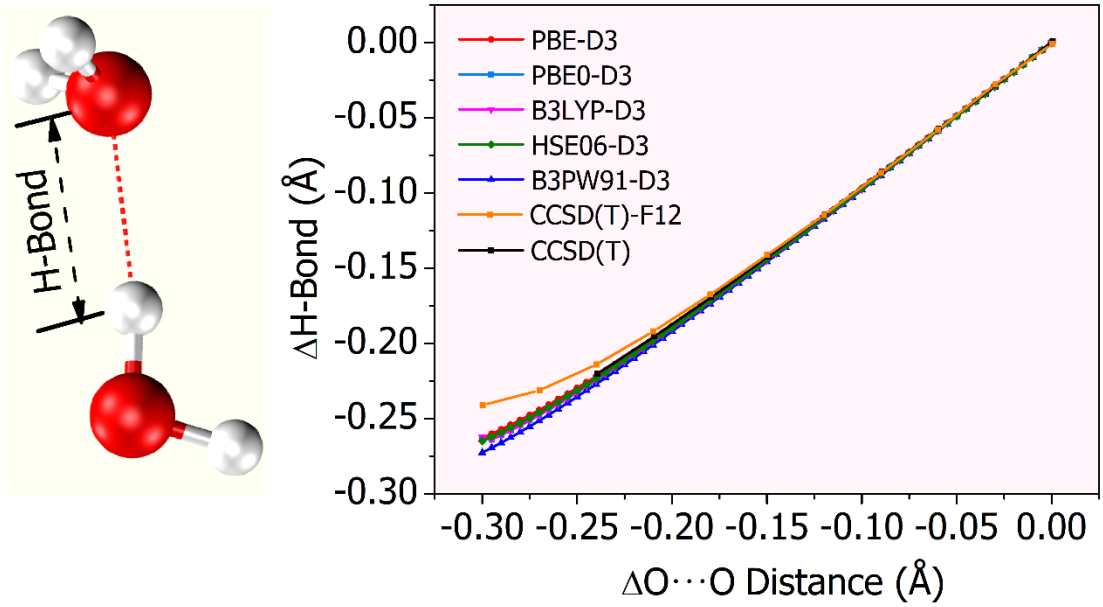

FIG. S2. The bond length of H-bond in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE09-D3 method and aug-cc-pVTZ basis set in Gaussian 09 and CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

TABLE S10. The bond length of H-bond in the scan of water dimer with PBE0-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	H-Bond Distance (Å)	ΔO ··O Distance(Å)	ΔH-Bond Distance(Å)
2.88434	1.923819	0	0
2.85434	1.894467	-0.03	-0.02935
2.82434	1.865156	-0.06	-0.05866
2.79434	1.836032	-0.09	-0.08779
2.76434	1.807278	-0.12	-0.11654
2.73434	1.779023	-0.15	-0.1448
2.70434	1.751377	-0.18	-0.17244
2.67434	1.724582	-0.21	-0.19924
2.64434	1.699165	-0.24	-0.22465
2.61434	1.67609	-0.27	-0.24773
2.58434	1.660319	-0.30	-0.26350

TABLE S11. The bond length of H-bond in the scan of water dimer with PBE-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	H-Bond Distance (Å)	ΔO ··O Distance(Å)	ΔH-Bond Distance(Å)
2.89236	1.92086	0	0
2.86236	1.89162	-0.03	-0.02924
2.83236	1.86243	-0.06	-0.05843
2.80236	1.83346	-0.09	-0.08740
2.77236	1.80493	-0.12	-0.11593
2.74236	1.77701	-0.15	-0.14385
2.71236	1.74980	-0.18	-0.17106
2.68236	1.72359	-0.21	-0.19727
2.65236	1.69889	-0.24	-0.22196
2.62236	1.67658	-0.27	-0.24428
2.59236	1.65795	-0.30	-0.26291

TABLE S12. The bond length of H-bond in the scan of water dimer with B3PW91-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	H-Bond Distance (Å)	ΔO ··O Distance(Å)	ΔH-Bond Distance(Å)
2.90831	1.94699	0	0
2.87831	1.91754	-0.03	-0.02945
2.84831	1.88805	-0.06	-0.05894
2.81831	1.85870	-0.09	-0.08829
2.78831	1.82972	-0.12	-0.11726
2.75831	1.80124	-0.15	-0.14575
2.72831	1.77328	-0.18	-0.1737
2.69831	1.74602	-0.21	-0.20096
2.66831	1.71987	-0.24	-0.22712
2.63831	1.69556	-0.27	-0.25143
2.60831	1.67432	-0.30	-0.27266

TABLE S13. The bond length of H-bond in the scan of water dimer with B3LYP-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	H-Bond Distance (Å)	ΔO ··O Distance(Å)	ΔH-Bond Distance(Å)
2.90919	1.94685	0	0
2.87919	1.91760	-0.03	-0.02925
2.84919	1.88828	-0.06	-0.05857
2.81919	1.85913	-0.09	-0.08772
2.78919	1.83040	-0.12	-0.11645
2.75919	1.80224	-0.15	-0.14462
2.72919	1.77466	-0.18	-0.17219
2.69919	1.74789	-0.21	-0.19896
2.66919	1.72241	-0.24	-0.22444
2.63919	1.69923	-0.27	-0.24762
2.60919	1.68464	-0.30	-0.26221

TABLE S14. The bond length of H-bond in the scan of water dimer with HSE06-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	H-Bond Distance (Å)	ΔO ··O Distance(Å)	ΔH-Bond Distance(Å)
2.87668	1.915422	0	0
2.84668	1.886087	-0.03	-0.02933
2.81668	1.856931	-0.06	-0.05851
2.78668	1.827978	-0.09	-0.08744
2.75668	1.799378	-0.12	-0.11604
2.72668	1.771236	-0.15	-0.14419
2.69668	1.743726	-0.18	-0.1717
2.66668	1.717137	-0.21	-0.19829
2.63668	1.692017	-0.24	-0.2234
2.60668	1.669298	-0.27	-0.24612
2.57668	1.650566	-0.30	-0.26486

TABLE S15. The bond length of H-bond in the scan of water dimer with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	H-Bond Distance (Å)	ΔO ··O Distance(Å)	ΔH-Bond Distance(Å)
2.91369	1.95299	0	0
2.88369	1.92368	-0.03	-0.02931
2.85369	1.89487	-0.06	-0.05812
2.82369	1.86610	-0.09	-0.08689
2.79369	1.83778	-0.12	-0.11521
2.76369	1.80979	-0.15	-0.1432
2.73369	1.78261	-0.18	-0.17038
2.70369	1.75660	-0.21	-0.19639
2.67369	1.73164	-0.24	-0.22135

TABLE S16. The bond length of H-bond in the scan of water dimer with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

O ··O Distance(Å)	H-Bond Distance (Å)	ΔO ··O Distance(Å)	ΔH-Bond Distance(Å)
2.91308	1.95412	0	0
2.88308	1.92712	-0.03	-0.027
2.85308	1.89705	-0.06	-0.05707
2.82308	1.86851	-0.09	-0.08561
2.79308	1.84051	-0.12	-0.11361
2.76308	1.81378	-0.15	-0.14034
2.73308	1.78747	-0.18	-0.16665
2.70308	1.76304	-0.21	-0.19108
2.67308	1.74102	-0.24	-0.2131
2.64308	1.72381	-0.27	-0.23031
2.61308	1.71390	-0.30	-0.24022

Part 5. The energies of water dimer in the scan with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

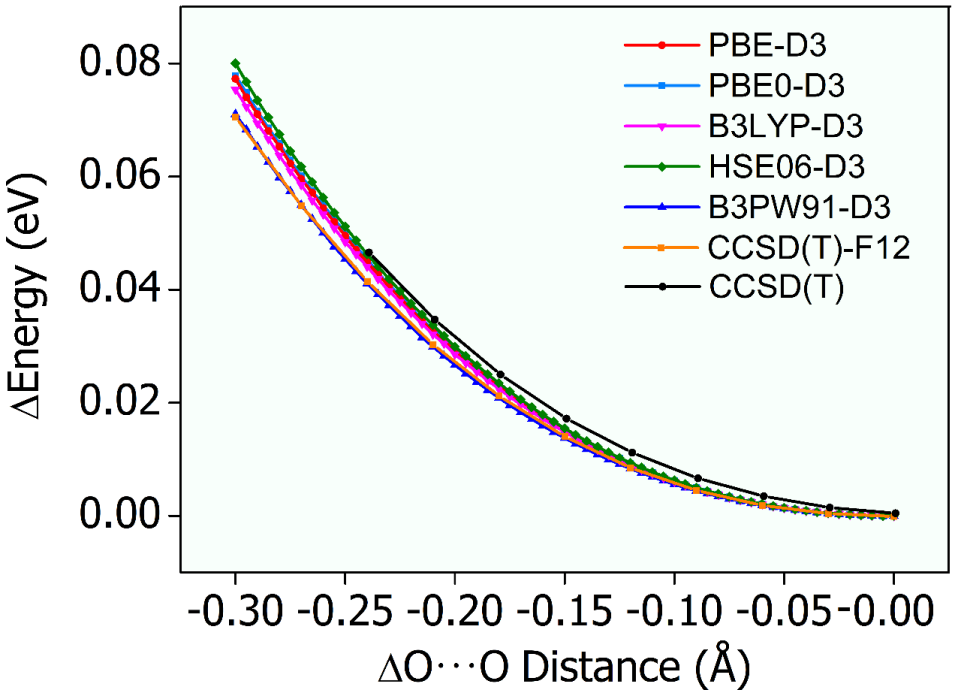

FIG. S3. The energies of the water dimer scanned with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE09-D3 method and aug-cc-pVTZ basis set in Gaussian 09 and CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

