

Hexamers: From Covalently Bound Organic Structures to Hydrogen Bonded Water Clusters

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KEYWORDS:

ab initio calculations · clusters · hydrogen bonds · vibrational spectroscopy · water chemistry

Cyclic hexamers are most common in chemistry. This structural motif is found for the saturated hydrocarbon cyclohexane, which exists in two possible non-planar arrangements, a chair and a boat conformation.^[1] Both structural isomers shown in Figure 1 satisfy the need for

rings (Figure 2). Adamantane includes four chair conformers and bicyclo[2.2.2]octane can be represented by three boat conformers. In twistane, the six-membered ring maintains five twist-boat conformations. Diamond represents another prominent polycyclic structure. This

forming four covalent bonds, the water molecule has also four sites to build hydrogen bonds. In an almost tetrahedral coordination, each water molecule is involved in four hydrogen bonds, the two lone electron pairs as bond acceptors and both hydrogen atoms as bond donors. Hydrogen bonds are about ten times weaker than covalent bonds. Recently, it was shown by Compton scattering experiments on ice^[2] and NMR measurements of internucleotide scalar coupling in biomolecules^[3] that hydrogen bonds have covalent character and can be regarded as weak covalent bonds. Because of the tetrahedral arrangement and the covalent character of the hydrogen bond, the structural motifs of organic molecules can be found in all known crystalline phases of ice.^[4–7] In Figure 3,

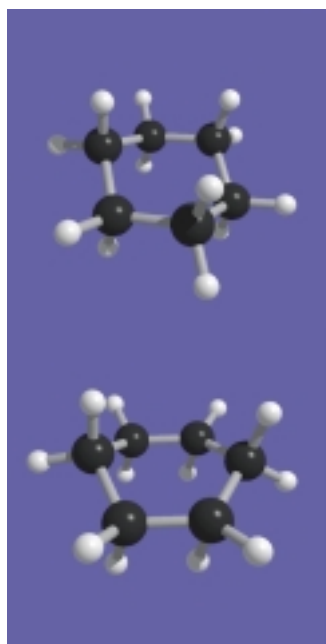


Figure 1. Chair (above) and boat (below) conformations of cyclohexane.



Figure 2. Adamantane (above), twistane (center), and bicyclo[2.2.2]octane (below) are all composed of chair and boat conformations.

tetrahedral bond angles and represent constituents of larger organic molecules. Adamantane, twistane, and bicyclo[2.2.2]octane all contain cyclohexane

form of elemental carbon, in which each atom is bonded to four other carbon atoms, is an extended three-dimensional network of adamantane units. In common, all of these structures have carbon atoms, each covalently bound in a tetrahedral fashion. These possible tetrahedral structures establish the relationship to the hydrogen bond networks of water. Whereas the carbon atom with four equivalent hybrid orbitals is capable of

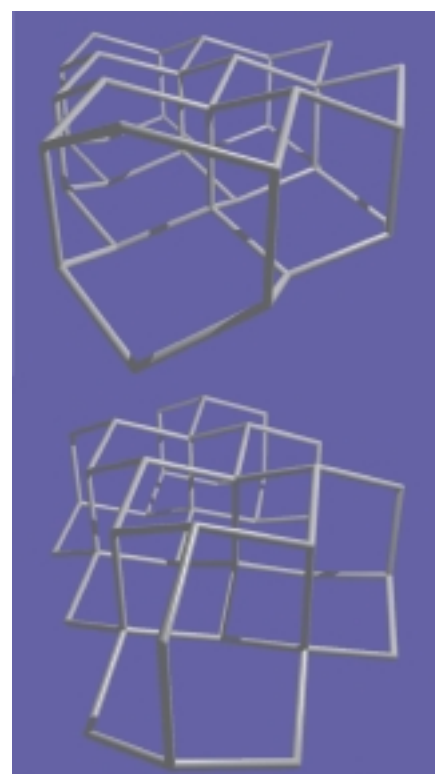


Figure 3. The structure of hexagonal ice I_h (above) and cubic ice I_c (below). Each line represents a hydrogen bond $O-H\cdots O$ and vertices correspond to the oxygen atomic positions.

