CHIN. PHYS. LETT. Vol. 38, No. 1 (2021) 013101

# Uncooperative Effect of Hydrogen Bond on Water Dimer

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(Received 16 November 2020; accepted 7 December 2020; published online 16 December 2020)

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.

DOI: 10.1088/0256-307X/38/1/013101

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

Supported by the National Natural Science Foundation of China (Grant Nos. 11974136 and 11674123).
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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).

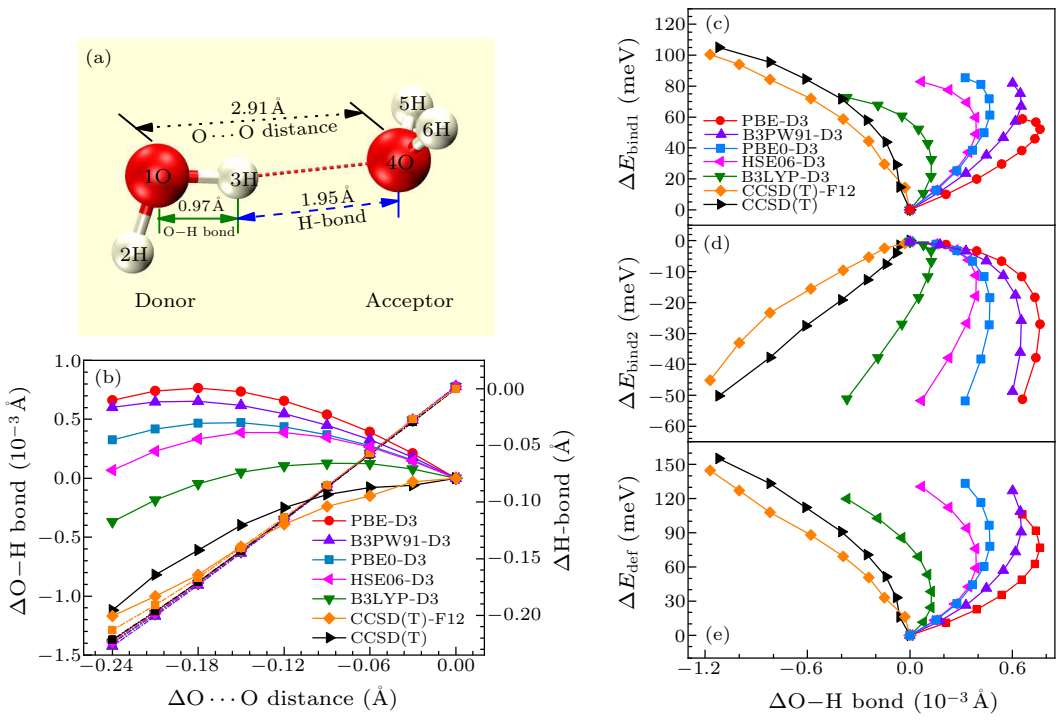


**Fig. 1.** The structural parameters in the water dimer, the O–H distance and binding energies of O–H bond during the compression. (a) The stable structure of the water dimer optimized with the CCSD(T) method. (b) The O–H bond length (solid line) and the H-bond length (dotted line) in the water dimer 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.

