

Structure and stability of spiro-cyclic water clusters[†]

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Abstract. The structure and stability of spiro-cyclic water clusters containing up to 32 water molecules have been investigated at different levels of theory. Although there exist minima lower in energy than these spiro-cyclic clusters, calculations at the Hartree–Fock level, density functional theory using B3LYP parametrization and second order Møller–Plesset perturbation theory using 6-31G* and 6-311++G** basis sets show that they are stable in their own right. Vibrational frequency calculations and atoms-in-molecules analysis of the electron density map confirm the robustness of these hydrogen bonded clusters.

Keywords. Hydrogen bonding; water clusters; spiro-cyclic; atoms-in-molecules.

1. Introduction

H-bonding in water clusters has been the subject of several experimental and theoretical investigations due to its importance in various real life systems.^{1–8} High level *ab initio* calculations predict the structure and stability of small water clusters with near quantitative accuracy.^{9–23} These studies have been found to be extremely useful in interpreting the high-resolution spectral data obtained from size and mass selective beam techniques.^{24–33} These calculations provide valuable information on H-bonding and also take us beyond what is easily obtained experimentally. The 12-mer, 16-mer and 20-mer of the water molecule seem to prefer stacked cube and stacked pentagonal geometries.⁹ The much anticipated buckyball structure is not the most stable geometry for the water 20-mer!^{9,34}

It is well-known from the crystal structure database that the water molecule plays different roles in the stabilization of crystal structures and displays a variety of structural topologies in crystal structures and in confined environments.^{35–42} The surge in activity in the area of supramolecular chemistry exemplifies the importance of water mediated crystallization and H-bonding interaction.

Most of the structural arrangements and shapes exhibited by water clusters in various environments

are already known in organic chemistry. For example, water hexamer exists in boat and chair forms and these structural motifs are known for cyclohexane. Similarly, water octamer assumes the shape of a cubane. In all these organic moieties, every carbon atom is invariably sp^3 hybridized and forms a maximum of four covalent bonds in a tetrahedral fashion. The oxygen atom in water also exhibits $\sim sp^3$ hybridization and can form a maximum of four hydrogen bonds as illustrated in scheme 1. In classical organic chemistry, spiro-cyclic molecules⁴³ are also interesting from structure and reactivity point of view. Hence, it is interesting to probe the possibility of the existence of analogous spiro-cyclic motifs in water clusters. In the present study, the structure and stability of spiro-cyclic water clusters have been investigated and compared with the most stable water clusters using *ab initio* and density functional theoretic methods.

2. Computational details

Geometries of all the water clusters under investigation have been optimized without any constraint at different levels of theory using the G98W suite of programs.⁴⁴ Stabilization energies (SEs) of all the clusters have been calculated using the supermolecule approach and corrected for basis set superposition error (BSSE) following the procedure adopted by Boys and Bernardi.⁴⁵

[†]Dedicated to the memory of the late Professor S K Rangarajan

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$$SE = - \left(E_{\text{cluster}} - \sum_{i=1}^n E_i \right), \quad (1)$$

where E_{cluster} is the energy of the cluster, n the total number of molecules in the cluster and E_i the energy of the i th monomer in its specific location computed using the basis set for the n -mer. The relative population of various conformers for each $(\text{H}_2\text{O})_n$ cluster as a function of temperature is computed using the Boltzmann distribution formula:

$$\frac{n}{N} = \frac{e^{[-\Delta E_n/k_B T]}}{\sum e^{[-\Delta E_n/k_B T]}}, \quad (2)$$

where k_B is the Boltzmann constant, ΔE_n is the relative energy of the conformer with respect to the most stable geometry and T is the temperature. To ensure that the optimized geometries obtained correspond to true minima in the energy space, vibrational frequencies were calculated at HF/6-31G* and HF/6-311++G** levels. They were scaled by a factor of 0.8929 and 0.9070, respectively. The theory of atoms-in-molecules (AIM)⁴⁶ was used to characterize the hydrogen-bonding interaction using the topological properties of the electron density at the hydrogen bond critical point (HBCP) using the AIM2000 package.⁴⁷

3. Results and discussion

3.1 Geometries

Various spiro-cyclic water clusters considered in this study are represented schematically in scheme 1. The size of the rings formed in each cluster is used in the nomenclature. For example, the cluster 3-3 has two trimer rings arranged in a spiro-cyclic fashion. The optimized geometries of different spiro-cyclic water clusters are shown in figures 1 and 2. Of all the water clusters considered, 3-3, 3-4, 3-5, 3-6 and 4-4 retain their spiro-cyclic structures at all levels of calculation. However the clusters, 4-5, 4-6, 5-5, 5-6 and 6-6 rearrange from the initial spiro-cyclic structure during optimization. The increase in the cluster size in each ring decreases the donor-acceptor interaction between the nearby water molecules and as a consequence the spiro-cyclic structure collapses.