TABLE S17. The energy of water dimer in the scan with PBE0-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Energy (Hartree)	ΔO ··O Distance (Å)	ΔEnergy (eV)
2.88434	-152.7686487	0	0
2.85434	-152.7686305	-0.03	0.000495159
2.82434	-152.7685721	-0.06	0.002084063
2.79434	-152.7684673	-0.09	0.00493798
2.76434	-152.768309	-0.12	0.009243713
2.73434	-152.7680899	-0.15	0.015205398
2.70434	-152.7678018	-0.18	0.023045431
2.67434	-152.767436	-0.21	0.03292531
2.64434	-152.7669835	-0.24	0.04544237
2.61434	-152.7664361	-0.27	0.06013631
2.58434	-152.7657887	-0.30	0.07782346

TABLE S18. The energy of water dimer in the scan with PBE-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Energy (Hartree)	ΔO ··O Distance (Å)	ΔEnergy (eV)
2.89236	-152.7695183	0	0
2.86236	-152.7695002	-0.03	0.000491376
2.83236	-152.7694423	-0.06	0.002067846
2.80236	-152.7693383	-0.09	0.004898905
2.77236	-152.7691813	-0.12	0.009169753
2.74236	-152.768964	-0.15	0.015082704
2.71236	-152.7686783	-0.18	0.02285724
2.68236	-152.7683156	-0.21	0.0326532
2.65236	-152.7678674	-0.24	0.04489815
2.62236	-152.7673253	-0.27	0.05959209
2.59236	-152.7666829	-0.30	0.07727924

TABLE S19. The energy of water dimer in the scan with B3PW91-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Energy (Hartree)	ΔO ··O Distance (Å)	ΔEnergy (eV)
2.90831	-152.8798045	0	0
2.87831	-152.8797882	-0.03	0.00044441
2.84831	-152.8797357	-0.06	0.001873695
2.81831	-152.879641	-0.09	0.004449597
2.78831	-152.8794978	-0.12	0.008347274
2.75831	-152.8792989	-0.15	0.013757963
2.72831	-152.8790368	-0.18	0.020890021
2.69831	-152.8787033	-0.21	0.0299321
2.66831	-152.8782899	-0.24	0.04108861
2.63831	-152.8777882	-0.27	0.05496622
2.60831	-152.8771909	-0.30	0.07102071

TABLE S20. The energy of water dimer in the scan with B3LYP-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Energy (Hartree)	ΔO ··O Distance (Å)	ΔEnergy (eV)
2.90919	-152.9408586	0	0
2.87919	-152.9408409	-0.03	0.000484084
2.84919	-152.9407839	-0.06	0.002034049
2.81919	-152.9406816	-0.09	0.004818197
2.78919	-152.9405273	-0.12	0.00901612
2.75919	-152.9403139	-0.15	0.014822049
2.72919	-152.9400338	-0.18	0.022446055
2.69919	-152.9396787	-0.21	0.03210898
2.66919	-152.9392406	-0.24	0.04408182
2.63919	-152.9387117	-0.27	0.05850365
2.60919	-152.9380886	-0.30	0.07537447

TABLE S21. The energy of water dimer in the scan with HSE06-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Energy (Hartree)	ΔO ··O Distance (Å)	ΔEnergy (eV)
2.87668	-152.7817129	0	0
2.84668	-152.7816946	-0.03	0.000499349
2.81668	-152.7816355	-0.06	0.002106975
2.78668	-152.7815291	-0.09	0.005001164
2.75668	-152.7813683	-0.12	0.009379115
2.72668	-152.7811449	-0.15	0.015457943
2.69668	-152.7808502	-0.18	0.023474794
2.66668	-152.7804751	-0.21	0.03374164
2.63668	-152.7800099	-0.24	0.0462587
2.60668	-152.7794457	-0.27	0.06176897
2.57668	-152.7787758	-0.30	0.08000034

TABLE S22. The energy of water dimer in the scan with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Energy (Hartree)	ΔO ··O Distance (Å)	ΔEnergy (eV)
2.91369	-15267518072	0	0
2.88369	-152.6751436	-0.03	0.001010344
2.85369	-152.6750688	-0.06	0.003045999
2.82369	-152.6749527	-0.09	0.006203564
2.79369	-152.6747858	-0.12	0.01074644
2.76369	-152.6745629	-0.15	0.016811772
2.73369	-152.6742765	-0.18	0.024605819
2.70369	-152.6739168	-0.21	0.034391439
2.67369	-152.6734787	-0.24	0.046313666

TABLE S23. The energy of water dimer in the scan of water dimer with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

O ··O Distance(Å)	Energy (Hartree)	ΔO ··O Distance (Å)	ΔEnergy (eV)
2.91308	-152.7476678	0	0
2.88308	-152.7476496	-0.03	0.00050
2.85308	-152.7475966	-0.06	0.00194
2.82308	-152.7474991	-0.09	0.00459
2.79308	-152.7473525	-0.12	0.00858
2.76308	-152.7471504	-0.15	0.01408
2.73308	-152.7468857	-0.18	0.02128
2.70308	-152.7465514	-0.21	0.03038
2.67308	-152.7461408	-0.24	0.04155
2.64308	-152.7456488	-0.27	0.05954
2.61308	-152.7450741	-0.30	0.07058

Part 6. The bond angles of O-H ··O in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

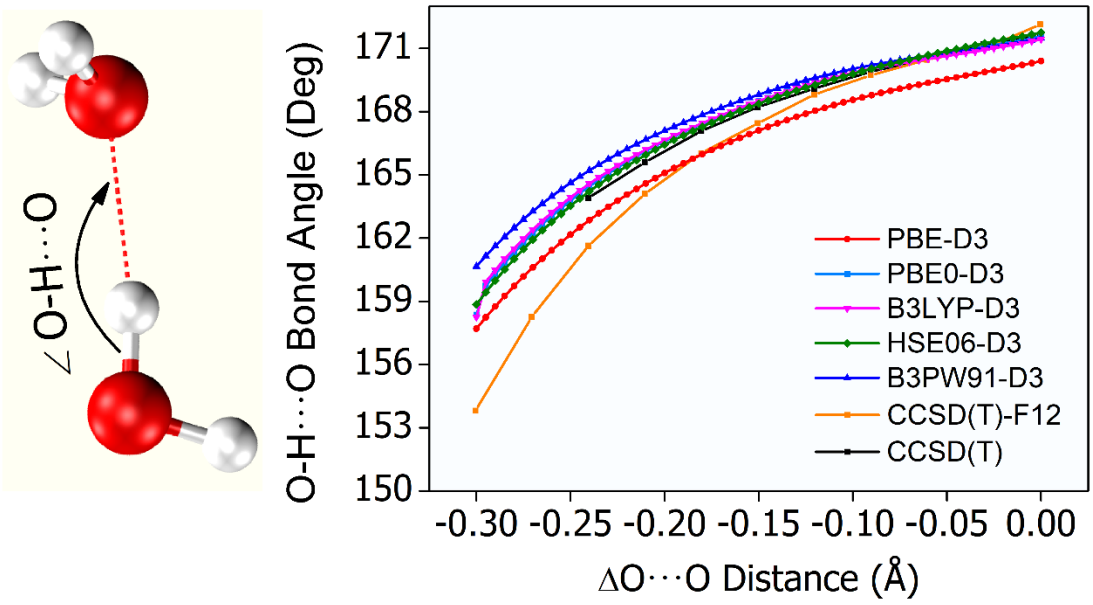

FIG. S4. The bond angles of the water dimer in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method with VTZ-F12 basis set.

TABLE S24. The bond angles of the water dimer scanned with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method with VTZ-F12 basis set at different O ··O distance (Å).

