# Structures, Relative Stabilities and Binding Energies of Neutral Water Clusters, $(H_2O)_{2-30}$

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**SUPPORTING INFORMATION:**

## 1 Structures of neutral water clusters

$(H_2O)_{2-7}$. Small size water clusters have been extensively investigated in the literature and their structures are known. Our investigations confirm previous results on the structures of neutral water clusters lower than the heptamer. There is only one linear isomer belonging to the $C_s$ point group on the PES of the water dimer. Cyclic structure is found to be unstable for the water dimer, contrary to the case of ammonia dimer where both cyclic and linear isomers are reported as most stable structures[1]. From trimer to pentamer, the most stable isomers are 2D cyclic structures. The first occurrence of 3D structures starts from the water hexamer. The most stable structure of the water hexamer has been a controversy between the **Prism** and the **Cage** isomers. In this work, we found that the most stable hexamer is the **Prism** isomer, while the **Cage** isomer is found to be the second most stable one, lying 0.8 kcal/mol above **Prism** (Figure 1). Bates and Tshumper[2] found that the **Prism** is consistently the most stable water hexamer, lying 0.06 kcal/mol below the nearly isoenergetic **Cage** isomer at the electronic MP2 CBS limit, 0.25 kcal/mol below at the electronic CCSD(T) CBS limit, and 0.09 kcal/mol below at the harmonic ZPVE corrected CCSD(T) CBS limit. Elsewhere, at the M06-2X/aug-cc-pVTZ level of theory, we found that the **Prism** isomer is the most stable water hexamer lying 0.6 kcal/mol below the **Cage** isomer. All these results show that the announced controversy is due to the closed energies of the concerned isomers, which in turn renders the global minimum energy structure sensible to the computational level. In addition, Manna and coworkers[3] performed extensive benchmark calculations at the MP2 and CCSD(T) levels of theory. They found that the **Prism** isomer is the most stable, followed by the **cage** isomer. Pérez and coworkers[4] investigated the water hexamer at using broadband experimental spectroscopy. They found that the relative isomer populations at different expansion conditions establish that the cage isomer is the minimum energy structure.

As far as the water heptamer is concerned, its relative stability exhibits the same trend as that of the water hexamer (see Figure 1). The most stable water heptamer is a Prism like isomer, **W7_1**, followed by **W7_2** lying 2.2 kcal/mol above **W7_1**. We reported five isomers on the PES of the water heptamer, Figure 1. Our relative stabilities for the water hexamer and the water heptamer are consistent with the reported results from Shields *et al.*[5] at MP2/CBS-e. Furthermore, the **W7_1** isomer has been reported previously as the most stable water heptamer at MP2 levels of theory[6,7].

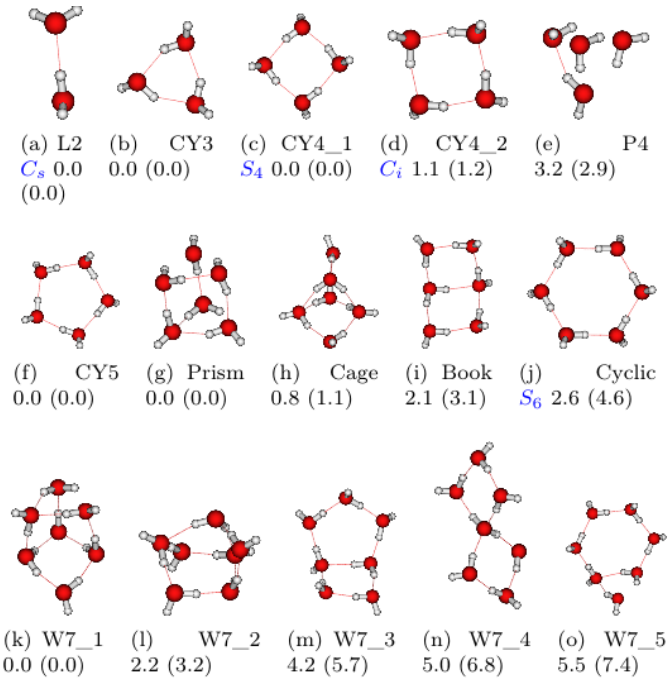


**Fig. S 1** Optimized structures of the neutral water clusters $(H_2O)_{n=2-7}$ at the M06-2X/6-31++g(d,p) level of theory. The caption of each sub-figure indicates the name of the isomer (*e.g.* "Cage" or "W7_4"), followed by its symmetry point group when different from $C_1$ (there is no indication for $C_1$ point group). Numbers represent the zero-point corrected (ZPE) relative electronic energy and the ZPE uncorrected relative energies in parenthesis. All energies are expressed in kcal/mol. L = linear, P = Prism, CY = Cyclic and W = Water. W is used for isomers that are not L, P, Cy or Book.

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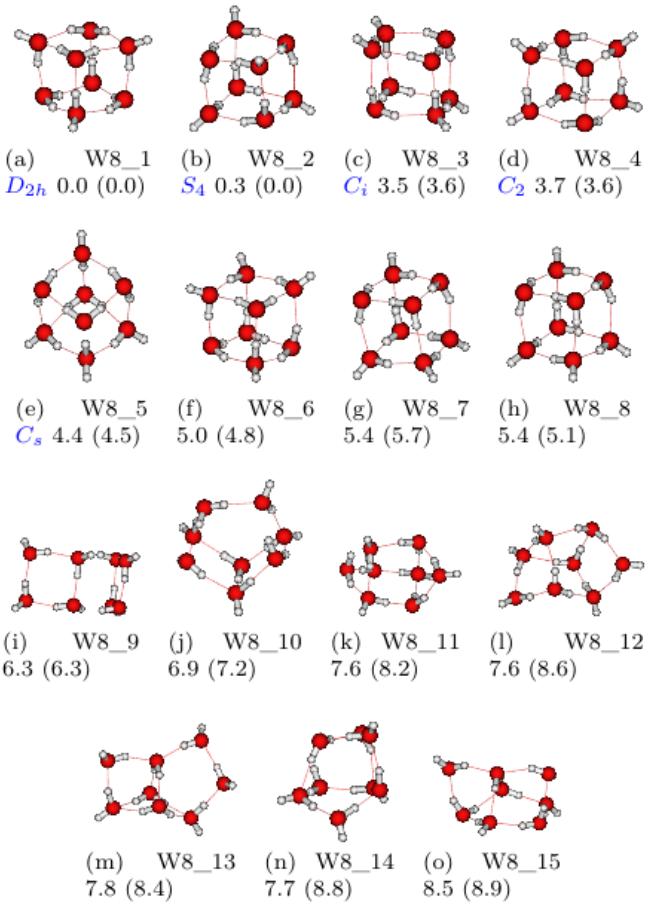


**Fig. S 2** Optimized structures of the water octamer $(H_2O)_{n=8}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

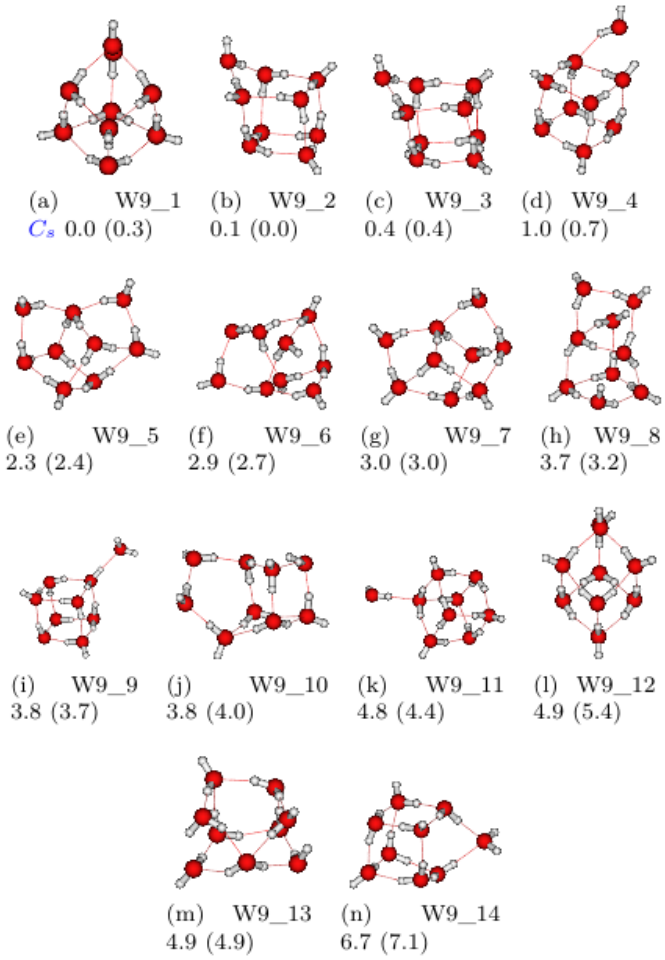


**Fig. S 3** Optimized structures of the water nonamer $(H_2O)_{n=9}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

## 2 Relative population of neutral water clusters

The following figures are reporting the relative population of neutral water clusters. The population of water 19-mer, 21-mer, 28-mer, 29-mer and 30-mer are dominated exclusively by the most stable isomer. Thus these population are not presented as figures.

## References

1 Malloum, A.; Fifen, J. J.; Dhaouadi, Z.; Nana, E. S. G.; Jaidane, N.-D. Structures and relative stabilities of ammonia clusters at different temperatures: DFT vs. ab initio. *Phys. Chem. Chem. Phys.* **2015**, *17*, 29226–29242.

