# Fluxional Hydrogen Bonds in Small Water Clusters $(H_2O)_n$ (n = 2-6)

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#### Abstract



Understanding the fluxional bonding nature of hydrogen bonds (HBs) and their networks in small water clusters and bulk water remains a huge challenge in both chemistry and physics. Detailed natural bonding orbital (NBO) and non-covalent interactions-reduced density gradient (NCI-RDG) analyses performed in this work at *ab initio* theoretical level unveil the existence of fluxional hydrogen bonds (FHBs) in small neutral water clusters ( $H_2O$ )<sub>n</sub> (n=2-6). The fluxional mechanisms of linear water dimer ( $H_2O$ )<sub>2</sub> and cyclic water trimer ( $H_2O$ )<sub>3</sub>, tetramer ( $H_2O$ )<sub>4</sub>, and pentamer ( $H_2O$ )<sub>5</sub> from their transition states (TSs) to ground states (GSs) mainly involve one 3c-2e FHB which fluctuates backward and forward through a weak 4c-2e van der Waals interaction in the TS, while that of the triangular prism water hexamer ( $H_2O$ )<sub>6</sub> involves two 3c-2e FHBs on two neighboring edges perpendicular to each other in a concerted mechanism. It is the FHBs that facilitate the structural fluxionalities of water clusters and their assemblies.

Keywords Small water clusters · Structural fluxionality · Non-covalent bonding · Fluxional hydrogen bonds

# Introduction

As the most important substance on earth, water is commonly recognized as the source of life on planets in the universe [1]. The unique properties of bulk water in gas, liquid, and solid phases originate from the hydrogen-bond networks formed between neighboring water molecules under specific conditions [2–4]. Small neutral water clusters (H<sub>2</sub>O)<sub>n</sub> and their assemblies in gas phases provide vital information on the hydrogen-bond networks in bulk water in bottom-up approaches [5, 6]. The nature of the interaction between the water molecules is the same in the clusters as in the bulk (many-body forces beyond the three-body term are relatively weak) [7]. (H<sub>2</sub>O)<sub>n</sub> assemblies are known to be held together by hydrogen-bond networks in one dimensional (1D), two dimensional (2D), and three dimensional

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(3D) structures. The structures of water dimer  $(H_2O)_2$ , trimer  $(H_2O)_3$ , tetramer  $(H_2O)_4$ , pentamer  $(H_2O)_5$  and hexamer  $(H_2O)_6$  have been studied extensively [8–25]. It is known that  $(H_2O)_2$  has a linear ground state (GS) structure [9–13],  $(H_2O)_3$ ,  $(H_2O)_4$ , and  $(H_2O)_5$  possess cyclic GS geometries with all oxygen atoms on a 2D plane [14-23], while  $(H_2O)_6$ is the smallest water cluster with a 3D triangular prism GS structure (the smallest droplet of water) [7, 24]. Recent joint infrared spectroscopic and quantum theoretical investigations identified edge-bridged prism-like isomers in water heptamer  $(H_2O)_7$ , ice cubes in water octamer  $(H_2O)_8$ , and edge-bridged ice cubes in water nonamer  $(H_2O)_0$  [26–28], indicating the increasing complicity of hydrogen-bond networks in bigger water clusters. A hydrogen bond (HB) O-H--:O mainly originates from the non-covalent bonding interaction between an electronegative O atom in one H<sub>2</sub>O as a lone-pair (LP) donor and a polarized H-O group with an unfilled antibonding orbital (BD\*) as a LP acceptor in another neighboring H<sub>2</sub>O. HBs can easily fluctuate under ambient conditions due to their weak non-covalent bonding nature. Quantum simulations have identified structural rearrangements that involve free hydrogen flips that break no HBs and bifurcations that break one HB in small water clusters from water dimer to pentamer [7–23]. Bifurcational tunneling pathways were experimentally observed in water dimer, trimer, and pentamer [11, 12, 14-22]. Jeremy et

al. recently reported a tunneling motion that involves the concerted breaking of two HBs in water hexamer [7]. The rearrangements of HBs in small water clusters have been studied extensively in literature, however, the fluxional bonding nature of HBs and their networks in small water clusters from their ground states to transition states (TSs) still remains unclear.