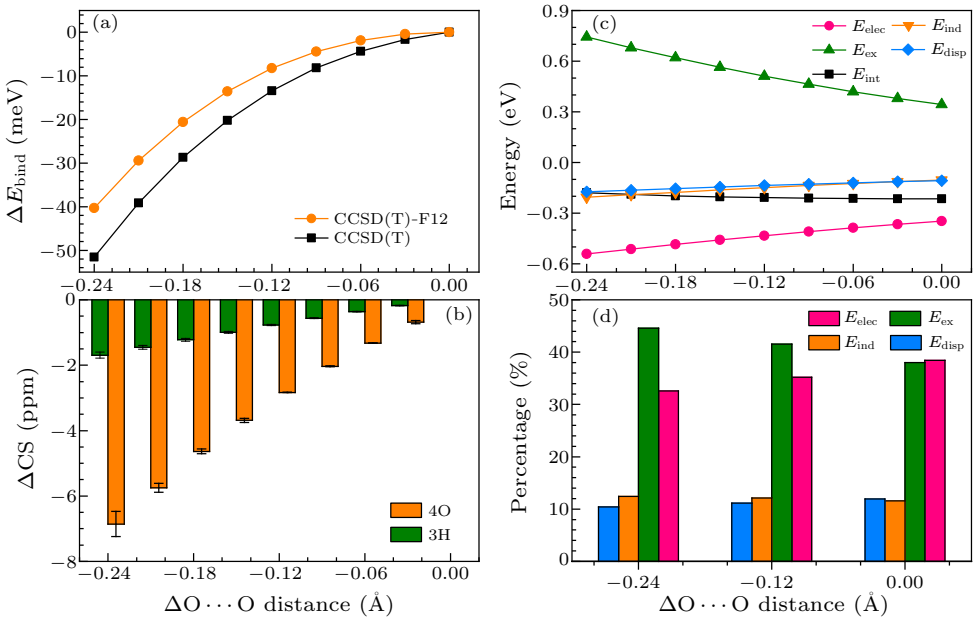


**Fig. 2.** The related experimental properties and energy decomposition as well as the corresponding percentage of the four terms in the total interaction during the compression of the water dimer. (a) The binding energies of H-bond during compression of water dimer. (b) The NMR chemical shift of the 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.

We acknowledge D. Zhang, X. Yang and F. Yu for discussion. Z. Wang also acknowledges the High-Performance Computing Center of Jilin University and the National Supercomputing Center in Shanghai.

## References

[1] Kennedy D and Norman C 2005 *Science* **309** 75
[2] Kamb B, Narten A H and Levy H A 1970 *Science* **167** 1520
[3] Chaplin M F 2001 *Biochem. Mol. Biol. Education* **29** 54
[4] Derjaguin B and Churaev N 1971 *Nat. Phys. Sci.* **232** 131
[5] Chaplin M 2015 *Water Structure and Science* (Aptarimas: Vanduo)
[6] Ekwall P, Mandell L and Fontell K 1969 *J. Colloid Interface Sci.* **31** 508
[7] Chen M, Ko H Y and Remsing R C 2017 *Proc. Natl. Acad. Sci. USA* **114** 10846
[8] Dyke T R, Mack K M and Muenter J S 1977 *J. Chem. Phys.* **66** 498
[9] Pfeilsticker K 2003 *Science* **300** 2078
[10] Harries J E, Burroughs W J and Gebbie H A 1969 *J. Quant. Spectrosc. Radiat. Transfer* **9** 799
[11] Curtiss L A, Frurip D J and Blander M 1978 *Chem. Phys. Lett.* **54** 575
[12] Sciortino F and Fornili S L 1989 *J. Chem. Phys.* **90** 2786
[13] Guevara-Vela J M, Chávez-Calvillo R, García-Revilla M, Hernndez-Trujillo J, Christiansen O, Francisco E, Pendas A M and Rocha-Rinza T 2013 *Chem. - Eur. J.* **19** 1
[14] Stokely K M, Mazza M G, Stanley H E and Franzese G 2010 *Proc. Natl. Acad. Sci. USA* **107** 1301
[15] Mehring M, Markus S and Ludwig R 2003 *Chem. - Eur. J.* **9** 837
[16] Ludwig R 2001 *Angew. Chem. Int. Ed.* **40** 1808
[17] Yoon B J, Morokuma K and Davidson E R 1985 *J. Chem. Phys.* **83** 1223
[18] Frank H S and Wen W Y 1957 *Discuss. Faraday Soc.* **24**

133
[19] Saenger W 1979 *Nature* **279** 343
[20] Kar T and Scheiner S 2004 *J. Phys. Chem. A* **108** 9161
[21] Sun C and Sun Y 2016 *The Attribute of Water: Single Notion, Multiple Myth*, in *Springer Ser. Chem. Phys.* (Heidelberg: Springer-Verlag) vol 113 p 1
[22] Masella M and Flament J P 1998 *J. Chem. Phys.* **108** 7141
[23] Argaman N 2000 *Am. J. Phys.* **68** 69
[24] Cook R L, De Lucia F C and Helminger P 1974 *J. Mol. Spectrosc.* **53** 62
[25] Fang Y, Xiao B and Tao J 2013 *Phys. Rev. B* **87** 214101
[26] Abascala J L F and Vega C 2005 *J. Chem. Phys.* **123** 234505
[27] Xantheas S S 2000 *Chem. Phys.* **258** 225
[28] Sun C, Zhang X and Zheng W 2012 *Chem. Sci.* **3** 1455
[29] Kowalski K and Piecuch P 2000 *J. Chem. Phys.* **113** 18
[30] Knizia G, Adler T B and Werner H J 2009 *J. Chem. Phys.* **130** 054104
[31] Geerlings P, Proft F D and Langenaeker W 2003 *Chem. Rev.* **103** 1793
[32] Elstner M, Porezag D, Seifert G, Frauenheim T and Suhai S 1998 *MRS Proc.* **538** 541
[33] Allinger N L 1976 *Adv. Phys. Org. Chem.* **13** 1
[34] Lane J R 2013 *J. Chem. Theory Comput.* **9** 316
[35] Klopper W, van Duijneveldt-van de Rijdt J G C M and van Duijneveldt F B 2000 *Phys. Chem. Chem. Phys.* **2** 2227
[36] Skinner H A 1945 *Trans. Faraday Soc.* **41** 645
[37] Kirchner B 2005 *J. Chem. Phys.* **123** 204116
[38] Afonin A V, Ushakov I A, Vashchenko A V, Kondarshov E V and Rulev A Y 2010 *Magn. Reson. Chem.* **48** 661
[39] Parthasarathi R, Subramanian V and Sathyamurthy N 2008 *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry* **38** 18
[40] Pople J A, Bernstein H J and Schneider W G 1959 *High-Resolution Nuclear Magnetic Resonance* (New York: McGraw-Hill)
[41] Bickelhaupt F M and Baerends E J 2000 *Reviews in computational chemistry* **15** 1

