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 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.

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 (H$_2$O)$_{120}$ (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
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 (H₂O)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-pVQZ 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-pVQZ 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-pVQZ 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 = 2 k), 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 (H₂O)ₖₐ enantiomeric cluster with motif kₐ, there are 2⁹ isomers; thus, for the enantiomer set of the 3ₐ polymer, there are 8 isomers, while 6₁₂ has 64 isomers.

3.2. Tetragonality

The melting of hexagonal ice Ih 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 Ih 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 Nc to be at least 4.7 [30].

Fig. 1. Mixed, tube and space-filling models of enantiomeric (R)- and (S)-5₁₄₀₁₀₁₀ helical (H₂O)₁₃ 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.)
To assess the effects of different arrangements of water molecules on the structural features of helices ranging from 3\(_6\) to 6\(_{12}\) and, possibly, to describe the deviation from tetragonality, we compare four categories of angles: the \(\text{H} \rightarrow \text{O} \rightarrow \text{H}\) valence bond, the \(\text{L}_\text{p} \rightarrow \text{O} \rightarrow \text{L}_\text{p}\) angle (measured as \(\text{O}(\text{H}) \cdot \cdot \cdot \text{O} \cdot \cdot \cdot (\text{H})\text{O}\)), the \(\text{O}(\text{H}) \cdot \cdot \cdot \text{O}(\text{H}) \cdot \cdot \cdot \text{O}(\text{H})\) angle along the “backbone” of a helix and the longitudinal \(\text{O}(\text{H}) \cdot \cdot \cdot \text{O}(\text{H}) \cdot \cdot \cdot \text{O}(\text{H})\) angle along the twisted edge of a prism. As expected, the average angle between the valence bonds of water molecules involved in helices is nearly intact and ranges from 104.1° to 105.1° (Table S1) (monomer exhibits the angle of 104.8° by these calculations). Surprisingly, the angle between lone pairs in all helical species is almost independent of the helical-shape, ranging from 82.4° to 88.8°, with considerable deviation from 109.47°. Likewise, that the \(\text{O}(\text{H}) \cdot \cdot \cdot \text{O}(\text{H}) \cdot \cdot \cdot \text{O}(\text{H})\) longitudinal arrangement is highly distorted from tetragonality; indeed, the hydrogen bonds align the nearest oxygen atoms, with angles that average is commonly in the range of 171.7–176.9°. It seems that the linearity of hydrogen bonds forces the major rehybridization of oxygen atoms. The structure of the individual helix is probed by observing successive angles along its “backbone”. As a direct consequence of their geometry, the four group isomers, denoted \(3_6\), \(4_8\), \(5_{10}\) and \(6_{12}\) (Fig. 2), can be distinguished by their \(\text{O}(\text{H}) \cdot \cdot \cdot \text{O}(\text{H}) \cdot \cdot \cdot \text{O}(\text{H})\) structural helical angles (on average): 77.7°, 97.0°, 111.3° and 121.6°, respectively.

### 3.3. H-bonds and dipole–dipole interactions

The helical clusters shown in Fig. 2 may be categorized into four classes, based exclusively on the size of the helix, which determines its hydrogen bonding network. The fully cooperative nature of hydrogen bonds restricts the hydrogen bond configurations, defines them, and therefore limits the number of likely candidates. There are two types of distinct, topologically non-equivalent, interdependent sub-networks of cooperative hydrogen bonds: “backbone” and longitudinal. Importantly, hydrogen bond geometries (Table S2) are approximately consistent with the conventional picture of an essentially linear hydrogen bond [31]. The three-dimensional network of hydrogen bonds in a helix is tetragonally distorted but remains flexible enough to enable water molecules to approach each other closely. The average length and angles of hydrogen bonds in \(4_8\), \(5_{10}\) and \(6_{12}\) clusters are similar: 1.81–1.76 Å and >170° (“intact”) [31,32] for “backbone” and ca 1.96 Å and ca 150° (“broken”) [32,33] for longitudinal cooperative chains. The average of longitudinal hydrogen bond length defines the pitch of individual helices and generally, rather little depends on the helix size. For the most stable cluster, i.e., \(5_{10}01010\) [34], “backbone” hydrogen bonds as short as 1.692 Å (178.7°) were found, while the longest hydrogen bond has a length of 1.779 Å (174.3°). Structures of \(3_6\) have hydrogen bonds ca 0.1 Å longer and angles ca 10° sharper than in both \(5_{10}\) and \(6_{12}\) clusters (Table S2), as can be expected, considering their closed-packed assembly. Interestingly, on the basis of natural bond analysis (NBO) analysis, such clusters, linked by extensive hydrogen bonding, can be considered to be connected by extensive but complementary electron delocalization on the surface of the helical structure [35].