In 2019, our group proposed the concept of intramolecular covalent fluxional bonds (FBs) in chemistry which form and break constantly under certain conditions at finite temperatures [29]. Multicenter-two-electron (mc-2e) FBs with small activation energy barriers on the potential energy surfaces facilitate the structural fluxionalities of planar  $B_{19}^{-}$ , tubular Ta@ $B_{20}^{-}$ , and cage-like  $B_{39}^{-}$ . Multi-center FBs were also studied in other fluxional boron clusters [30–34]. Recently, typical covanlent  $\pi$ -FBs and  $\sigma$ -FBs were explored in the prototypical fluxional molecule bullvalene (C<sub>10</sub>H<sub>10</sub>) and its analogs, unveiling the importance of FBs in fluxional organic molecules [35, 36].

Based on extensive noncovalent bonding analyses at *ab initio* theoretical level, we extend in this work the previously reported intramolecular covalent FBs to intermolecular noncovalent fluxional hydrogen bonds (FHBs) in small water clusters  $(H_2O)_n$  (n=2-6), aiming to establish the foundations to comprehend the fluxionalities of bigger water clusters and bulk water in bottom-up approaches. We focus on bifurcation pathways which involve one 3c-2e FHB in linear water dimer  $(H_2O)_2$  and cyclic water trimer  $(H_2O)_3$ , tetramer  $(H_2O)_4$ , and pentamer  $(H_2O)_5$  that fluctuates backward and forward through a weak van der Waals interaction in the corresponding transition states and the fluxional pathway in triangular prism water hexamer (H<sub>2</sub>O)<sub>6</sub> which involves two FHBs in a concerted mechanism. More complicated FHB networks in concerted mechanisms are expected to exist in bigger  $(H_2O)_n$   $(n \ge 7)$  and bulk water.

### **Theoretical Methods**

The GS and TS structures of  $(H_2O)_n$  (n=2-6) and GS structures of  $(H_2O)_n$  (n=7-9) were optimized at the second-order Møller-Plesset perturbation theory (MP2) with aug-cc-pVTZ basis set [37–39]. Frequency checks were performed at the same level of theory to ensure that all reported structures are true GSs or TSs of the systems. Intrinsic reaction coordinate (IRC) calculations were performed on  $(H_2O)_n$  (n=2-6) to confirm the fluxional mechanisms of these small water clusters from their TSs to GSs and GSs' [40, 41]. To obtain more accurate activation energies, single-point CCSD(T) calculations [42–44] at the MP2 geometries were performed on these neutral clusters with the same basis set. All the calculations in this work were implemented using the Gaussian 09 package [45]. Natural

bonding orbital (NBO) analyses were performed using the NBO 6.0 program [46] at  $\omega$ B97XD/aug-cc-pVTZ level [47]. The non-covalent interactions reduced density gradient (NCI-RDG) approach [48] was utilized to explore the bonding nature and types of intermolecular interactions in which topological parameters were computed with Multiwfn program [49] and visualized by VMD software [50]. Core-valence bifurcation (CVB) indexes [51–54] are also calculated using the Multiwfn program [49] to further help compare the relative hydrogen bond strengths in the concerned species.

# **Results and Discussion**

### **Structural Fluxionalities in Small Water Clusters**

The optimized GS and TS structures of small water clusters from dimer  $(H_2O)_2$  to hexamer  $(H_2O)_6$  are collectively depicted in Fig. 1, with the GS structures of edge-bridged prism-like  $(H_2O)_7$ , ice-cube  $(H_2O)_8$ , and edge-bridged cubic  $(H_2O)_9$  attached in Fig.S1. We choose neutral species to study in this work to avoid the impact of extra charges on the structures and bonding patterns of water clusters.