# 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.

**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.

**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.

**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.

**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 8.** The binding energies of H-bond in the 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.

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**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 as well as NMR chemical shift of water dimer scanned with PBE0-D3 method, aug-cc-pVTZ basis set in Gaussian 09.

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**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.

**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.

**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.

**Part 15.** The comparison of structures and 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.

**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 $\varphi_i$ into virtual orbitals $\varphi_a$. $T_{ij}^{ab}$ denotes an electron is excited from occupied orbital $\varphi_i$ and $\varphi_j$ into virtual orbitals $\varphi_a$ and $\varphi_b$ 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.

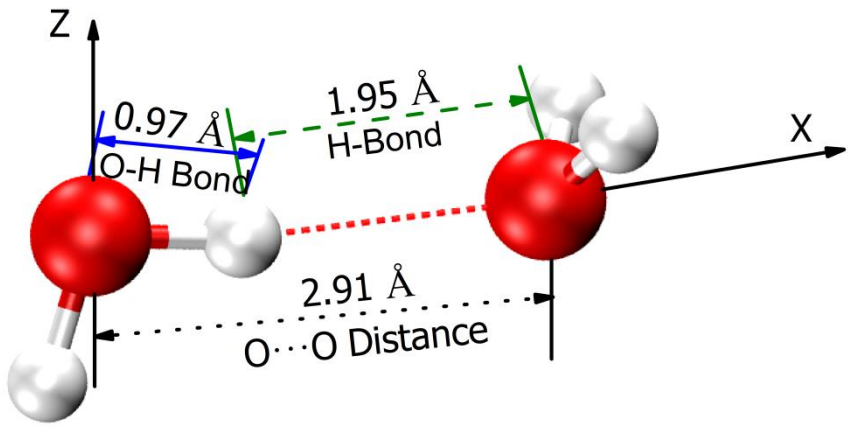


FIG. S1. The stable structure of water dimer optimized with CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09[20] and Molpro 2012[21]. It is similar with the former research[28].

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.

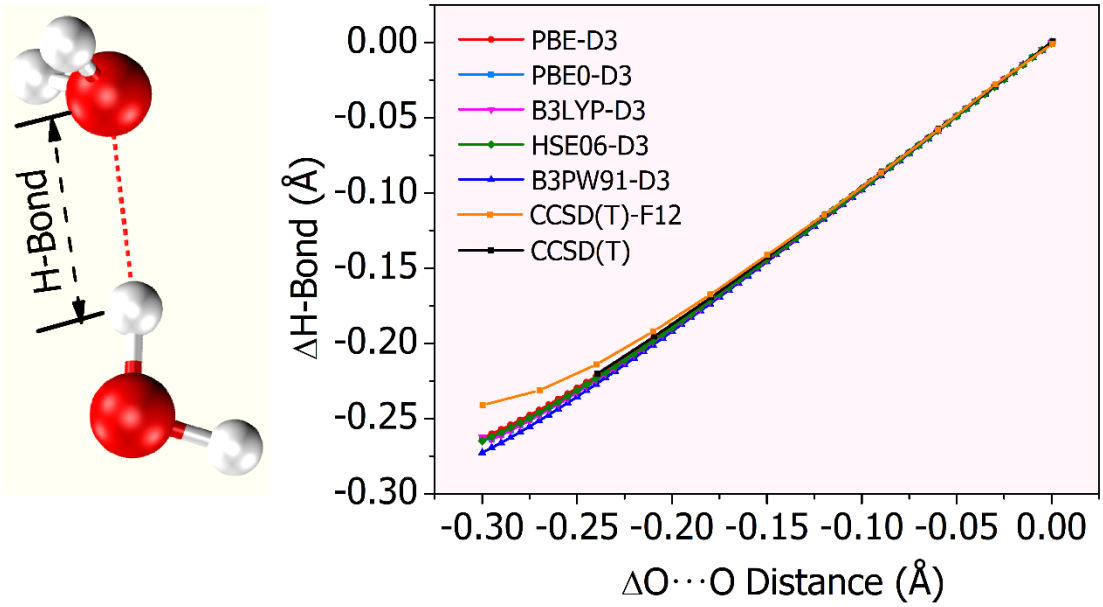


FIG. S2. The bond length of H-bond in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE09-D3 method and aug-cc-pVTZ basis set in Gaussian 09 and CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

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.

