



Liquid water: The helical perspective of structure



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ABSTRACT

The structure of water, especially the bulk liquid, is a fundamental question. We show that the infinite network of perfectly tetragonal oxygen atoms in ice I_h can be converted into the helical geometry, retaining the four-fold connectivity but being non-tetrahedral with respect to neighboring oxygen atoms. Thus, liquid water appears as a racemic mixture of *two types* of discrete, helical clusters of water molecules joined tightly together by *two types* of hydrogen bonds, which are very similar in all cluster entities.

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1. Introduction

Despite the importance of water, its anomalous behavior is not yet well understood, and the development of a satisfactory model for liquid water remains a challenge [1]. Experimental structural measurements demonstrate that each water molecule is four coordinated, i.e., satisfies the bulk ice rule [2], and cooperative hydrogen bonding forms the fundamental structure of the three dimensional network of water as a liquid [3]. Understanding the topology of this network over the full phase diagram is crucial for the development of the model [4,5]. At present, there are two well-established alternative and complementary approaches to the problem of modeling water. The Stanley and Teixeira statistical “percolation” model [6] distinguishes only between H-bonded and non-H-bonded water molecules, while Sceats’ and Rice’s continuum model [7] describes water as a fully, hydrogen bonded network. Another approach is Weinhold’s quantum cluster equilibrium (QCE) model [8], which assumes, at defined temperature and pressure, that a chemical equilibrium of a multi-component, molecular mixture of clusters, minimized by ab initio calculations, satisfactorily tests a wide range of thermodynamic properties. Thus, the study of small, neutral water complexes, the so-called cluster approach, holds great promise for obtaining a molecular description of the local structures of bulk liquid and, thereby, better rationalizing the unusual properties of water. For water dimers, hexamers [9], and up to $(\text{H}_2\text{O})_{20}$ (eicosamers) or even more complex systems, these investigations [10] enable tracking of topological changes in the hydrogen bonding of

structural isomers. However, computer simulations of much larger water clusters and aggregates of clusters are unable to resolve the issue at a satisfying ab initio level because of the exponentially increasing numbers of clusters and H-bond configurations with increasing numbers of water molecules. Because of current hardware limitations, ab initio molecular dynamics simulations of liquid water at large volumes would not be able to properly describe the structure of liquid water because of a relatively low level of theory and inadequate basis sets.

The present paper does not establish an accurate account of the molecular behavior responsible for water anomalies. Rather, this analysis provides an alternative approach to the current concepts of the organization of water molecules in the bulk [6,7]. Based on a topologically new class of helical, inherent water structures, we attempt to develop illustrative, helical, eicosamer clusters with water molecules mostly involved in a fully (i.e., four) coordinated environment and, consequently, totally involved in two systems of cooperative hydrogen bonds. From our point of view, the concept of the helical morphology of water clusters attempts to address water’s unusual properties and is perhaps the first step toward the development of a new, realistic molecular model, applicable to bulk and supercooled water.

2. Computational details

In this study, the DFT exchange–correlation functional X3LYP [11], designed to produce an improved description of hydrogen bonds and non-covalent interactions, was chosen because of its high performance for water dimer [11,12], as well as smaller [13] and larger [14] water clusters. Particularly, X3LYP has

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demonstrated its ability to reproduce the stability of eicosamer water clusters in the binding energies, ranking the edge-sharing prism is the lowest energy structure and the face-sharing pentagonal prism is the second lowest energy $(\text{H}_2\text{O})_{20}$ isomer and, moreover, the difference in energy of these structures for X3LYP is 1.6 kcal/mol, compared to 2.4 kcal/mol for the MP2/CBS benchmark [14].

All calculations were performed using Gaussian 09 package [15]. The geometries of all clusters were optimized with Dunning's aug-cc-pVDZ basis set [16] and are expected to correspond to true structure/energy relationships and reduced basis set errors [14]. For the geometry optimization, the optional LOOSE convergence criteria were used, which correspond to an RMS force accuracy of 0.0017 au. Because optimizations for the relatively large and structurally flexible helical eicosamers using larger basis sets are quite expensive, it would be reasonable to calculate reliable energies at a higher level with aug-cc-pVDZ basis set geometries followed by single point energies with the aug-cc-pVTZ. Additionally, single point calculations using the second-order Møller–Plesset perturbation theory (MP2) in the aug-cc-pVDZ basis set were performed for comparison. The effect of basis set superposition error (BSSE) [17,18] correction and zero-point energy (ZPE) [19,20] were also assessed. The self-consistent reaction field (SCRF) technique was used as a polarizable continuum model (PCM) [21] in a simulation of the water continuum at the X3LYP/aug-cc-pVDZ level.

All figures were prepared using the structure editor in the UCSF Chimera visualization system [22,23].