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the two prominent polymorphs are shown. Hexagonal ice I_h is ordinary ice, gels below the freezing point at normal pressure, and is composed of chair and boat conformers. The metastable cubic ice I_c can be formed by warming vitreous ice at low temperatures or by warming any of the quenched high-pressure ices. From Figure 3 it can be easily seen that the cubic lattice includes adamantane-like structures and is isomorphous with diamond. That the structural motifs of isomeric cyclic hexamers of covalently bonded organic molecules are present in the hydrogen bonded polymorphs of ice has been known for long time.^[4–7] On the other hand, the microscopic properties of liquid water remain poorly understood. However, computer simulations^[8] and thermodynamic models^[9] suggest that the cyclic hexamer is also one of the prominent morphologies in liquid water.

The structural motifs of ice crystals are fairly well understood; those of liquid water can be supposed by theoretical models. But what about pure isolated water clusters in the gas phase or in an inert environment? Do they exist as hexamers at all? And, if so, do they form quasiplanar rings or three-dimensional cage structures? These questions were intensively addressed by a palette of experimental and theoretical methods. In particular, vibration-rotation-tunneling (VRT) spectroscopy, infrared (IR) spectroscopy, and quantum mechanical methods were used to solve the puzzle of small water clusters. Recent research in this field is an excellent example for a fruitful interplay between theory and experiment.

First of all, enormous progress in laser spectroscopy has facilitated new, highly detailed studies of water clusters. Far-infrared (FIR) VRT spectroscopy of clusters has been developed by Saykally and coworkers^[10–13] to study the structure and dynamics of isolated water clusters. Low frequency van der Waals vibrations in clusters can be measured with tunable FIR lasers to resolve rotational and tunneling motions. The resulting VRT spectra can be analyzed in terms of permutation-inversion (PI) group theory and scattering theory to yield pair potentials of unprecedented accuracy and detail for important, weakly bound systems. FIR-VRT

spectroscopy is also a powerful probe of the tunneling dynamics that occur in hydrogen-bonded clusters. This method allows investigation of the cooperative (nonpairwise) effects in hydrogen bonding through the VRT spectroscopy of water clusters. In a series of beautiful experiments, Saykally et al. characterized the cyclic water trimer,^[10] tetramer,^[11] and pentamer.^[12] The results unambiguously establish that the structures of the water clusters (Figure 4) responsible for the observed spectra were indeed the quasiplanar rings predicted by theory.^[14–16] These spectra permitted estimates of the oxygen–oxygen interatomic distances, R_{O-O} , to be extracted for each of the clusters, which yields a quantitative experimental measure of the hydrogen bond cooperativity. In Figure 5, the R_{O-O} distances obtained from VRT spectroscopy and theoretical studies of water clusters are plotted. Cooperative effects are manifest, as all methods produced an exponential R_{O-O} contraction with increasing cluster size and convergent to the bulk (ordered ice) value of about 2.759 Å.^[5, 6] Experiment and theory strongly suggest that the water trimer,

tetramer, and pentamer ($n=3–5$) have cyclic, quasiplanar minimum energy structures. Larger water clusters were expected to have three-dimensional geometries, with the hexamer ($n=6$) representing the transition from cyclic to such three-dimensional structures.

Indeed, a cagelike hexamer, bound by eight hydrogen bonds, is in best agreement with the measured rotational constants from VRT measurements by the Saykally group.^[18] This three-dimensional water hexamer, shown in Figure 6, turned out to be the absolute minimum structure in a gas-phase experiment at temperatures about 5 K.

Forced by the surprising experimental results for the water hexamer in the gas phase, Kim and Kim^[19] performed extensive ab initio (MP2) and density functional theory (DFT) calculations on the five lowest energy structures of the water hexamers, as shown in Figure 6. The authors demonstrated that the ring, book, bag, cage, and prism structures are nearly isoenergetic, to within 0.7 kcal mol⁻¹. Their high performance MP2 calculations showed that the lowest energy conformer is the cage followed by

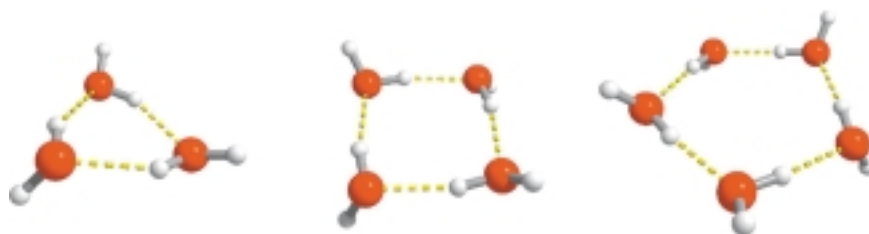


Figure 4. Ring structures of the water trimer, tetramer, and pentamer. Hydrogen bonds are indicated with a broken line.