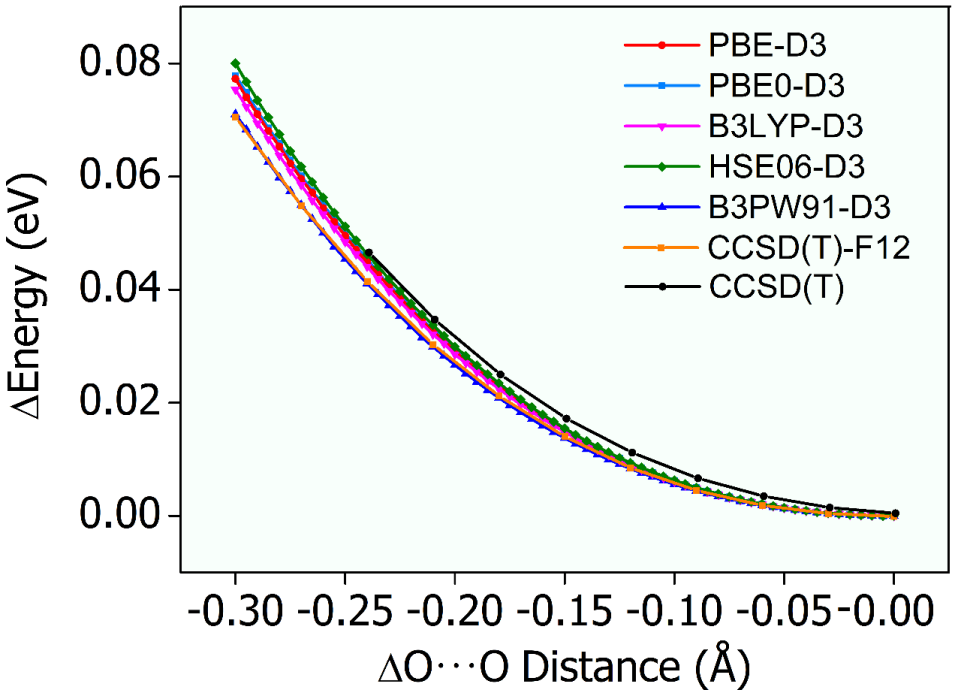


FIG. S3. The energies of the water dimer scanned with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE09-D3 method and aug-cc-pVTZ basis set in Gaussian 09 and CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012.

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.