2 Bates, D. M.; Tschumper, G. S. CCSD (T) complete basis set limit relative energies for low-lying water hexamer structures. *J. Phys. Chem. A* **2009**, *113*, 3555–3559.

3 Manna, D.; Kesharwani, M. K.; Sylvetsky, N.; Martin, J. M. Conventional and explicitly correlated ab initio benchmark study on water clusters: Revision of the BEGDB and WATER27 data sets. *J. Chem. Theory Comput.* **2017**, *13*, 3136–3152.

4 Pérez, C.; Muckle, M. T.; Zaleski, D. P.; Seifert, N. A.; Temelso, B.; Shields, G. C.; Kisiel, Z.; Pate, B. H. Structures of cage, prism, and book isomers of water hexamer from broadband rotational spectroscopy. *Science* **2012**, *336*, 897–901.

5 Shields, R. M.; Temelso, B.; Archer, K. A.; Morrell, T. E.; Shields, G. C. Accurate predictions of water cluster formation,$(H_2O)_{n=2-10}$. *J. Phys. Chem. A* **2010**, *114*, 11725–11737.

6 Liu, X.; Lu, W.-C.; Wang, C.; Ho, K. Energetic and fragmentation stability of water clusters $(H_2O)_n$, n = 2-30. *Chem. Phys. Lett.* **2011**, *508*, 270–275.

7 Temelso, B.; Archer, K. A.; Shields, G. C. Benchmark Structures and Binding Energies of Small Water Clusters with Anharmonicity Corrections. *J. Phys. Chem. A* **2011**, *115*, 12034–12046.

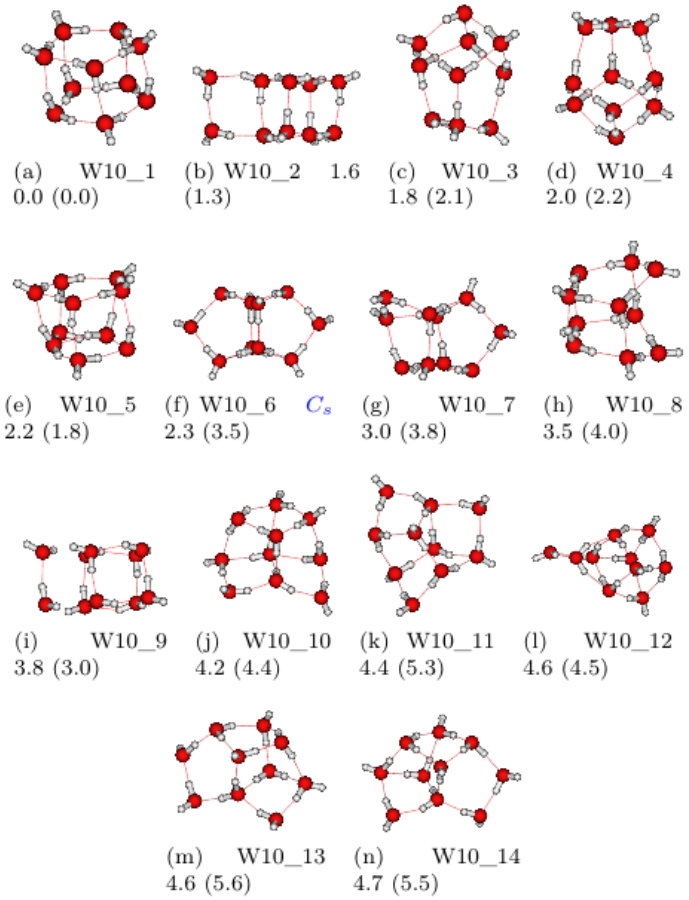


**Fig. S 4** Optimized structures of the water decamer $(H_2O)_{n=10}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

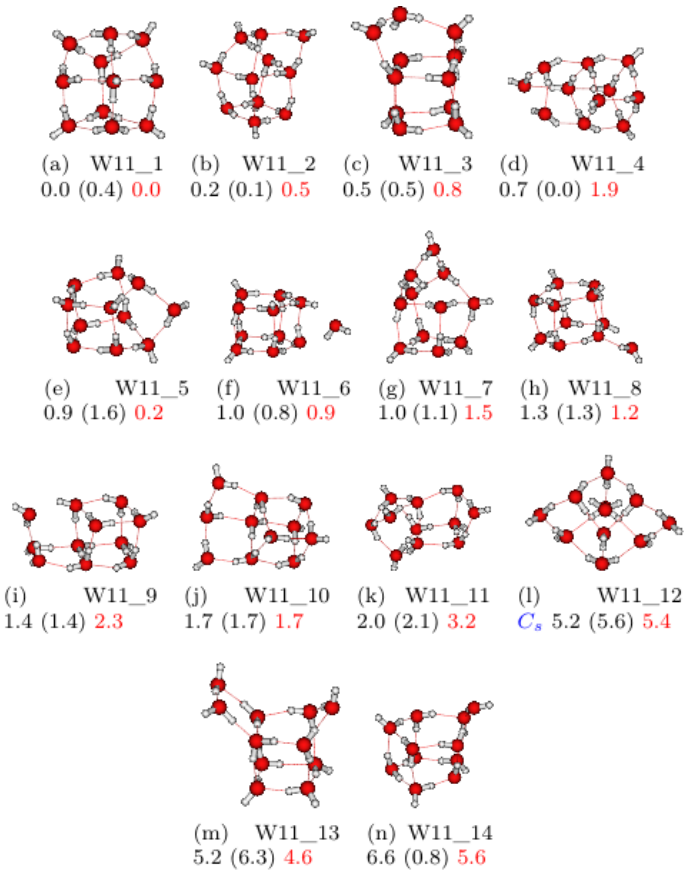


**Fig. S 5** Optimized structures of the water undecamer $(H_2O)_{n=11}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1. Numbers in red color represent the ZPE uncorrected relative energies as computed at the MP2/aug-cc-pVTZ level of theory.

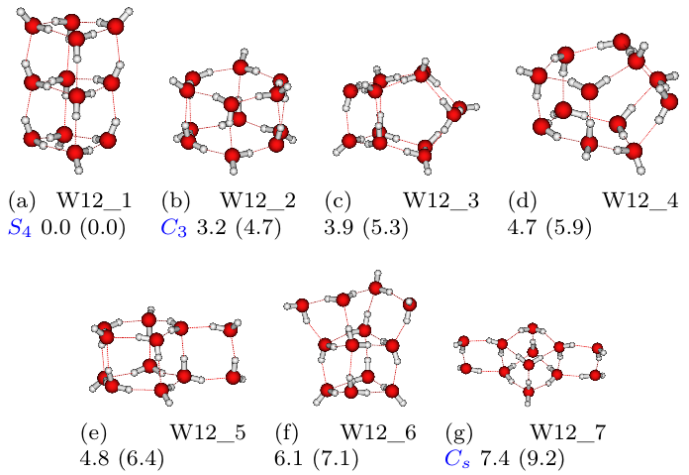


**Fig. S 6** Optimized structures of the water dodecamer $(H_2O)_{n=12}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

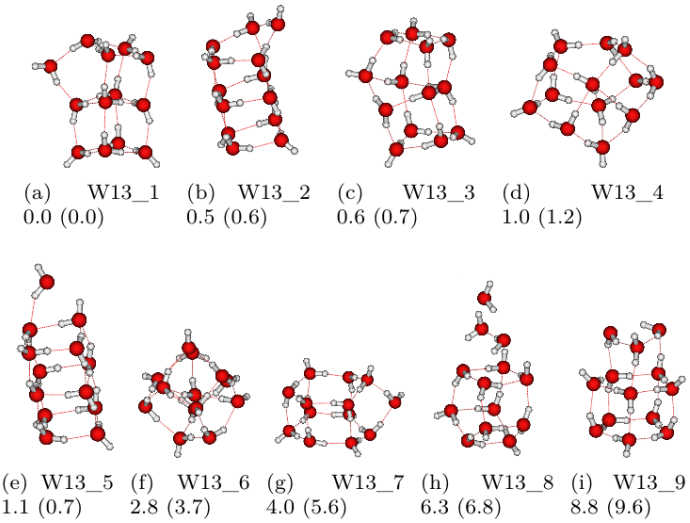


**Fig. S 7** Optimized structures of the water tridecamer $(H_2O)_{n=13}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

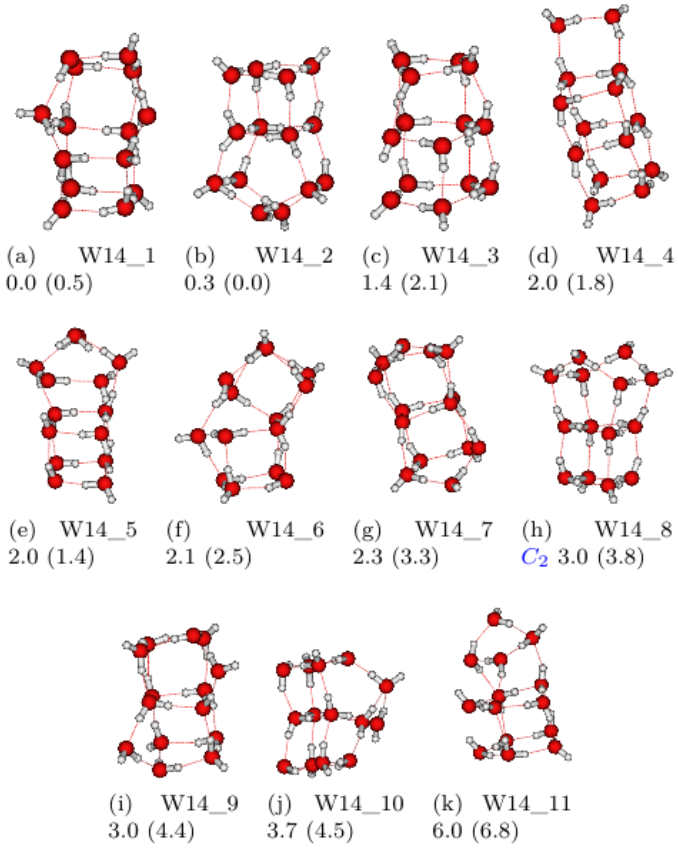


**Fig. S 8** Optimized structures of the water tetradecamer $(H_2O)_{n=14}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