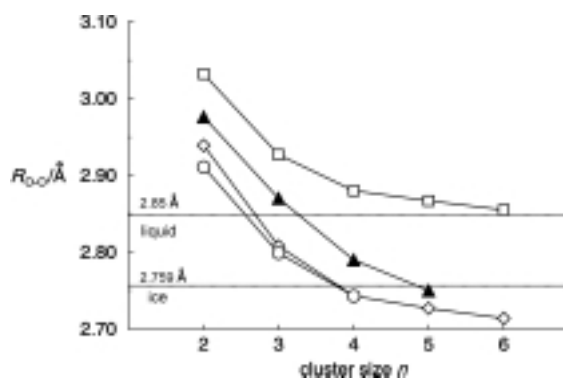


Figure 5. The R_{O-O} distances versus cluster size n obtained from VRT spectroscopy^[10–13] (\blacktriangle) and three different levels of theory^[14–16]: Hartree–Fock (HF, \square), Møller–Plesset second-order perturbation (MP2, \circ), and density functional theory (DFT, B-LYP level, \diamond). The experimental R_{O-O} distances in liquid water at 298 K^[17] and hexagonal ice at 183 K^[5, 6] are shown for comparison, as indicated by dotted lines.

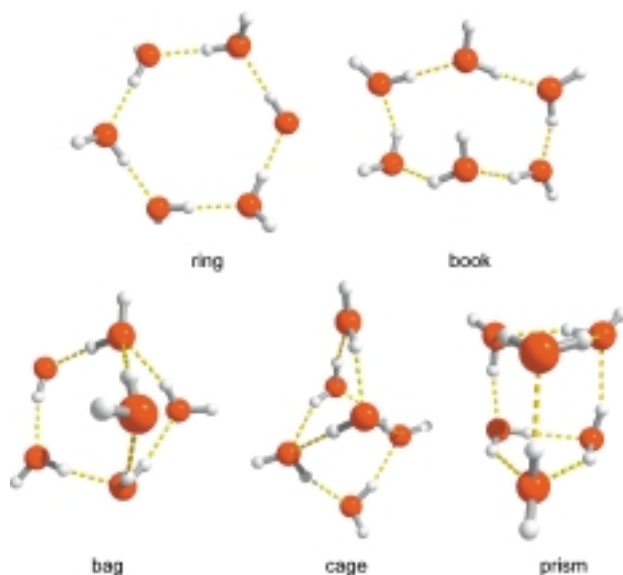


Figure 6. Five calculated water hexamer isomers showing quasiplanar and cagelike clusters. Hydrogen bonds are indicated with a broken line.

the book and prism structures lying less than 0.1 and 0.2 kcal mol⁻¹ higher in energy. The ring and the bag structures exist only slightly higher (0.5 and 0.7 kcal mol⁻¹) than the cage hexamer. The lowest energy structure of the water hexamer, at low temperatures, is now believed to be a three-dimensional cage from both experimental and theoretical viewpoints. At high temperatures, the populations of the five hexamer isomers would be almost the same. The ab initio calculations clearly showed that zero-point vibrational effects can alter the energy ordering of the low-lying hexamer structures. Thus, there was some hint that other hexamer isomers could be detected experimentally by changing the physical and chemical conditions. This proved to be the case. Nauta and Miller^[20] recently reported the experimental observation of the cyclic water hexamer, a higher energy isomer than the cage structure characterized in the gas phase by the Saykally group. The cyclic hexamer was formed in liquid helium droplets and studied with infrared spectroscopy. The infrared spectrum for the OH stretches of water clusters formed in liquid helium were compared with that of the corresponding complexes formed in a free jet expansion.^[21] The vibrational frequency shifts resulting from the interaction with the helium were negligible and the bands for the dimer, trimer, tetramer, and pentamer

are essentially in coincidence with gas-phase bands. An additional peak in the spectrum shifted further to the red than the pentamer was assigned to the cyclic isomer of the water hexamer. The most compelling support for this assignment comes from comparing the frequency shifts for all of these cyclic complexes with corresponding ab initio and DFT calculations, as shown in Figure 7. In correspondence with the changes in the intra- and intermolecular geometries, the frequency shifts vary smoothly with cluster size n and the cyclic hexamer peak is