As shown in Fig. 1, the linear structure of  $C_s$  GS (1) of  $(H_2O)_2$  with the lowest vibrational frequency of  $v_{min} =$ 127.95 cm<sup>-1</sup> is maintained by a 3c-2e HB between O1-H2--:O4 (LP (O4) $\rightarrow$ BD\* (O1-H2)), while its degenerate isomer  $C_s$  GS' (3) contains an equivalent 3c-2e HB between O1-H3--:O4 (LP (O4) $\rightarrow$ BD\* (O1-H3)).  $C_{2v}$  TS (2) as the transition state between the two equivalent ground states with one imaginary frequency at  $v_{\min} = -231.33 \text{ cm}^{-1}$  lies 1.93 kcal·mol<sup>-1</sup> higher in energy than  $C_s$  GS (1). It is interesting to notice that the 3c-2e HB in the  $C_s$  GS has been changed into a weak 4c-2e bonding interaction between O1-H(2,3)--:O4 in  $C_{2\nu}$  TS (2) (which is, in fact, a weak 4c-2e van der Waals interaction in nature as detailed below) which shares the same lone pair from :O4, with the two H<sub>2</sub>O molecules located in two planes perpendicular to each other. As tabulated in Table S1, the distances of R = 3.019 Å between O1--O4 and  $r_1 = 2.521$  Å between H2--O4 in the  $C_{2\nu}$  TS (2) have been shortened to R = 2.909 Å and  $r_1 = 1.948$  Å in the  $C_s$  GS (1), respectively, while the bond length  $r_2 = 0.962$  Å between O1-H2 in the TS has been elongated to  $r_2 = 0.969$ Å in the GS. Such a distance variation originates from the fact that the :O4 lone pair and the O1-H2 anti-bonding orbital possesses an optimum overlap in  $C_s$  GS (1) to form the 3c-2e HB between two H<sub>2</sub>O molecules, while the 4c-2e interaction in  $C_{2\nu}$  TS (2) is a weak van der Waals interaction in nature as discussed below. Inspiringly, the calculated bond length changes  $\Delta R = R_{GS} - R_{TS}$ ,  $\Delta r_1 = r_{1,GS} - r_{1,TS}$ , and  $\Delta r_2 = r_{2,GS} - r_{2,TS}$  from the TSs to GSs tabulated in Table



**Fig. 1** Optimized structures of the ground states (GSs/GSs') and transition states (TSs) of (a)  $(H_2O)_2$ , (b)  $(H_2O)_3$ , (c)  $(H_2O)_4$ , (d)  $(H_2O)_5$ , and (e)  $(H_2O)_6$  at MP2/aug-cc-pVTZ level, with the lowest vibrational fre-

S1 show the same variation trend for the whole  $(H_2O)_n$ (n=2-6) series. As shown in Fig. 1 (a), in the  $C_s GS(1) \rightarrow C_{2\nu} TS(2) \rightarrow C_s GS'(3)$  fluxional process, H2 and H3 rotate clock-wise inside the paper plane, while H5 and H6 rotate anti-clock-wise perpendicular to the paper. Such a GS  $\rightarrow$  TS  $\rightarrow$  GS' structural fluctuation is vividly demonstrated in an IRC scanning process shown in Video S1. Such fluxional processes occur reversibly, randomly, and continuously in molecular dynamics simulations, resulting in structural fluctuations equivalent to atomic mutations between H2 $\leftrightarrow$ H3 in the LP acceptor H<sub>2</sub>O on the left.