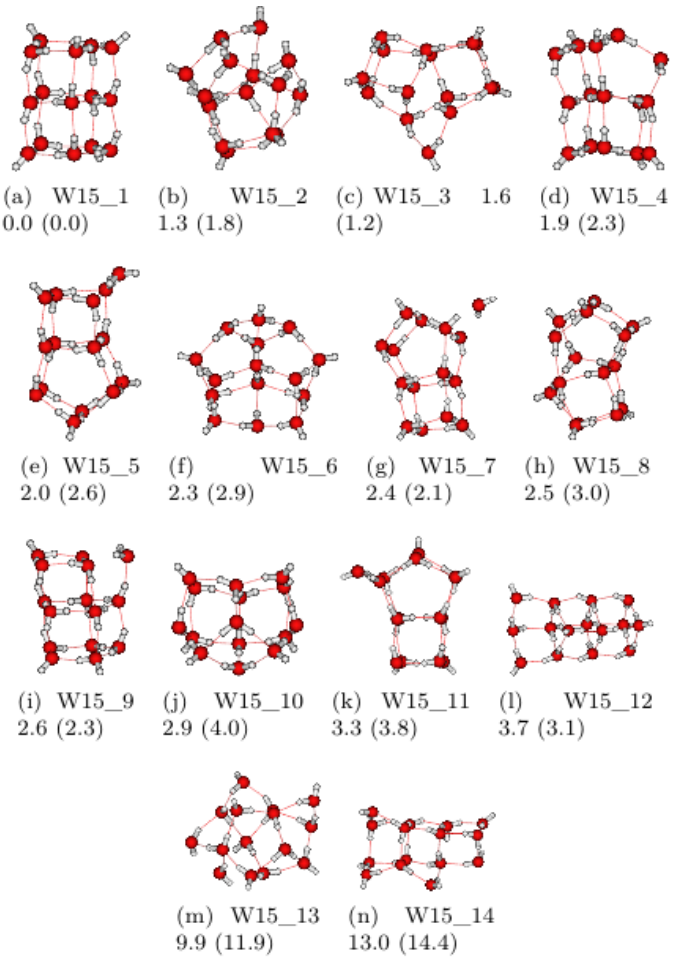


**Fig. S 9** Optimized structures of the water pentadecamer $(H_2O)_{n=15}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

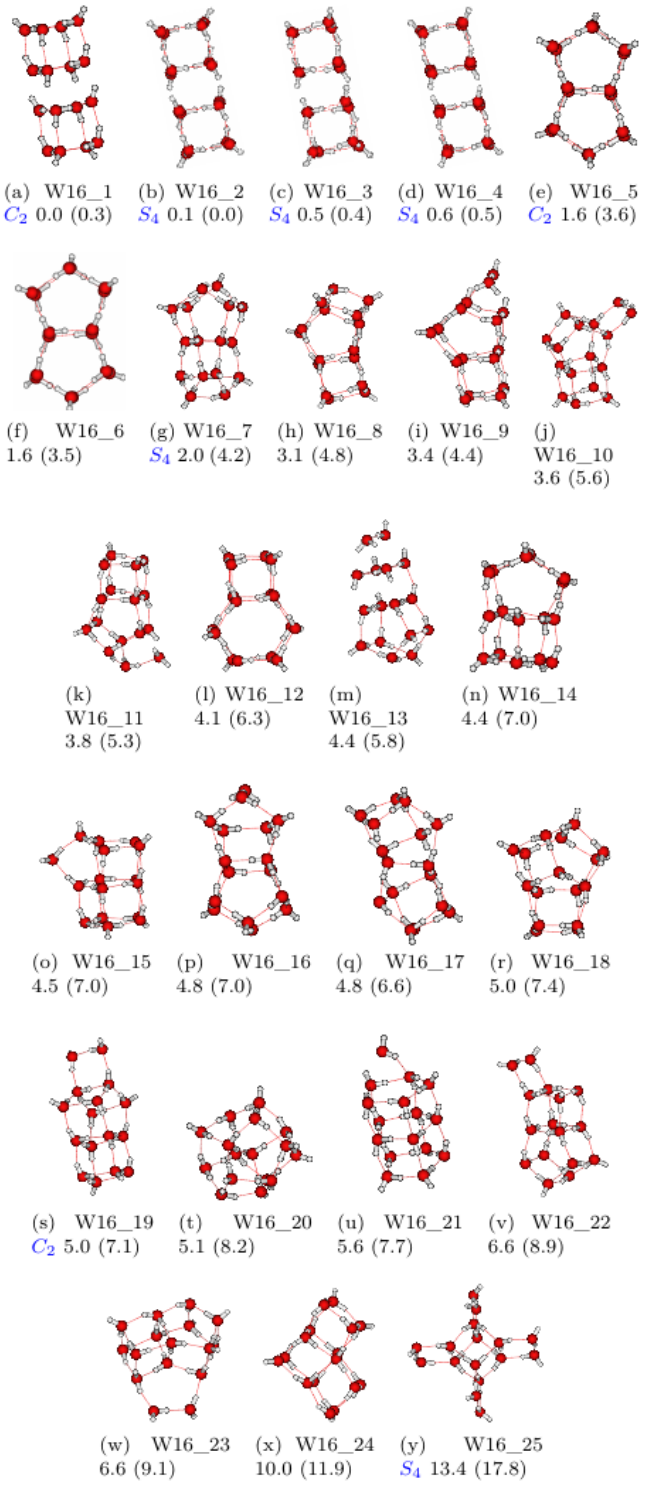


**Fig. S 10** Optimized structures of the water hexadecamer $(H_2O)_{n=16}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

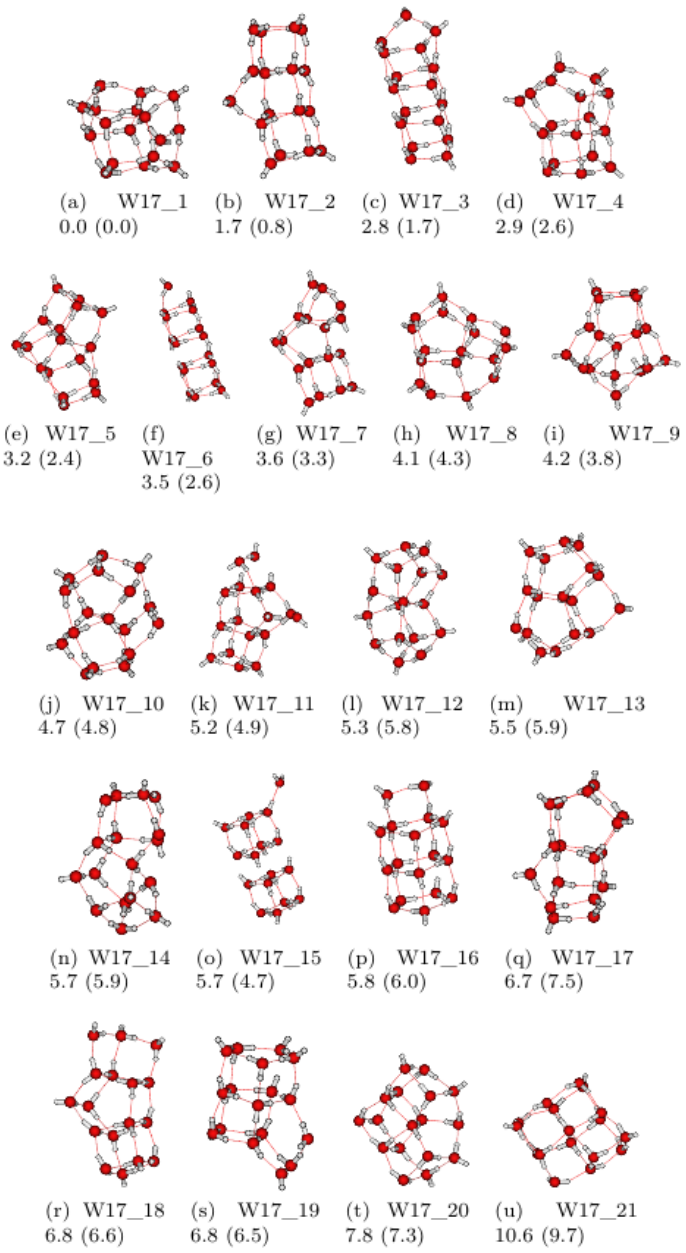


**Fig. S 11** Optimized structures of the water heptadecamer $(H_2O)_{n=17}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