In all the spiro-cyclic water clusters, the central water molecule, which is shared by both the rings, is

tetra-coordinated. In this mode of interaction, the central water molecule accepts two protons and also donates two protons, resulting in an overall stabilization of the spiro-cyclic structure. A close scrutiny

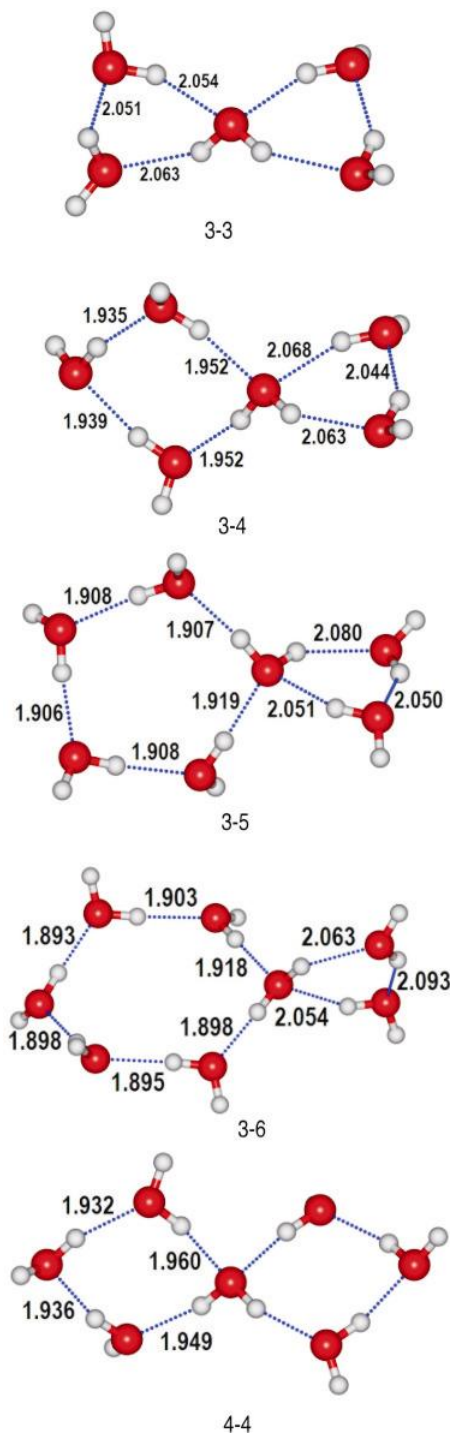
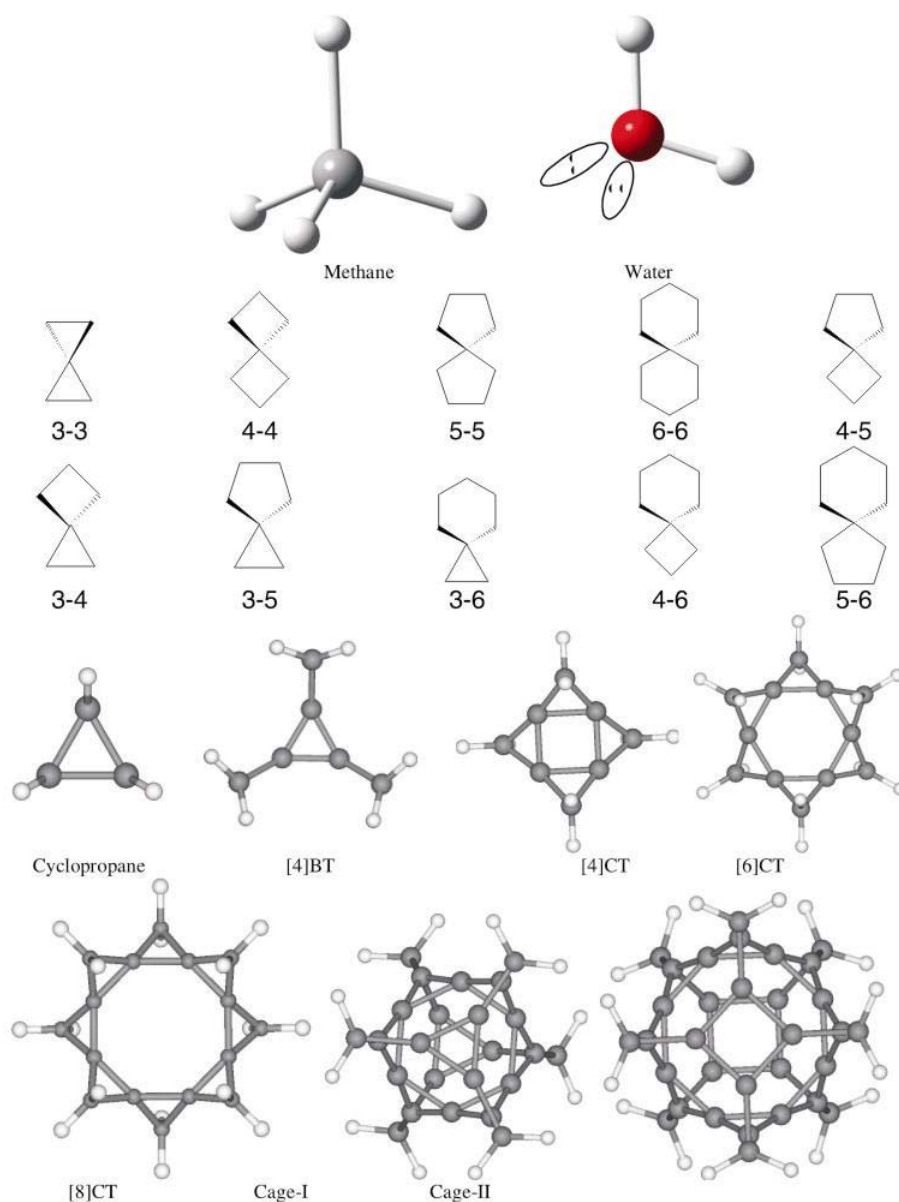


Figure 1. Optimized geometries of different spiro-cyclic water clusters obtained using HF/6-311++G** calculation. These clusters are found to be stable without any reorganization during energy minimization at DFT and MP2 levels of theory.



