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Chirality Properties of Modeling Water in Different Aqueous Systems

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Abstract

The research addresses the problem of chirality existence in modeling water with various impurity molecules using new numerical algorithm of chirality determination. It is based on asymmetry analysis of molecular system composed of water molecules. The following molecular systems are investigated: (1) small water clusters such as $(\text{H}_2\text{O})_n$, $\text{K}^+(\text{H}_2\text{O})_m$, and $\text{Na}^+(\text{H}_2\text{O})_m$ ($n = 4\div 8$, $m = 5\div 10$) at temperature 1 K; (2) $(\text{H}_2\text{O})_n$, $\text{K}^+(\text{H}_2\text{O})_p$, and $\text{Na}^+(\text{H}_2\text{O})_p$ ($n = 4\div 9$, $p = 5\div 8$) at temperature 300 K; and (3) chiral biological molecules of L-valine, D-valine, L-glycerose, and D-glycerose and left or right water clusters $(\text{H}_2\text{O})_4$ with water molecule's shell with thickness varied from 4 to 14 Å with a step of 2 Å. The systems (1), (2) are investigated by Monte Carlo method and the interaction is simulated with Poltev-Malenkov potentials. Systems (3) are initiated using Solvate software, and then aqueous systems are optimized by the conjugate gradient algorithm using the MMFF94 potential. It is revealed that there is no predominance of right-handed or lefthanded substructures in all studied configurations of water molecules. But in small aqueous systems (2), (3), the number of types of water structures, taking into account chirality, depends on the presence of impurity ion and its type.

Keywords: chirality, water structure, small water clusters, biological molecules, numerical simulation, computer modeling, Monte Carlo procedure, Poltev-Malenkov potential, MMFF94 potential, conjugate gradients

1. Introduction

Chirality is the structural characteristic of molecules, which determines their physical, chemical, and biological properties. Chiral molecules differ not only in properties associated with rotation of the polarization plane for plane-polarized light but also in being involved in processes of metabolism and catabolism and also in pharmacological activity [1]. Besides, the presence of some chiral impurity allows one to control chemical reaction and to change its rate [2] and also influences the twisting abilities of nematic liquid crystals [3].

In biological systems, fundamental role is played by homochirality of chiral compounds, such as amino acids, phospholipids, sugars, etc. This property influences formation of macromolecular prebiological systems [4–6].

Thus, the research of chirality is important for many areas of science. Since biologically significant molecules and ions are typically surrounded by water environment, the analysis of their possible influence on chiral properties of model water systems is of vital importance. However, the problem of chiral properties of model water systems received little attention in scientific literature because of its complexity.

For simplicity, we will consider only protium water molecule $^1\text{H}_2^{16}\text{O}$ (H_2O), without her ortho- and paraomers.

Any molecule can be either symmetric or asymmetric. Chirality is a special case of asymmetry when the molecule does not coincide with its mirror image. For assessment of symmetry of a molecule, it can be likened to a geometrical Figure.

Properties of symmetry of geometrical figures are characterized by operations of symmetry and symmetry elements, which can be expressed in five possible types of symmetry elements of acyclic figures [7–15]: axis of rotation (C_n), axis of rotation inversion (S_n), identical transformation (E), symmetry plane (σ), and center of inversion (i).

Water molecule possesses an axis of symmetry passing through the center of oxygen and the midpoint between two hydrogen atoms. Therefore, a single H_2O molecules has no chirality. Only a structure formed by the H_2O molecules by means of hydrogen bonds can possess chirality. For the analysis of chirality of water system, it is possible to present its structure in the form of a geometrical figure with centers of oxygen atoms depicted by vertices and hydrogen bonds between the H_2O molecules represented by edges. But the structure of liquid water is not rigid and permanent; therefore the search of symmetry elements or classification to a certain group of symmetry is relevant only for concrete water configuration, but not for water system in general.

Molecules can be not only classified as being chiral and achiral but they can be also distinguished by the chirality type. According to what element, addition makes a molecule chiral; the following types of chirality exist [16]: (1) central (center of chirality), (2) axial (chirality axis), (3) planar (chirality plane), (4) spiral (spiral), and (5) topological.

For the molecule to possess central chirality, it here must contain an asymmetric atom of carbon or such atoms as Si, P, S, or (less frequently) N.

The axial chirality arises because substituting groups do not belong to one plane with respect to some axis. This type of chirality is observed in allenes, where substituting group belongs to perpendicular planes. Similar situation is observed also in substituted biphenyls, in which the rotation about the bond connecting aromatic rings hindered, and also in spirocyclic compounds [17, 18].

The spiral chirality is observed in molecules with spiral location of the elements with respect to each other. This type of chirality is observed in proteins and nucleic acids.

Besides, there are L- and D-configurations of amino acids, hydroacids, and carbohydrates. Historically glyceric aldehyde was chosen as a reference. Glyceric aldehyde configuration rotating the polarization plane to the left is denoted as L, and its dextrorotatory enantiomer as D. Other structures are assigned to L- or D-row according to comparison with the reference [19].

The above-stated classification according to chirality type is not applicable to model water systems due to their low atomic variability in the absence of impurities and also due to large flexibility of the formed configurations. Conventional concepts of L- and D-configurations are applicable only for the chiral compounds containing carbon. Therefore they cannot be used for model water systems containing only the H_2O molecules. Also, it is impossible to determine chirality by searching the symmetry elements, for example, using the V.I. Sokolov classification tree [20] for such complex, but at the same time, homogeneous by the atomic structure, structure as water system.

The available methods of molecule chirality assessment are based on its comparison with its mirror image obtained by operations of symmetry. Distances between similar atoms are used for calculation of chirality degree. The main drawback of such methods is ambiguity in matching between atoms of the original molecule and its image if identical atoms are present. All available methods allowing comparison of structures according to chirality and its sign are not applicable for systems with flexible structure. The water system contains hydrogen bonds with variable lengths and angles, which fall into one structural type. Therefore, in this case these methods are inapplicable. The methods based on search of symmetry elements do not allow to distinguish chiral structures with opposite sign of chirality; therefore they are not applicable to model water systems. Simplex representation allows analysis of the systems containing not less than four various structural elements. However, the water system without impurity does not possess such variety of atomic structure. Model water system consisting only of water molecules has only one structural element—the H_2O molecule. Therefore, the method of simplex representation is not suitable for studies of chirality of such systems.

For the analysis of chirality of model water structures, it is necessary to take into account the variability of the hydrogen bond grid, the presence of only two kinds of atoms, and also the directed nature of hydrogen bond. Besides, the method has to allow classification of ambidextral water clusters, that is, their sign of chirality is to be determined.

The chirality sign can be determined not only for carbon-contained compounds (e.g., organic) but also for structures with helicoid shape. They can be divided into right and left. Molecules of water are connected with each other by hydrogen bonds having asymmetry with respect to donor or acceptor oxygen of two H_2O molecules. Therefore this bond is directional. Therefore, the sequence of connected water molecules will have some joint direction of twist. Model of water system can be presented in the form of a connected grid of hydrogen bonds or a set of groups of such grids, for each of which it is possible to allocate twist elements. If we search in water system elements of twist, each of them can be classified as left or right twist element; then it is possible to reveal the prevailing direction of elements of twist. Using this approach, it is possible to analyze chirality of instant configurations of model water systems. In this case, the minimal object to determine an element of twist is water cluster $(\text{H}_2\text{O})_4$ which does not contain water molecules without hydrogen bonds. Respectively, in the case of the system which is in gas phase, this cluster can be absent. Therefore, chirality properties of such model water system cannot be determined on the basis of the approach described above. Therefore, before analysis of chirality properties of a system, it is necessary to study its structure. It is especially necessary when it is required to compare two water systems or their instant equilibrium configurations. Before comparison of chirality properties of two configurations, it is useful to find out whether they have similar structure.

2. Methodology

2.1 Method to determine structure types of water configurations

Comparison of the structures of two model water systems involves two important problems:

1. The order of numbering of atoms and molecules for each system can be arbitrary; therefore for systems with large number of particles, the description

of their structure via properties of each particle bonds does not allow to carry out the comparative analysis of structural properties of two systems.

2. Average characteristics of structure do not represent its local features.

A technique has been proposed [21, 22] to solve these problems. It involves analysis of the structure of hydrogen bond grid for each hydrogen-connected figure (a group of water molecules connected with hydrogen bonds) in a configuration of model water system according to the theory of graphs. It allows finding exact correspondence between each H₂O molecule in one configuration and the same molecule in other configuration if their types of structure are identical. Also it allows to reveal all unique types of hydrogen bond grids structures, which are formed during thermal motion (except for chirality effect), and to calculate weight coefficients of their occurrence in sampling set. The approach is suitable for small clusters but demands essential computational power already for a system composed of more than 12 H₂O molecules.

To reduce the computational time, the search of correspondence between molecules of two configurations was later abandoned; instead an individual code was assigned to each analyzed configuration [23]. Thus, the properties characterizing structure of a configuration are described by a single integer number. It is composed of codes of the three following matrices:

- The matrix “T1” characterizes number of hydrogen bonds of each molecule of water of a cluster and types of atoms through which the considered molecule is connected with this hydrogen bond (hydrogen-connected figures are investigated composed of water molecules, which are within the first coordination sphere (FCS) of each water molecule in the system).
- The matrix “T2” characterizes which water molecules are connected with hydrogen bonds and through which hydrogen atom (hydrogen-connected figures are investigated composed of water molecules, connected with each H₂O molecule via its hydrogen atoms).
- The matrix “T3” characterizes which water molecules are connected with hydrogen bonds and through which hydrogen atom—within the first coordination sphere (hydrogen-connected figures are investigated composed of water molecules, which are within the first coordination sphere (FCS) and connected with each H₂O molecule via its hydrogen atoms).