ΔO ··O Distance	PBE0 -D3	PBE -D3	B3PW91-D3	B3LYP -D3	HSE06 -D3	CCSD (T)	CCSD(T)-F12
0	171.57	170.40	171.49	171.43	171.75	171.56	172.13
-0.03	171.08	169.88	171.04	170.93	171.24	171.16	170.96
-0.06	170.60	169.37	170.65	170.51	170.68	170.47	170.46
-0.09	170.05	168.79	170.21	170.03	170.04	169.85	169.71
-0.12	169.36	168.04	169.60	169.38	169.28	169.05	168.80
-0.15	168.49	167.11	168.81	168.51	168.38	168.16	167.43
-0.18	167.43	165.98	167.85	167.46	167.29	167.03	166.02
-0.21	166.13	164.59	166.68	166.19	165.94	165.54	164.08
-0.24	164.46	162.85	165.21	164.58	164.22	163.86	161.26
-0.27	162.23	160.61	163.27	162.40	161.93		158.25
-0.30	158.37	157.70	160.66	158.24	158.85		153.79

Part 7. The binding energies of O-H bond with and without deformation energies of monomers as well as the monomers' deformation energies in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) methods and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

TABLE S25. The binding energies of O-H bond with deformation energies of monomers in the water dimer scanned with PBE0-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding energy (meV)
2.88434	-0.201332751	0	0
2.85434	-0.201304749	-0.03	-0.761962422
2.82434	-0.201234649	-0.06	-2.669453523
2.79434	-0.201117246	-0.09	-5.864106556
2.76434	-0.200947453	-0.12	-10.48434388
2.73434	-0.200716107	-0.15	-16.77949988
2.70434	-0.200415781	-0.18	-24.95167067
2.67434	-0.200037266	-0.21	-35.25144234
2.64434	-0.199574665	-0.24	-47.83927815
2.61434	-0.199017522	-0.27	-62.99969632

TABLE S26. The binding energies of O-H bond with deformation energies of monomers in the water dimer scanned with PBE-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.89236	-0.206128027	0	0
2.86236	-0.206095369	-0.03	-0.888656838
2.83236	-0.206026784	-0.06	-2.754923273
2.80236	-0.205912013	-0.09	-5.877956954
2.77236	-0.2057442	-0.12	-10.4443165
2.74236	-0.205516	-0.15	-16.6538667
2.71236	-0.205219597	-0.18	-24.71928873
2.68236	-0.204846748	-0.21	-34.86488287
2.65236	-0.204388377	-0.24	-47.33761615
2.62236	-0.203836764	-0.27	-62.34755749
2.59236	-0.203186065	-0.30	-80.05372798

TABLE S27. The binding energies of O-H bond with deformation energies of monomers in the water dimer scanned with B3LYP-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.90919	-0.2029277	0	0
2.87919	-0.202897551	-0.03	-0.82041165
2.84919	-0.20282773	-0.06	-2.720310881
2.81919	-0.202712063	-0.09	-5.867725618
2.78919	-0.2025437	-0.12	-10.44905121
2.75919	-0.202315483	-0.15	-16.659064
2.72919	-0.202020022	-0.18	-24.69885327
2.69919	-0.201649704	-0.21	-34.77557637
2.66919	-0.201195928	-0.24	-47.1232751

TABLE S28. The binding energies of O-H bond with deformation energies of monomers in the water dimer scanned with B3PW91-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.90831	-0.202141135	0	0
2.87831	-0.202109073	-0.03	-0.872439082
2.84831	-0.202040447	-0.06	-2.739821169
2.81831	-0.201929253	-0.09	-5.765521102
2.78831	-0.201768774	-0.12	-10.13231517
2.75831	-0.201552042	-0.15	-16.02980962
2.72831	-0.2012718	-0.18	-23.65547469
2.69831	-0.200920206	-0.21	-33.22269902
2.66831	-0.200489052	-0.24	-44.95483051

TABLE S29. The binding energies of O-H bond with deformation energies of monomers in the water dimer scanned with HSE06-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.87668	-0.200153075	0	0
2.84668	-0.200128564	-0.03	-0.66696882
2.81668	-0.200063204	-0.06	-2.445479781
2.78668	-0.199950523	-0.09	-5.511642472
2.75668	-0.199783284	-0.12	-10.0623829
2.72668	-0.199553588	-0.15	-16.31264076
2.69668	-0.19925282	-0.18	-24.4968388
2.66668	-0.198871708	-0.21	-34.86727744
2.63668	-0.198400863	-0.24	-47.67944073

TABLE S30. The binding energies of O-H bond with deformation energies of monomers in the water dimer scanned with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.91308	-0.60607363	0	0
2.88308	-0.60605647	-0.03	-0.46694076
2.85308	-0.60600239	-0.06	-1.93851164
2.82308	-0.60590486	-0.09	-4.592400471
2.79308	-0.60575827	-0.12	-8.58126096
2.76308	-0.60555621	-0.15	-14.07951562
2.73308	-0.60529141	-0.18	-21.28498842
2.70308	-0.60495717	-0.21	-30.37999306
2.67308	-0.60454656	-0.24	-41.55310177

TABLE S31. The binding energies of O-H bond with deformation energies of monomers in the water dimer scanned with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.91369	-0.19959799	0	0
2.88369	-0.19954407	-0.03	-1.46721712
2.85369	-0.19945267	-0.06	-3.95430252
2.82369	-0.19931885	-0.09	-7.59567854
2.79369	-0.19913354	-0.12	-12.63814895
2.76369	-0.19889181	-0.15	-19.21586398
2.73369	-0.19858654	-0.18	-27.52256595
2.70369	-0.19820866	-0.21	-37.80505863
2.67369	-0.19775418	-0.24	-50.17191391

TABLE S32. The binding energies of O-H bond without deformation energies in the water dimer scanned with PEB0-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.88434	-0.206893811	0	0
2.85434	-0.207354579	-0.03	12.53795805
2.82434	-0.207818739	-0.06	25.16821581
2.79434	-0.208301986	-0.09	38.31784992
2.76434	-0.208722083	-0.12	49.74910939
2.73434	-0.209140537	-0.15	61.13566119
2.70434	-0.209524391	-0.18	71.58071238
2.67434	-0.209871276	-0.21	81.01980012
2.64434	-0.210031145	-0.24	85.36999547

TABLE S33. The binding energies of O-H bond without deformation energies in the water dimer scanned with PEB-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.89236	-0.210595467	0	0
2.86236	-0.210964229	-0.03	9.911035319
2.83236	-0.211330054	-0.06	19.86549939
2.80236	-0.211681223	-0.09	29.42115905
2.77236	-0.21200264	-0.12	38.16723704
2.74236	-0.21228375	-0.15	45.81652125
2.71236	-0.212515467	-0.18	52.12177254
2.68236	-0.212681488	-0.21	56.63936997
2.65236	-0.212754347	-0.24	58.62193622

TABLE S34. The binding energies of O-H bond without deformation energies in the water dimer scanned with B3LYP-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.90919	-0.206832041	0	2.20384E-09
2.87919	-0.207226311	-0.03	10.73092996
2.84919	-0.2076307	-0.06	21.73369781
2.81919	-0.208030953	-0.09	32.62544478
2.78919	-0.2084088	-0.12	42.9063048
2.75919	-0.208754613	-0.15	52.31532438
2.72919	-0.209063612	-0.18	60.72570026
2.69919	-0.209322754	-0.21	67.77607036
2.66919	-0.209503168	-0.24	72.68629531

TABLE S35. The binding energies of O-H bond without deformation energies in the water dimer scanned with B3PW91-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.90831	-0.207042835	0	-7.34865E-10
2.87831	-0.207472243	-0.03	11.68549184
2.84831	-0.207909187	-0.06	23.57588251
2.81831	-0.208342603	-0.09	35.36858569
2.78831	-0.208757794	-0.12	46.66740922
2.75831	-0.209145412	-0.15	57.21330438
2.72831	-0.20949969	-0.18	66.85361746
2.69831	-0.209808896	-0.21	75.26753077
2.66831	-0.210048892	-0.24	81.79844288

TABLE S36. The binding energies of O-H bond without deformation energies in the water dimer scanned with HSE06-D3 method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.87668	-0.205768255	0	0
2.84668	-0.206229964	-0.03	12.56495136
2.81668	-0.206687694	-0.06	25.01969817
2.78668	-0.207134953	-0.09	37.18900159
2.75668	-0.207563194	-0.12	48.84428922
2.72668	-0.207962048	-0.15	59.69739657
2.69668	-0.20831816	-0.18	69.3853289
2.66668	-0.208612088	-0.21	77.38509079
2.63668	-0.208812663	-0.24	82.84361739

TABLE S37. The binding energies of O-H bond without deformation energies in the water dimer scanned with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.91369	-0.20600603	0	0.0000000
2.88369	-0.20654213	-0.03	14.58863343
2.85369	-0.2070717	-0.06	28.9987627
2.82369	-0.20761228	-0.09	43.70848508
2.79369	-0.2081349	-0.12	57.9294979
2.76369	-0.2086424	-0.15	71.7390804
2.73369	-0.20911328	-0.18	84.55219608
2.70369	-0.20951757	-0.21	95.55333127
2.67369	-0.20986733	-0.24	105.0706506

TABLE S38. The binding energies of O-H bond without deformation energies in the water dimer scanned with CCSD(T)-F12 method and aug-cc-pVTZ basis set in Molpro 2012.