Scheme 1. Schematic representation of spirocyclic models (organic and water cluster) considered in this study.

of the structures reveals that the two rings are orthogonal to each other, similar to their organic counter parts. A comparison of the geometries obtained from *ab initio* calculations for 3-6, 4-6, 5-6 and 6-6 clusters shows that the hexamer ring adopts a chair form in all the cases. The pentamer ring found in 3-5, 4-5, 5-5 and 6-5 clusters deviates slightly from the planar arrangement. The trimer and tetramer rings are planar as observed in the most stable water clusters. Some of these clusters are not stable at higher level calculations. However, these spiro-cyclic structures (for example 6-6 and 4-4)

are observed in certain crystals^{48,49} suggesting that the stabilization of these structural motifs must be arising from additional interaction with the host molecules and crystal packing. In contrast, the 3-3, 3-4, 3-5, 3-6 and 4-4 spiro clusters seem to be stable even in the absence of any host lattice and associated packing effect.

A search of the crystal structure database for spiro-cyclic structures reveals several exotic spiro-cyclic and spiro-annulated structures.^{48,49} Some of the spiro-cyclic and spiro-annulated water clusters optimized at the HF/6-311++G** level of theory are

shown in figure 3. The possibility of forming such structures in the absence of a host or a crystal packing environment has been examined. The spiro-annulated structures are classified as unbranched (**U**), branched (**B**) and cyclic (**C**). The total number of trimer rings present in each cluster is denoted as $[n]$. For example, the cluster [4] is a spiro-annulated water cluster with four trimer rings.

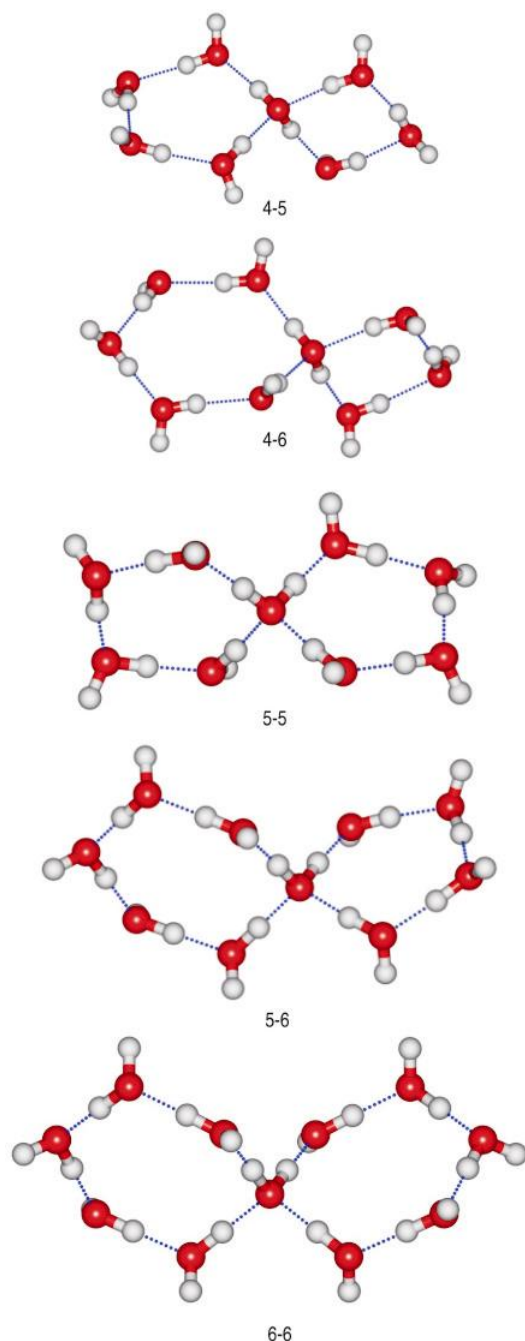


Figure 2. Optimized geometries of spiro-cyclic water clusters obtained using HF/3-21G level of calculations. These geometries were found to reorganize upon optimization with a larger basis set.

In this investigation, one **B**, four **C** and two caged spiro-annulated clusters have been studied. In general, all the **C** structures have an even number of spiro-annulated trimer rings ($[n]$) with a planar central ring. Any two adjacent trimer rings are arranged in an up and down fashion with respect to the central planar ring and hence $(n/2)$ trimer rings are above and $(n/2)$ trimer rings are below the central plane. Along with these structures, two cage structures consisting of only spiro-annulated trimer rings have been studied. These rings are interconnected in a beautiful manner that results in a regular cage structure. It is important to note that in all these clusters, the basic spiro-cyclic 3–3 cluster is observed without any structural deformation. In addition, these clusters are stable without any host and packing environment. All the spiro-annulated structures are similar in shape to that of the corresponding organic molecules as illustrated in scheme 1.