To describe the structure of a water cluster configuration, the codes of all three matrices “T1”, “T2”, and “T3” are written sequentially in the combined code as follows:

0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
“T1”									“T2”									“T3”									

If the combined codes of two various configurations coincide, they are attributed to one structural type (i.e., they have identical structure); otherwise they are attributed to different structural types (i.e., their structures differ). To calculate the codes of abovementioned matrices, tables are to be completed. Initially, all the table cells contain zeros.

However, the practice of using the technique [23] revealed several configurations having various structures, for which identical combined code is assigned. Therefore this technique is modified, its description being given below.

2.1.1 Description of matrix “T1”

The code of matrix “T1” has fixed dimension— 1×10 (1 row and 10 columns). Columns 1–4 contain information on hydrogen bonds of oxygen atoms of water molecules belonging to the cluster. Columns 5–7 and 8–10, respectively, contain information on hydrogen bonds of the first and second hydrogen atoms of water molecules belonging to the cluster.

For each molecule, every bond is registered as a separate row. Each cell of a row, except columns 4, 7, and 10, contains either zero (“0”) in the absence of hydrogen bond or one (“1”) if bond is present. For oxygen atom of each molecule, 4 columns (1–4) are provided. In case the molecule has only one bond via oxygen atom, “1” is assigned only to column 1; if there are two bonds, “1” is assigned to columns 1 and 2; if there are three bonds, to columns 1, 2, and 3; and in the case of four and more bonds, the first three bonds are represented in columns 1–3 and all the others in column 4. If the molecule has bond via its first hydrogen atom, values are assigned to columns 5–7. In the case of one bond via the first hydrogen atom, “1” is assigned only to column 5; in the case of two bonds, “1” is assigned to columns 5 and 6; if there are three and more bonds, the first two bonds are represented in columns 5 and 6; and the others in column 7. For bonds via the second hydrogen atom, columns 8–10 are similarly completed. As a result, we obtain the complete table. The example for a cluster of $K^+(H_2O)_6$ is presented in **Table 1**.

The first molecule of this cluster is connected with hydrogen bond via its first hydrogen atom; therefore “1” is assigned in the first row to column 6 (**Table 1**). The second molecule has one hydrogen bond via oxygen atom; therefore “1” is assigned in the second row to column 2. Similarly the table is completed for the third, fourth, and fifth molecule. The sixth molecule has two hydrogen bonds via the oxygen atom; therefore “1” is assigned in the sixth row to columns 2 and 3. Then the values in each column of **Table 1** are summarized. Thus, in our case, code of matrix “T1” is composed of the 10 following numbers: 3, 1, 0, 0, 4, 0, 0, 0, 0, 0, that is, 3 1 0 0 4 0 0 0 0 0 (see **Table 1**).

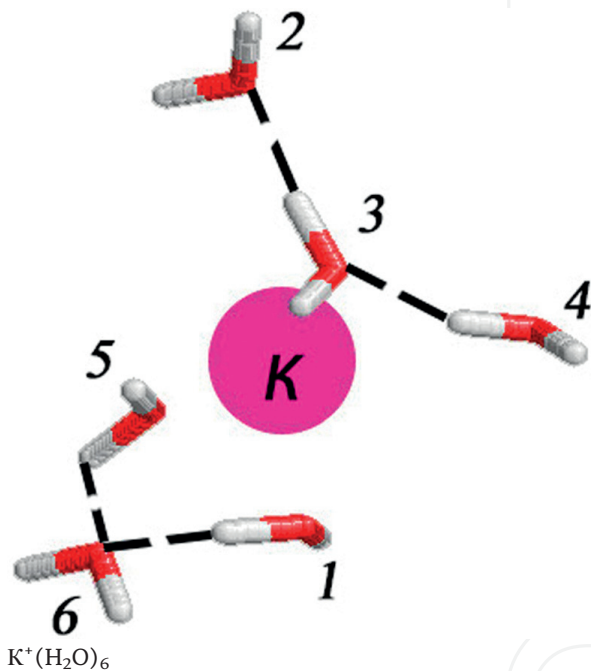
2.1.2 Description of matrix “T2”

The matrix “T2” has fixed dimension 1×8 (one row and eight columns). Completion of cells of this matrix is made sequentially implementing four independent methods:

1. The method of chains fills cells in columns 1 and 2 of matrix “T2”.
2. The method of reconsiderations fills cells in columns 3 and 4 of matrix “T2”.
3. The method of deadlocks fills cells in columns 5 and 6 of matrix “T2”.
4. The method of cycles fills cells in columns 7 and 8 of matrix “T2”.

2.1.2.1 Method of chains

An example of completing the table for $K^+(H_2O)_6$ cluster (see **Table 1**) is presented in **Table 2**. The principle is different in comparison with matrix “T1”.



	1	2	3	4	5	6	7	8	9	10	11
No of molecule	No of column of matrix "T1"										
	1	2	3	4	5	6	7	8	9	10	
1	0	0	0	0	1	0	0	0	0	0	
2	1	0	0	0	0	0	0	0	0	0	
3	1	0	0	0	1	0	0	0	0	0	
4	0	0	0	0	1	0	0	0	0	0	
5	0	0	0	0	1	0	0	0	0	0	
6	1	1	0	0	0	0	0	0	0	0	
Total	3	1	0	0	4	0	0	0	0	0	0

**Hereinafter in all tables, numbers in the very first line of the table denote numbers of columns.*

Table 1.
Table of matrix "T1".

1	2	3	4
No of initial molecule	No of the subsequent molecule in the chain	H ₁	H ₂
1	6	0	0
2	0	0	0
3	2	0	0
4	3	1	0
	2	0	0
5	6	0	0
6	0	0	0
Total		1	0

Table 2.
Method of chains result.

Each molecule of a water cluster is considered as initial for a chain of water molecules. Next molecule can be added to the chain only if it is connected with a molecule from the chain via its oxygen atom.

The first column (see **Table 2**) contains number of the initial water molecule for each chain. Note that it is assigned only once and no more values are written to column 1 until the beginning of the next considered chain.

The second column contains numbers of the subsequent molecules from the chain. If water molecule, which is considered as initial, has no hydrogen bonds, then its number is assigned to the first column, and all other columns in this row are filled with a “0” symbol. Then the next H₂O molecule is considered.

It is possible that the subsequent water molecule in the considered chain does not have hydrogen bonds via hydrogen atoms; then the “0” symbol is assigned to the third and the fourth columns. In the case of one hydrogen bond, the third column is filled with “1”, and the fourth column contains “0”. In case both hydrogen atoms of the subsequent molecule in the chain are involved in hydrogen bonds, “1” is assigned to the third and fourth columns.

In the case of chain branching (both hydrogen atoms of the subsequent molecule of the chain are involved in hydrogen bonds), first the “branch” with the smallest serial number of the subsequent molecule is considered. When all the molecules in the considered branch have no more hydrogen bonds via hydrogen atoms, consideration comes back to the branching point, and second “branch” of the chain is similarly analyzed.

If the considered chain forms a closed loop, then consideration finishes when the number of the subsequent molecule coincides with the number of initial molecule of the chain. Note that in this case the initial molecule is not registered in the second column as a subsequent molecule.

Finally, the sum of the cells of column 3 of **Table 2** is assigned to the cell 1 of matrix “T2”. The sum of the cells of column 4 of **Table 2** is assigned to the cell 2 of matrix “T2”. The code of matrix “T2” for K⁺(H₂O)₆ cluster (see **Table 1**) takes the following form: 1 0 0 0 0 0 0.

More illustrative example of method of chains in the case of configuration with large number of branching points is presented in **Table 3**.

Search begins from molecule 1. It is connected via hydrogen atom only with molecule 3, which is reflected in the second column. Water molecule 3 has two bonds; therefore “1” is assigned to the third and fourth columns. Then, bond between molecules 3 and 4 is considered since 4 < 5. Molecule 4 has no bonds via

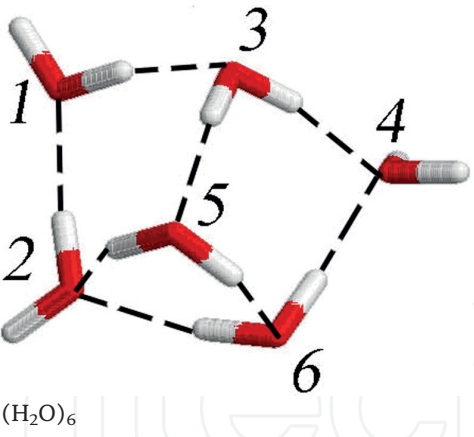
 (H ₂ O) ₆	1	2	3	4
	No of initial molecule	No of the subsequent molecule in the chain	H ₁	H ₂
1		3	1	1
		4	0	0
		5	1	1
		2	1	0
		6	1	1
2		1	1	0
		3	1	1
		4	0	0
		5	1	1
		6	1	1
3		4	0	0
		5	1	1
		2	1	0
		1	1	0
		6	1	1
		4	0	0
4		0	0	0
5		2	1	0
		1	1	0
		3	1	1
		4	0	0
		6	1	1
		2	1	0
6		1	1	0
		3	1	1
		4	0	0
		5	1	1
		4	0	0
Total			23	13

Table 3.
Method of chains result for cluster (H₂O)₆.

hydrogen atoms; therefore the third and fourth columns contain zeros. Next, bond between molecules 3 and 5 is considered. Molecule 5 has two bonds: with molecules 2 and 6. First, we pass to molecule 2 possessing one bond with molecule 1, which is the initial molecule of the chain; therefore it is not registered in the second column.

Then, from molecule 5 we pass to molecule 6, which is connected with molecules 2 and 5, but these molecules are already taken into account in the considered chain. Hence, consideration of the chain, beginning from molecule 1, finishes with molecule 6.