O ··O Distance(Å)	Binding energy (Hartree)	ΔO ··O Distance(Å)	ΔBinding Energy (meV)
2.91308	-0.61426895	0	0
2.88308	-0.61484691	-0.03	15.72686956
2.85308	-0.61541195	-0.06	31.102173
2.82308	-0.61596123	-0.09	46.04863108
2.79308	-0.61650019	-0.12	60.71427164
2.76308	-0.61698862	-0.15	74.00494037
2.73308	-0.61745855	-0.18	86.7922056
2.70308	-0.61782139	-0.21	96.66544484
2.67308	-0.61805705	-0.24	103.0779891
2.64308	-0.61804537	-0.27	102.7601646
2.61308	-0.61766411	-0.30	92.38569876

TABLE S39. The deformation energies of monomers of O-H bond in the water dimer scanned with PBE0-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Deformation Energies (Hartree)	ΔO ··O Distance(Å)	ΔDeformation Energies (meV)
2.88434	0.00556238	0	0
2.85434	0.00605778	-0.03	13.4803294
2.82434	0.00659463	-0.06	28.08855475
2.79434	0.0071697	-0.09	43.73678452
2.76434	0.00777681	-0.12	60.25685473
2.73434	0.00841286	-0.15	77.56441128
2.70434	0.00907604	-0.18	95.61020226
2.67434	0.00975841	-0.21	114.1781723
2.64434	0.01043887	-0.24	132.6941694

TABLE S40. The deformation energies of monomers of O-H bond in the water dimer scanned with PBE-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Deformation Energies (Hartree)	ΔO ··O Distance(Å)	ΔDeformation Energies (meV)
2.89236	0.00446744	0	0
2.86236	0.00486886	-0.03	10.92303962
2.83236	0.00530327	-0.06	22.74377013
2.80236	0.00576921	-0.09	35.42246347
2.77236	0.00625844	-0.12	48.734901
2.74236	0.00676775	-0.15	62.59373541
2.71236	0.00729587	-0.18	76.96440873
2.68236	0.00783474	-0.21	91.6276003
2.65236	0.00836597	-0.24	106.0828998

TABLE S41. The deformation energies of monomers of O-H bond in the water dimer scanned with B3LYP-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Deformation Energies (Hartree)	ΔO ··O Distance(Å)	ΔDeformation Energies (meV)
2.90919	0.00390434	0	0
2.87919	0.00432876	-0.03	11.54891983
2.84919	0.00480297	-0.06	24.45264814
2.81919	0.00531889	-0.09	38.49134726
2.78919	0.0058651	-0.12	53.35426757
2.75919	0.00643913	-0.15	68.9741979
2.72919	0.00704359	-0.18	85.42215896
2.69919	0.00767305	-0.21	102.550395
2.66919	0.00830724	-0.24	119.8073391

TABLE S42. The deformation energies of monomers of O-H bond in the water dimer scanned with B3PW91-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Deformation Energies (Hartree)	ΔO ··O Distance(Å)	ΔDeformation Energies (meV)
2.90831	0.0049017	0	0
2.87831	0.00536317	-0.03	12.55706017
2.84831	0.00586874	-0.06	26.31412544
2.81831	0.00641335	-0.09	41.13350815
2.78831	0.00698902	-0.12	56.79806452
2.75831	0.00759337	-0.15	73.24303237
2.72831	0.00822789	-0.18	90.50895609
2.69831	0.00888869	-0.21	108.4899849
2.66831	0.00955984	-0.24	126.7526475

TABLE S43. The deformation energies of monomers of O-H bond in the water dimer scanned with HSE06-D3 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Deformation Energies (Hartree)	ΔO ··O Distance(Å)	ΔDeformation Energies (meV)
2.87668	0.00561518	0	0
2.84668	0.0061014	-0.03	13.20408877
2.81668	0.00662449	-0.06	27.43789076
2.78668	0.00718443	-0.09	42.6744181
2.75668	0.00777991	-0.12	58.87802438
2.72668	0.00840846	-0.15	75.98149843
2.69668	0.00906534	-0.18	93.85586011
2.66668	0.00974038	-0.21	112.2243736
2.63668	0.0104118	-0.24	130.4943832

TABLE S44. The deformation energies of monomers of O-H bond in the water dimer scanned with CCSD(T) method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Deformation Energies (Hartree)	ΔO ··O Distance(Å)	ΔDeformation Energies (meV)
2.91369	0.00640804	0	0
2.88369	0.00699806	-0.03	16.05506143
2.85369	0.00761903	-0.06	32.9522761
2.82369	0.00829343	-0.09	51.3033745
2.79369	0.00900136	-0.12	70.56685773
2.76369	0.00975059	-0.15	90.95415526
2.73369	0.01052674	-0.18	112.0739729
2.70369	0.01130891	-0.21	133.3576008
2.67369	0.01211315	-0.24	155.2417754

TABLE S45. The deformation energies of monomers of O-H bond in the water dimer scanned with CCSD(T)-F12 method and aug-cc-pVTZ basis set.

O ··O Distance(Å)	Deformation Energies (Hartree)	ΔO ··O Distance(Å)	ΔDeformation Energies (meV)
2.91308	0.00819532	0	0
2.88308	0.00879044	-0.03	16.19383753
2.85308	0.00940956	-0.06	33.04071185
2.82308	0.01005637	-0.09	50.64105876
2.79308	0.01074192	-0.12	69.29555981
2.76308	0.01143241	-0.15	88.0844832
2.73308	0.01216714	-0.18	108.0772212
2.70308	0.01286422	-0.21	127.0454651
2.67908	0.01351049	-0.24	144.6311181

Part 8. The binding energies of H-bond without deformation energies in the scan of water dimer calculated with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

TABLE S46. The binding energies of H-bond in the scan of water dimer calculated with CCSD(T) method and aug-cc-pVTZ in Gaussian 09.

O ··O Distance (Å)	ΔO ··O Distance (Å)	Binding Energy (Hartree)	ΔBinding Energy (meV)
2.91369	0	-0.00724569	0
2.88369	-0.03	-0.0071858	-1.62966679
2.85369	-0.06	-0.00708694	-4.31974625
2.82369	-0.09	-0.00694512	-8.17881027
2.79369	-0.12	-0.00675215	-13.42971694
2.76369	-0.15	-0.00650264	-20.21913355
2.73369	-0.18	-0.00618998	-28.72692481
2.70369	-0.21	-0.0058081	-39.11826149
2.67369	-0.24	-0.00534972	-51.59123967

TABLE S47. The binding energies of H-bond without deformation energies in the scan of water dimer calculated with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

O ··O Distance (Å)	ΔO ··O Distance (Å)	Binding Energy (Hartree)	ΔBinding Energy (meV)
2.91308	0	-0.00804609	0
2.88308	-0.03	-0.00802976	-0.44435563
2.85308	-0.06	-0.0079787	-1.833749291
2.82308	-0.09	-0.00788454	-4.39593705
2.79308	-0.12	-0.0077425	-8.26098749
2.76308	-0.15	-0.00754646	-13.59543193
2.73308	-0.18	-0.00728933	-20.59219636
2.70308	-0.21	-0.0069638	-29.45019319
2.67908	-0.24	-0.00656456	-40.31391283

Part 9. The energy decomposition and corresponding percentage of four parts E_{elec}, E_{ex}, E_{orb}, E_{disp} in Psi4 of water dimer with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

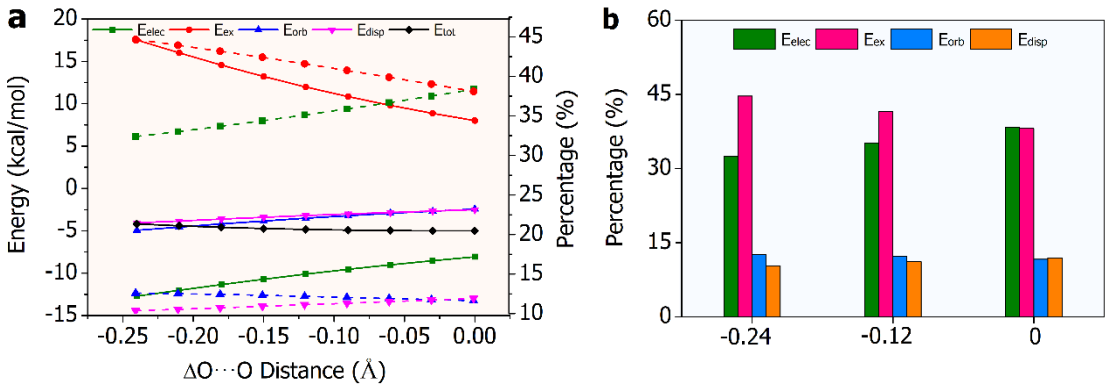

FIG. S5. The energy decomposition based on Symmetry-Adapted Perturbation Theory (SAPT)[25] and the corresponding percentage of the four terms in the total interaction. (a) The energy decomposition of water dimer scanned with CCSD(T) method and aug-cc-pVTZ basis set. (b) The percentage of the four parts E_{int}, E_{elec}, E_{ex}, E_{orb}, E_{disp} (kcal/mol) at ΔO ··O distance of 0 Å, 0.12 Å and 0.24 Å corresponding O···O distance of 2.91 Å, 2.79 Å and 2.67 Å in the Psi4[26-27].