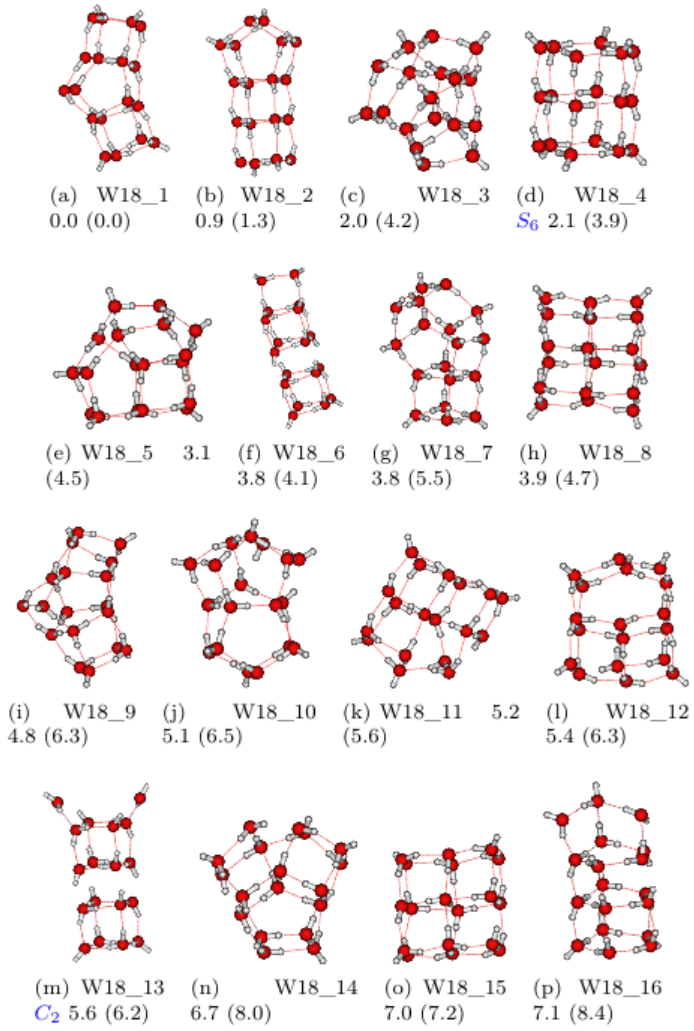


**Fig. S 12** Optimized structures of the water octadecamer $(H_2O)_{n=18}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

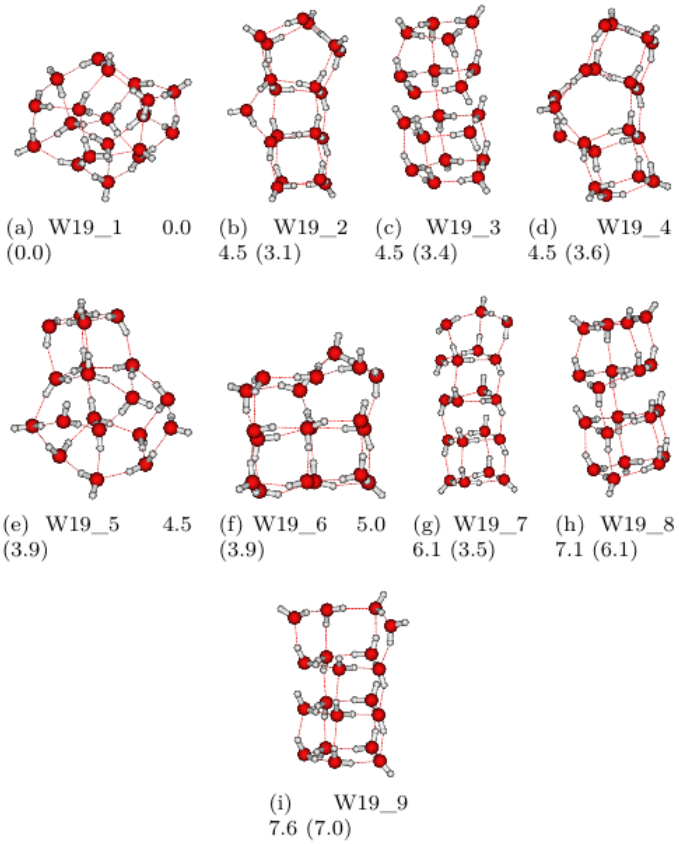


**Fig. S 13** Optimized structures of the water nonadecamer $(H_2O)_{n=19}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

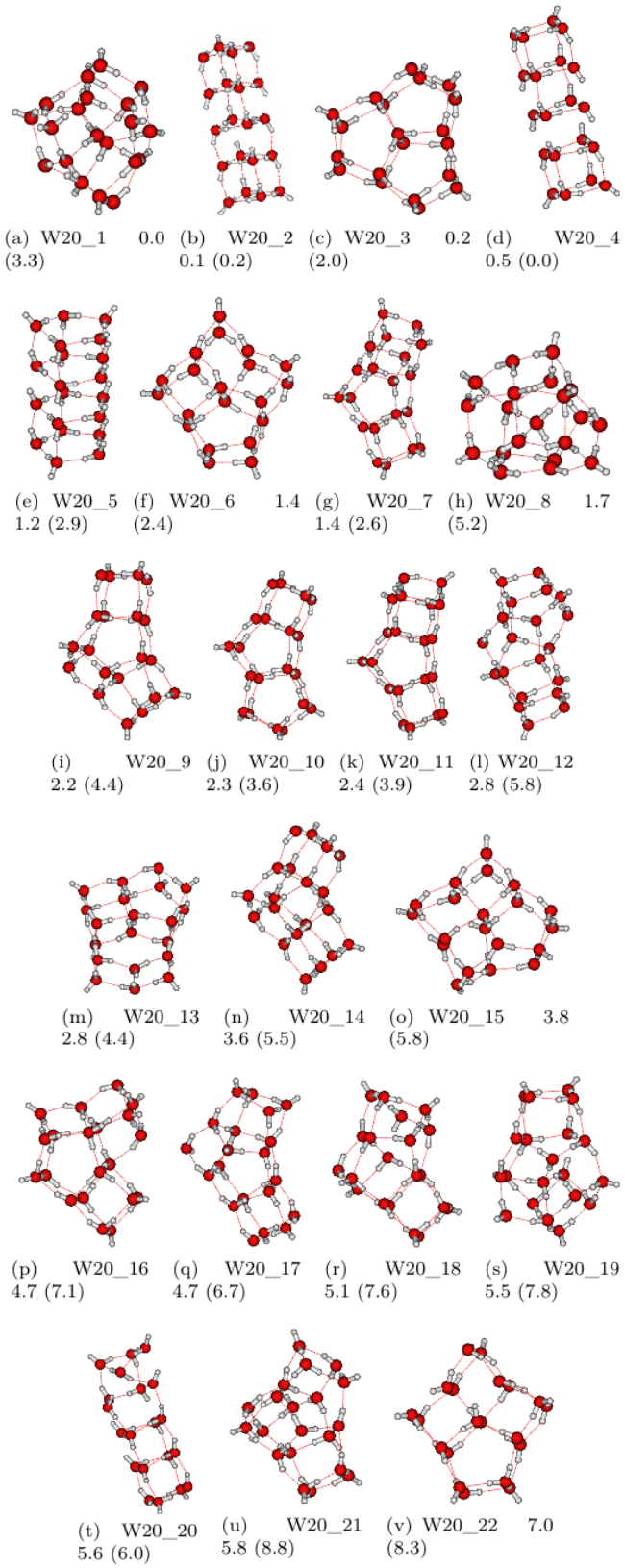


**Fig. S 14** Optimized structures of the water eicosamer $(H_2O)_{n=20}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

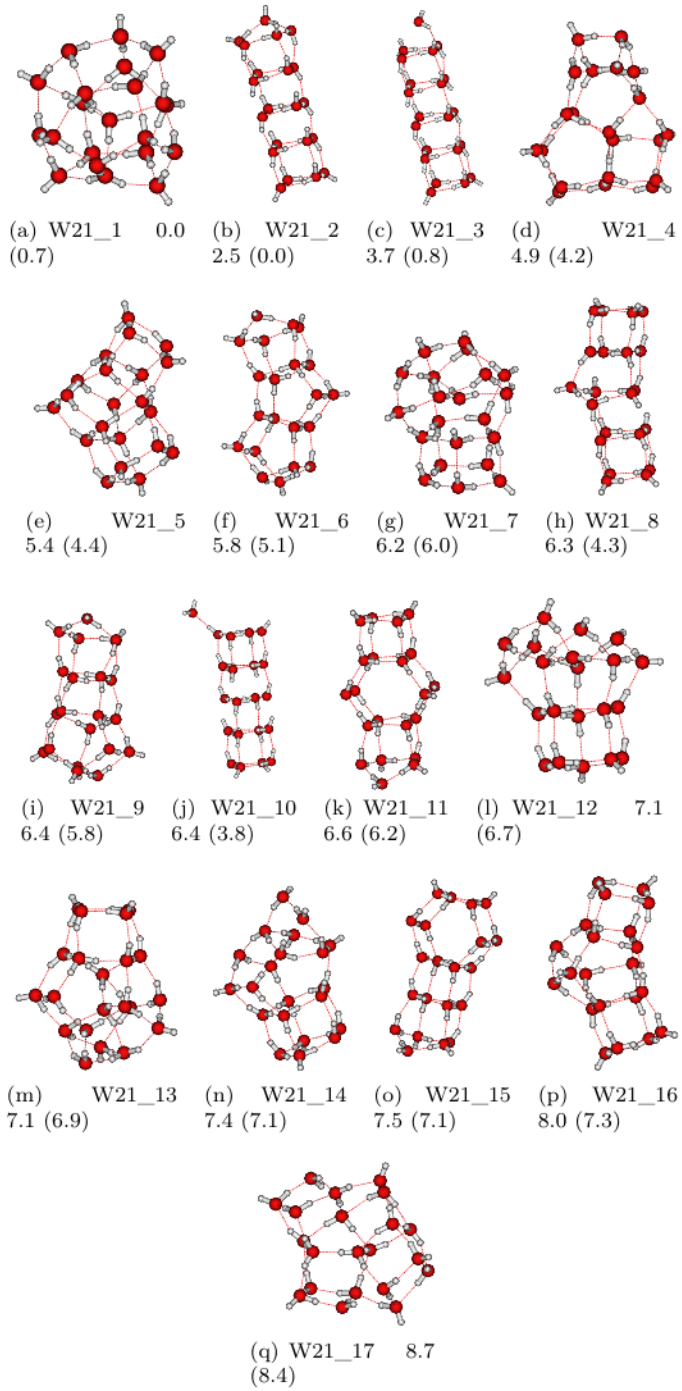


**Fig. S 15** Optimized structures of the water 21-mer $(H_2O)_{n=21}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