3.2 Energetics

Stabilization energies (SEs) obtained from HF calculations using the 6-31G* and 6-311++G** basis sets are listed in table 1 for different water clusters. SEs obtained from MP2/6-311++G** and DFT(B3LYP)/6-311++G** calculations are listed in table 2. The SEs obtained from HF/6-31G* and HF/6-311++G** levels of calculation are corrected for zero point energy (ZPE). For all other calculations, only BSSE corrections are included. As was expected, there is a decrease in the SE with an increase in the size of the basis set. Further, the SEs obtained from HF, DFT(B3LYP) and MP2 levels of theory using the 6-311++G** basis set follow the order HF < DFT(B3LYP) < MP2.

The SEs obtained from DFT(B3LYP)/6-311++G** calculations for the spiro-cyclic water clusters are compared with those of the most stable water clusters in figures 4a and b. Clearly, the spiro-cyclic water clusters are less stable than the most stable water clusters. The SE of the 3–3 cluster (with five water molecules), for example, is lower in energy than the most stable (cyclic) pentamer by 9.2 kcal/mol, despite the fact that the former has an additional hydrogen bond over the latter. The SE of the 3–4 cluster (six water molecules) is less than that of the most stable (cage) hexamer by 6.1 kcal/mol. The clusters 4–4 and 3–5 have seven water molecules each. However, the SE of the 4–4 cluster is larger than that of 3–5 by 1.9 kcal/mol and less than that of

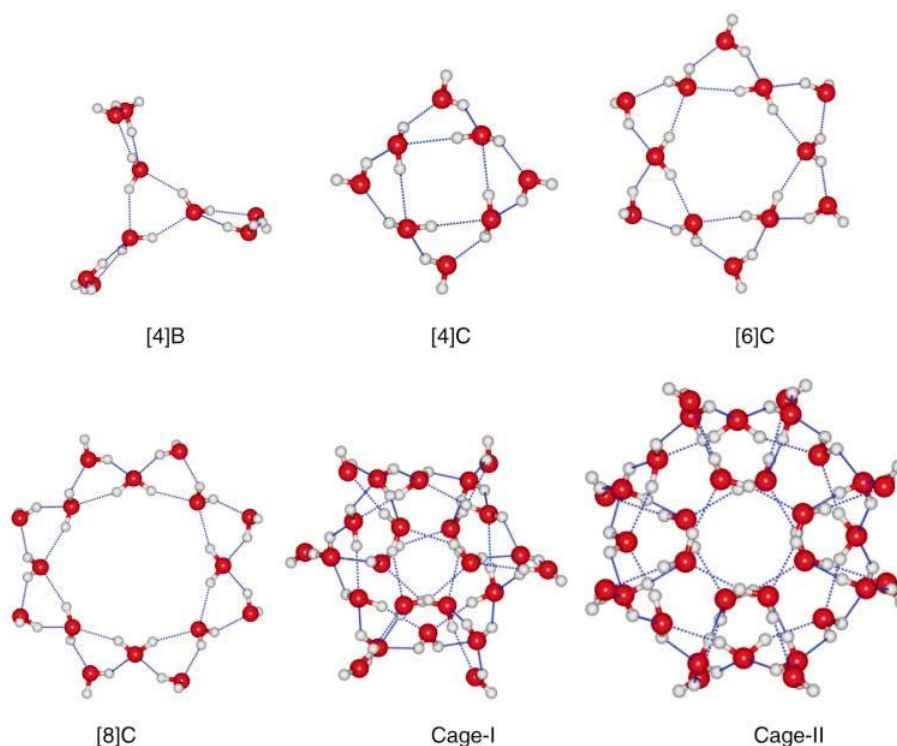


Figure 3. Optimized geometries of spiro-annulated and cage like spiro-cyclic water clusters obtained from HF/6-311++G** calculations.

Table 1. BSSE corrected and uncorrected stabilization energies for different spiro-cyclic water clusters calculated at HF level using 6-31G* and 6-311++G** basis sets. Total number (nW) of water molecules in each cluster is given in parentheses.

Cluster	HF/6-31G*			HF/6-311++G**		
	BSSE uncorrected	BSSE corrected	BSSE + ZPE corrected	BSSE uncorrected	BSSE corrected	BSSE + ZPE corrected
3-3 (5W)	34.8	28.2	16.9	26.9	24.9	12.6
3-4 (6W)	45.5	38.6	24.8	36.6	33.7	18.5
3-5 (7W)	55.8	48.3	31.9	45.2	41.5	24.5
3-6 (8W)	63.2	55.3	37.2	52.9	48.4	25.6
4-4 (7W)	57.6	50.0	33.2	46.4	42.7	25.5
[4]B (9W)	69.1	56.1	34.2	53.1	49.1	25.4
[4]C (8W)	63.4	50.1	30.3	48.1	44.3	26.8
[6]C (12W)	100.8	82.2	51.3	77.6	76.2	43.4
[8]C (16W)	134.9	109.8	68.6	104.4	102.8	65.8
Cage-I (24W)	229.0	184.3	116.5	173.0	170.0	103.1
Cage-II (32W)	311.8	250.0	158.1	234.4	–	–

the most stable heptamer by 6.2 kcal/mol. To gain further insight into the energetics of various spiro-cyclic clusters, the SE per H-bond has been calculated. It is evident from the results presented in figure 4b that the SE per H-bond for 3-3 cluster is less than that of the corresponding most stable cyclic pentamer. However, for other spiro-cyclic water

clusters such as 3-4, 3-5, 3-6 and 4-4, the SE per H-bond is larger than that of the corresponding most stable water clusters. The difference falls in the range 0.5–1.2 kcal/mol.