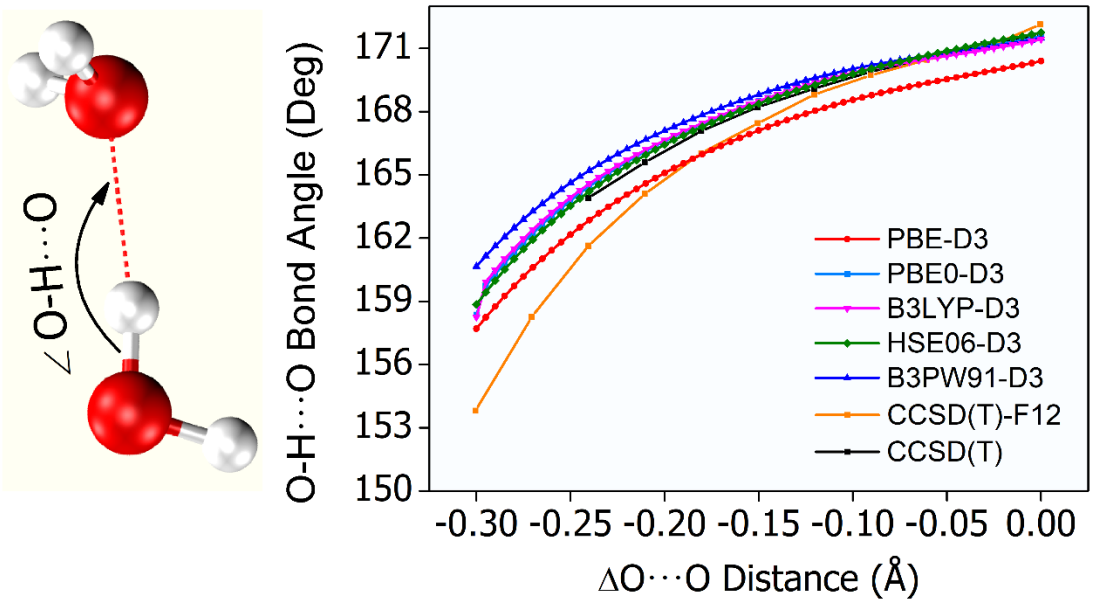


FIG. S4. The bond angles of the water dimer in the scan of water dimer with PBE0-D3, PBE-D3, B3PW91-D3, B3LYP-D3, HSE06-D3, CCSD(T) method and aug-cc-pVTZ basis set in Gaussian 09 as well as CCSD(T)-F12 method with VTZ-F12 basis set.

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.

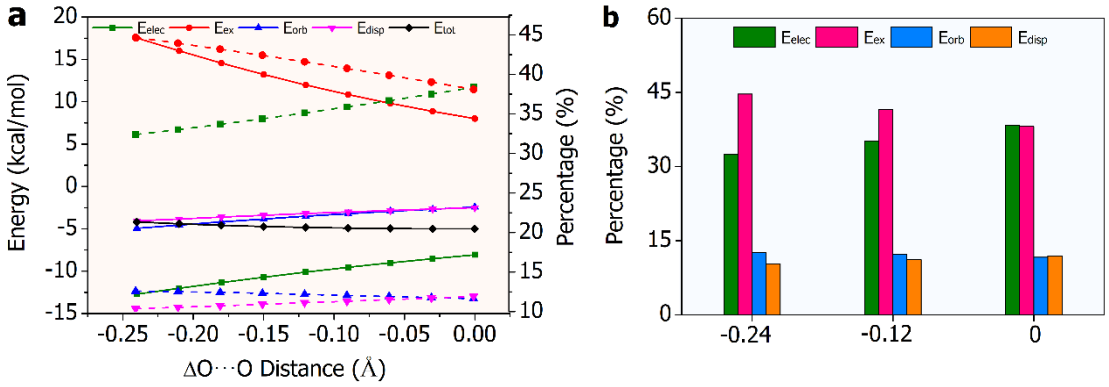


FIG. S5. The energy decomposition based on Symmetry-Adapted Perturbation Theory (SAPT)[25] and the corresponding percentage of the four terms in the total interaction. (a) The energy decomposition of water dimer scanned with CCSD(T) method and aug-cc-pVTZ basis set. (b) The percentage of the four parts $E_{int}$, $E_{elec}$, $E_{ex}$, $E_{orb}$, $E_{disp}$ (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.

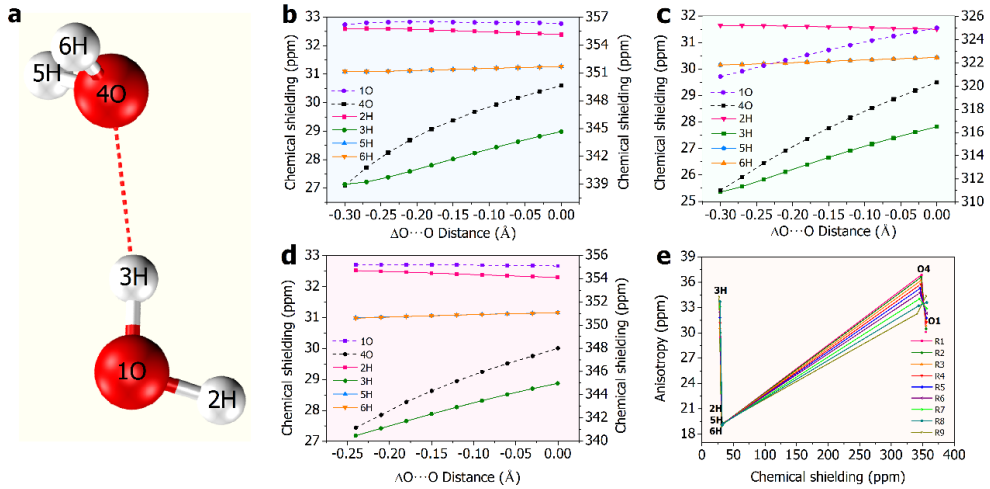


FIG. S6. The NMR chemical shift and the anisotropy of the water dimer scanned with CCSD(T)-F12, PBE0 and CCSD(T) methods. (a) The structure of the water dimer. (b) The NMR chemical shift of water dimer scanned with CCSD(T)-F12 method with VTZ-F12 basis set in CFOUR 2010[23-24]. (c) The NMR chemical shift 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.