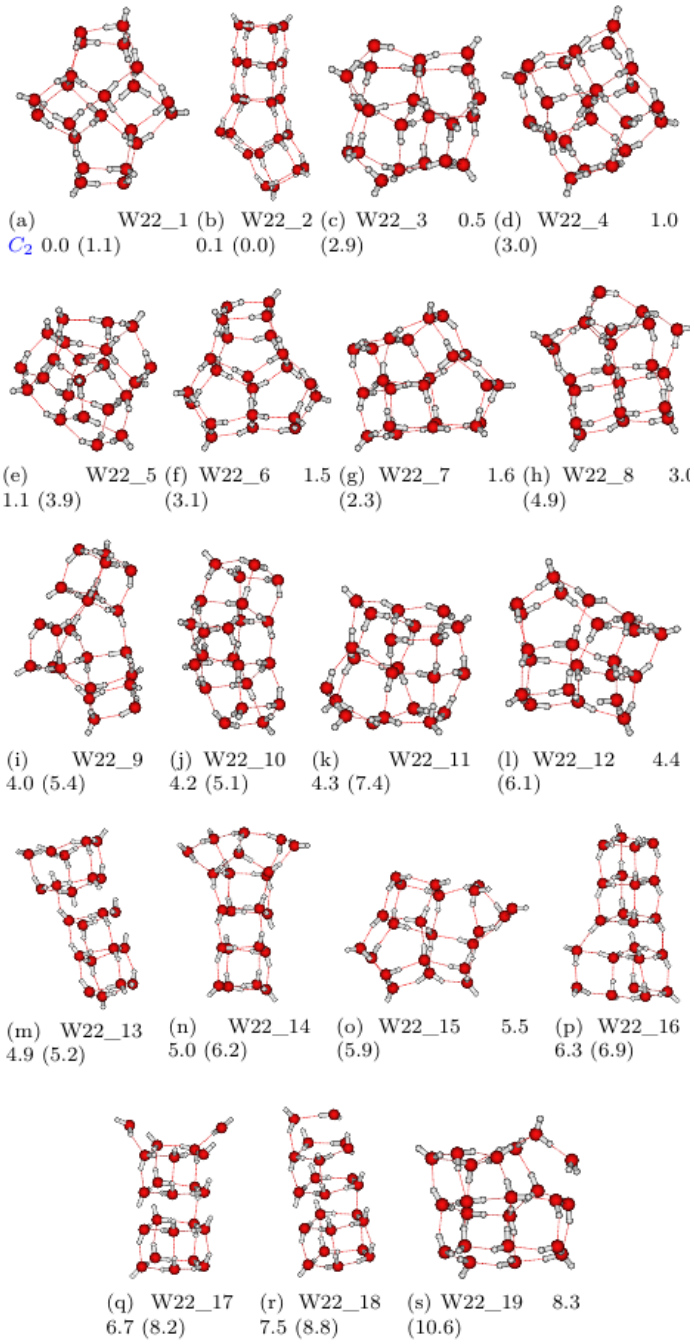


**Fig. S 16** Optimized structures of the water 22-mer $(H_2O)_{n=22}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

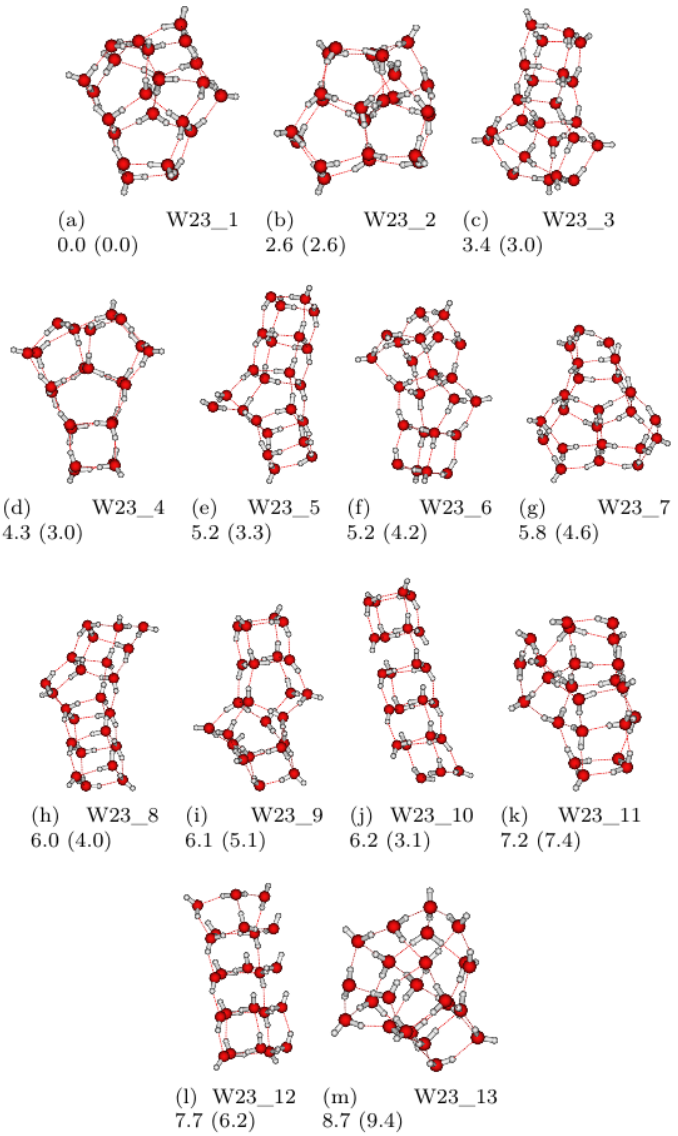


**Fig. S 17** Optimized structures of the water 23-mer $(H_2O)_{n=23}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

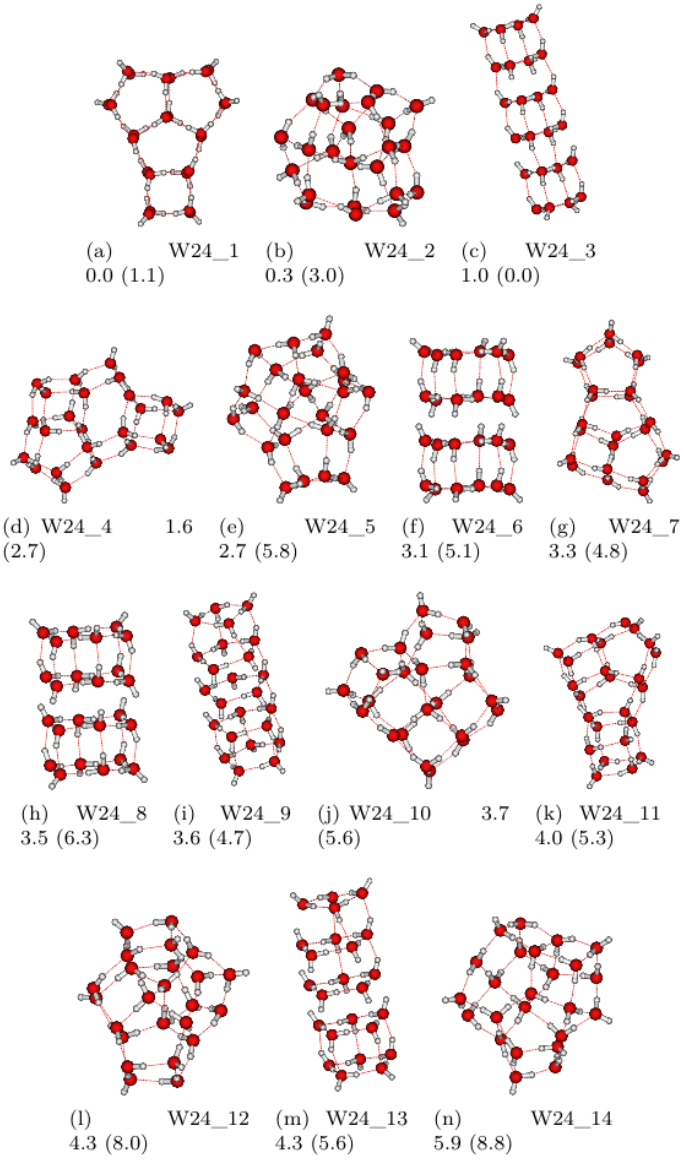


**Fig. S 18** Optimized structures of the water 24-mer $(H_2O)_{n=24}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