It is important to note from the SE values of various spiro-cyclic clusters that as the size of the spiro-cyclic water cluster increases, the difference bet-

Table 2. BSSE corrected and uncorrected stabilization energies for certain spiro-cyclic water clusters calculated at DFT(B3LYP) and MP2 levels of theory using the 6-311++G** basis set.

Cluster	DFT(B3LYP)/6-311++G**			MP2/6-311++G**	
	BSSE uncorrected	BSSE corrected	SE per H-bond	BSSE uncorrected	BSSE corrected
3-3	34.4	31.7	5.2	35.6	27.7
3-4	46.5	43.1	6.3	48.0	37.3
3-5	57.9	53.7	6.7	59.5	46.2
3-6	66.2	61.3	6.8	67.9	52.7
4-4	59.8	55.6	6.9	61.4	47.7

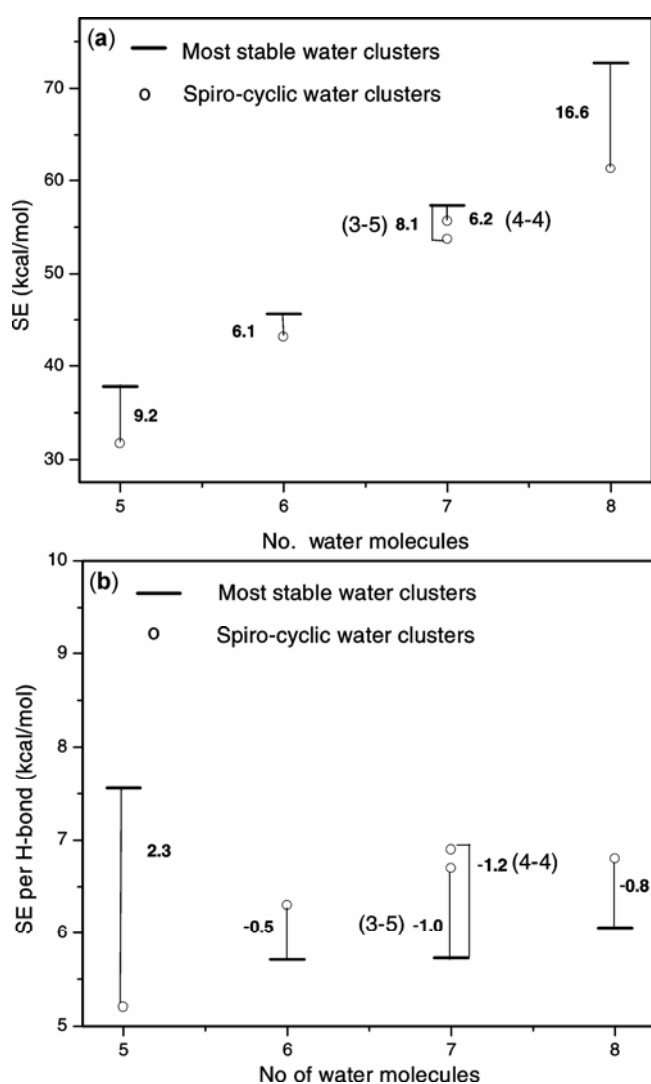


Figure 4. (a) BSSE corrected stabilization energy and (b) stabilization energy per H-bond of the most stable water cluster and the corresponding spiro-cyclic water cluster containing the same number of water molecules calculated at DFT(B3LYP)/6-311++G** level of theory. The differences in energies in kcal/mol units are included in the figure.

ween the SE of spiro-cyclic and the most stable water cluster also increases. This is partly because the number of unused potential hydrogen bonding interaction sites is more in spiro-cyclic water clusters than in the most stable water clusters. These sites would clearly contribute to hydrogen bond formation with the host molecules and hence the stability of spiro-cyclic clusters in organic and inorganic host lattices.

In addition to the spiro-cyclic water clusters, the SE of hitherto unreported cage-I and cage-II structures are also listed in table 1. These cages consist of 24 and 32 water molecules, respectively. Their SEs with BSSE corrections are 184 and 250 kcal/mol, respectively, at the HF/6-31G* level of calculation. The respective SE per H-bond for these clusters is 4.5 and 3.4 kcal/mol.

The population⁵⁰ of various conformers for different water clusters $[(\text{H}_2\text{O})_n]$, where $n = 5, 6, 7, 8$ as a function of temperature is illustrated in figure 5. It is evident from the figure that as the number of conformers increases for any particular $(\text{H}_2\text{O})_n$, the contribution by the spiro-cyclic water clusters also increases. When compared to the most stable conformation, the population is low for all other conformers investigated.