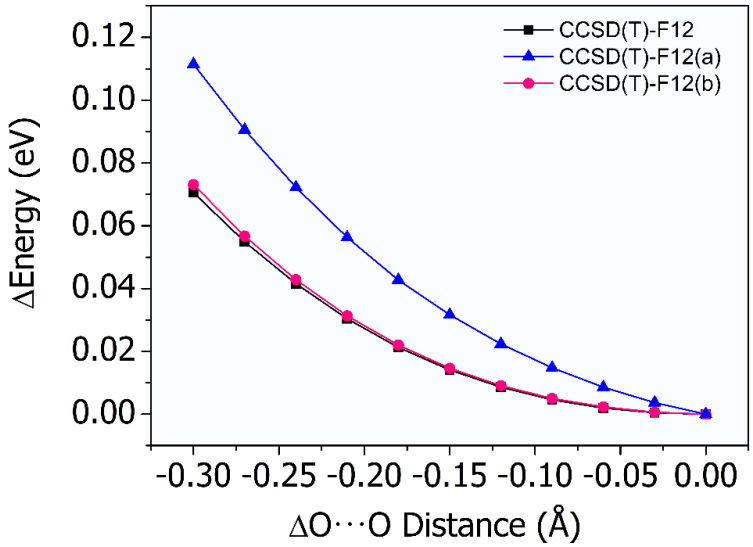


FIG. S7. The energy of water dimer scanned with CCSD(T)-F12 method and VTZ-F12 basis set in Molpro 2012 taking spin-orbital coupling into consideration. (a) The energy of water dimer containing spin-orbital coupling effect with single configuration. (b) The energy of water dimer containing spin-orbital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

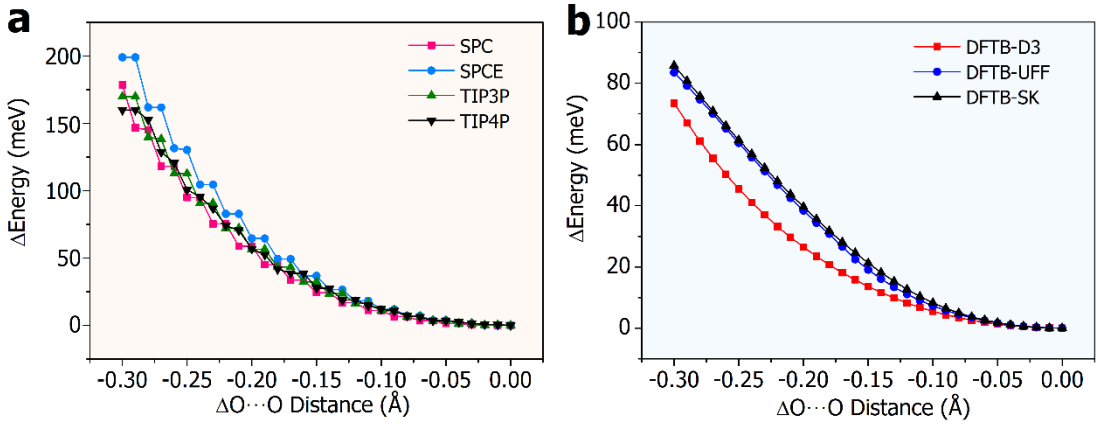


FIG. S8. The Δenergies (meV) in the scan of water dimer with methods of force field. (a) The Δenergies of water dimer calculated with force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs[29-30]. (b) The Δenergies of water dimer calculated with DFTB method and D3, UFF and SK dispersion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

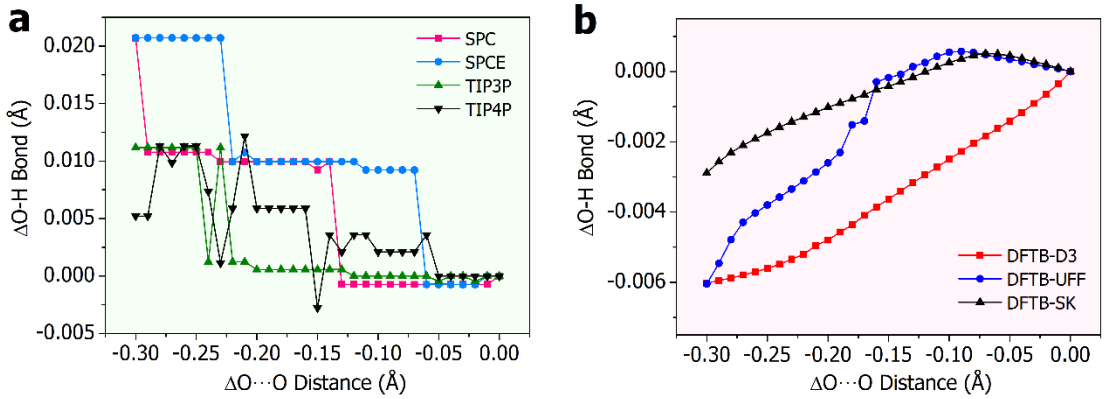


FIG S9. The ΔO-H bond length in the scan of water dimer with methods of force field. (a) The ΔO-H bond length of water dimer calculated with force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs. (b) The ΔO-H bond length of water dimer calculated with DFTB method and D3, UFF and SK dispersion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