The multilateral contacts along the walls of many composed cylindrical helices constitute the assembly of helices and by extension, perhaps, the nano-drop of bulk water [36]. Fig. 4 shows the optimized structure of right-handed 19 mer and 11 mer helical clusters, anti-parallelly oriented along both contacting seams to avoid, at least in the middle of the helix, intercluster hydrogen bonding. Fig. 4 reveals that, although the distance between pairs of close oxygen atoms is 3.2–3.4 Å, the resulting energy of association of 2.2 kcal/mol cannot be attributed solely to van der Waals forces. Apparently, two types of dipole–dipole interactions exist between clusters of self-organizing associates. One is made of long-range, dipole–dipole interactions (parallel or anti-parallel) between the “total” dipole moment of the “central” cluster and the individual dipole moments of each neighboring cluster. The second consists of local dipole interactions between the longitudinal hydrogen bonds connecting the various helices. Thus, we expect that the main force causing the assembly of helical clusters to form tightly associated aggregates is electrostatic but reinforced by van der Waals forces as a mechanism of secondary importance. Notably, hydrogen bonds stabilize the structure of clusters at the lowest level but do not finally lead to the formation of a continuous medium. The “water continuum” with regards to hydrogen bonds, as predicted by the random network of hydrogen bonds theory [7,37], does not exist here.

### 3.4. Energy

Table 1 shows the relative energies of helical 20-mer clusters (eicosamers) in vacuum, which reflect their stability. The
structures have a total of 33–36 “backbone” and longitudinal hydrogen bonds (with a maximum of 40 hydrogen bonds for 20 water molecules). For $4_8$ and $6_{12}$, longitudinal hydrogen bonds have an alternating parallel and anti-parallel topology, but for odd numbers of water molecules per turn, as in $3_6$ and $5_{10}$ species, these structures are either mostly parallel or mostly anti-parallel. As would be expected, the energies of water eicosamers differ moderately within the category, but the energies of two $5_{10}$ structures, calculated in vacuum, differ by approximately 11 kcal/mol despite having the same number of hydrogen bonds, irrespective of the applied calculation method. However, the use of dielectric approximations of the well-known polarizable continuum model (PCM) considerably reduces the energy differences between the helical isomers (Table S9). Therefore, the presented examples are only of illustrative value and, at present, we are not able to indicate the most stable patterns. Bearing in mind the limited accuracy of the computational data and considering the average H-bond energy (Table 1) we conclude that the helical $5_{10}$ and $6_{12}$ structures are energetically favored over $3_6$ and $4_8$ isomers and, thus, preferentially represented in bulk water under standard conditions. These observations support the “two-state-model”, in which the equilibrium of topological isomers $5_{10} \rightleftharpoons 6_{12}$ defines “backbone” and longitudinal hydrogen bonding and thus explains both “a crude sort of isosbestic point at $\sim 1.44 \mu m$ for the [near IR] spectra in the range 0–80 °C” [38]. The Raman isosbestic point, indicative of two state behavior, was also observed [7,32,33].

The propensity of water molecules to form clusters is controlled by the energy gap between the ice and dimer structures. If we assign all the binding energy of ice to H-bonds, we obtain the upper energy limit for the H-bond at 5.85 kcal/mol, defined as the energy of sublimation [39]. The lower limit of the dissociation enthalpy of the water dimer at 4.9 kcal/mol, was established experimentally [39] and is in perfect agreement with the value predicted by the density functional theory (DFT) model [40].