precisely where it is expected theoretically. Better agreement with experimental and theoretical values cannot be expected since the theoretical values are based on harmonic frequency calculations. Theoretical methods were mostly helpful in characterizing the measured species clearly as cyclic hexamers. On the other hand, the experimental frequencies support theory. As shown in Figure 7, the calculated frequency shifts can be scaled to the experimental data. Increasing cluster size obviously does not require different scaling factors. The cage isomer characterized in the gas phase^[18] has an intense OH vibrational band, which is shifted further to much lower. It wavenumbers was shown earlier that several calculated local minima^[19] lie lower in energy than the cyclic hexamer. Obviously, the path between this hexamer and the three-dimensional cage structure will involve a great deal of hydrogen bond rearrangement, which is expected to be difficult in liquid helium.

So far, a cage and a quasiplanar water hexamer could be detected experimentally. Both structures were characterized by theoretical methods. Distinct chair and boat conformers of water hexamers do not exist as free species and require a crystal host for stability. Recently, cyclic water hexamers with an icelike chair conformer were found included inside the channels of an organic host.^[22] The average R_{O-O} distance is 2.776 Å. For

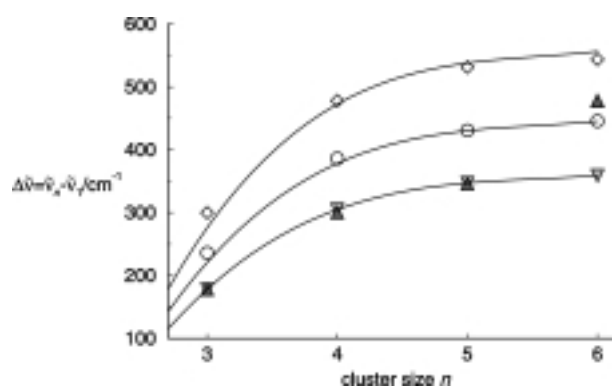


Figure 7. The red-shifted signals of the vibrational spectra of cyclic water clusters from the trimer to the hexamer, $\bar{\nu}_n$, compared to that of the water monomer, $\bar{\nu}_1$, from experimental^[20, 21] (in the gas phase, \blacktriangle ; in liquid helium droplets, \blacktriangledown) and theoretical^[14–16] (DFT at the B-LYP level, \diamond ; MP2, \circ) studies. The shifts are taken in both cases relative to the average of the symmetric and asymmetric O–H stretches of the monomer. The frequency shifts are essentially the same for the data collected in the gas phase and in liquid helium droplets up to the pentamer. The cage hexamer detected in the gas phase is red shifted further than the quasiplanar ring hexamer that exists in liquid helium. The solid curves present a guideline; they are obtained by scaling the fitted experimental curve to the theoretical data.

comparison, the analogous value in ice I_h is 2.759 Å at 183 K. However, there is a wide variation in the value of the angle $\angle(\text{O-O-O})$: With an average of 116.5° it lies considerably far from the value of 109.3° for hexagonal ice. The hexamers are self-assembled by O–H...O hydrogen bonds into extended tapes along the channels, which consist of fused four- and six-membered water rings. The observed inter-hexamer $R_{\text{O-O}}$ value of 2.854 Å is close to the separation of 2.85 Å found in liquid water.^[17] This supramolecular association of water molecules into tapes is presumably enforced by the shape of the host channels, whose relatively narrow openings preclude the formation of more stable, three-dimensional clusters, as found in the gas phase. There are no O–H...N hydrogen bonds between the water tapes and the organic host. Thus, the water clusters can be removed by heating without changing the structure of the host. As opposed to the inclusion complexes of water clusters previously described with strong interactions with the host, the water clusters resemble more closely an environment found in liquid water or ice. IR spectra suggest that

the water tapes are more similar to liquid water than with hexagonal ice.^[22]

In the future, we can expect that larger water clusters with a variety of isomers will be measured and calculated. Results from these studies are yielding important insights into cooperative effects in hydrogen bonding, aqueous solvation, and hydrogen bond network arrangements. There is some promise that we can enhance our understanding of the bulk phase, in particular, of liquid water.

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