Next, consideration of a chain with initial molecule 2 begins. It is connected only with molecule 1, which, in turn, has only one bond with molecule 3. Molecule 3 has two bonds: with molecules 4 and 5. Therefore, we consider molecule 4, which does not have hydrogen bonds via hydrogen atoms. Therefore, from molecule 3 we pass to molecule 5, connected with molecules 2 and 6. Molecule 2 is not considered since it is the initial molecule of this chain, so we consider only molecule 6, possessing two bonds. But molecule 2 is not considered since it is the initial molecule of the chain, and molecule 4 was already considered. Thus, consideration of this chain comes to an end.

Next, we consider the chain, beginning from molecule 3. It has two bonds; therefore the branches beginning from molecules 4 and 5 will be considered separately. The branch, which begins from molecule 4, contains only one molecule (4), since molecule 4 has no bonds via hydrogen atoms. Then, we consider the branch beginning from molecule 5, which has two hydrogen bonds via hydrogen atoms. First, we consider molecule 2, connected only with molecule 1. Molecule 1 is connected with molecule 3, but since consideration of the chain began from molecule 3, it is not registered in the second column of **Table 3**. Next, we pass from molecule 5 to molecule 6, which has two bonds via hydrogen atoms. Molecule 2 is not considered since it was already taken into account within the branch beginning from molecule 5, whereas molecule 4 is considered since it was considered within other branch. Consideration of this chain finishes with molecule 4 since it has no hydrogen bonds via hydrogen atoms.

The chain beginning from molecule 4 is empty since there are no molecules, bonded to molecule 4 via its hydrogen atoms.

The chain beginning from molecule 5 has two independent branches growing from molecules 2 and 6. First, we consider the branch beginning from molecule 2. It is connected bonded only to molecule 1. From molecule 1 we pass to molecule 3, which has two hydrogen bonds via hydrogen atoms. First, we consider the deadlock molecule 4. Molecule 5 is not considered since it is the initial molecule of this chain. Now we consider the branch beginning from molecule 6, which has two hydrogen bonds via hydrogen atoms. First, we will consider molecule 2. Such consideration is possible since molecule 2 was already considered but within other branch beginning from it. Next, we pass to molecule 1 and then to molecule 3. First, we consider the deadlock molecule 4, and consideration of molecule 5 is impossible since it is the initial molecule of the chain. We come back to molecule 6, but consideration of molecule 4 became impossible since it has been already considered within this branch of the described chain.

The chain, which begins from molecule 6, also has two independent branches, growing from molecules 2 and 4. First, the branch from molecule 2 is considered. It is connected only with molecule 1. From here we pass to molecule 3, possessing two hydrogen bonds via hydrogen atoms. Next, molecule 4 is considered, which is not bonded to other molecules via hydrogen atoms. Then we pass to molecule 5. From here we can pass neither to molecule 2 since the considered branch begins from it nor to molecule 6 since it is the initial molecule of the chain. Consideration of this branch comes to an end. Now we pass to consideration of the branch beginning from molecule 4, which is deadlock. Therefore, consideration of this chain is finished.

As a result of method of chains implementation, the total value of cells of column 3 in **Table 3** is assigned to column 1 of matrix "T2". Total value of cells of

column 4 in **Table 3** is assigned to column 2. The code of matrix “T2” is determined: 23 13 0 0 0 0 0 0.

2.1.2.2 Method of reconsiderations

An example of completing the table for cluster $(\text{H}_2\text{O})_6$ (a) using method of reconsiderations is presented in **Table 4**. It is required since there are structural types of water clusters, which do not differ according to method of chains with taking into account matrix “T1.” **Table 4** provides example of two clusters (a) and (b), which have different structures but are not distinguished by the codes of matrix “T1” and matrix “T2” if only method of chains is used. In fact, codes of matrices “T1” and “T2” are identical for both clusters: “T1”: 6 1 0 0 6 0 0 1 0 0 and “T2”: 33 5 0 0 0 0 0 0.

To distinguish clusters with such complex structure (see **Table 4**), it is required to develop and apply one more method—the method of reconsiderations. It implies reconsideration of already considered molecule(s) for the analysis of water molecule chain beginning with one of the H_2O molecules in a cluster connected by hydrogen bonds via atoms of hydrogen. Only the molecules meeting the following condition are reconsidered: not less than two water molecules must exist in the analyzed chain, which are directly connected to each other and to reconsidered molecule(s) via hydrogen atoms and have identical number of hydrogen bonds via hydrogen atoms with water molecules. First, the quantity of molecules of N meeting this condition, which go before the reconsidered water molecule in the chain, is determined. Then, a chain of water molecules beginning from one of this molecules is constructed. In each direction of formation of hydrogen bonds via hydrogen atoms of this molecule, N-1 water molecules subsequently connected by hydrogen bonds via hydrogen atoms are considered as described below. First, one of the reconsidered molecule is considered (if $N-1 \geq 1$); next, from this molecule of N-2 of steps are made (if $N-2 \geq 1$): at the first step, all molecules connected to reconsidered molecule(s) via oxygen atoms are considered; at the second step, all molecules connected to neighbors of reconsidered molecule(s) via oxygen atoms are considered, etc.

Information obtained using method of reconsiderations is added to **Table 4** as follows: number of water molecule preceding the repeated molecule is assigned to column 1. The sequence of water molecules numbers in the chain, starting with number of the reconsidered molecule is written to column 2. Columns 3 and 4 are completed similarly to columns 3 and 4 of **Table 3** for method of chains.

For example, cluster (b) (**Table 4**) does not contain molecules meeting the condition of application for method of reconsiderations, whereas cluster (a) does.

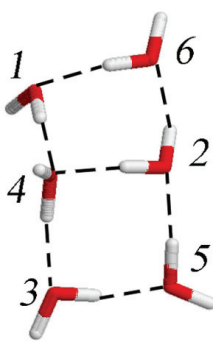
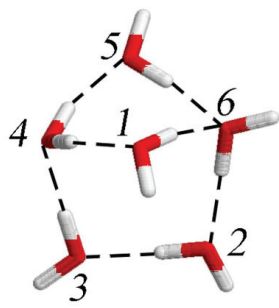
		1	2	3	4
		No of the molecule preceding the reconsidered molecule	No of reconsidered molecules	H ₁	H ₂
	a) $(\text{H}_2\text{O})_6$	1	4	1	0
		1	4	1	0
		Total		2	0
	b) $(\text{H}_2\text{O})_6$				

Table 4.
The method of reconsiderations corresponding to (a) left cluster $(\text{H}_2\text{O})_6$. Right cluster $(\text{H}_2\text{O})_6$ – (b).

Beginning consideration of cluster (a) from molecule 3, the following chain is formed: 3, 5, 2, 4, and 6; then after molecule 6, molecule 1 is considered, and after molecule 4—molecule 3, but this is the initial molecule of the chain. Further, after molecule 1 we consider molecule 4, but it has already been considered in this chain and can be reconsidered molecule. It is preceded by two molecules (1 and 6) both having one hydrogen bond via hydrogen atoms, that is, $N-1 = 2-1 = 1$. Thus, one step should be made from molecule 1 toward the reconsidered molecule. The chain beginning from molecule 5 is considered similarly.

Eventually, the total value of cells of column 3 in **Table 4** is assigned to column 3 of matrix “T2”. Total value of cells of column 4 in **Table 4** is assigned to column 4 of matrix “T2”. After application of method of reconsiderations, the code of matrix “T2” for cluster (a) will be 33 5 2 0 0 0 0 0 and for cluster (b) 33 5 0 0 0 0 0 0.

2.1.2.3 Method of deadlocks

An example of completing the table for cluster (a) $(H_2O)_6$ using method of deadlocks is presented in **Table 5**. This method is required because if the considered water molecule does not possess hydrogen bonds via hydrogen atoms, it is described by zero values: 0, 0, written in columns 3 and 4 of the table using methods of chains and reconsiderations. Therefore, such deadlock molecule does not make contribution to the value of matrix “T2”. Thus, clusters which differ only in the position of deadlock, water molecule cannot be distinguished by methods of chains and reconsiderations. **Table 5** presents an example of two clusters, which have different structures, but identical codes of matrices “T1” and “T2” are determined using only methods of chains and reconsiderations: “T1” is 6 0 0 0 4 0 0 2 0 0 and “T2” is 12 6 0 0 0 0 0 0. Therefore, the method of deadlocks is developed and applied. It is similar to method of reconsiderations, but the steps are made from a deadlock water molecule via molecules, connected with the preceding ones via hydrogen atoms.

For example, cluster (a) in **Table 5** contains two deadlock molecules—water molecules 3 and 6. The method of deadlocks for this cluster is applied three times and only for molecule 6 since it is preceded by two molecules with identical number of hydrogen bonds via their hydrogen atoms—molecules 1 and 2. Molecule 3 is preceded by molecules with different numbers of hydrogen bonds via hydrogen atoms: molecule 2 has two hydrogen bonds, and molecule 5 has only one. The first time method of deadlocks in **Table 5** is applied for cluster (a) to consider the chain beginning from molecule 2: after molecule 2 molecule 1 is considered and then molecule 6, which is deadlock, so its number is assigned to column 1 of **Table 5**. It is

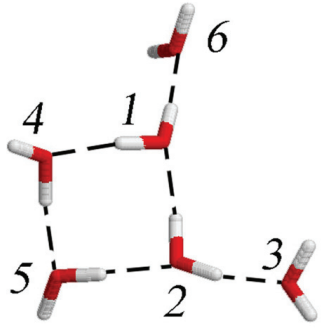
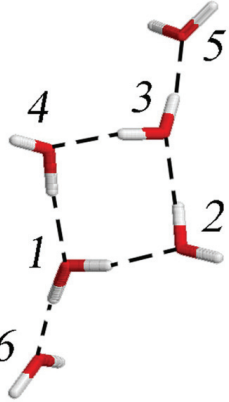
 a) $(H_2O)_6$	1	2	3	4
	No of deadlock molecule	No of preceding molecule	H ₁	H ₂
	6	1	1	1
	6	1	1	1
	6	1	1	1
Total			3	3
 b) $(H_2O)_6$				

Table 5.
The method of reconsiderations corresponding to (a) left cluster $(H_2O)_6$. Right cluster $(H_2O)_6$ – (b).