3.3 Atoms-in-molecules

The AIM theory has been used to characterize the hydrogen bonding interaction in spiro-cyclic water clusters and the resulting parameters are listed in table 3. Figure 6 gives the AIM topology for all the spiro-cyclic water clusters. The electron density (ρ) values at the HBCPs are $\sim 10^{-2} e/a_0^3$ indicating non-covalent interaction. The values of the Laplacian of electron density at the HBCPs are all positive, a

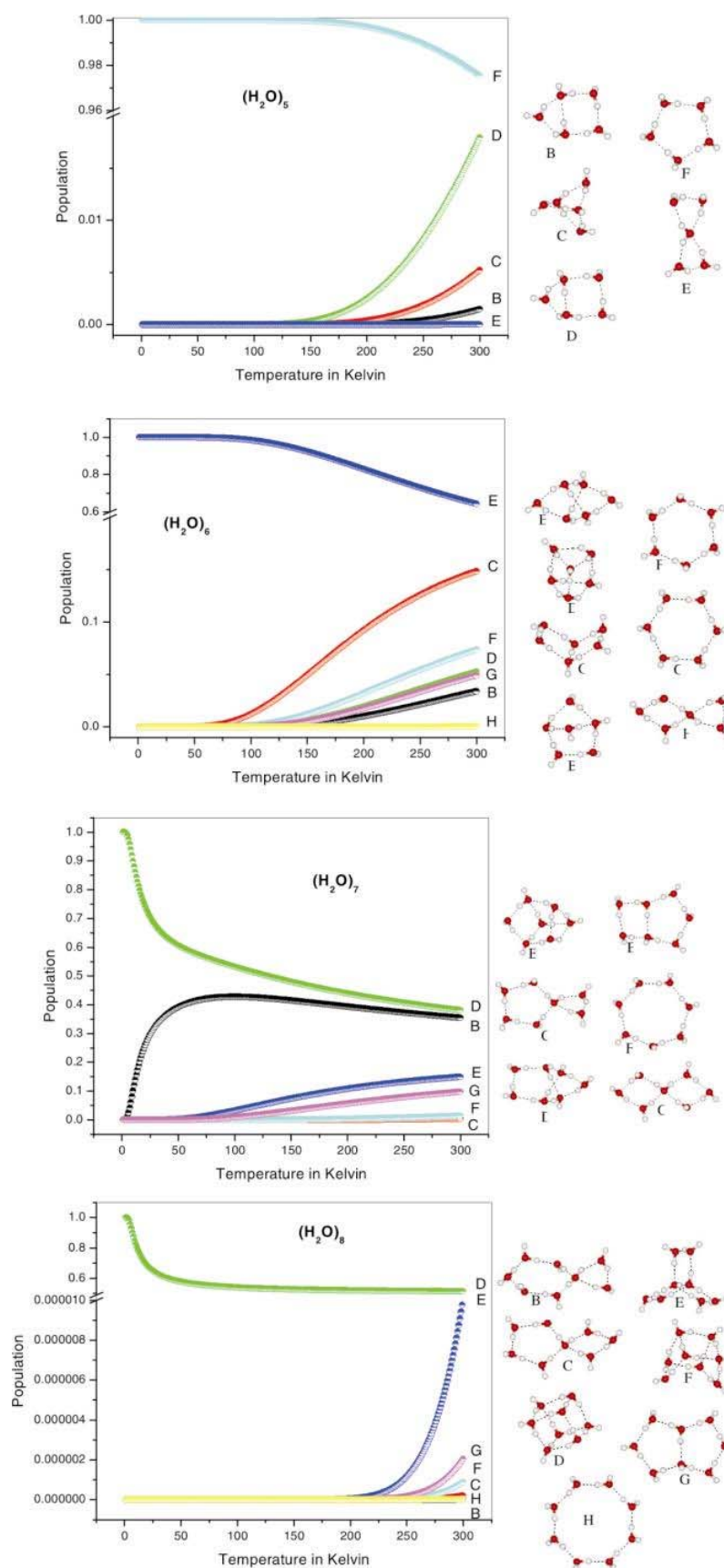


Figure 5. Relative population of different conformers of various water clusters as a function of temperature obtained using DFT(B3LYP)/6-311++G** calculations.

Table 3. Ranges of electron density and Laplacian of electron density at the HBCPs for different spiro-cyclic water clusters calculated at HF level using 6-311++G** basis set.

Cluster	HF/6-31G*	
	Electron density (e/a_0^3)	Laplacian of electron density (e/a_0^5)
3-3	0.018–0.020	0.022–0.024
3-4	0.023–0.030	0.020–0.025
3-5	0.024–0.032	0.020–0.027
3-6	0.022–0.031	0.019–0.026
4-4	0.022–0.032	0.024–0.025
[4]B	0.023–0.025	0.020–0.021
[4]C	0.021–0.026	0.020–0.022
[6]C	0.022–0.025	0.019–0.021
[8]C	0.022–0.024	0.019–0.020
Cage-I	0.021–0.026	0.018–0.022
Cage-II	0.020–0.025	0.019–0.023