TABLE S48. The four parts E_{int}, E_{elec}, $E_{ex,}$ E_{orb}, E_{disp} (kcal/mol) of energy decomposition of water dimer scanned with CCSD(T)-F12 method and VTZ-F12 basis set at different O ··O distance (Å) in the Psi4.

O ··O Distance	ΔO ··O Distance	E_{int}	E_{elec}	E_{ex}	E_{orb}	E_{disp}
2.91308	0	-4.9855	-8.0039	7.9141	-2.4133	-2.4823
2.88308	-0.03	-4.9777	-8.4519	8.7451	-2.6340	-2.6369
2.85308	-0.06	-4.9510	-8.9346	9.6679	-2.8818	-2.8024
2.82308	-0.09	-4.8998	-9.4547	10.687	-3.1526	-2.9795
2.79308	-0.12	-4.8214	-10.007	11.797	-3.4451	-3.1663
2.76308	-0.15	-4.7115	-10.591	12.996	-3.7538	-3.3622
2.73308	-0.18	-4.5671	-11.206	14.291	-4.0844	-3.5675
2.70308	-0.21	-4.3811	-11.854	15.679	-4.4246	-3.7813
2.67308	-0.24	-4.1513	-12.514	17.121	-4.7587	-3.9993
2.64308	-0.27	-3.8698	-13.144	18.524	-5.0416	-4.2090
2.61308	-0.30	-3.5306	-13.702	19.793	-5.2203	-4.4005

TABLE S49. The percentage of four parts E_{int}, E_{elec}, $E_{ex,}$ E_{orb}, E_{disp} (kcal/mol) of energy decomposition of water dimer scanned with CCSD(T)-F12 method and VTZ-F12 basis set in the Psi4.

O ··O Distance(Å)	ΔO ··O Distance(Å)	E_{elec}	E_{ex}	E_{orb}	E_{disp}
2.91308	0	38.4548	38.0233	11.5951	11.9265
2.88308	-0.03	37.6177	38.9225	11.7234	11.7362
2.85308	-0.06	36.7879	39.8071	11.8659	11.5390
2.82308	-0.09	35.9852	40.6754	11.9991	11.3402
2.79308	-0.12	35.2171	41.5165	12.1236	11.1426
2.76308	-0.15	34.4963	42.3276	12.2256	10.9502
2.73308	-0.18	33.8060	43.1114	12.3208	10.7616
2.70308	-0.21	33.1692	43.8709	12.3798	10.5799
2.67308	-0.24	32.5951	44.5937	12.3944	10.4165
2.64308	-0.27	32.1215	45.2714	12.3208	10.2860
2.61308	-0.30	31.7806	45.9057	12.1074	10.2061

TABLE S50. The four parts E_{int}, E_{elec}, $E_{ex,}$ E_{orb}, E_{disp} (kcal/mol) of energy decomposition in the Psi4 of water dimer scanned with CCSD(T) method and aug-cc-pVTZ method at different O ··O distance (Å) in Gaussian 09.

O ··O Distance	ΔO ··O Distance	E_{int}	E_{elec}	E_{ex}	E_{orb}	E_{disp}
2.91369	0	-5.0035	-8.0601	8.0039	-2.4445	-2.5028
2.88369	-0.03	-4.9979	-8.5275	8.8717	-2.6786	-2.6634
2.85369	-0.06	-4.9704	-9.0150	9.8038	-2.9289	-2.8302
2.82369	-0.09	-4.9203	-9.5425	10.838	-3.2069	-3.0092
2.79369	-0.12	-4.8422	-10.106	11.971	-3.5080	-3.1992
2.76369	-0.15	-4.7335	-10.707	13.209	-3.8351	-3.4004
2.73369	-0.18	-4.5890	-11.343	14.550	-4.1845	-3.6112
2.70369	-0.21	-4.4069	-12.022	16.005	-4.5550	-3.8346
2.67369	-0.24	-4.1808	-12.708	17.524	-4.9352	-4.0613

TABLE S51. The percentage of four parts E_{int}, E_{elec}, $E_{ex,}$ E_{orb}, E_{disp} (kcal/mol) of energy decomposition in the Psi4 of water dimer scanned with CCSD(T) method and aug-cc-pVTZ method in Gaussian 09.

O ··O Distance(Å)	ΔO ··O Distance(Å)	E_{elec}	E_{ex}	E_{orb}	E_{disp}
2.91369	0	38.36086	38.09323	11.63426	11.91163
2.88369	-0.03	37.49791	39.01136	11.77871	11.71200
2.85369	-0.06	36.6791	39.8885	11.9170	11.5152
2.82369	-0.09	35.8780	40.7502	12.0573	11.3142
2.79369	-0.12	35.1098	41.5890	12.1868	11.1142
2.76369	-0.15	34.3711	42.4026	12.3107	10.9154
2.73369	-0.18	33.6708	43.1893	12.4208	10.7189
2.70369	-0.21	33.0131	43.9493	12.5078	10.5296
2.67369	-0.24	32.3955	44.6714	12.5803	10.3527

Part 10. The NMR chemical shift of water dimer scanned with CCSD(T)-F12, CCSD(T) methods and VTZ-F12, aug-cc-pVTZ basis set respectively, anisotropy scanned with CCSD(T) method and aug-cc-pVTZ basis set in CFOUR 2010[6,7] as well as NMR chemical shift of water dimer scanned with PBE0-D3 method, aug-cc-pVTZ basis set in Gaussian 09.

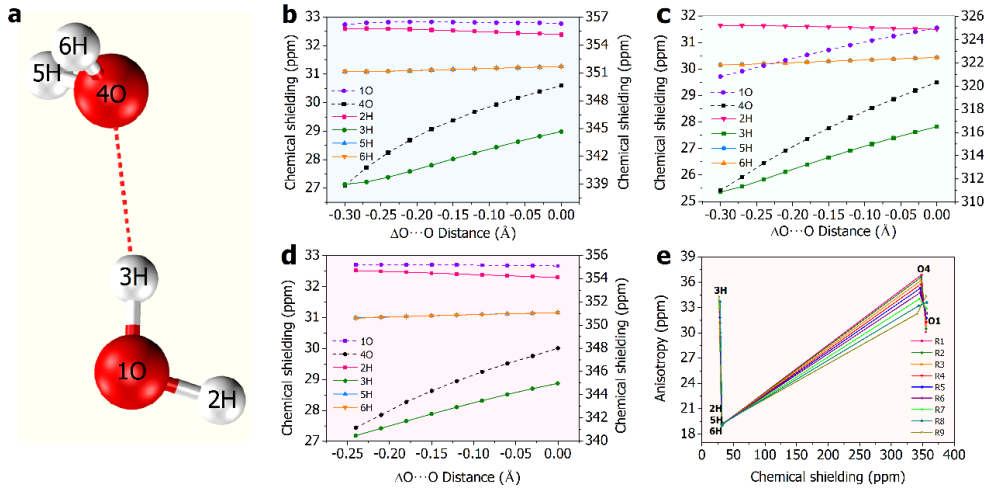

FIG. S6. The NMR chemical shift and the anisotropy of the water dimer scanned with CCSD(T)-F12, PBE0 and CCSD(T) methods. (a) The structure of the water dimer. (b) The NMR chemical shift of water dimer scanned with CCSD(T)-F12 method with VTZ-F12 basis set in CFOUR 2010[23-24]. (c) The NMR chemical shift of water dimer scanned with PBE0 method with aug-cc-pVTZ basis set in Gaussian 09. (d) The NMR chemical shift of water dimer scanned with CCSD(T) method with aug-cc-pVTZ basis set in CFOUR 2010. (e) The anisotropic corresponding to the NMR chemical shift of water dimer scanned with CCSD(T) method and aug-cc-pVTZ basis set in CFOUR 2010.