As shown in Fig. 1 (b), (c), and (d), the cyclic GS structures of  $C_1$  (H<sub>2</sub>O)<sub>3</sub> (**4**),  $S_4$  (H<sub>2</sub>O)<sub>4</sub> (**7**), and  $C_1$  (H<sub>2</sub>O)<sub>5</sub> (**10**) possess three, four, and five 3c-2e HBs, respectively. Interestingly and intriguingly, one of the 3c-2e HBs in the GSs has been transferred to a weak 4c-2e van der Waals interaction in their TSs  $C_1$  (H<sub>2</sub>O)<sub>3</sub> (**5**),  $C_1$  (H<sub>2</sub>O)<sub>4</sub> (**8**), and  $C_1$ (H<sub>2</sub>O)<sub>5</sub> (**11**), generating the energy barriers of  $\Delta E_a = 2.20$ , 3.51 and 3.07 kcal·mol<sup>-1</sup> on the corresponding potential energy surfaces, respectively. We notice that the intermediate state  $C_i$  (H<sub>2</sub>O)<sub>4</sub> (**9**) lies 0.91 kcal·mol<sup>-1</sup> higher than its GS  $S_4$  (H<sub>2</sub>O)<sub>4</sub> (**7**). The GS  $\rightarrow$  TS  $\rightarrow$  GS' structural fluctuations in (H<sub>2</sub>O)<sub>3</sub>, (H<sub>2</sub>O)<sub>4</sub>, and (H<sub>2</sub>O)<sub>5</sub> are also well demonstrated in their IRC scanning processes shown in Video S2, Video S3, and Video S4, similar to the situation in (H<sub>2</sub>O)<sub>2</sub> (Video S1).

As the first 3D water cluster, triangular prism  $C_1$  (H<sub>2</sub>O)<sub>6</sub> (13) possesses nine slightly different 3c-2e HBs in its 3D HB network. The  $C_1$  TS (14) has the highest activation energy barrier of  $\Delta E_a = 3.94 \text{ kcal} \cdot \text{mol}^{-1}$  in the series due to fact that the fluxional process from the GS to the TS of (H<sub>2</sub>O)<sub>6</sub> involves two 3c-2e HBs on two neighboring edges

quencies  $v_{\min}$  indicated. The energy barriers  $\Delta E_a$  between the TSs and GSs are calculated at the single-point CCSD(T)/ aug-cc-pVTZ level



**Fig. 2** Cohesive energies  $(E_{\rm coh})$  and average hydrogen bond energies  $(E_{\rm coh/HB})$  of the GSs (n=2-9, black real lines) and TSs (n=2-6, red dashes lines) of neutral  $(H_2O)_n$  at CCSD(T)/ aug-cc-pVTZ level

of the triangular prism perpendicular to each other: one on a horizontal edge on the top (GS (O1-H3--:O7) (13)  $\rightarrow$  TS (O1-H2--:O7) (14)) and the other on a neighboring vertical edge (GS (O1-H2--:O4) (13)  $\rightarrow$  TS (O1-H2'--:O4) (14)). The two HBs fluctuate simultaneously in a concerted mechanism. A similar but reversible process happens from TS (14) to GS' (15). (H<sub>2</sub>O)<sub>6</sub> has the largest  $\Delta R$  and  $\Delta r_1$  values in horizontal direction in the series (Table S1). Such a concerted fluxional mechanism is clearly demonstrated in the IRC scanning process in Video S5.

Fig. 2 shows the variations of the total cohesive energies  $E_{\rm coh} = nE_{\rm H2O} - E_{(H2O)n}$  of the GSs of  $(\rm H_2O)_n$  clusters with respect to  $(\rm H_2O)_n = n\rm H_2O$  and the corresponding average hydrogen bond energies  $(E_{\rm coh/HB})$  with the number (n) of