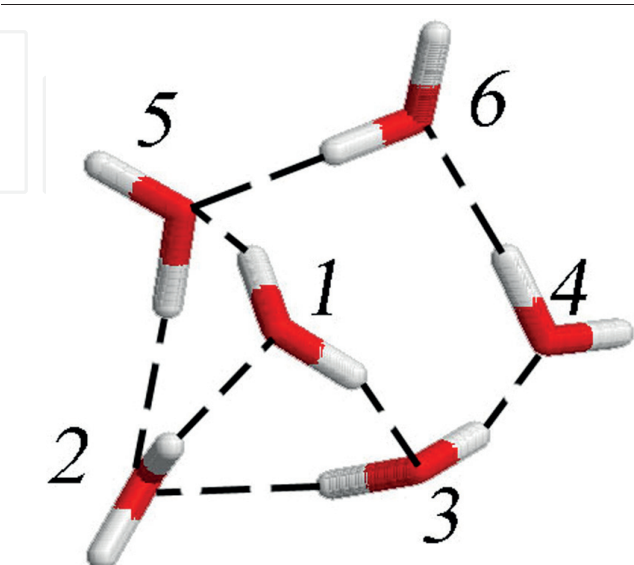
preceded by two water molecules with identical number of hydrogen bonds ($N = 2$): molecules 1 and 2; therefore it is necessary to make $N-1 = 2-1 = 1$ step from the deadlock molecule. Thus, after molecule 6 molecule 1 is considered; its number is assigned to column 2 of **Table 5**. Columns 3 and 4 of **Table 5** are completed similarly to **Table 3**. Two more times the method of deadlocks is applied to cluster (a) in **Table 5** to consider the chains beginning from molecules 4 and 5. Eventually, the total value of cells of column 3 in **Table 5** is assigned to column 5 of matrix “T2”. Total value of cells of column 4 in **Table 5** is assigned to column 6 of matrix “T2”. The code of matrix “T2” for cluster (a) $(\text{H}_2\text{O})_6$ from **Table 5** is 12 0 6 0 0 3 3 0 0.

For cluster (b) $(\text{H}_2\text{O})_6$ from **Table 5**, the method of deadlocks is not applied, since deadlock molecules (molecules 6 and 5) are not preceded by two or more molecules having identical number of hydrogen bonds via hydrogen atoms. Therefore, for this cluster the method of deadlocks does not give any contribution to code of matrix “T2”.

2.1.2.4 Method of cycles

An example of completing the table for cluster (a) $(\text{H}_2\text{O})_6$ using method of cycles is given in **Table 6**. **Tables 6** and 7 present two clusters (a) and (b), which have different structures but identical codes of matrices “T1” and “T2”, determined using methods of chains, reconsiderations, and deadlocks: “T1” is 6 2 0 0 6 0 0 2 0 0 and “T2” is 35 11 5 0 0 0 0 0. To distinguish them the following method of cycles is developed and applied:

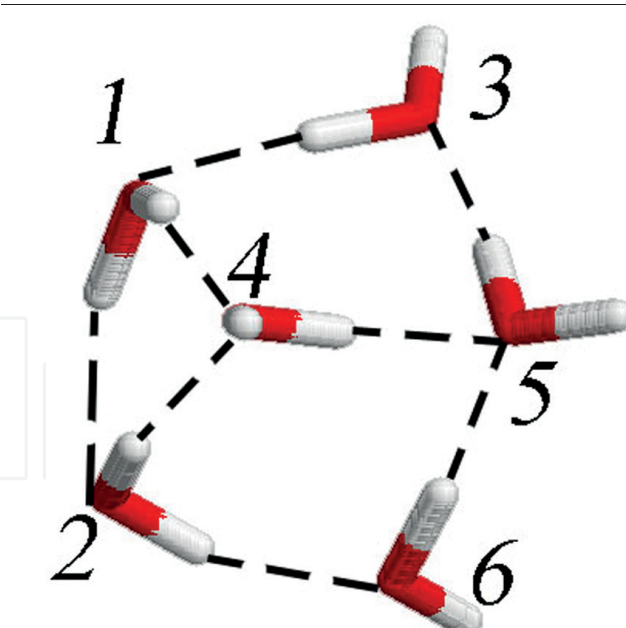
The method of cycles involves the following procedure: each water molecule of the cluster is considered as initial for a closed loop of molecules called a cycle. Numbers of initial molecules are assigned to column 1 in **Table 6**. For each hydrogen bond of this molecule via its hydrogen atoms, we determine the length of the shortest cycle (number of water molecules involved in the cycle except the initial water molecule). If there are several cycles with the same length via the same hydrogen bond of the initial water molecule, then numbers of water molecules forming all cycles with this length are assigned to column 2 in **Table 6**. If the shortest cycle length is less than 3 molecules, “1” is assigned to column 3 in **Table 6**; otherwise “0” is



(a) $(\text{H}_2\text{O})_6$

1	2	3	4
No of initial molecule	No of the molecules involved in the cycle	<3	≥3
1	3,2	1	0
	5,2	1	0
2	1,3	1	0
	1,5	1	0
3	2,1	1	0
	4,6,5,1	0	1
4	6,5,1,3	0	1
5	2,1	1	0
6	5,1,3,4	0	1
Total		6	3

Table 6.
The method of cycles corresponding to (a) cluster $(\text{H}_2\text{O})_6$.



(b) (H₂O)₆

	1	2	3	4
No of initial molecule	No of the molecules involved in the cycle		<3	≥3
1		2,4	1	0
		4,2	1	0
2		4,1	1	0
		6,5,4	0	1
3		1,4,5	0	1
4		5,6,2	0	1
5		3,1,4	0	1
6		5,4,2	0	1
Total			3	5

Table 7.
The method of cycles corresponding to (b) cluster (H₂O)₆.

assigned. If it exceeds, or is equal to 3 molecules, then “1” is assigned to column 4 in **Table 6**; otherwise “0” is assigned. For the next hydrogen bond via hydrogen atom of the considered initial water molecule (if present), the shortest cycle length is determined again. It can be larger than the shortest cycle length for other hydrogen bond of the same initial water molecule.

Let us illustrate the application of method of cycles for the example of cluster (a) (H₂O)₆ shown in **Table 6**. Consideration begins with molecule 1. It has two hydrogen bonds via its hydrogen atoms. For one of them, the shortest cycle is via molecules 3 and 2. Other cycles exist, for example, via molecules 3, 4, 6, and 5. But it is longer than the cycle including molecules 3 and 2; therefore it is not described in **Table 6**. The cycle including molecules 3 and 2 has length 2 which is less than 3; therefore “1” is assigned to column 3 in **Table 6**. For the second hydrogen bond, the shortest cycle is via molecules 5 and 2. Its length is also less than 3; therefore “1” is assigned to column 3 in **Table 6**.

The most interesting in this example is consideration of the cycles beginning from molecule 3. It has two hydrogen bonds via its hydrogen atoms. For one of them, it is possible to get back to molecule 3, passing only two molecules: water molecules 2 and 1. But for the second bond, the shortest cycle includes four molecules: 4, 6, 5, and 1. Therefore, in this case “1” is assigned to column 4 in **Table 6**. Similarly, the table for or all initial water molecules can be completed.

Eventually, the total value of cells of column 3 in **Table 6** is assigned to column 7 of matrix “T2”. Total value of cells of column 4 in **Table 6** is assigned to column 8 of matrix “T2”. The code of matrix “T2” for cluster (a) (H₂O)₆ (**Table 6**) is 35 11 5 0 0 0 6 3, and for cluster (b) (H₂O)₆ (**Table 7**), it is 35 11 5 0 0 0 3 5.

2.1.3 Description of matrix “T3”

The matrix “T3” has fixed dimension 1x9 (one row, nine columns). The first eight columns of matrix “T3” are completed similarly to matrix “T2” but for the molecules which belong to FCS of the impurity particle in the cluster. Any molecules and atoms except for water molecules can be such impurity particle. For the

H₂O molecule in the proposed method, zero radius of FCS = 0 is prescribed. If the system does not contain impurity particle, then this matrix is completed with zero values. Number of water molecules belonging to FCS is assigned to column 9 of matrix “T3”.

An example of construction of matrix “T3” for cluster of K⁺(H₂O)₆ presented in **Table 1** is given in **Table 8**. This cluster does not contain molecules meeting the condition of application for methods of deadlocks, reconsiderations, and cycles. After consideration of all water molecules belonging to FCS (molecules 1, 3, 4, 5, and 6) as initial for the chains, summation of all the values obtained in columns is performed. In the case under consideration, the code of matrix “T3” is 1 0 0 0 0 0 0 0 5.

2.1.4 Description of matrix “T4”

The matrix “T4” has fixed dimension 1 × 28 (1 row, 28 columns) and characterizes relative positioning and the sequence of interaction of molecules within elementary structure (elementary structure is the structure composed of four water molecules, three of which are subsequently connected with hydrogen bonds, and the fourth has at least one hydrogen bond with any of the first three molecules via any atom).

To take into account chirality of water system within one structural type, the matrix “T4” is introduced. The table structure for matrix of chirality “T4” is presented in **Table 9**.