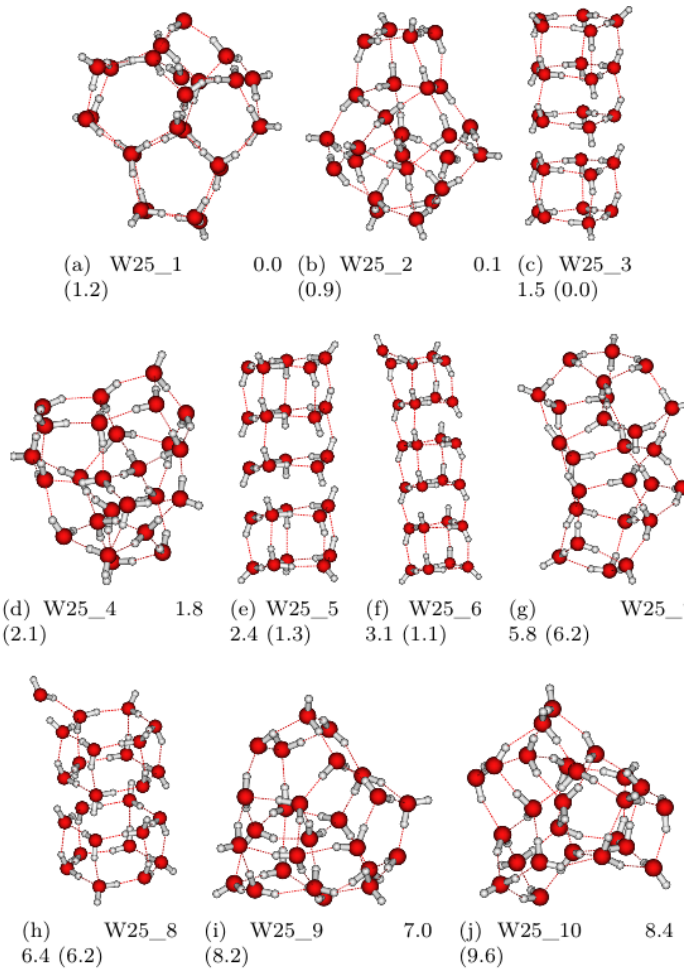


**Fig. S 19** Optimized structures of the water 25-mer $(H_2O)_{n=25}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

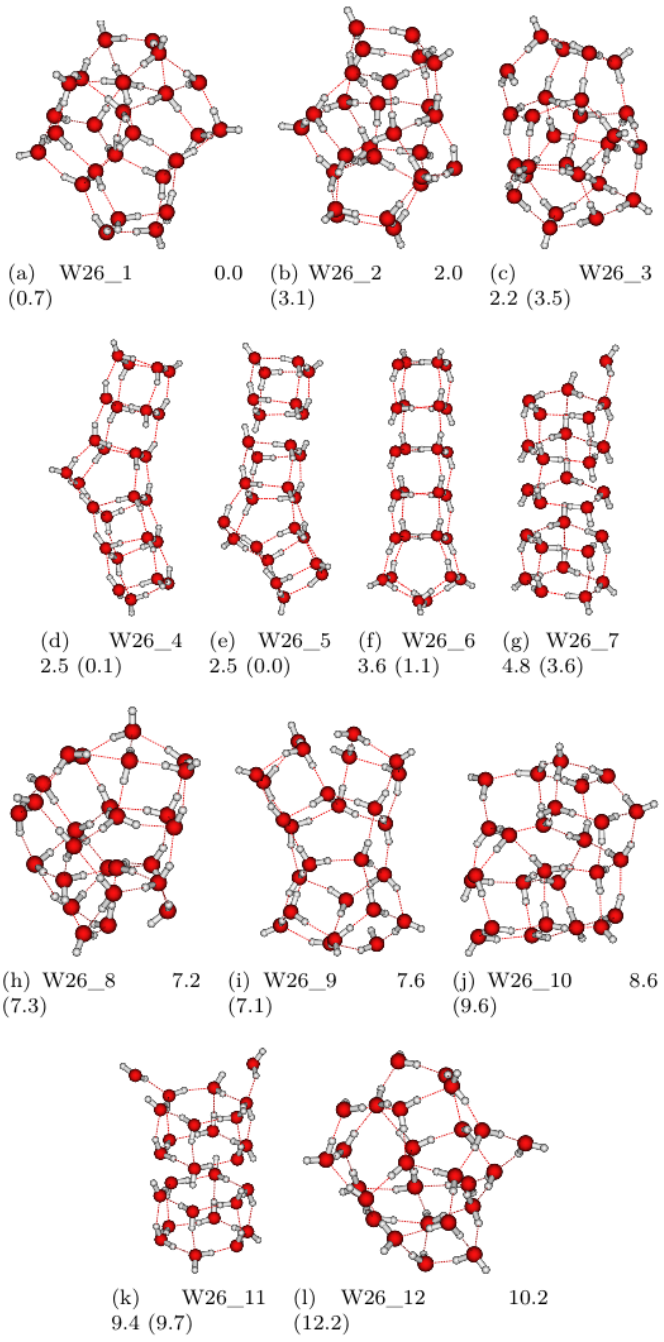


**Fig. S 20** Optimized structures of the water 26-mer $(H_2O)_{n=26}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

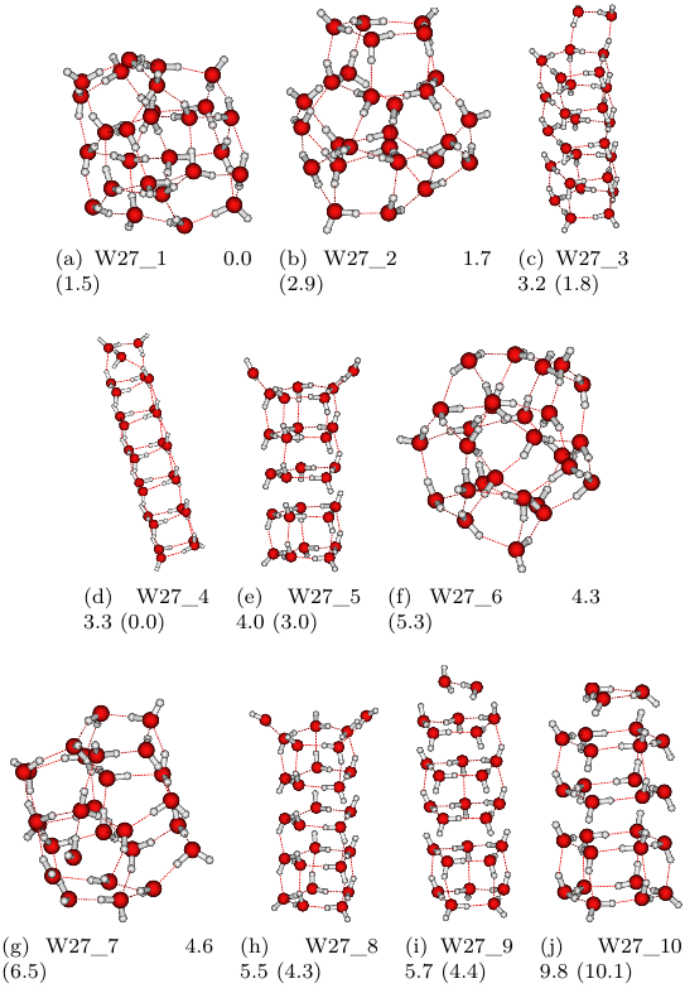


**Fig. S 21** Optimized structures of the water 27-mer $(H_2O)_{n=27}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

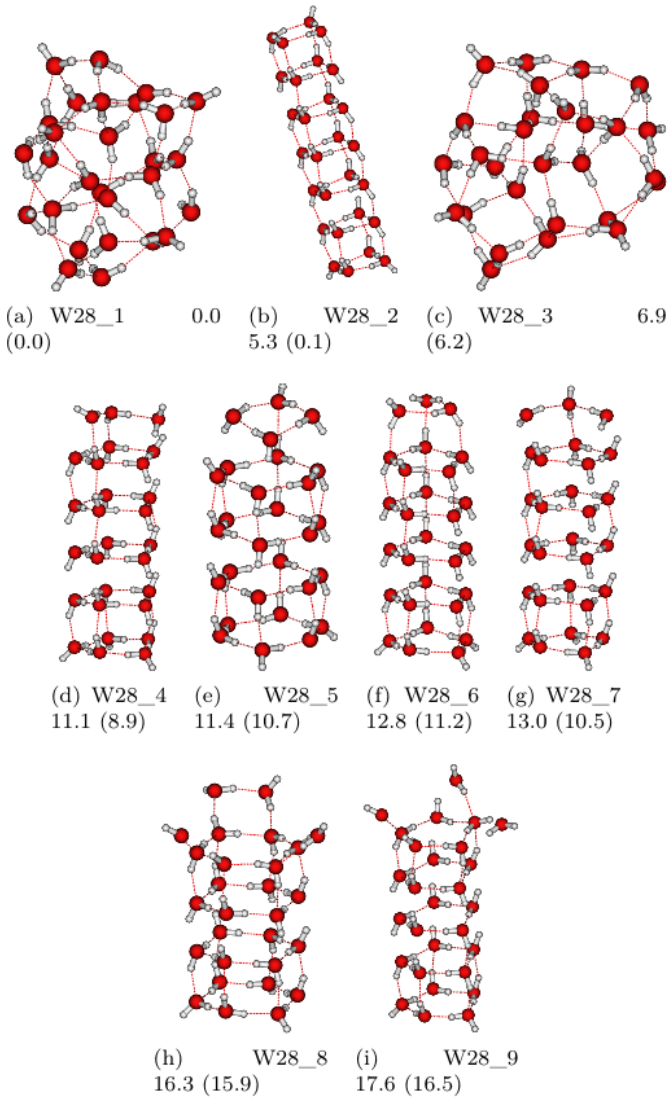


**Fig. S 22** Optimized structures of the water 28-mer $(H_2O)_{n=28}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