Part 11. The energy of water dimer taking spin-orbital coupling into consideration scanned with CCSD(T)-F12 method and VTZ-F12 basis set.

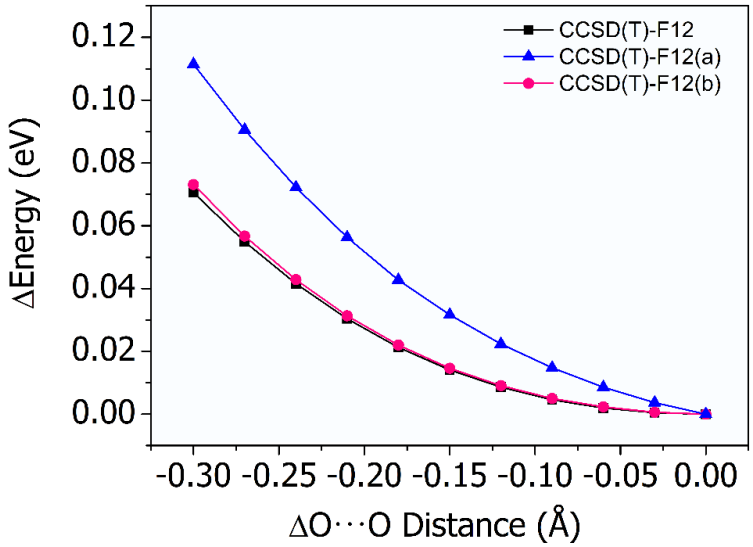

FIG. S7. The energy of water dimer scanned with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012 taking spin-orbital coupling into consideration. (a) The energy of water dimer containing spin-orbital coupling effect with single configuration. (b) The energy of water dimer containing spin-orbital coupling effect with multiconfiguration excitation.

TABLE S52. The energy of water dimer scanned with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012 taking spin-orbital coupling into consideration at different O ··O distance (Å).

O ··O Distance	ΔO ··O Distance	CCSD(T)-F12	CCSD(T)-F12(a)	CCSD(T)-F12(b)
2.91308	0	-152.7476678	-152.1340772	-152.6824589
2.88308	-0.03	-152.7476496	-152.1339418	-152.682436
2.85308	-0.06	-152.7475966	-152.1337618	-152.6823733
2.82308	-0.09	-152.7474991	-152.1335348	-152.682275
2.79308	-0.12	-152.7473525	-152.1332565	-152.6821248
2.76308	-0.15	-152.7471504	-152.1329147	-152.6819222
2.73308	-0.18	-152.7468857	-152.1325072	-152.6816505
2.70308	-0.21	-152.7465514	-152.1320078	-152.6813087
2.67308	-0.24	-152.7461408	-152.131422	-152.6808842
2.64308	-0.27	-152.7456488	-152.1307481	-152.6803737
2.61308	-0.30	-152.7450741	-152.129983	-152.679771

Part 12. The energies in the scan with methods of force field in Gromacs and DFTB with SPC, SPCE, TIP3P and TIP4P models of water and D3, UFF as well as SK dispersion respectively.

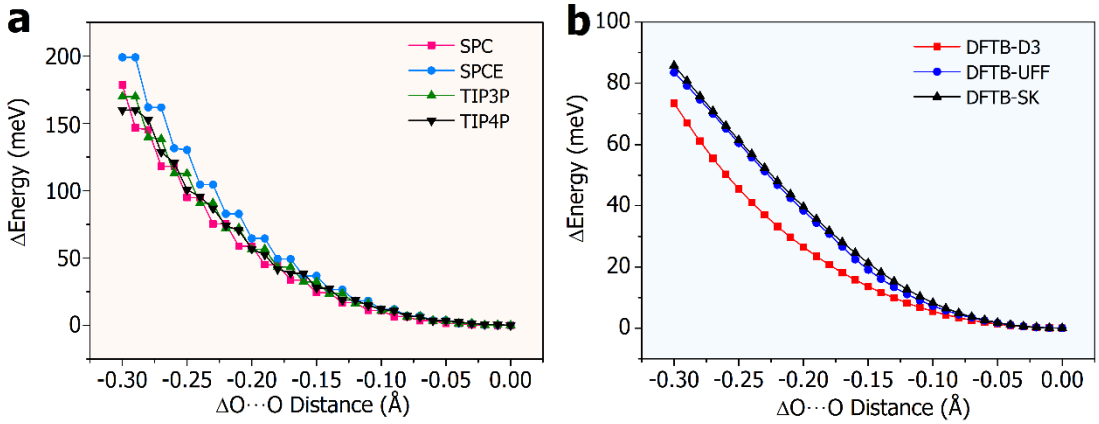

FIG. S8. The Δenergies (meV) in the scan of water dimer with methods of force field. (a) The Δenergies of water dimer calculated with force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs[29-30]. (b) The Δenergies of water dimer calculated with DFTB method and D3, UFF and SK dispersion in DFTB[31-32].

TABLE S53. The energies (eV) in the scan of water dimer with methods of force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs.

O ··O	Water Models			
Distance (Å)	SPC	SPCE	TIP3P	TIP4P
2.41		-0.129504		
2.42		-0.129502		
2.43		-0.166678	-0.122446	-0.117324
2.44	-0.121593	-0.166701	-0.122433	-0.117336
2.45	-0.153442	-0.197000	-0.152615	-0.124671
2.46	-0.154929	-0.198351	-0.153941	-0.148671
2.47	-0.182034	-0.223976	-0.179597	-0.156537
2.48	-0.181986	-0.223985	-0.179590	-0.176626
2.49	-0.205145	-0.245717	-0.201547	-0.181781
2.50	-0.205165	-0.245680	-0.201535	-0.190472
2.51	-0.224764	-0.263971	-0.220116	-0.203132
2.52	-0.224770	-0.263950	-0.220128	-0.206782
2.53	-0.241319	-0.279209	-0.235825	-0.220494
2.54	-0.241276	-0.279185	-0.235793	-0.224965
2.55	-0.255106	-0.291792	-0.248976	-0.235510
2.56	-0.255097	-0.291778	-0.248990	-0.238621
2.57	-0.266498	-0.302023	-0.259851	-0.238565
2.58	-0.266494	-0.301990	-0.259880	-0.249536
2.59	-0.275816	-0.310216	-0.268736	-0.249789
2.60	-0.275801	-0.310226	-0.268587	-0.258596
2.61	-0.283252	-0.316625	-0.275861	-0.258449
2.62	-0.283272	-0.316561	-0.275861	-0.262505
2.63	-0.289023	-0.321366	-0.281451	-0.265188
2.64	-0.289084	-0.321427	-0.281327	-0.266559
2.65	-0.293505	-0.324774	-0.285704	-0.270223
2.66	-0.293522	-0.324756	-0.285714	-0.271049
2.67	-0.296637	-0.326990	-0.288780	-0.273775
2.68	-0.296673	-0.327007	-0.288794	-0.273748
2.69	-0.298727	-0.328209	-0.290721	-0.274665
2.70	-0.298759	-0.328276	-0.290845	-0.275870
2.71	-0.299828	-0.328474	-0.291945	-0.276418
2.72	-0.299825		-0.291868	-0.276769
2.73	-0.300049		-0.292219	-0.277266
2.74	-0.300077			

TABLE S54. The energies (eV) of water dimer in the scan with DFTB method and D3, UFF and SK dispersion in DFTB.