H<sub>2</sub>O molecules at CCSD(T)/aug-cc-pVTZ in the size range between n = 2-9. The corresponding  $E_{\rm coh}$  and  $E_{\rm coh/HB}$  of the TSs of  $(H_2O)_n$  (n=2-6) are depicted in dashed lines for comparison. Interestingly, the cohesive energies of  $(H_2O)_{\mu}$ clusters increase almost perfectly linearly with the number of H<sub>2</sub>O molecules involved, with the average slopes of  $E_{\rm coh} = 11.66 \text{ kcal} \cdot \text{mol}^{-1}$  and  $E_{\rm coh} = 10.20 \text{ kcal} \cdot \text{mol}^{-1}$  for the GSs and TSs, respectively. As expected, the GSs have slightly higher  $E_{\rm coh}$  and  $E_{\rm coh/HB}$  than their TSs due to the existence of weak van der Waals interactions in the TSs. For the GSs of  $(H_2O)_n$  (n=2-9),  $E_{coh/HB}$  lies in a narrow range between 5.216 and 7.456 kcal·mol<sup>-1</sup>, with the average value of  $E_{\rm coh/HB} = 6.284 \text{ kcal} \cdot \text{mol}^{-1}$ , while for the TSs of  $(H_2O)_n$  (n=2-6),  $E_{coh/HB}$  lies between 3.291 and  $6.842 \text{ kcal} \cdot \text{mol}^{-1}$ , with obviously an lower average value of  $E_{\rm coh/HB} = 5.192 \text{ kcal} \cdot \text{mol}^{-1}$ . Specific variations depend on the sizes and geometries of specific clusters.

# Donor-Acceptor Orbital Overlapping Patterns and Hydrogen bond Strengths

To better comprehend the donor-acceptor orbital-overlap bonding patterns and hydrogen bond strengths in the concerned small water clusters, we performed detailed natural bond orbital (NBO) analyses on  $(H_2O)_n$  (n=2-6) using

(a) (H,O),

Fig. 3 Donor-acceptor orbital overlapping patterns and the corresponding stabilization energies  $(E(2)/\text{kcal}\cdot\text{mol}^{-1})$  of the concerned FHBs in linear (a)  $(H_2O)_2$ and cyclic (b)  $(H_2O)_3$ , (c)  $(H_2O)_4$ , and (d)  $(H_2O)_5$  in the fluxional processes GS $\rightarrow$ TS $\rightarrow$ GS'



the second-order perturbation theory of Fock matrix at  $\omega$ B97XD/aug-cc-pVTZ level. The in-phase donor-acceptor orbital overlaps lead to loss of occupancy from the localized Lewis NBOs (bond or lone pair as the LP donor) into the empty non-Lewis NBOs (anti-bond or Rydberg as the LP acceptor) [46]. In this approach, the stabilization energy (*E*(2)) is used to estimate the strength of the donor-acceptor interactions [55]. The calculated stabilization energies *E*(2) of donor-acceptor interactions and corresponding orbital overlapping patterns between the neighboring LP donor and acceptor are shown in Fig. 3 for linear and cyclic (H<sub>2</sub>O)<sub>n</sub> (*n*=2–5). As compared in Table S2, the calculated *E*(2) values at M06-2X/aug-cc-pVTZ and TPSSh/aug-cc-pVTZ levels exhibit the same variation trends from the ground states to the transition states as that obtained at  $\omega$ B97XD.

In the fluctuating process of water dimer  $(H_2O)_2$  from  $C_s$  GS (1) to  $C_{2\nu}$  TS (2) in Fig. 3 (a), the 3c-2e HB in  $C_s$  GS (1) (LP (O4)  $\rightarrow$  BD\* (O1-H2)) with the stabilization energy of E(2)=8.43 kcal·mol<sup>-1</sup> has been transferred into a weak 4c-2e van der Waals interaction in  $C_{2\nu}$  TS (2) (LP (O4)  $\rightarrow$  BD\* (O1-H2)+BD\* (O1-H3)) which has an obviously lower stabilization energy of  $E(2)=2\times0.07=0.14$  kcal·mol<sup>-1</sup>. Continued clock-wise rotation of the LP acceptor H<sub>2</sub>O on the left generates the next ground state  $C_s$  GS' (3) and completes the  $C_s$  GS (1)  $\rightarrow C_{2\nu}$  TS (2)  $\rightarrow C_s$  GS'