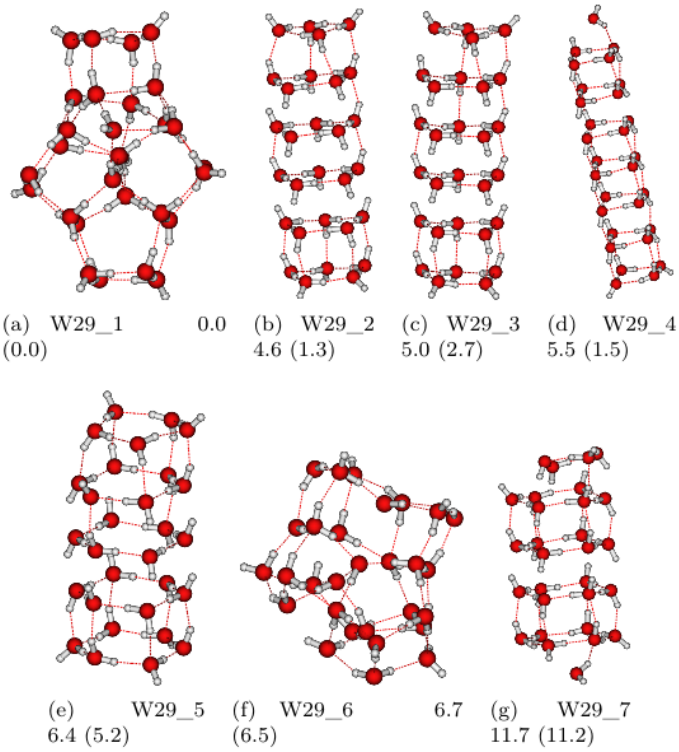


**Fig. S 23** Optimized structures of the water 29-mer $(H_2O)_{n=29}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

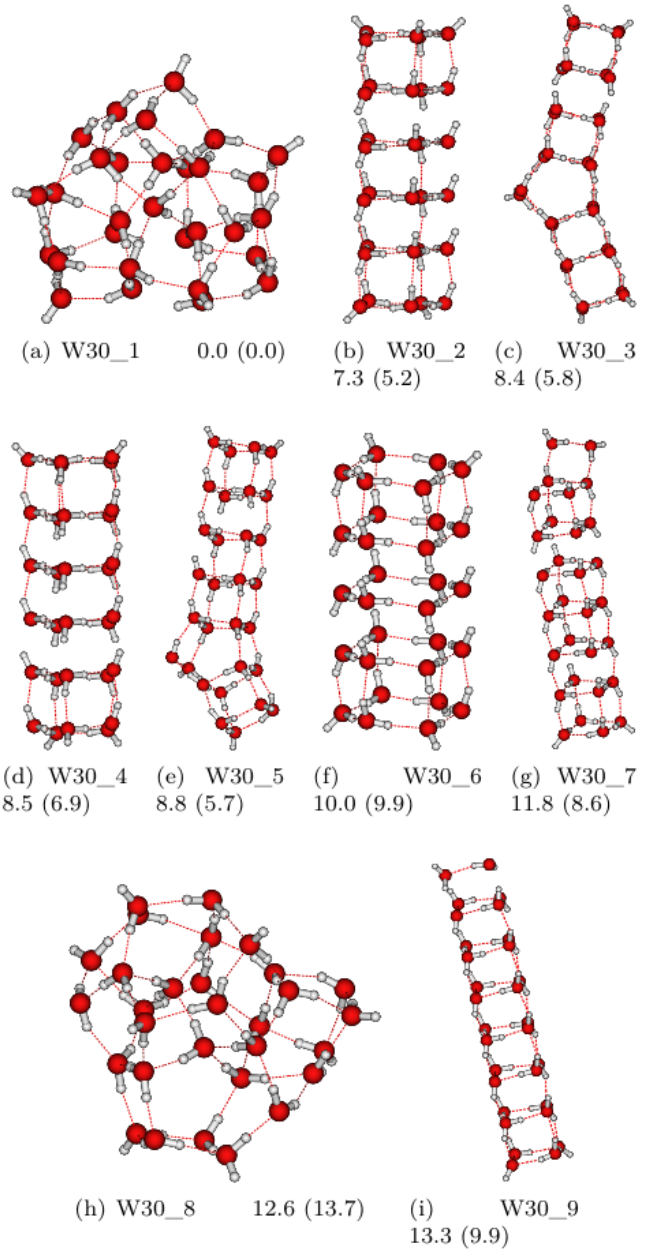


**Fig. S 24** Optimized structures of the water 30-mer $(H_2O)_{n=30}$ at the M06-2X/6-31++g(d,p) level of theory. Details are provided in the caption of Figure 1.