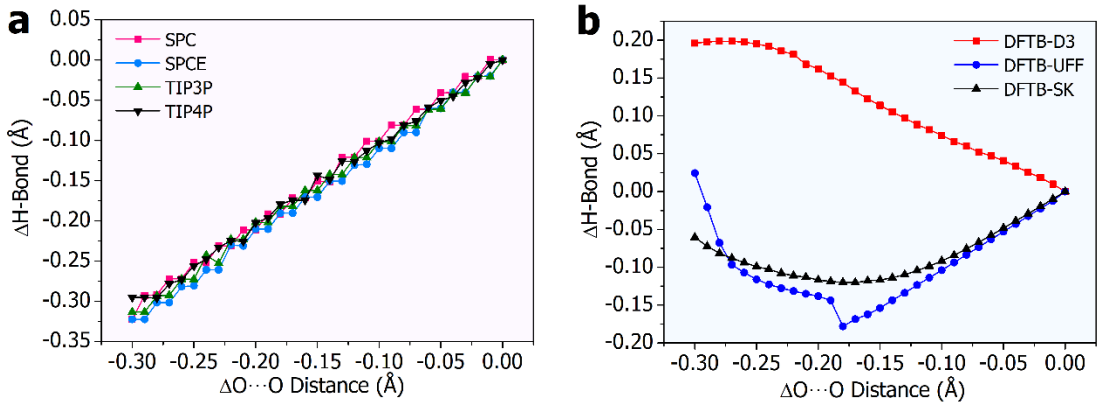


FIG S10. The ΔH-bond length (Å) in the scan of water dimer with methods of force field. (a) The ΔH-bond length of water dimer calculated with force field of OPLSAA and SPC, SPCE, TIP3P, TIP4P models in Gromacs. (b) The ΔH-bond length of water dimer calculated with DFTB method and D3, UFF and SK dispersion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

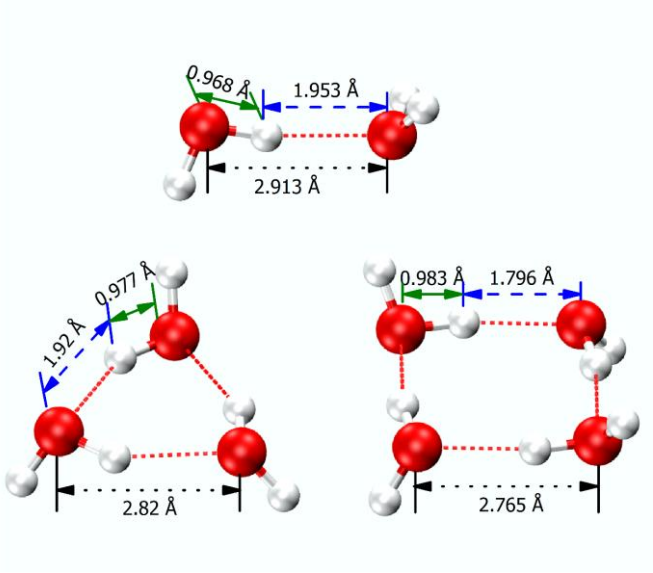


FIG S11. The structures of water dimer, water trimer and water tetramer calculated with CCSD(T) method and aug-cc-pVDZ basis set in Gaussian 09.