The developed method for the analysis of chirality of water systems is based on decomposing water configuration into a set of elementary structures composed of four water molecules, connected with hydrogen bonds. In each of them, three water molecules which are subsequently connected with hydrogen bonds determine the direction of twist, and the fourth water molecule is required as a reference point, with respect to which the direction of twist is defined: right or left.

Mirror image of chiral structure composed of four water molecules has different directions of twist; hence the original structure and its image cannot be matched using translation and rotation. For mirror image of achiral system, the direction of twist with respect to the fourth molecule remains the same; therefore the original structure and its image can be matched.

Realization of the proposed technique involves four stages:

At the first stage for each water configuration under consideration, its mirror image is constructed. For plane reflection in yz plane, the sign of all coordinate x values is changed, that is,

1	2	3	4
No of initial molecule	No of the subsequent molecule in the chain	H ₁	H ₂
1	6	0	0
3	2	0	0
4	3	1	0
	2	0	0
5	6	0	0
6	0	0	0
Total		1	0

Table 8.
Method of chain result.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	
1	One neighbor of the first molecule								Two neighbors of the first molecule								Three neighbors of the first molecule								Sign of chirality (0 or 1)				
2	3				2		1				3				2		1				3				2		1		
3	+	0	—	+	0	—	+	0	—	+	0	—	+	0	—	+	0	—	+	0	—	+	0	—	+	0	—		
4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>*Numbers in the leftmost column of the table are row numbers.</i>																													

Table 9.
Structure of chirality matrix “T4”*.

$$x_0 = x_k \times (-1), \quad (1)$$

where x_0 are new coordinates x of mirror image configuration and x_k are original coordinates x of the studied configuration. All further calculations are performed independently for the original configuration and its mirror image.

At the second stage, we search for three water molecules, which are subsequently connected with hydrogen bonds. All molecules in configuration are tried as initial molecule. Two vectors are constructed for each of the obtained sets of three molecules: $\vec{a}_1$ and $\vec{a}_2$. The vector $\vec{a}_1$ is drawn oxygen atom of the first water molecule to oxygen atom of the second molecule and the vector $\vec{a}_2$ is similarly from the second to the third water molecule. The twist vector $\vec{a}_0$ is cross product of these two vectors (**Figure 1 (a)**):

$$\vec{a}_0 = [\vec{a}_1 \times \vec{a}_2] \quad (2)$$

At the third stage we search for the fourth H_2O molecule in elementary structure. It must have hydrogen bond with any of the first three molecules via any atom. The vector $\vec{a}_3$ connects oxygen atoms of the fourth water molecule and the molecule with which it has hydrogen bond (**Figure 1 (b)**).

It is necessary to consider all hydrogen bonds between the molecules belonging to thus determined elementary structure. For this purpose, we determine number of water molecules within elementary structure, possessing hydrogen bond with the first molecule (neighbors of the first molecule).

Next, the elementary structures which form closed loops are excluded (see **Figure 2**). Also, reconsideration of identical elementary structures is prohibited.

To avoid closed loops, that is, sets 1-2-3-1, 2-3-1-2, and 3-1-2-3, where figures denote serial numbers of water molecules in configuration (the order is determined by the file with initial coordinates of the molecules), it is necessary to ensure that the number of the fourth molecule does not coincide with the number of molecules 1, 2, or 3 belonging to the elementary structure.

Duplicates of elementary structures arise if the fourth H_2O molecule has two hydrogen bonds with water molecules belonging to this elementary structure. To eliminate such duplicates, elementary structures are ordered so that the number of water molecule increases, for example, configuration 2-1-4-3 after ordering becomes 1-2-3-4. Next, the ordered elementary structures are saved, and

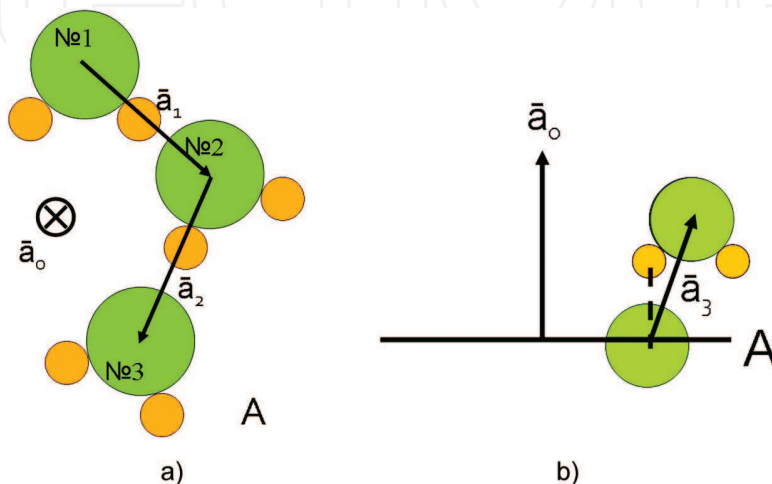


Figure 1.

The scheme of vector construction for elementary structure composed of four water molecules (right configuration).

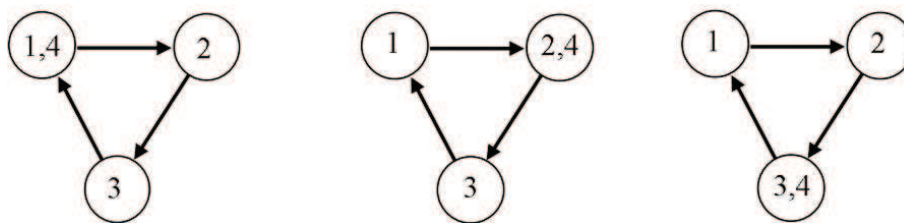


Figure 2.
 Possible elementary structures forming closed loops.

calculations are performed only for those elementary structures which differ after ordering. **Figure 3** shows example where the fourth water molecule is connected with two molecules belonging to elementary structure. Two combinations of water molecule numbers are possible: 1-2-3-4 and 4-2-3-1. After ordering they take form: 1-2-3-4 and 1-2-3-4; that is, calculation is to be performed only for one of two combinations: 1-2-3-4. Without ordering the calculation would be performed for two combinations, and, since their vectors of twist ($\vec{a}_{0_1}$, $\vec{a}_{0_2}$) have opposite direction, after summation they would cancel each other, and the structure would be considered as achiral. But if four molecules of this structure are not coplanar, it is chiral. Therefore, correct performance of the proposed algorithm requires special treatment of cases with the fourth molecule having two bonds and subsequent ordering of molecules in configuration in ascending order of the serial number.

If the fourth water molecule does not have two hydrogen bonds with other molecules from elementary structure, ordering in ascending order of serial number is performed only for the first three molecules from the structure. For example, for three combinations of molecules, 1-3-2-4, 2-3-1-4, and 4-1-3-2 (after ordering, 1-2-3-4, 1-2-3-4, and 1-3-4-2), calculations are performed only twice, since after ordering there are only two different sequences: 1-2-3-4 and 1-3-4-2. For three combinations, 6-5-7-8, 8-6-7-4, and 7-6-8-5 (after ordering, 5-6-7-8, 6-7-8-4, and 6-7-8-5), three calculations are performed as all these sequences are different.

Next, vector $\vec{a}_3$ is drawn from the center of oxygen atom of water molecule, with which the fourth molecule has hydrogen bond, to the center of oxygen atom of the fourth molecule.

At the fourth stage of the method matrices “T4” (see **Table 9**) are constructed for the original configuration and its mirror image. Initial values of all cells in matrix “T4” are zero.

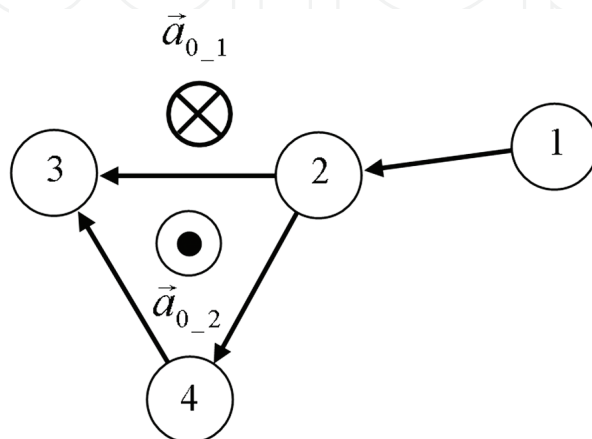


Figure 3.
 The scheme of structure in which the fourth molecule is connected with two molecules belonging to elementary structure.

The first row in **Table 9** characterizes number of molecules belonging to elementary structure, with which molecule 1 is connected with hydrogen bonds, no matter via which atom. Since in this method we consider structures composed of four molecules, three variants are possible: (1) only one molecule is connected to molecule 1 (columns from 1 to 9), (2) two molecules are connected to molecule 1 (columns from 10 to 18), and (3) all three other molecules from elementary structure are connected to molecule 1 (columns from 19 to 27).

The second row in **Table 9** characterizes with which molecule from the considered elementary structure the fourth molecule from the same structure has hydrogen bond. Titles of columns ("3", "2", "1") correspond to serial number of this molecule in elementary structure and combine, in fact, several columns in **Table 9**. Bond can be realized either via hydrogen or via oxygen atom of the fourth molecule. If the fourth water molecule has more than one hydrogen bond with other molecules belonging to elementary structure, then completion of **Table 9** has the following specific features:

1. If the fourth molecule has hydrogen bonds with water molecules 1, 2, and 3 simultaneously, values are added for the original configuration to cells of row 4 and for the mirror image to cells of row 5 in corresponding group of columns "3" (columns from 1 to 3, or from 10 to 12, or from 19 to 21);
2. If the fourth molecule has hydrogen bonds with water molecules 1 and 2, values are added for the original configuration to cells of row 4 and for the mirror image to cells of row 5 in corresponding group of columns "2" (columns from 4 to 6, or from 13 to 15, or from 22 to 24);
3. If the fourth molecule has hydrogen bonds with water molecules 1 and 3, values are added for the original configuration to cells of row 4 and for the mirror image to cells of row 5 in corresponding group of columns "3" (columns from 1 to 3, or from 10 to 12, or from 19 to 21);
4. If the fourth molecule has hydrogen bonds with water molecules 2 and 3, values are added for the original configuration to cells of row 4 and for the mirror image to cells of row 5 in corresponding group of columns "3" (columns from 1 to 3, or from 10 to 12, or from 19 to 21).