Our model assumes that helices interact via dipole–dipole and van der Waals forces across lateral contacts. The DFT calculations allow prediction of an energy of ca 0.2 kcal/mol per involved longitudinally bonded water molecule. Assuming a net 2 mol of hydrogen bonds/mol of water, ca 0.1 kcal/mol per hydrogen bond is provided by dipole–dipole and van der Waals forces. Taking into account the most stable ($5_{10}01010$) of the considered structures, with a basis set superposition error (BSSE) energy of ca 5.6 kcal/mol (Table 1), we obtain 5.5 kcal/mol, a value close to the experimental energy obtained from melting and sublimation enthalpy of ice (5.6 kcal/mol) [41]. We are aware that real cluster stability in the condensed phase cannot be concluded exclusively on the basis of electronic energy, but needs to consider the factor of vibrational entropy. A short discussion of this aspect is presented in Supporting Information.

### 3.5. Radial distribution

At present, there is no direct proof for the helical structuring of liquid water. As an initial test of this hypothesis, we assessed the oxygen–oxygen radial distribution function (rdf) of pure water [42]. Although the rdf cannot tell much about the higher order of oxygen correlations, it does reveal function irregularities, which can reflect intrinsic, non-nearest neighbor packing effects: the

### Table 1

Relative energies, water and hydrogen bond binding energies (kcal/mol) of eicosamer helical clusters$^a$.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$n_m$</th>
<th>$\Delta E$</th>
<th>$E_{EBSSE}$</th>
<th>$E_{BSSE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3_6010$</td>
<td>36</td>
<td>24.75</td>
<td>-8.92</td>
<td>-4.96</td>
</tr>
<tr>
<td>$4_80101$</td>
<td>34</td>
<td>7.16</td>
<td>-9.80</td>
<td>-5.77</td>
</tr>
<tr>
<td>$5_{10}01010$</td>
<td>34</td>
<td>0.00</td>
<td>-10.16</td>
<td>-5.98</td>
</tr>
<tr>
<td>$6_{12}010101$</td>
<td>33</td>
<td>6.12</td>
<td>-9.85</td>
<td>-5.97</td>
</tr>
<tr>
<td>$4_81010$</td>
<td>35</td>
<td>7.52</td>
<td>-9.78</td>
<td>-5.59</td>
</tr>
<tr>
<td>$5_{10}10101$</td>
<td>34</td>
<td>11.22</td>
<td>-9.60</td>
<td>-5.65</td>
</tr>
<tr>
<td>$6_{12}101010$</td>
<td>34</td>
<td>7.26</td>
<td>-9.80</td>
<td>-5.76</td>
</tr>
<tr>
<td>Dimer</td>
<td>1</td>
<td>-2.56</td>
<td>-5.11</td>
<td>-2.44</td>
</tr>
</tbody>
</table>

$^a$ all geometries were optimized at the X3LYP level of theory using the aug-cc-pVDZ basis.

$^b$ Number of hydrogen bonds in the cluster.

$^c$ $\Delta E$ corresponds to the electronic energy.

$^d$ $\Delta E_{BSSE}$ corresponds to basis set superposition error (BSSE) binding energies.

$^e$ kcal/mol.

$^f$ The binding energy is given relative to twenty fully separated water molecules.

$^g$ Averaged over the number of hydrogen bonds in the cluster.

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**Fig. 4.** Space-filling molecular models of the optimized (X3LYP/aug-cc-pVdz) association of two anti-parallelly arranged right-handed $4_8$(H$_2$O)$_{19}$ and $4_8$(H$_2$O)$_{11}$ helical clusters. With the exception of those ending the clusters, all oxygen atoms are four coordinated and water molecules exclusively form intra-cluster hydrogen bonds. Note the lack of inter-cluster hydrogen bonding in the space between the associate participants.
strongest evidence for any water model. The second broad band of the oxygen–oxygen radial distribution function, which represents the tetragonal coordination of oxygen atoms, has a maximum of 4.5 Å at 4 °C, a weak, local maximum at 3.7 Å and two inflection points at ca. 4.1 Å and 4.8 Å, of which the latter two are best observed at 25 °C and 4 °C, respectively, for D₂O [143].