(3)  $C_s \text{ GS'}$ 3c-2e HB LP (O4)  $\rightarrow$  BD\* (O1-H3) E(2) = 8.43 kcal/mol



(6)  $C_1$  GS' 3c-2e HB LP (O4)  $\rightarrow$  BD\* (O1-H3) E(2) = 10.27 kcal/mol



(9)  $C_i$  GS' 3c-2e HB LP (O4)  $\rightarrow$  BD\* (O1-H3) E(2) = 18.72 kcal/mol



(3) fluxional process. Such a process clearly evidences the existence of an FHB in water dimer and traces its bonding pattern evolution from the 3c-2e HB in  $C_s$  GS (1) to a weak 4c-2e van der Waals interaction in  $C_{2v}$  TS (2) and finally to a 3c-2e HB in  $C_s$  GS'(3). Such a fluctuating process is reversible in nature and occurs randomly in ambient conditions, evidencing the existence of FHBs in water clusters which form and break constantly under certain conditions at finite temperatures.

Fig. 3 (b), (c), and (d) demonstrate in similar ways evolutions of orbital overlapping patterns of the FHBs in  $(H_2O)_3$ ,  $(H_2O)_4$  and  $(H_2O)_5$  in the processes of  $GS \rightarrow TS \rightarrow GS'$ , respectively. They all contain one FHB which fluctuates from a 3c-2e HB in the GS, to a weak 4c-2e van der Waals interaction in the TS, and finally to a 3c-2e HB in the GS' sharing the same LP from :O4. The stabilization energies of the LP (O4)  $\rightarrow$  BD\* (O1-H2) interactions in the GSs of  $(H_2O)_3$ ,  $(H_2O)_4$  and  $(H_2O)_5$  are E(2) = 10.27, 18.64, and 21.17 kcal·mol<sup>-1</sup>, respectively, while the corresponding values of the 4c-2e van der Waals interactions in the TSs  $(LP (O4) \rightarrow BD^* (O1-H2)+BD^* (O1-H3))$  appear to be much lower, with E(2) = 0.07, 0.46, and 0.66 kcal·mol<sup>-1</sup>. It is noticed that GS (H<sub>2</sub>O)<sub>4</sub> and GS (H<sub>2</sub>O)<sub>5</sub> possess the highest E(2) values and therefore the strongest hydrogen bonds in the  $(H_2O)_n$  series (n=2-6). Opposite but similar orbital overlapping pattern evolutions happen from the TSs to the GSs', further evidencing the fluxional nature of the FHBs in these cyclic water clusters.

Fig. 4 shows specifically the evolution of the two FHBs in the smallest 3D triangular prism  $C_1$  GS (H<sub>2</sub>O)<sub>6</sub> (13) in the process of GS  $\rightarrow$  TS  $\rightarrow$  GS'. The two 3c-2e FHBs on one vertical edge and a neighboring horizontal edge in the GS, TS, and GS' possess the stabilization energies  $E(2) = 7.91/4.71, 0.46/0.98, 7.95/11.39 \text{ kcal·mol}^{-1}$ , respectively. They form an FHB network with two 3c-2e FHBs in



**Fig. 4** Donor-acceptor orbital overlapping patterns and the corresponding stabilization energies  $(E(2)/ \text{ kcal} \cdot \text{mol}^{-1})$  of the two 3c-2e FHBs in triangular prism (H<sub>2</sub>O)<sub>6</sub>

a concerted mechanism to facilitate the fluxionality of the system. Such fluxional processes could also be realized via a tunneling motion which involves the concerted breaking of two HBs as reported in previous experiments [7]. Experimentally, an HB network with twelve HBs was observed in water ice-cube  $(H_2O)_8$  [27]. Experimental observations of the edge-bridged prism-like  $(H_2O)_7$  [26] and edge-bridged cubic  $(H_2O)_9$  [28] provide further evidence to support the high stabilities of triangular prism  $(H_2O)_6$  and ice cube  $(H_2O)_8$ . Though the fluxional processes of these large water clusters may possess much more complicated mechanisms, the fluxional bonding nature of the HBs is expected to remain basically unchanged.