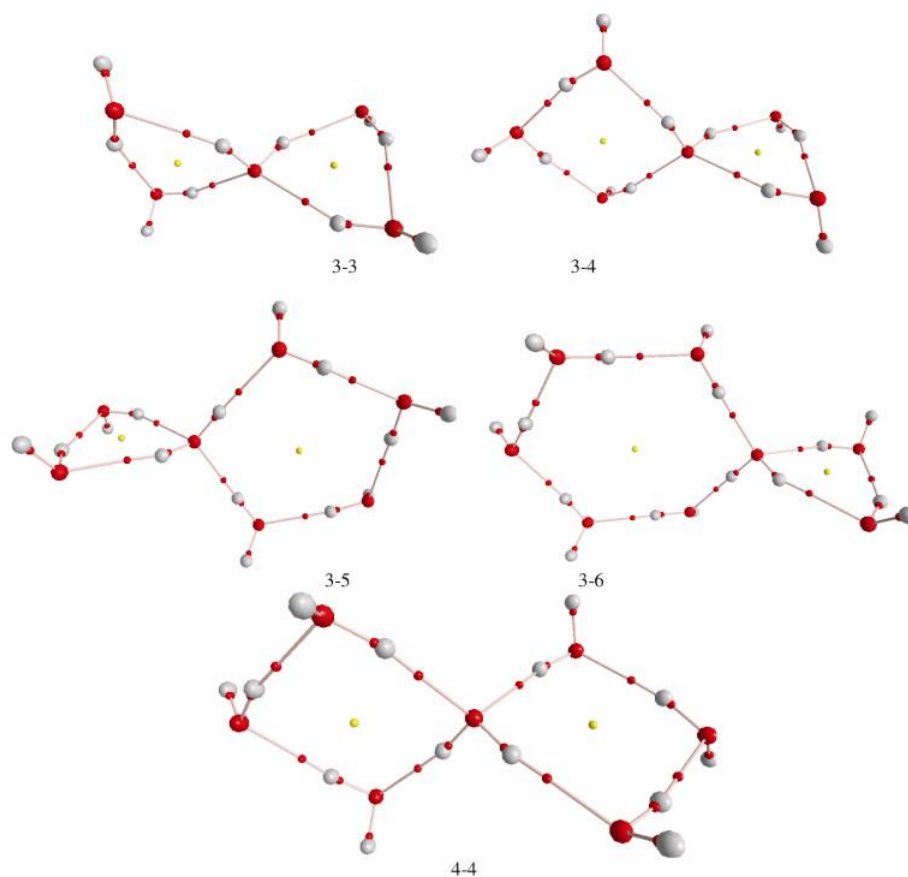


Figure 6. AIM derived molecular graph of spiro-cyclic water clusters obtained from HF/6-311++G** calculations. The red spheres represent oxygen atoms and the grey spheres represent the hydrogen atoms. While the red dots indicate bond critical points, the yellow dots represent ring critical points.

characteristic of non-covalent interactions.⁵¹ The molecular graphs show rich electron density topological features in spiro-cyclic clusters and the presence of the ring structure is confirmed by the

presence of ring critical points. The molecular graphs further confirm that there is no other short contact or non-bonded interaction between the spiro-cyclic rings.

Table 4. Calculated ranges of vibrational frequencies of various spiro-cyclic water clusters at the HF/6-311++G** level, along with computed red shifts in the O–H stretching mode.

Species	Scaled frequencies		Red shifts	
	ss	as	ss	as
Water	3757	3849		
3–3	3522–3594	3554–3737	40–234	2–295
3–4	3441–3562	3582–3708	71–192	31–157
3–5	3423–3558	3575–3705	75–210	35–164
3–6	3427–3563	3576–3708	71–206	31–163
4–4	3461–3589	3599–3736	44–172	3–139
[4]B	3487–3563	3595–3706	71–146	34–145
[4]C	3509–3578	3617–3711	55–123	28–122
[6]C	3493–3567	3579–3708	66–140	31–161
[8]C	3487–3568	3590–3711	65–146	29–149
Cage-I	3486–3569	3590–3701	64–147	30–149

3.4 Vibrational frequencies

Symmetric and asymmetric O–H stretching frequencies for a water molecule and spiro-cyclic and spiro-annulated water clusters as computed by the HF/6-311++G** method and scaled by a factor of 0.9070 are reported in table 4. The calculated red shifts fall in the range 40–234 cm⁻¹ for symmetric stretching and 3–295 cm⁻¹ for asymmetric stretching. This again is characteristic of hydrogen bonded systems.

4. Conclusions

Hartree–Fock, density functional and second order Møller–Plesset perturbation theoretic calculations using reasonably large basis sets show that several spiro-cyclic clusters are stable in their own right. Frequency calculations and atoms-in-molecules analysis of the electron density topology of these clusters reveal the hydrogen bonding in these clusters and their robustness. While they may not be common in gas phase, they are stable enough and they have enough potential hydrogen bonding sites that they can be formed in host lattices and in crystal packing environments.