If the fourth water molecule has only one hydrogen bond with other molecule from elementary structure, then completion of **Table 9** has the following features:

1. If the fourth molecule has hydrogen bond with water molecule 3, values are added for the original configuration to cell of row 4 and for the mirror image to cell of row 5 in corresponding group of columns "3" (columns from 1 to 3, or from 10 to 12, or from 19 to 21).
2. If the fourth molecule has hydrogen bond with water molecule 2, values are added for the original configuration to cell of a line 4 and for her mirror image to cell of row 5 in corresponding group of two columns (columns from 4 to 6, or from 13 to 15, or from 22 to 24);
3. If the fourth molecule has hydrogen bond with water molecule 1, values are added for the original configuration to cell of row 4 and for the mirror image to cell of row 5 in corresponding group of columns "1" (columns from 7 to 9, or from 16 to 18, or from 25 to 27).

The third row in **Table 9** characterizes the position of the fourth molecule of elementary structure with respect to the plane passing through oxygen atoms of other three water molecules belonging to the elementary structure. The following scalar product is calculated:

$$t = (\vec{a}_0, \vec{a}_3) \quad (3)$$

If $t > 0$, then 1 is added for the original configuration to the value in cell of row 4 and for the mirror image to the value in cell of row 5 of the corresponding “+” column in **Table 9**. If $t = 0$, then 1 is added for the original configuration to the value in cell of row 4 and for the mirror image to the value in cell of row 5 of the corresponding “0” column. If $t < 0$, then 1 is added for the original configuration to the value in cell of row 4 and for the mirror image to the value in cell of row 5 of the corresponding “-” column (**Figure 4**). These calculations are performed for each identified elementary structure of the considered water configuration and its mirror image.

The last column 28 in **Table 9** is completed with results of comparison of values in corresponding cells of rows 4 and 5 in columns from 1 to 27. If values are equal, then the original configuration is considered achiral, and no new value is assigned to column 28 cell “The sign of chirality”, so the value remains zero. If at least for one of the compared cell values for the original configuration (row 4) and for the mirror image (row 5) is not equal, then the original configuration is considered chiral and 1 is assigned to column 28 cell “The sign of chirality”.

Table 9 is used for completion of matrix “T4” with dimension 1×28 (1 row, 28 columns). Values of cells of matrix “T4” in columns from 1 to 27 are copied from the corresponding cells of row 4 in **Table 9**. The value of cell in column 28 of matrix “T4” is copied from column 28 in **Table 9**.

This method allows classification of chiral configurations according to the sign of chirality. If the total value of the “+” columns exceeds the total value of the “-” columns, that is, there are more right-handed structures than left-handed, then the configuration is considered to be right. If the total value of the “+” columns is less than the total value of the “-” columns, then the configuration is considered to be left. If these two values are equal, the configuration has no dominating direction of twist.

Figure 5 presents an example of chiral configurations of one structural type with different types of chirality. This structural type had the greatest weight coefficient in the sampling set. Two configurations have identical structure, but opposite directions of twist, which is represented by different matrices “T4”.

Besides, configurations shown in **Figure 5** differ not only by chirality type but also by its sign. Cluster configuration (a), twisted outwards, is right ($\Sigma “+” = 5$, $\Sigma “-” = 3$), whereas configuration (b), twisted inwards, is left ($\Sigma “+” = 3$, $\Sigma “-” = 5$).

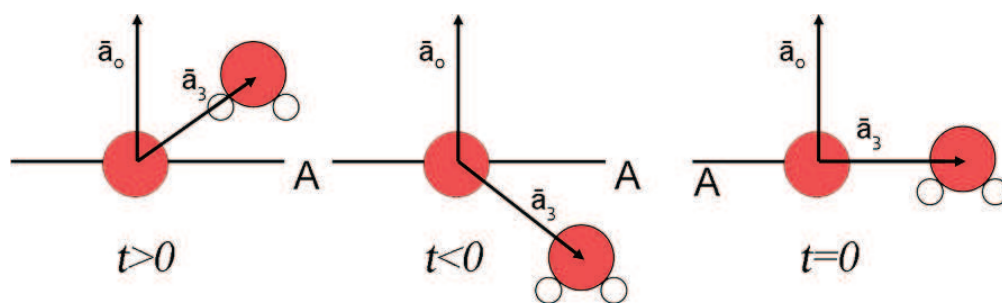


Figure 4.
 Variants of relative positioning of vector of twist $\vec{a}_0$ and vector $\vec{a}_3$.

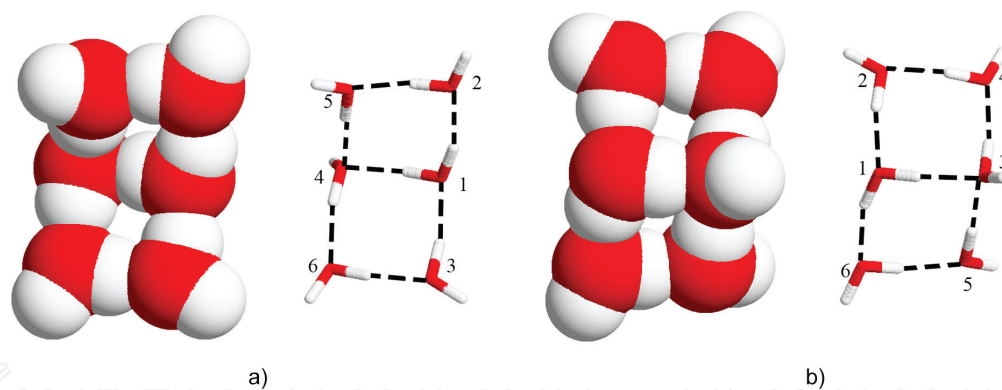


Figure 5.

An example of chiral configurations belonging to one structural type but to different types of chirality with corresponding matrices “T4”.

For better understanding of the above-described algorithm, we will present one more example of calculation of matrix “T4” for chiral configuration of cluster $(\text{H}_2\text{O})_5$ (a) and its mirror image (b) (see **Figure 6**).

2.2 Results

2.2.1 Influence of number of water molecules in cluster $(\text{H}_2\text{O})_n$ ($n < 10$) on its chirality properties

Clusters $(\text{H}_2\text{O})_n$ with $n = 4 \div 8$ at temperature $T = 1$ K are obtained as in [24]. Cluster optimization is performed using Monte Carlo method with periodic boundary conditions, interaction between the atoms is taken into account with Poltev-Malenkov potential functions, and water molecules are described by rigid model.

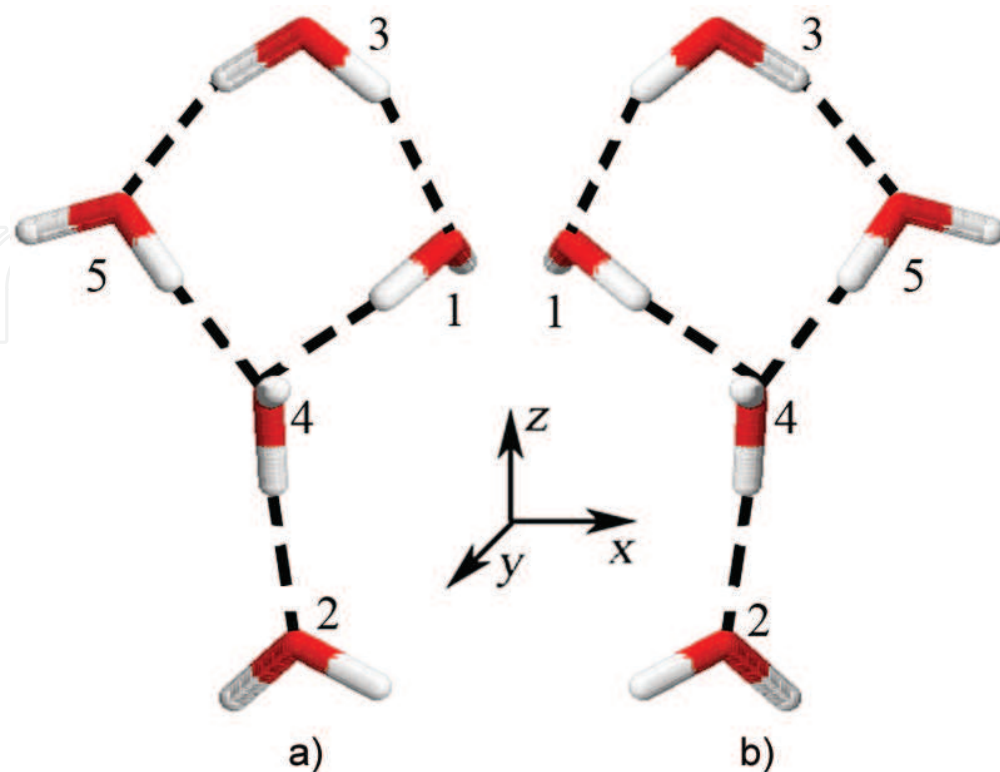


Figure 6.