To estimate the proportion of oxygen–oxygen distances in helical clusters, we provide a graphical representation of the calculated distribution data (Fig. S2). The relatively small discrepancy between pairs of histograms gives us a direct insight into the degree to which the structural data are affected by the topology effects of hydrogen bonding. Obviously, for all clusters, the first peak at 2.8 Å and the first minimum at 3.2 Å are the same as those found in the experimentally determined radial distribution function; however, analysis of oxygen–oxygen distributions within the range of 3.0–4.0 Å, across the set of helical clusters (Fig. S2), shows that the various clusters differ – the maximum of 3.4–3.6 Å for 5₁₀ shifts from lower to greater distances of oxygen pairs, accompanied by a gradual decrease in intensity with increasing helical size. Despite this, helical clusters 5₁₀ and 6₁₂, predicted to be present in liquid water (vide supra) (Fig. S2), show a sufficient number of adjacent oxygen atoms, which range from 3.4 to 4.0 Å, to appreciably contribute to the distinctive feature of experimental distribution function at 3.7 Å. This cannot be explained by tetragonal coordination and thus proves the concept of individual helical features forming the structural components of liquid water. Astonishingly, calculated distributions of helical clusters in 5₁₀ and 6₁₂ above 4.0 Å are also in fair agreement with the observed inflexion points at the lower and upper ends of the 4.0–5.0 Å range [42].

The functions gOH(r) and gHH(r) are even more stringent tests of the helical model for liquid water. The histograms of oxygen–hydrogen distances for a complete set of clusters are plotted (Fig. S2). The distinct peak at 1.86 Å for the O–H pair distribution function [44] is represented by distances of ca. 1.7–2.0 Å at the short-distance end of the histogram. The apparent peak at 3.3 Å, present in the experimental function [44], is related to the 3.0–3.6 Å O–O distribution in 5₁₀ and 6₁₂ clusters, but an inflexion point at 2.6 Å and minor peak at 4.2 Å have no counterpart in the radial distribution function. However, assuming some level of inter-cluster ordering, these differences may be due to contributions from the lateral interactions of pairs of O–H atoms belonging to adjacent clusters. Surprisingly, an excellent agreement is found between the H–H neutron rdf and 5₁₀ and 6₁₂ histograms. The major peak at 2.3 Å, peak at 3.8 Å and a broad peak at 4.6 Å correspond to the ranges of 2.2–3.0 Å, 3.6–4.2 Å and 4.6–4.8 Å, respectively, for H–H distances in the 5₁₀ and 6₁₂ clusters.

3.6. X-ray spectroscopy and scattering

Further evidence for the helical alignment of water molecules comes from non-resonantly excited X-ray emission spectroscopy (XES) spectra [45, 46] of the gas phase, liquid and ice, interpreted in terms of two different H-bonding motifs in liquid water. The splitting of the 1b₁ peak, its changes with varying temperature, and the comparison with gas phase and ice spectra allows assignment of the low energy component to tetrahedral species and the high-energy fragment to distorted H-bonding [47]. On the basis of our helical model, we can give a definitive assignment in terms of H-bond coordination: low-energy species correspond to “main-chain”, almost linear H-bonding, while high-energy corresponds to longitudinal cooperativity. The transfer of intensity with increasing temperature [47] may indicate weakened longitudinal H-bonding and, therefore, the increase of the helical pitch value and consequent extension of the helical cluster along the axis. Both linear and distorted H-bond components are structurally integrated in each cluster. This result does not exclude an equilibrating mixture of helical clusters of different sizes, topologies and chiralities.

This interpretation also applies to the Wernet et al. [48] experiment related to the structure of the first coordination shell and explains why, upon heating, some water molecules change from a tetrahedral H-bonding not to a less coordinated environment but, rather, a less bonded one. Indeed, bearing in mind that the minimum H-bond parameters are necessary to account for experimentally observed XAS pre- and main-edge intensities [48], some H-bonds likely do not fulfill the criteria at elevated temperature (the average values calculated for 5₁₀ and 6₁₂ are 2.87 Å for O–O distances and Ω = 26.6° for H-bond angles, with interpolated minimum XAS values of 2.87 Å and 24°) (Ref. [48] Suppl.). This result strongly suggests that a water molecule is, in fact, asymmetrically bonded by one strong and one weakened (but not broken) donor H-bond. It is important to note that the isosbestic point measured by X-ray absorption spectroscopy (XAS) [48] at 538.8 eV, as well as that by X-ray Raman scattering spectroscopy (XRS) [48], again strongly supports the two different components of H-bond coordination.