### Hydrogen Bonds Versus Van Der Waals Interactions in Water Clusters

The Non-covalent Interactions-Reduced Density Gradient (NCI-RDG) method has been widely used to characterize the strengths and identify the types of non-covalent interactions in chemistry. Reduced density gradient RDG has been developed by Johnson et al. and defined by the following equation [48]:

$$RDG(r) = \frac{1|\nabla\rho(r)|}{2(3\pi^2)^{\frac{1}{3}}\rho(r)^{\frac{4}{3}}}$$

Fig. 5 shows the plots of RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue  $(\sin(\lambda_2)\rho)$  for  $(H_2O)_2$ ,  $(H_2O)_3$ ,  $(H_2O)_4$  and  $(H_2O)_5$ . They help discern different types of noncovalent interactions, with the blue regions with sign $(\lambda_2)\rho < 0$  representing strong non-covalent bonding attractions like H-bond and halogenbond etc., green regions with  $sign(\lambda_2)\rho \approx 0$  standing for weak van der Waals interactions, and the red regions with  $sign(\lambda_2)\rho > 0$  identifying strong repulsions such as steric effect in rings and cages [56]. Fig. 5 (a) exhibits an obvious spike around -0.024 a.u for  $C_s$  GS (1) of (H<sub>2</sub>O)<sub>2</sub>. This spike corresponds to the light blue isosurface between O1-H2 and O4 in Fig. 5 (a') which is located exactly at the area of orbital overlap between the lone pair of :O4 and antibonding orbital of O1-H2 (LP (O4)  $\rightarrow$  BD\* (O1-H2)) in Fig. 3 (a), clearly indicating the existence and location of the much concerned HB in the  $C_s$  GS (1) of water dimer. In contrast, Fig. 5 (b) possesses an obvious spike around -0.01 a.u. which corresponds to the green isosurface of  $C_{2\nu}$  TS (2) of  $(H_2O)_2$  in Fig. 5 (b'), evidencing that the strong HB in  $C_{\rm s}$  GS (1) has been transferred into a weak van der Waals interaction (LP (O4)  $\rightarrow$  BD\* (O1-H2)+BD\* (O1-H3)) in the  $C_{2\nu}$  TS (2). Interestingly, the isosurface between O4 and O1-H3 (LP (O4)  $\rightarrow$  BD\* (O1-H3)) becomes light blue again in Fig. 5 (c') with a spike occurring at -0.024 a.u. in

 $C_s$  GS' (3) in Fig. 5 (c), showing that the HB goes backward and forward through a weak 4c-2e van der Waals interaction in the  $C_{2\nu}$  TS (2), corresponding to an H2 $\leftrightarrow$ H3 mutation in the LP acceptor H<sub>2</sub>O on the left.

As shown in Fig. 5 (d), (d'), (e), (e'), (f), and (f'), water trimer (H<sub>2</sub>O)<sub>3</sub> exhibits similar but more complicated RDG-sign( $\lambda_2$ ) $\rho$  plots. Figure 5 (d'), (e'), and (f') contain three, two, and three light blue disks, indicating that  $C_1$ GS (4),  $C_1$  TS (5), and  $C_1$  GS' (6) of (H<sub>2</sub>O)<sub>3</sub> contain three, two, and three effective HBs, respectively, while the additional green spike at -0.01 a.u. in Fig. 5 (e) and green disk in Fig. 5 (e') clearly indicate the existence and location of the weak 4c-2e van der Waals bond in  $C_1$  TS (5) at the bottom. Similarly, Fig. 5 (g'), (h'), and (i') exhibit four, three, and four blue disks, indicating the locations of the four, three, four effective HBs in  $S_4$  GS (7),  $C_1$  TS (8), and  $C_i$  GS' (9) of  $(H_2O)_4$ , respectively, with Fig. 5 (h) containing an additional green spike at around -0.015 a.u. indicating the existence of a weak 4c-2e van der Waals bond in  $C_1$  TS (8) at the bottom. As indicated in Fig. 5 (j, k, l) and Fig. 5 (j', k', l'), the biggest cyclic water cluster (H<sub>2</sub>O)<sub>5</sub> also contains a weak van der Waals bonding interaction in its  $C_1$  TS (11).