O ··O	E(eV)	E(eV)	E(eV)
Distance(Å)	DFTB-D3	DFTB-UFF	DFTB-SK
2.35	-222.8348		
2.36	-222.8412		
2.37	-222.8472		
2.38	-222.8528		
2.39	-222.8580		
2.40	-222.8628		
2.41	-222.8672		
2.42	-222.8713		
2.43	-222.8751		
2.44	-222.8786		
2.45	-222.8818		
2.46	-222.8848		
2.47	-222.8876		
2.48	-222.8902		
2.49	-222.8925		
2.50	-222.8947		
2.51	-222.8966		
2.52	-222.8984		
2.53	-222.9001		
2.54	-222.9015		
2.55	-222.9028		
2.56	-222.9039		-221.9887
2.57	-222.9049		-221.9937
2.58	-222.9057		-221.9986
2.59	-222.9064	-222.4331	-222.0035
2.60	-222.9070	-222.4374	-222.0083
2.61	-222.9074	-222.4419	-222.0130
2.62	-222.9078	-222.4466	-222.0176
2.63	-222.9081	-222.4514	-222.0221
2.64	-222.9082	-222.4561	-222.0265
2.65	-222.9083	-222.4608	-222.0307
2.66		-222.4653	-222.0348
2.67		-222.4698	-222.0388

2.68	-222.4741	-222.0427
2.69	-222.4782	-222.0464
2.70	-222.4822	-222.0499
2.71	-222.4858	-222.0532
2.72	-222.4900	-222.0563
2.73	-222.4941	-222.0592
2.74	-222.4975	-222.0618
2.75	-222.5005	-222.0641
2.76	-222.5032	-222.0662
2.77	-222.5055	-222.0680
2.78	-222.5075	-222.0695
2.79	-222.5093	-222.0708
2.80	-222.5108	-222.0718
2.81	-222.5121	-222.0727
2.82	-222.5132	-222.0733
2.83	-222.5141	-222.0739
2.84	-222.5149	-222.0742
2.85	-222.5155	-222.0744
2.86	-222.5160	-222.0745
2.87	-222.5163	
2.88	-222.5165	
2.89	-222.5166	

Part 13. The length of O-H bonds in the scan of water dimer with methods of force field in Gromacs and DFTB with SPC, SPCE, TIP3P and TIP4P models of water and D3, UFF as well as SK dispersion respectively.

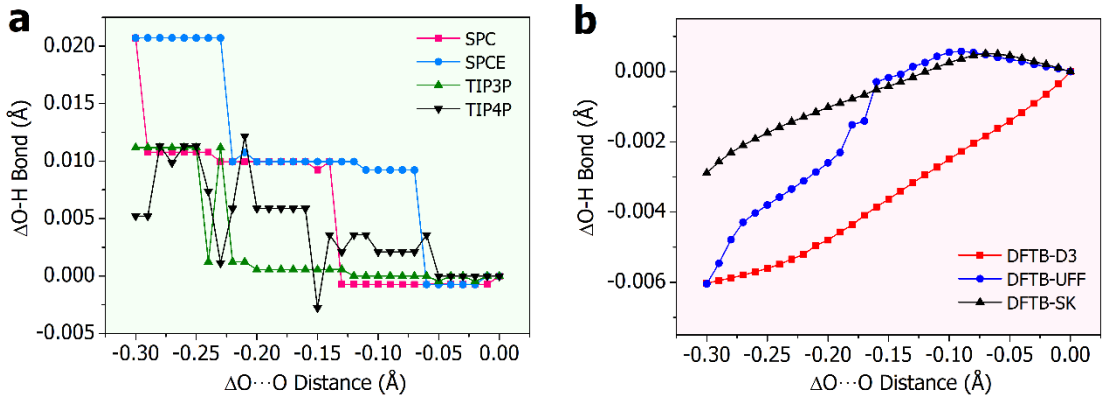

FIG S9. The ΔO-H bond length in the scan of water dimer with methods of force field. (a) The ΔO-H bond length of water dimer calculated with force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs. (b) The ΔO-H bond length of water dimer calculated with DFTB method and D3, UFF and SK dispersion in DFTB.

TABLE S55. The O-H bond length (Å) of water dimer in the scan with methods of force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs.

O ··O	Water Models			
Distance (Å)	SPC	SPCE	TIP3P	TIP4P
2.41		1.046232		
2.42		1.046232		
2.43		1.046232	0.985750	0.980664
2.44	1.046232	1.046232	0.985750	0.980664
2.45	1.036292	1.046232	0.985750	0.986762
2.46	1.036292	1.046232	0.985750	0.985292
2.47	1.036290	1.046230	0.985748	0.986762
2.48	1.036290	1.046230	0.985748	0.986762
2.49	1.036290	1.035470	0.975807	0.982804
2.50	1.036290	1.036290	0.985748	0.976574
2.51	1.035470	1.035470	0.975807	0.981324
2.52	1.035470	1.035470	0.975807	0.987622
2.53	1.035472	1.035472	0.975140	0.981324
2.54	1.035472	1.035472	0.975140	0.981324
2.55	1.035472	1.035472	0.975140	0.981327
2.56	1.035472	1.035472	0.975140	0.981327
2.57	1.035472	1.035472	0.975140	0.981327
2.58	1.035472	1.035472	0.975140	0.972676
2.59	1.034747	1.035472	0.975142	0.979030
2.60	1.035472	1.034747	0.975142	0.977548
2.61	1.024793	1.034747	0.974578	0.979030
2.62	1.024793	1.034747	0.974578	0.979030
2.63	1.024793	1.034747	0.974578	0.977548
2.64	1.024793	1.034747	0.974578	0.977548
2.65	1.024791	1.024791	0.974576	0.977548
2.66	1.024791	1.024791	0.974576	0.977548
2.67	1.024791	1.024791	0.974576	0.979030
2.68	1.024791	1.024791	0.974114	0.975447
2.69	1.024891	1.024793	0.974576	0.975447
2.70	1.024793	1.025525	0.974576	0.975450
2.71	1.024793	1.025525	0.974114	0.975450
2.72	1.024793		0.974576	0.975450
2.73	1.024793		0.974576	0.975450
2.74	1.025525			

TABLE S56. The O-H bond length (Å) of water dimer in the scan with DFTB method and D3, UFF and SK dispersion in DFTB.

O ··O	O-H (Å)	O-H (Å)	O-H (Å)
Distance(Å)	DFTB-D3	DFTB-UFF	DFTB-SK
2.35	0.970712		
2.36	0.970798		
2.37	0.970859		
2.38	0.970952		
2.39	0.971041		
2.40	0.971139		
2.41	0.971254		
2.42	0.971400		
2.43	0.971539		
2.44	0.971787		
2.45	0.971948		
2.46	0.972172		
2.47	0.972376		
2.48	0.972647		
2.49	0.972891		
2.50	0.973109		
2.51	0.973341		
2.52	0.973574		
2.53	0.973801		
2.54	0.974016		
2.55	0.974249		
2.56	0.974466		0.97487
2.57	0.974696		0.97519
2.58	0.974910		0.97545
2.59	0.975118	0.969191	0.97566
2.60	0.975333	0.969775	0.97584
2.61	0.975580	0.970449	0.97601
2.62	0.975832	0.970946	0.97618
2.63	0.976103	0.971204	0.97633
2.64	0.976390	0.971435	0.97646
2.65	0.976743	0.971658	0.9766
2.66		0.971891	0.97674
2.67		0.972119	0.97686
2.68		0.972374	0.97698

2.69		0.972635	0.9771
2.70		0.972925	0.97725
2.71		0.973718	0.97734
2.72		0.973825	0.97746
2.73		0.974941	0.97760
2.74		0.975061	0.97775
2.75		0.975153	0.97788
2.76		0.975373	0.97802
2.77		0.975489	0.97812
2.78		0.975663	0.97822
2.79		0.975781	0.97827
2.80		0.975808	0.97826
2.81		0.975778	0.97821
2.82		0.975716	0.97813
2.83		0.975639	0.97804
2.84		0.975582	0.97796
2.85		0.975522	0.97786
2.86		0.975437	0.97776
2.87		0.975377	
2.88		0.975316	
2.89		0.975235	

Part 14. The length of H-bonds in the scan of water dimer with methods of force field in Gromacs and DFTB with SPC, SPCE, TIP3P and TIP4P models of water and D3, UFF as well as SK dispersion respectively.

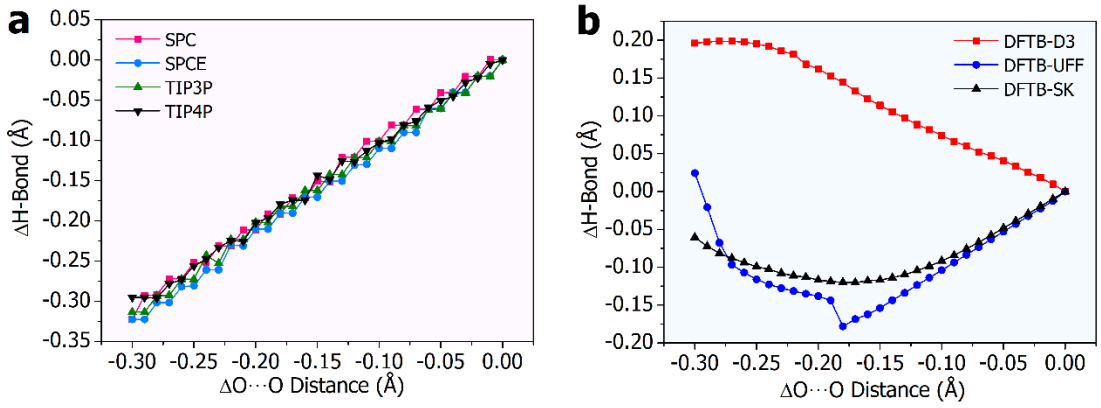

FIG S10. The ΔH-bond length (Å) in the scan of water dimer with methods of force field. (a) The ΔH-bond length of water dimer calculated with force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs. (b) The ΔH-bond length of water dimer calculated with DFTB method and D3, UFF and SK dispersion in DFTB.