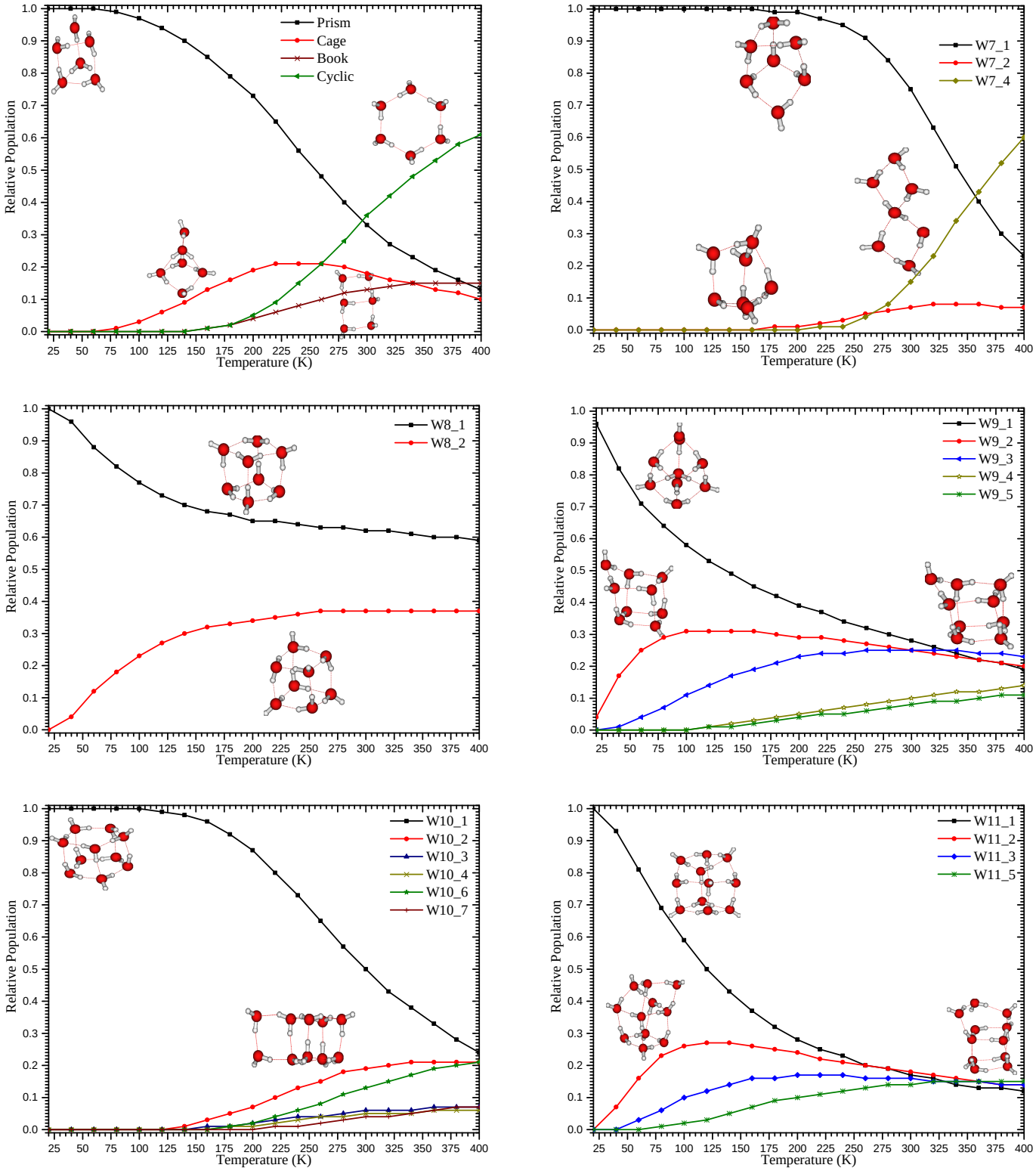


**Fig. S 25** Relative population of neutral water clusters, $(H_2O)_{n=6-11}$.

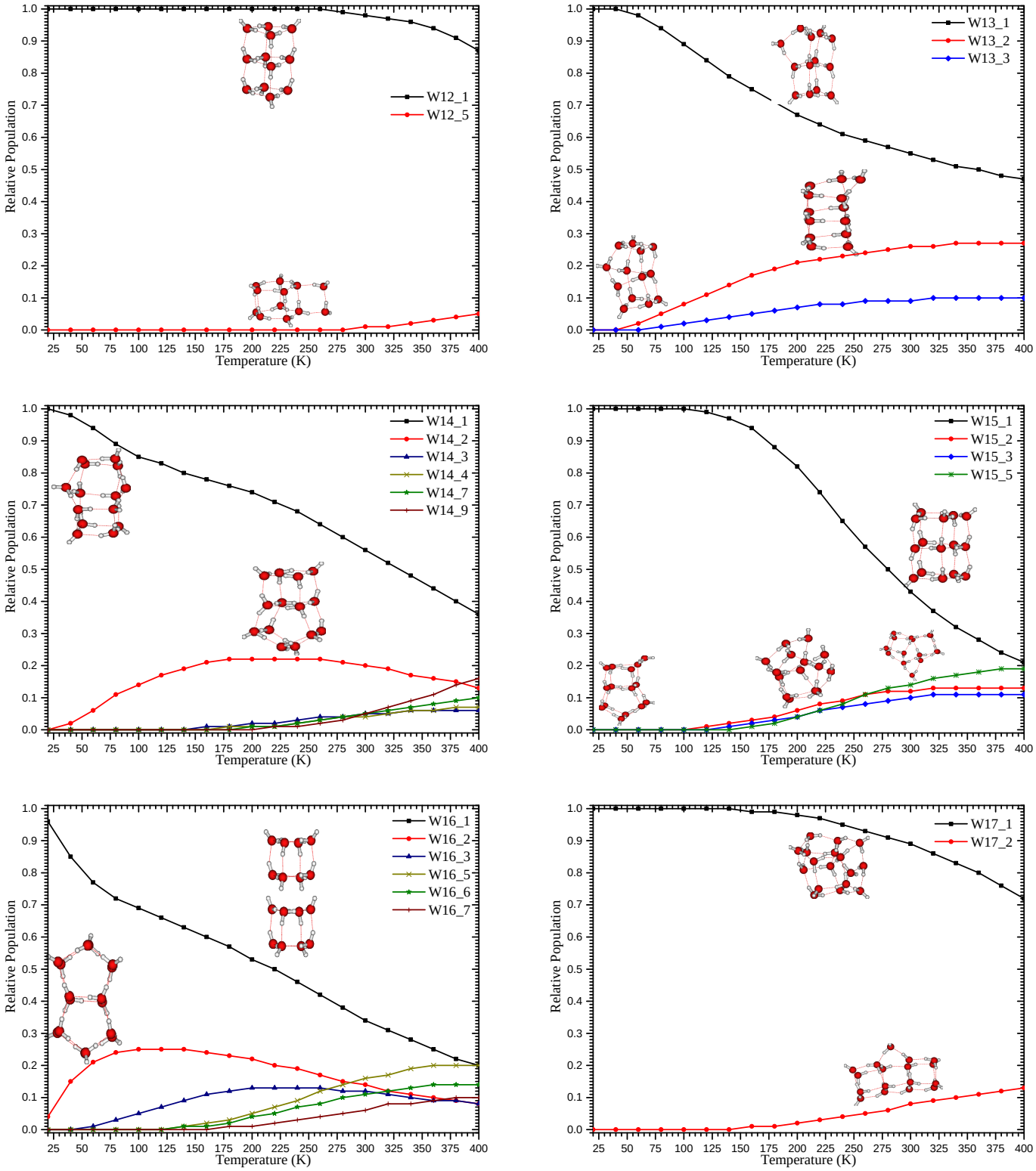


**Fig. S 26** Relative population of neutral water clusters, $(H_2O)_{n=12-17}$.

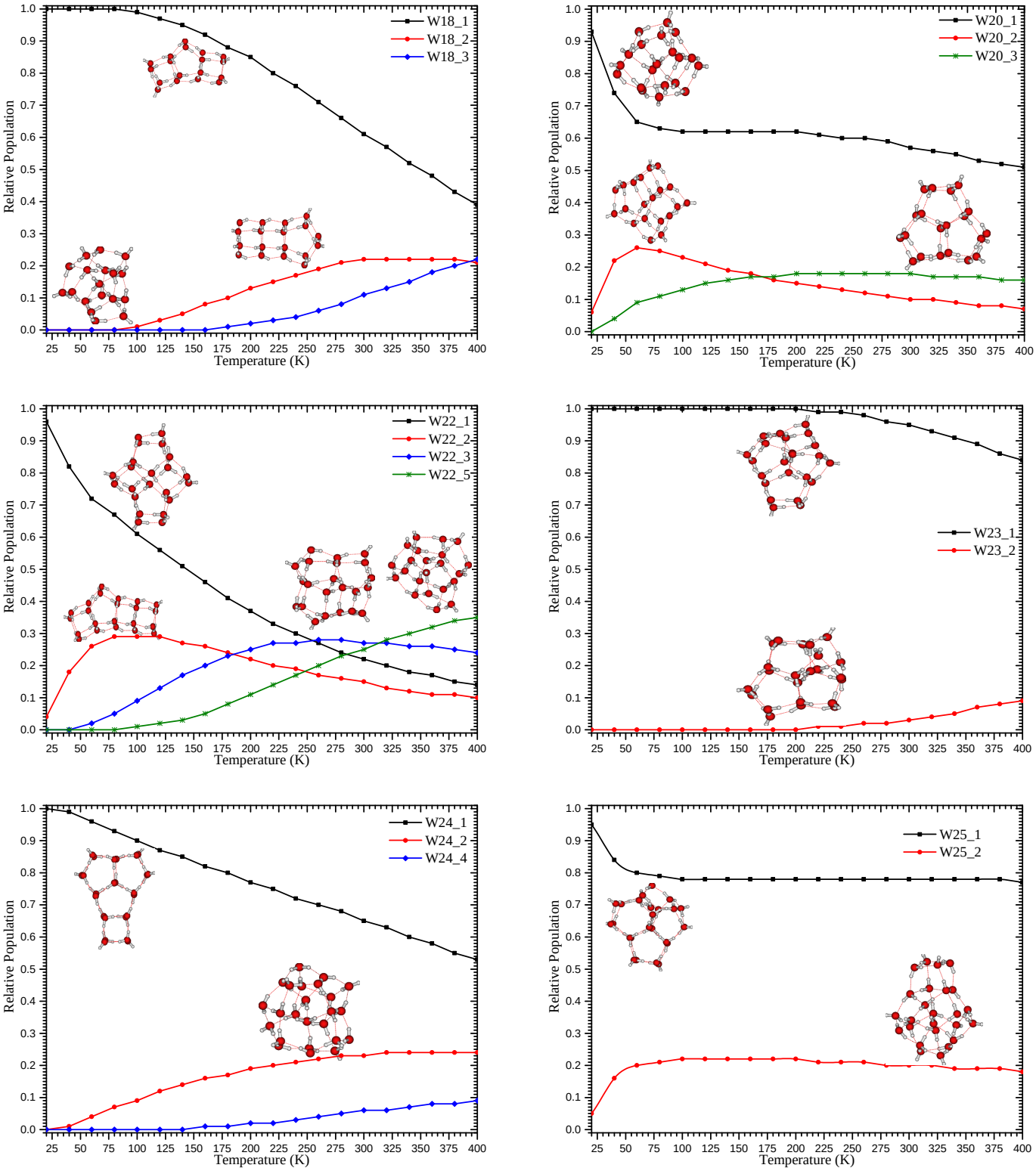


**Fig. S 27** Relative population of neutral water clusters, $(H_2O)_{n=18-25}$.

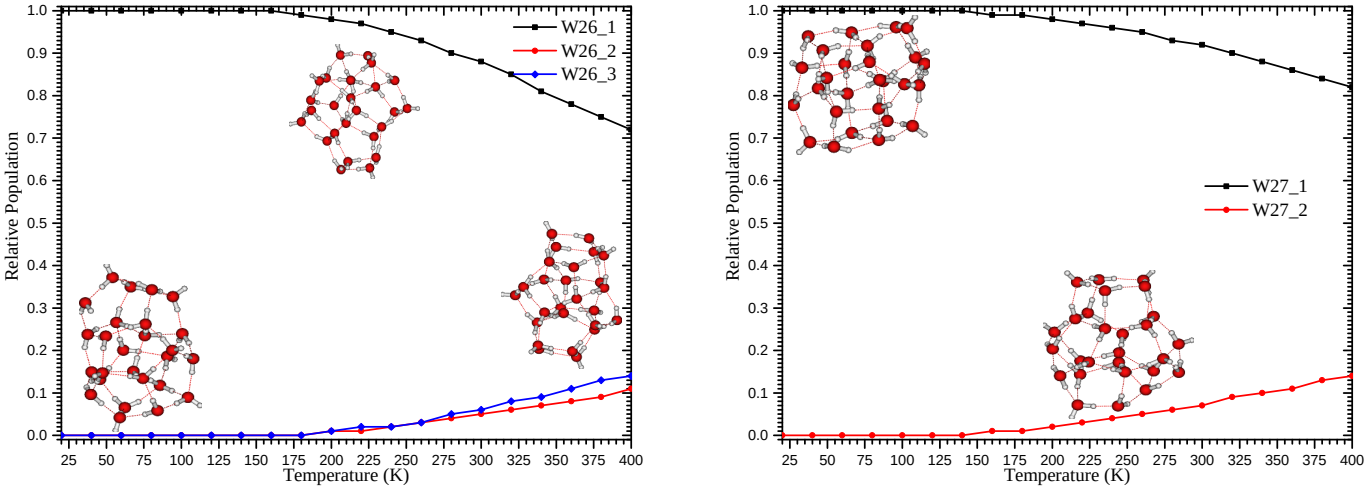


**Fig. S 28** Relative population of neutral water clusters, $(H_2O)_{n=26-27}$.