The 3D FHB network of the triangular prism  $(H_2O)_6$  becomes more complicated as shown in Fig.S2. The boundaries between different types of the non-valent interactions become vaguer than that in smaller  $(H_2O)_n$  (n=2-5). But the two green disks, one on a vertical edge and the other on a neighboring horizontal edge in  $C_1$  TS (14), can still be easily recognized which represent the two weak van der Waals

interactions in the TS, well supporting the green spike at around -0.01 a.u. in Fig.S2 (b). There exist thus two FHBs in (H<sub>2</sub>O)<sub>6</sub> which fluctuate backward and forward through the weak van der Waals bonding interactions in  $C_1$  TS (**14**). The edge-bridged prism-like (H<sub>2</sub>O)<sub>7</sub>, ice cube (H<sub>2</sub>O)<sub>8</sub>, and edge-bridged cubic (H<sub>2</sub>O)<sub>9</sub> which possess more than one TSs in the fluxional processes are expected to have more complicated HB networks with more concerted FHBs fluctuating backward and forward through the TSs. Such complicated situations are beyond the scope of the current work.

Interestingly, as shown in Table S3, GS  $(H_2O)_4$  (7), GS'  $(H_2O)_4$  (9), GS  $(H_2O)_5$  (10), and GS'  $(H_2O)_5$  (12) possess the most negative calculated CVB indexes, indicating that they have the strongest HBs in the series as noticed above, well in line with the corresponding E(2) values indicated in Figs. 3 and Fig. 4 and color-filled iso-surfaces shown in Fig. 5. It is also noticed that the transition states have much higher positive CVB indexes than their corresponding ground states, further evidencing that these transition states possess typical weak van der Walls interactions.

### Conclusions

Based on detailed NBO and NCI-RDG analyses, we have evidenced in this work the existence of non-covalent FHBs in small  $(H_2O)_n$  clusters (n=2-6) in the fluxional processes  $GS \rightarrow TS \rightarrow GS'$  which fluctuate backward and forward through weak multi-center van der Waals interactions in



**Fig. 5** The RDG vs.  $sign(\lambda_2)\rho$  plots (a-l) and color-filled RDG isosurfaces (a'-l') of the GSs, TSs, GSs' of linear and cyclic water clusters  $(H_2O)_n$  (n=2-5). GS  $(H_2O)_4$  and GS  $(H_2O)_5$  appear to have the strongest hydrogen bonds in color-filled isosurfaces in the series

transition states. It is the FHBs that facilitate the structural fluxionalities of small water clusters, their assemblies, and bulk water as well. Such hydrogen bonding fluctuations could also be realized via bifurcational tunneling pathways which involve the breaking of more than one hydrogen bonds. Further theoretical and experimental studies of FHBs in bigger water clusters and bulk water are of great importance in chemistry, physics, materials science, life science, and climate changes.

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Authors' contributions Si-Dian Li and Qiang-Chen designed the project and finalized the manuscript; Cai-Yue Gao and Yuan-Yuan Ma performed the calculations and prepared the first draft. All authors read and approved the final manuscript.

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**Data Availability** The data presented in this article are available on request from the corresponding author.

### Declarations

Ethical Approval Not applicable.

Competing Interests The authors declare no conflict of interest.

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