3. Results and discussion

3.1. Helicity

The theory of hydrogen bonding predicts that when water molecules are involved in cluster structures, the equilibrium of polymerization is displaced toward the species with the strongest, i.e., cooperative binding [3]. The regular, space-curved arrangement makes optimal use of hydrogen bonds more readily than many possible water-cluster configurations. In contrast to rings [9], the helix, a tube-shaped aggregation of polymerized water molecules, is a species that enables the full connectivity of oxygen atoms and great, even infinite, cooperative binding. Indeed, the high propensity of small water molecules for hydrogen bonding and the flexibility of hydrogen bonds should favor the formation of clusters that are minimally affected by ligand packing and geometrical constraints of helical types. The helical structure is stabilized by both the “backbone”—cooperative hydrogen bonds wound on the surface of a cylinder, around an imaginary axis inside the helix—and by much shorter outwards chains of hydrogen bonds, cooperative but longitudinally oriented. Strictly speaking, helical type of cluster assembles from a number of single-file water chains or “water wires” [24–28]: the side-by-side association of such repetitive, wire oligomers, rigidified by extra (“backbone”) hydrogen bonds, leads to the formation of a hollow helix. Such helical entities, either right-handed or left-handed, can undergo continuous polymerization (or depolymerization) by the addition (or dissociation) of a water molecule at either end. Thus, temperature-dependent changes of the helical cluster mass through growing or shortening at the ends of individual helices, as well as re-winding to achieve a different handedness or type of helicity, is not difficult to envisage.

There are a few possible helical types [29] anticipated in water polymerization, varying by size, i.e., number of water molecules per turn (k), and number of atoms in a pseudo-ring ($r = 2k$), which is formed by a longitudinal hydrogen bond and a segment of helical

“backbone” (“main-chain”) connecting, neighboring extremities (Fig. 1). The helices in the water clusters presented here are described as right-handed [29] (Fig. 2) because, starting from the first proton-donor molecule of water, consecutive molecules traced out a clockwise relation, moving away from the observer. Complexity arises, in part, from the wide range of helical geometries and the ability of each longitudinal structure to assume a parallel or anti-parallel motif. Thus, for each $(\text{H}_2\text{O})_n$ enantiomeric cluster with motif k , there are 2^k isomers; thus, for the enantiomer set of the 3_6 polymer, there are 8 isomers, while 6_{12} has 64 isomers.

3.2. Tetragonality

The melting of hexagonal ice I_h at 273 K is an endothermic process, with a residual enthalpy of only 1.4 kcal/mol, which corresponds to approximately one-fourth of its hydrogen bonds, per water molecule [1]. This means that the infinitely extending tetragonal ice lattice is reorganized into individual species that conserve the majority of hydrogen bonding in a more limited space. It seems that the helix, due to its spatial curvature, forms a compact sub-lattice that, although it preserves the four-fold connectivity of oxygen in ice, is actually a pseudo-tetragonal network. It should be noted that the four-coordinate structures toward which water molecules tend are not the same as tetragonal structures. Thus, water molecules in a melting I_h ice crystal lose their perfect tetragonal, spatial organization but retain their maximum, four-fold hydrogen bonding. Moreover, although basic tetragonality is not conserved, the curling of water chains into a helix, a more compact species than linear polymeric chains, affords the denser packing of water molecules and the increased coordination number of each oxygen atom. Indeed, we observe the partial reorganization of ice tetragonality: the central oxygen atom migrates and takes its place at the center of a triangular bipyramid, and one of its ligands forms the bipyramidal vertex. As can be seen from Fig. 3, the outward bipyramidal vertex is not occupied but provides considerable room for the extra coordination of an oxygen atom from a water molecule of an adjacent cluster. It is worth remembering that a simple model to account for X-ray data predicts the coordination number N_c to be at least 4.7 [30].

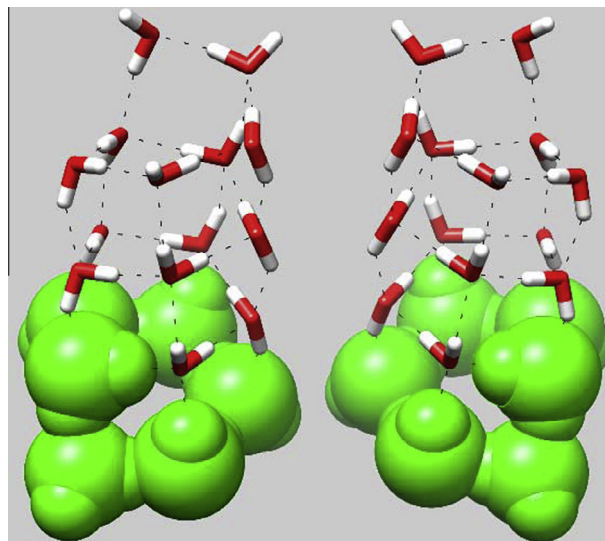


Fig. 1. Mixed, tube and space-filling models of enantiomeric (R)- and (S)- $5_{10}1010$ helical $(\text{H}_2\text{O})_{20}$ cluster. Oxygen atoms (red) and hydrogen atoms (white), hydrogen bonds are shown as dashed lines. Green spheres are used to display the chiral character of five repeating units of the first turn of the helical cluster. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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