TABLE S57. The H-bond (Å) of water dimer in the scan with methods of force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs.

O ··O	Water Models			
Distance (Å)	SPC	SPCE	TIP3P	TIP4P
2.41		1.368538		
2.42		1.368538		
2.43		1.389388	1.450551	1.461403
2.44	1.389388	1.389388	1.450551	1.461403
2.45	1.419190	1.409255	1.470408	1.460616
2.46	1.420211	1.410283	1.471529	1.478276
2.47	1.440070	1.430140	1.491375	1.483577
2.48	1.440070	1.430140	1.491375	1.500468
2.49	1.459932	1.460994	1.521151	1.508940
2.50	1.459932	1.459932	1.511225	1.523484
2.51	1.480846	1.480846	1.541007	1.531962
2.52	1.480846	1.480846	1.541007	1.531146
2.53	1.500700	1.500700	1.561987	1.554155
2.54	1.500700	1.500700	1.561987	1.560256
2.55	1.520559	1.520559	1.581836	1.577210
2.56	1.520559	1.520559	1.581836	1.582432
2.57	1.540421	1.540421	1.601687	1.582432
2.58	1.540421	1.540421	1.601687	1.613102
2.59	1.561345	1.560288	1.621541	1.607917
2.60	1.560288	1.561345	1.621541	1.631011
2.61	1.591132	1.581202	1.642528	1.630122
2.62	1.591132	1.581202	1.642528	1.643805
2.63	1.610994	1.601063	1.662377	1.653209
2.64	1.610994	1.601063	1.662377	1.658373
2.65	1.630860	1.630860	1.682231	1.675411
2.66	1.630860	1.630860	1.682231	1.680566
2.67	1.650729	1.650729	1.702087	1.697617
2.68	1.650729	1.650729	1.703233	1.706168
2.69	1.671197	1.670599	1.721947	1.711289
2.70	1.671646	1.671197	1.723080	1.728381
2.71	1.691509	1.691065	1.744106	1.734388
2.72	1.691509		1.742930	1.751486
2.73	1.712453		1.763944	1.756588
2.74	1.712015			

TABLE S58. The H-bond length (Å) of water dimer in the scan with DFTB method and D3, UFF and SK dispersion in DFTB.

O ··O	H-bond (Å)	H-bond (Å)	H-bond (Å)
Distance(Å)	DFTB-D3	DFTB-UFF	DFTB-SK
2.35	2.057322		
2.36	2.059012		
2.37	2.059947		
2.38	2.059837		
2.39	2.058775		
2.40	2.056329		
2.41	2.053098		
2.42	2.046959		
2.43	2.042514		
2.44	2.029502		
2.45	2.023549		
2.46	2.014004		
2.47	2.005527		
2.48	1.993891		
2.49	1.983708		
2.50	1.975180		
2.51	1.966514		
2.52	1.958344		
2.53	1.949845		
2.54	1.943003		
2.55	1.935687		
2.56	1.927637		1.82704
2.57	1.921368		1.81528
2.58	1.913639		1.80600
2.59	1.908365	1.942548	1.79942
2.60	1.902137	1.897330	1.79363
2.61	1.894682	1.850381	1.7883
2.62	1.886814	1.821453	1.78478
2.63	1.879600	1.810924	1.77971
2.64	1.871171	1.802123	1.77643
2.65	1.861336	1.795477	1.77451
2.66		1.790428	1.77067
2.67		1.786563	1.76882
2.68		1.782994	1.76755

2.69	1.779941	1.76737
2.70	1.774342	1.7696
2.71	1.739960	1.77075
2.72	1.749456	1.77368
2.73	1.755850	1.77778
2.74	1.764261	1.78322
2.75	1.774468	1.78899
2.76	1.784267	1.79586
2.77	1.794593	1.80327
2.78	1.804248	1.81183
2.79	1.814166	1.82058
2.80	1.824415	1.82981
2.81	1.834641	1.83919
2.82	1.844765	1.84873
2.83	1.854964	1.85834
2.84	1.865195	1.868
2.85	1.875251	1.87773
2.86	1.885681	1.88752
2.87	1.895729	
2.88	1.905778	
2.89	1.918116	

Part 15. The comparison of structures and binding energies of H-bond in water dimer, water trimer, water tetramer calculated with CCSD(T) method and aug-cc-pVDZ basis set in Gaussian 09.

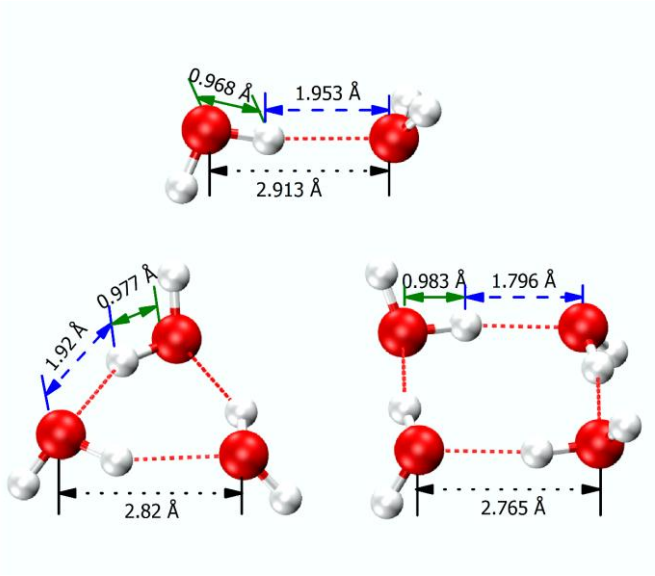

FIG S11. The structures of water dimer, water trimer and water tetramer calculated with CCSD(T) method and aug-cc-pVDZ basis set in Gaussian 09.

TABLE S59. The O-H bond length, H-bond length as well as O ··O distance in water dimer, water trimer and water tetramer calculated with CCSD(T) method and aug-cc-pVDZ basis set in Gaussian 09.

Water	O-H bond (Å)	H-bond (Å)	O···O Distance (Å)
Dimer	0.968	1.953	2.913
Trimer	0.977	1.920	2.820
Tetramer	0.983	1.796	2.765

TABLE S60. The binding energies of H-bond in water dimer, water trimer and water tetramer calculated with CCSD(T) method and aug-cc-pVDZ basis set in Gaussian 09.

Water	Binding energies (Hartree)	Binding energies (Kcal/mol)	ΔBinding energies (meV)
Dimer	-0.00725	-4.54952	0
Trimer	-0.00791	-4.94398	18
Tetramer	-0.01309	-8.18490	159

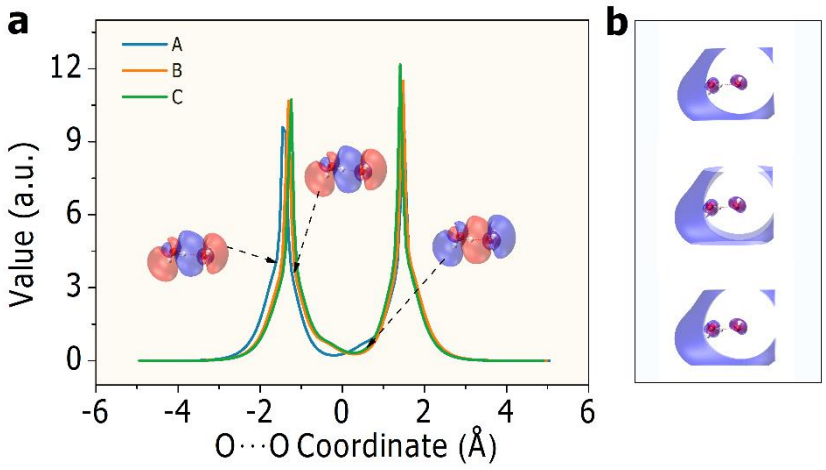

Figure S12. The lowest unoccupied orbitals and the integral of the unoccupied orbitals in the direction of O ··O distance of water dimer calculated with CCSD(T) and PBE0-D3 method. The value of the isosurface is 0.004. (a) The lowest unoccupied orbitals and the integral of the unoccupied orbitals in the direction of O ··O distance of water dimer calculated with CCSD(T) method. A, B and C represent the water dimer at ΔO···O distance of 0, 012, 0.24 Å respectively. The peak value corresponding to the position of two water monomers. (b) The lowest unoccupied orbitals of water dimer calculated with PBE0-D3 method. i, ii and iii denotes the water dimer at ΔO···O distance of 0, 012, 0.24 Å respectively.

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