An example of chiral water configuration of cluster $(\text{H}_2\text{O})_5$ with its mirror image and corresponding matrix “T4”.

For each value of n , 20 10,000 sampling sets are simulated. Averaging of all results presented below is performed for all 20 sampling sets. The error of each experiment is estimated with significance level of 0.05.

The proposed method of accounting for chirality properties of model water systems is further development of approach for examination of their structural properties formulated in [21]. Using this approach, the increase of number of structural types with increasing number of water molecules in cluster at temperature 1 K has been obtained earlier without taking into account chirality (see Figure 7).

Figure 8 presents dependences of number of types of structures with and without taking into account chirality on number of water molecules in cluster. From Figure 8 one can see that when all matrices—“T1”, “T2”, “T3” and “T4”—are taken into account, number of types of structures increases. Also, the error increases with increasing number of molecules in cluster. This is explained by the fact that number of types becomes comparable with number of configurations in the sampling set. Consequently, no studies were performed for cluster $(\text{H}_2\text{O})_n$ at temperature 1 K with $n > 8$ using 10,000 sampling set.

Taking chirality of water system into account does not change qualitatively the growth of number of structural types with increasing number of water molecules in cluster, but it becomes (3.10 ± 0.99) times quicker.

In Figure 9, the dependence of number of chiral and achiral configurations of cluster $(\text{H}_2\text{O})_n$ on number of water molecules in cluster is displayed for 10,000 sampling set. It follows that with increasing number of molecules in cluster the number of chiral configurations increases.

Figure 10 shows the dependence of numbers of the right, left configurations and configurations without domination of one of the directions of twist for chiral cluster on number of water molecules. One can see that numbers of the right and left configurations in 10,000 sampling set are equal within the accuracy; therefore, water cluster $(\text{H}_2\text{O})_n$ ($n \leq 8$) at temperature 1 K has no preferential direction of twist. When n is increased, the probability for a configuration to possess one of the directions of twist (either right or left) increases.

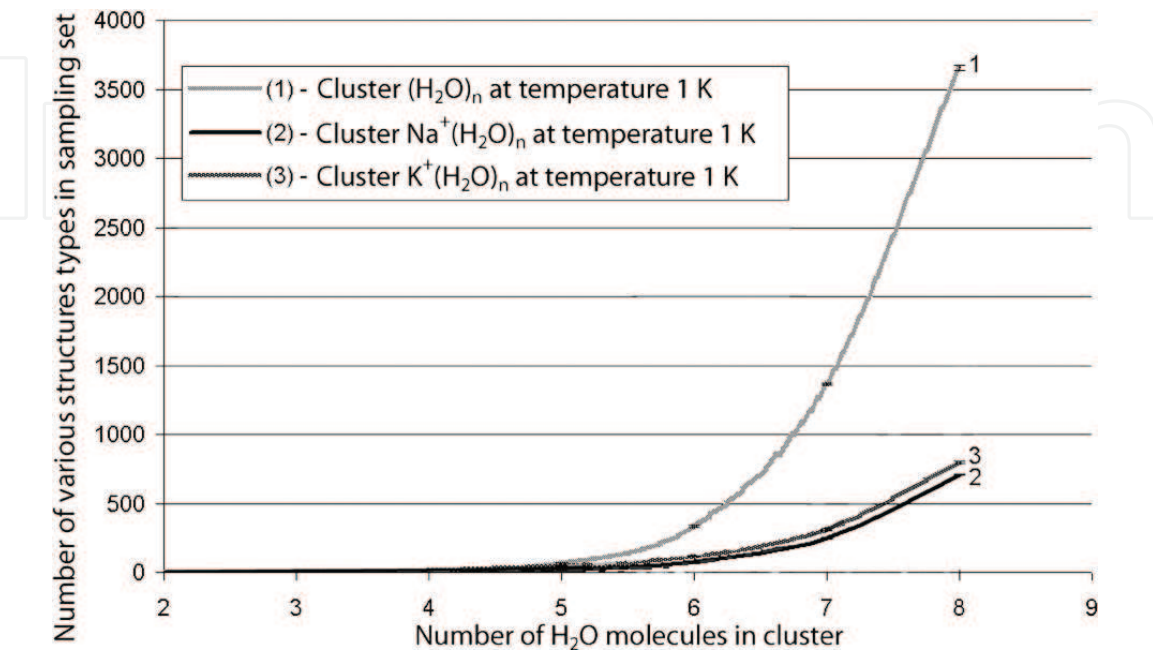


Figure 7.
Number of various types of structures without taking into account chirality as function of number of water molecules in clusters $(\text{H}_2\text{O})_n$, $\text{Na}^+(\text{H}_2\text{O})_n$ and $\text{K}^+(\text{H}_2\text{O})_n$ at temperature 1 K [24].

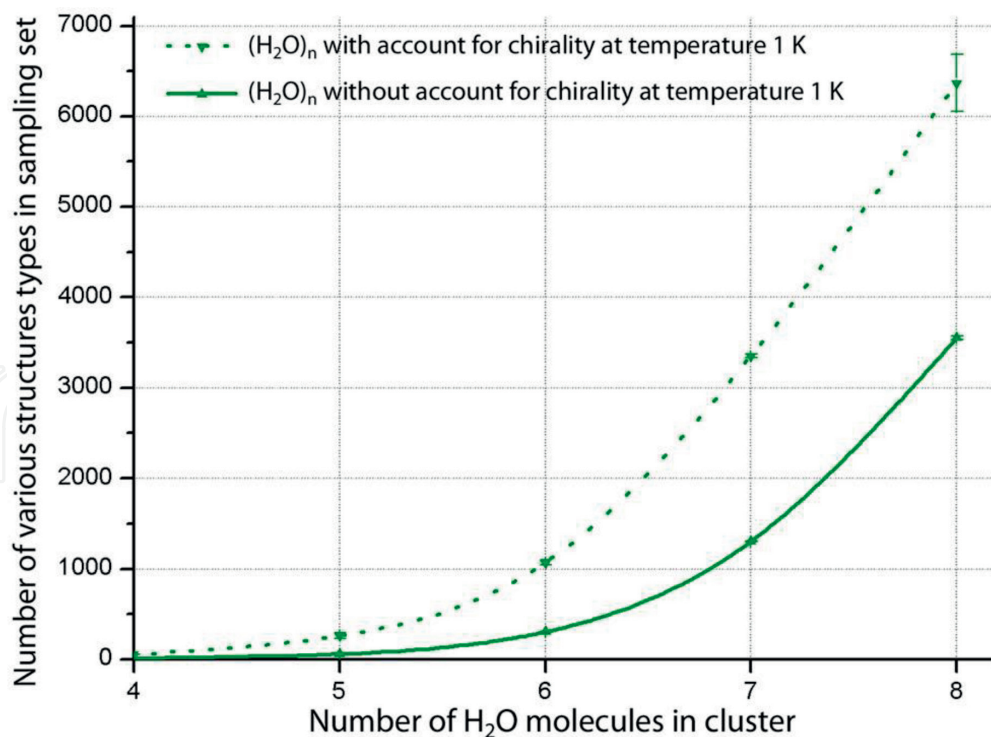


Figure 8.

Number of types of structures with and without taking into account chirality for clusters $(\text{H}_2\text{O})_n$ at temperature 1 K using 10,000 sampling as function of number of water molecules.

It can be concluded from the above results that number of water molecules ($n = 4 \div 8$) contained in a small water cluster influences its chirality properties but does not violate the balance between the right and left configurations in sampling set.

2.2.2 Dependence of chirality properties of water cluster $(\text{H}_2\text{O})_n$ ($n < 10$) on its temperature

Figure 11 presents the dependence of number of various structural types on number of water molecules in cluster $(\text{H}_2\text{O})_n$ where $n = 4 \div 9$ at temperature 300 K without taking into account chirality. It is obtained by taking into account only matrices “T1”, “T2”, and “T3”. In the range $n = 4 \div 8$, it coincides with similar dependence obtained in [21].

Also **Figure 11** presents curves for number of structural types with and without taking into account chirality at 1 and 300 K. Thick lines correspond to curves at 300 K, and dashed lines to dependences obtained taking into account chirality.

It follows from **Figure 11** that increasing temperature to 300 K does not change exponential increase of number of structural types; only the exponential factor is modified. Extrapolations using exponential dependence $y = ae^{bx}$ are obtained. Parameters of extrapolation curves are listed in **Table 10**. All curves shown in **Figure 11** have no significant deviation from exponential dependence.