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References

- Pauling L 1960 *The nature of the chemical bond* (Cornell University Press)
- Jeffrey G A 1997 *An introduction to hydrogen bonding* (Oxford University Press)
- Scheiner S 1997 *Hydrogen bonding. A theoretical perspective* (Oxford University Press)
- Desiraju G R and Steiner T 1999 *The weak hydrogen bond: In structural chemistry and biology* (Oxford University Press)
- Steiner T 2002 *Angew. Chem. Int. Ed.* **41** 48
- Desiraju G R 2002 *Acc. Chem. Res.* **35** 565
- Saenger W 1984 *Principles of nucleic acid structure* (Springer-Verlag)
- Schulz G E and Schirmer R H 1979 *Principles of protein structure* (Springer-Verlag)
- Maheshwary S, Patel N, Sathyamurthy N, Kulkarni A D and Gadre S R 2001 *J. Phys. Chem.* **A105** 10525
- Wales D J and Hodges M P 1998 *Chem. Phys. Lett.* **286** 65
- Wernet Ph, Nordlund D, Bergmann U, Cavalleri M, Odellius M, Ogasawara H, Naslund L-Å, Hirsch T K, Ojamae L, Glatzel P, Pettersson L G M and Nilsson A 2004 *Science* **304** 995
- James T, Wales D J and Hernández-Rojas J 2005 *Chem. Phys. Lett.* **415** 302
- Kim J and Kim K S 1998 *J. Chem. Phys.* **109** 5886
- Buck U, Ettischer I, Melzer M, Buch V and Sadlej J 1998 *Phys. Rev. Lett.* **80** 2578
- Harvey J N, Jung J O and Gerber R B 1998 *J. Chem. Phys.* **109** 8747
- Kim J, Mujumdar D, Lee H M and Kim K S 1999 *J. Chem. Phys.* **110** 9128
- Brudermann J, Melzer M, Buck U, Kazimirski J K, Sadlej J and Buch V 1999 *J. Chem. Phys.* **110** 10649
- Hodges M and Wales D J 2000 *Chem. Phys. Lett.* **324** 279
- Chaban G M, Xantheas S S and Gerber R B 2003 *J. Phys. Chem.* **A107** 4952

20. Myshakin E M, Diri K and Jordan K D 2004 *J. Phys. Chem.* **A108** 6752
21. Tachikawa H 2004 *J. Phys. Chem.* **A108** 7853
22. Choi Y C, Pak C and Kim K S 2006 *J. Chem. Phys.* **124** 094308
23. Ludwig R 2007 *Chem. Phys. Chem.* **8** 938
24. Matsumoto Y, Ebata T and Mikami N 2000 *J. Mol. Struct.* **552** 257
25. Guchhait N, Ebata T and Mikami N 2000 *J. Phys. Chem.* **A104** 11891
26. Fujii A, Patwari G N, Ebata T and Mikami N 2002 *Int. J. Mass Spectrom.* **220** 289
27. Miyazaki M, Fujii A, Ebata T and Mikami N 2004 *Science* **304** 1134
28. Steinbach C, Andersson P, Kazimirski J K, Buck U, Buch V and Beu T A 2004 *J. Phys. Chem.* **A108** 6165
29. Steinbach C, Andersson P, Melzer M, Kazimirski J K, Buck U and Buch V 2004 *Phys. Chem. Chem. Phys.* **6** 3320
30. Gruenloh C J, Hagemeister F C and Zwier T S 2000 *Recent theoretical and experimental advances in hydrogen-bonded clusters* (Kluwer) pp. 83–99
31. Zwier T S 2001 *J. Phys. Chem.* **A105** 8827
32. Zwier T S 2004 *Science* **304** 1119
33. Liu K, Cruzan J D and Saykally R J 1996 *Science* **271** 929
34. Ludwig R 2001 *Angew. Chem. Int. Ed.* **40** 1808
35. Atwood J L, Barbour L J, Ness T J, Raston C L and Raston P L 2001 *J. Am. Chem. Soc.* **123** 7192
36. Moorthy J N, Natarajan R and Venugopalan P 2002 *Angew. Chem. Int. Ed.* **41** 3417
37. Ghosh S K and Bharadwaj P K 2003 *Inorg. Chem.* **42** 8250
38. Ghosh S K and Bharadwaj P K 2004 *Angew. Chem. Int. Ed.* **116** 4490
39. Ghosh S K and Bharadwaj P K 2004 *Inorg. Chem.* **43** 3771
40. Saha B K and Nangia A 2005 *Chem. Commun.* **24** 3024
41. Mukherjee A, Saha M K, Nethaji M and Chakravarty A R 2004 *Chem. Commun.* **21** 716
42. Nangia A 2007 *Encyclopedia of supramolecular chemistry* (eds) J L Atwood and J W Steed (Taylor & Francis) pp. 1–9
43. Meijere A D, Kozhushkov S I and Schill H 2006 *Chem. Rev.* **106** 4926
44. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery J A Jr, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C and Pople J A 1998 Gaussian 03, Revision E.01, Gaussian, Inc., Pittsburgh, PA
45. Boys S F and Bernardi F 1970 *Mol. Phys.* **19** 553
46. Bader R F W 1990 *Atoms in molecules: a quantum theory* (Clarendon Press)
47. AIM 2000 Biegler-Konig F, Schonbohm J, Derdau R, Bayles D and Bader R F W 2000 Version 1 (Bielefeld, Germany)
48. Garcia R L, Murillo B M D, Barba V, Hopfl H, Beltran H I and Rivera L S Z 2005 *Chem. Commun.* **22** 5527
49. Choudhury S R, Jana A D, Colacio E, Lee H M, Mostafa G and Mukhopadhyay S 2007 *Crystal Growth & Design* **7** 212
50. Maciel G S, Bitencourt A C P, Ragni M and Aquilanti V 2007 *Int. J. Quantum Chem.* **107** 2697
51. Parthasarathi R, Subramanian V and Sathyamurthy N 2006 *J. Phys. Chem.* **A110** 3349