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 |

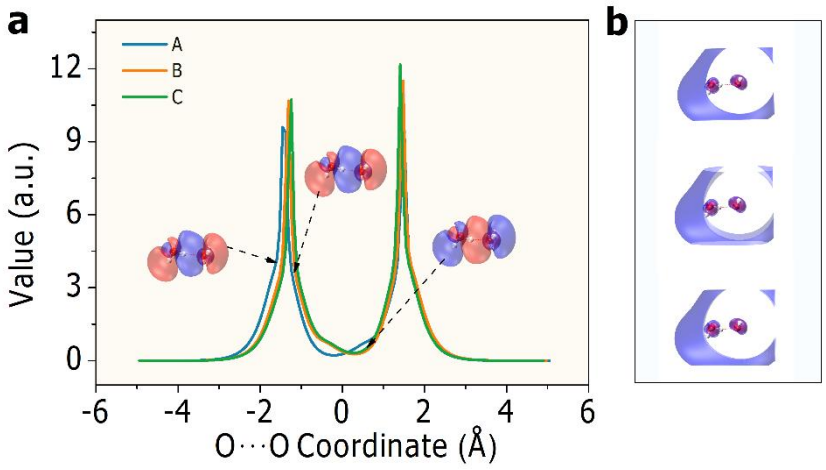


Figure S12. The lowest unoccupied orbitals and the integral of the unoccupied orbitals in the direction of O ··O distance of water dimer calculated with CCSD(T) and PBE0-D3 method. The value of the isosurface is 0.004. (a) The lowest unoccupied orbitals and the integral of the unoccupied orbitals in 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.

**References**


[1] Argaman N and Makov G 1998 *Am. J. Phys.* **68** 69-79

[2] Tunon N I, Martins-Costa M T C and Millot C et al. 1996 *J. Comput. Chem.* **17** 19-29

[3] Wallqvist A and Åstrand, P O 1995 *J. Chem. Phys.* **102** 6559-6565

[4] Madura J D, Pettitt B M and Calef D F 1988 *Mol. Phys.* **64** 325-336
[5] Jorgensen W L, Chandrasekhar J and Madura J D et al. 1983 *J. Chem. Phys.* **79** 926-935
[6] Kusalik P G and Svishchev I M 1994 *Science* **265** 1219- 1221
[7] Allinger N L 1976 *Adv. Phys. Org. Chem.* **13** 1-82
[8] Lang N D 1974 *Phys. Rev. B. Solid. State.* **28** 225- 225
[9] Trickey S B 1990 *Ed.: Adv. Quantum Chem.* (Academic Press, New York) **21**
[10] Gillan M J, Alfè D and Michaelides A 2016 *J. Chem. Phys.* **144** 130901.
[11] Wang B et al. 2016 *Sci. Rep.* ***6***, 22099.
[12] Silvestrelli P L 2009 *Chem. Phys. Lett.* **475** 285-288
[13] Levine I 2013 *Quantum Chemistry, Edition 7.* (United States Edition)
[14] Zhang C, Wu Jun, Galli G. and Gygi F 2011 *J. Chem. Theor. Comput.* **7**. 3054-3061
[15] Gaiduk A P, Gygi F and Galli G 2015 *J. Phys. Chem. Lett.* **6** 150607150530003
[16] Willow S Y, Zeng X C and Xantheas S S et al. 2016 *J. Phys. Chem. Lett.* 680-684
[17] Sun C Q, Sun Y and Ni Y et al. 2009 *J. Phys. Chem. C.* **113** 20009-20019
[18] Sun C and Sun Y 2016 *The Attribute of Water: single notion, multiple myth* Springer Ser. Chem. Phys. **113** (Heidelberg: Springer-Verlag) 1-494
[19] Kowalski K and Piecuch P 2000 *J. Chem. Phys.* **113** 18-35
[20] Frisch M J et al. 2009 Gaussian 09, Revision D.01. Gaussian, Inc., Wallingford CT.
[21] Werner H.-J, Knowles P J, Knizia G, Manby F R and Schütz M 2012 *Comput. Mol. Sci.* **2** 242-253
[22] Santra B, Michaelides A and Scheffler M 2009 *J. Chem. Phys.* **131** 124509(1)-124509(9)
[23] Stanton, J. F. et al. 2015 CFOUR, coupled-cluster techniques for computational chemistry, a quantum-chemical program package.
[24] Harding M E Metzroth T, Gauss J and Auer A A 2008 *J. Chem. Theor. Comput.* **4** 64-74
[25] Parker T M, Burns L A, Parrish R M, Ryno A G and Sherrill C D 2014 *J. Chem. Phys.* **140** 094106
[26] Parrish R M et al. 2017 *J. Chem. Theor. Comput.* **13** 3185-3197
[27] Turney Justin, M. et al. 2011 *Comput. Mol. Sci.* **2** 556-565
[28] Lane J R 2013 *J. Chem. Theor. Comput.* **9** 316- 323
[29] Berendsen H J C, Spoel D V D and Drunen R V 1995 *Comput. Phys. Commun.* **91** 43-56
[30] Spoel D V D, Lindahl E and Hess B et al. 2005 *J. Comput. Chem.* **26** 1701-1718.
[31] Elstner M, Porezag D, Jungnickel G, Elsner J, Haugk M, Frauenheim T, Suha, S and Seifert G 1998 *Phys. Rev. B* **58** 7260-7268
[32] Elstner M, Porezag D, Jungnickel G, Frauenheim T, Suhai S and Seifert G 1998 *Mater. Res. Soc*. **491** 131