Two types of hydrogen bonds, related to different local configurations, were observed via inelastic coherent neutron scattering (IINS) for low density amorphous (LDA) ice, suggesting a structural similarity to liquid water [49]. It should be stressed that bimodal hydrogen bonding, i.e., two different strengths of H-bonds, was established even for highly symmetric structures of ice Ih, but it is difficult to accept that random distribution throughout the lattice exceeds the propensity for the formation of infinite chains of hydrogen bonds [49].

4. Conclusions

A general hypothesis for the microstructure of water is the idea of helical clusters as the main constituents, determining water’s unusual properties. The transformation of the ice lattice into a mixture of 5₁₀ and 6₁₂ helical species, with major modifications to the tetragonality but conservation of the four-fold coordination and effective hydrogen bonding, may explain the latent heat of melting. The same structural reasoning explains the increase in density upon the melting of ice at 273 K and the density of water at 277 K. It is evident that the equilibrium of dense 5₁₀ and light 6₁₂ species could correspond to the maximum density encountered by liquid water under atmospheric pressure. Thus, it is not surprising that, under the extremely high pressure of 3000 bars [50] or more, water behaves as a standard liquid – the equilibrium is completely shifted toward the higher-packed 4₈ and 3₈ structures or simply to the most stable 3₈ structure, and the anomalous behavior vanishes. As explained above, the substantial orbital rehybridization of the sp³ oxygen atom, leading to an increase of the coordination number to 4.7 [30], is a natural consequence of a denser species. Special attention must be paid to the liquid–liquid critical point (LLCP) hypothesis [4, 5], which propose two forms of ice: LDA ice [51] and high density amorphous (HDA) ice [52], interpreted as the stable structures of arrested low density (LDL) and high density (HDL) water [53], respectively. Similarly, in our scenario, at normal P for both the ambient and the supercooled regimes, 5₁₀ and 6₁₂ clusters are in equilibrium on both sides of the L–L Widom line [5, 46]. We speculate that the very slow freezing of water exclusively transforms super-cooled mixtures of 5₁₀ and 6₁₂ helices of limited lengths into more stable, less dense 6₁₂ helices (or even the thermodynamically stable, individual 6₁₂ helix) i.e., into the LDL water phase [54]. Then, the decreasing density of super-cooled liquid is observed (0.9999 g/cm³ to 0.9775 g/cm³ from 273 K to 239 K, respectively) [55] and, being racemic, the mixture of near-infinite left-handed and right-handed, disordered, topologically invariant 6₁₂ polymers forms glassy water, i.e., LDA ice. If so, the
structurally similar ice \( I_h \) and LDA ice must have similar densities of 0.917 and 0.920 g/cm\(^3\), respectively [56]. Similarly, HDA ice is also experimentally obtained at high \( P \) from either LDA ice or ice \( I_h \). In this approach, HDA ice represents a super-molecular associate.

In summary, the melting of ice at 273 K is most likely related to the weakening of temperature-sensitive tetrahedral correlations between nearest neighboring water molecules and possibly causes the major loss of tetragonality (cf. Ref. 57). In liquid water, directional hydrogen bonds still control the formation of individual, or 48 \( H_2 \) associates.

References

[22] Chimera (v.1.9), Resource for Biocomputing, Visualization, and Informatics; University of California, San Francisco, CA, 2014.
[29] Abbreviations and symbols for the description of the conformation of polypeptide chains <http://www.chem.qmul.ac.uk/iupac/>.
[34] G010 notation means antiparallel (0) or parallel (1) direction to the helix axis of the consecutive longitudinal hydrogen bonds pattern, starting from the first proton donor water molecule of the helix main-chain.