Figure 12 presents dependences of number of chiral and achiral configurations and configurations to which the concept of chirality is not applicable in sampling set for cluster $(\text{H}_2\text{O})_k$ ($k = 4 \div 9$) at temperature 300 K. Chirality is not applicable if cluster does not contain four water molecules connected with hydrogen bonds, three of which are connected subsequently. From **Figures 9** and **12**, it is possible to draw a conclusion that increasing temperature to 300 K does not change the growth of number of chiral configurations in sampling set with increasing number of molecules in cluster. However, the curve for number of achiral configurations is

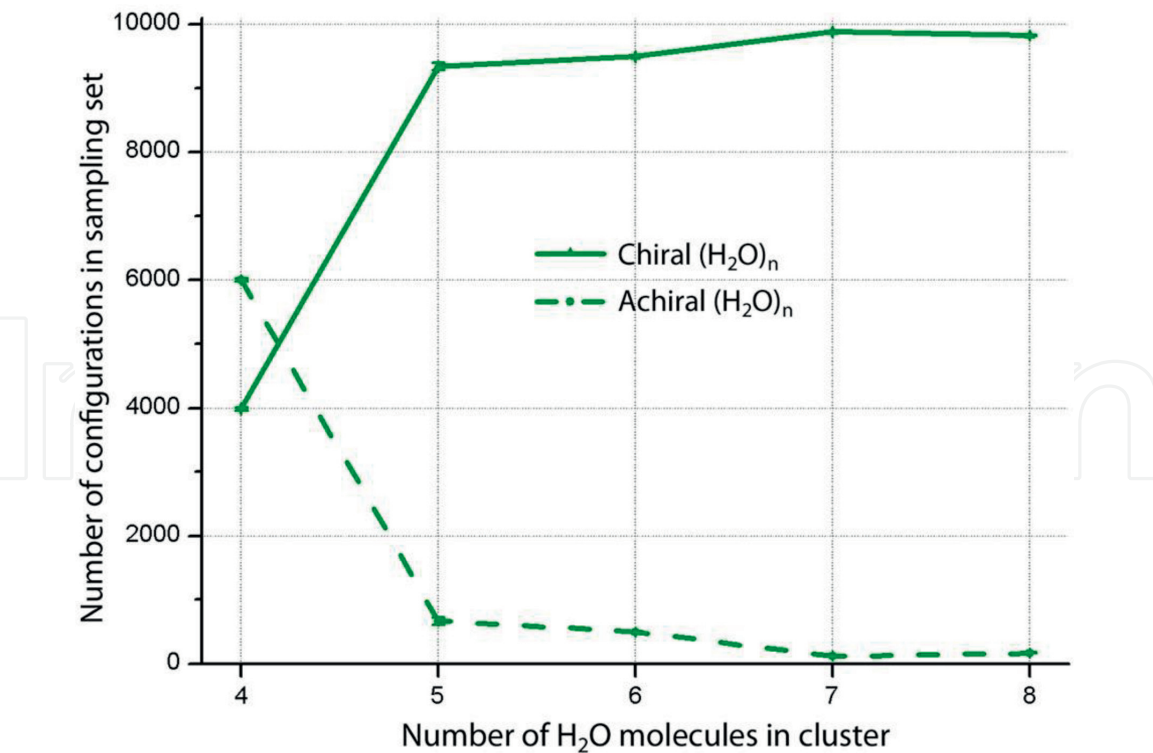


Figure 9.
Numbers of achiral and chiral configurations in cluster $(\text{H}_2\text{O})_n$ at temperature 1 K as functions of number of water molecules for 10,000 sampling set.

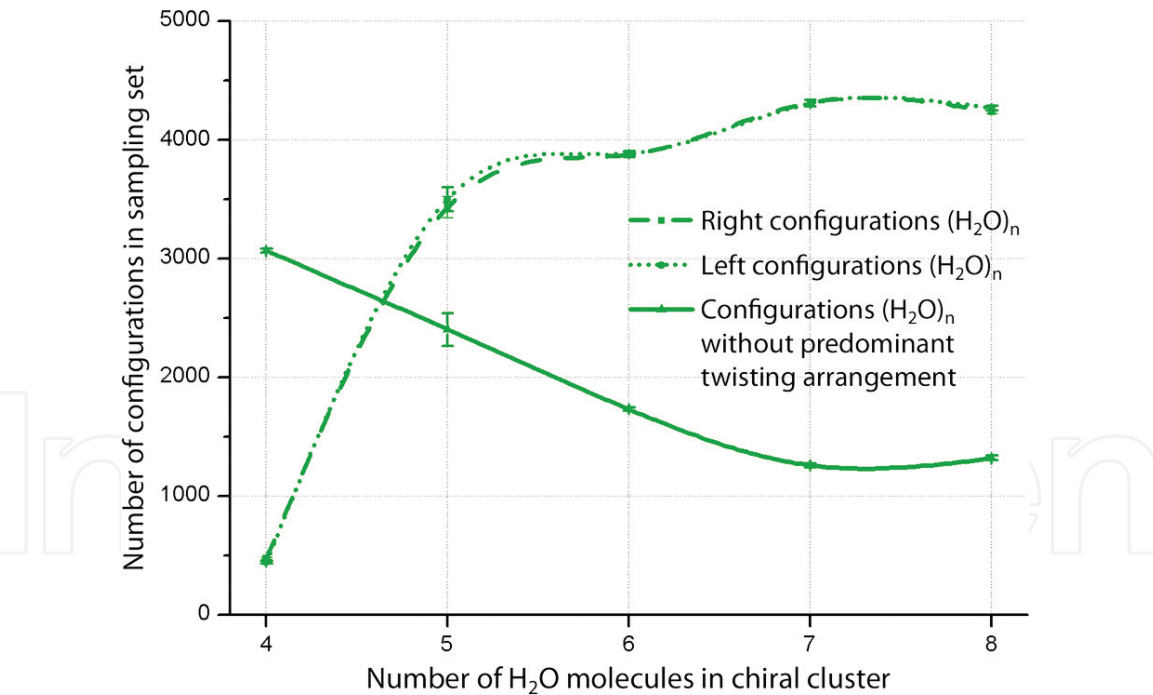


Figure 10.
Numbers of right, left, and configurations without domination of one of the directions of twist for chiral cluster $(\text{H}_2\text{O})_n$ at temperature 1 K as functions of number of water molecules for 10,000 sampling set.

changed from monotonically decreasing to dependence, which possess a maximum corresponding to cluster composed of eight water molecules.

Figure 13 shows dependences of number of the right, left configurations and configurations without domination of one of the directions of twist on number of water molecules for cluster $(\text{H}_2\text{O})_n$ ($n = 4 \div 8$) at temperature 1 K and $(\text{H}_2\text{O})_k$ ($k = 4 \div 9$) at temperature 300 K. It follows that at 300 K equality of numbers of the

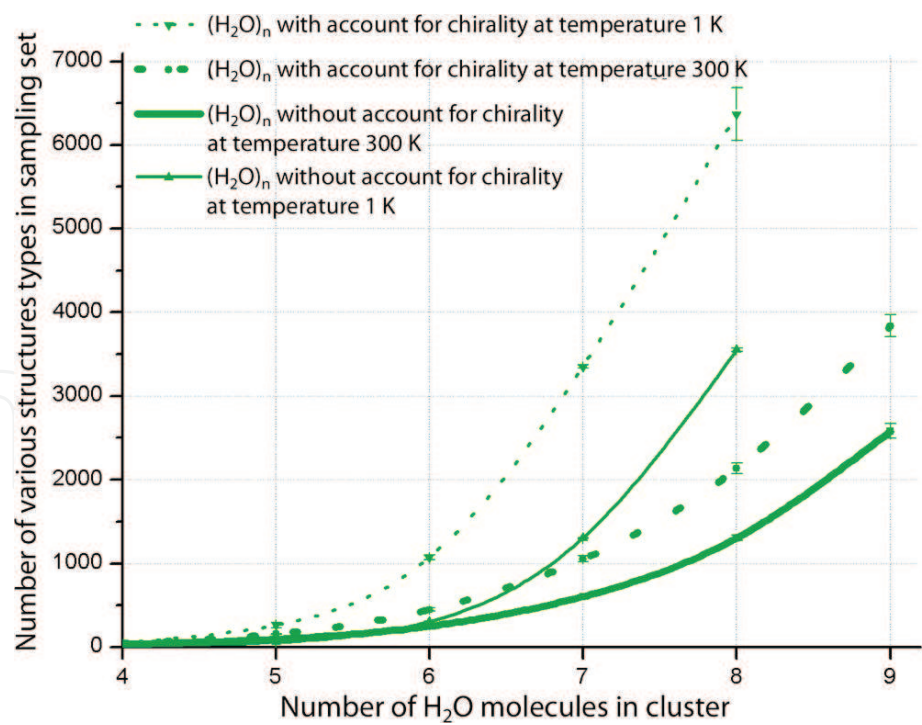


Figure 11. Number of types of structures as function of number of water molecules with and without taking into account chirality for clusters $(\text{H}_2\text{O})_n$ at temperature 1 K and $(\text{H}_2\text{O})_k$ at temperature 300 K, where $n = 4\div 8$ and $k = 4\div 9$, for 10,000 sampling set.

Type of dependence	a	b	Correlation coefficient
$(\text{H}_2\text{O})_n$ without chirality at 1 K	0.19 ± 0.13	1.24 ± 0.09	0.97
$(\text{H}_2\text{O})_k$ without chirality at 300 K	1.30 ± 0.27	0.86 ± 0.03	0.98
$(\text{H}_2\text{O})_n$ with chirality at 1 K	0.32 ± 0.17	1.32 ± 0.08	0.98
$(\text{H}_2\text{O})_k$ with chirality at 300 K	1.97 ± 0.72	0.86 ± 0.05	0.94

Table 10. Parameters of extrapolation curves.

right and left configurations in sampling set is also observed. But for cluster $(\text{H}_2\text{O})_n$ at temperature 1 K, the number of configurations without domination of one of the directions of twist decreases with increasing number of molecules in cluster. At 300 K quite different situation is observed: number of such configurations increases. Most likely, this can be attributed to the fact that at 1 K even for small number of water molecules contained in cluster, essentially all configurations in sampling set are chiral. When number of molecules increases, the numbers of the right and left configurations increase, and the number of configurations without domination of one of the directions of twist, respectively, decreases.

For cluster $(\text{H}_2\text{O})_k$ at 300 K, not all configurations in sampling set are chiral. Presumably, when the number of chiral configurations in sampling set is comparable with the sampling set, the type of dependence for number of right, left configurations and configurations without domination of one of directions of twist can be the same as observed at 1 K; that is, the numbers of the right and left configurations continue to grow, and the number of configurations without domination of one of the directions of twist decreases.

It is recognized that study of water clusters $(\text{H}_2\text{O})_n$ with $n \geq 8$ requires sampling set exceeding 10,000 configurations, as at $n = 8$ the number of various structural types taking into account chirality approaches the size of the sampling set.

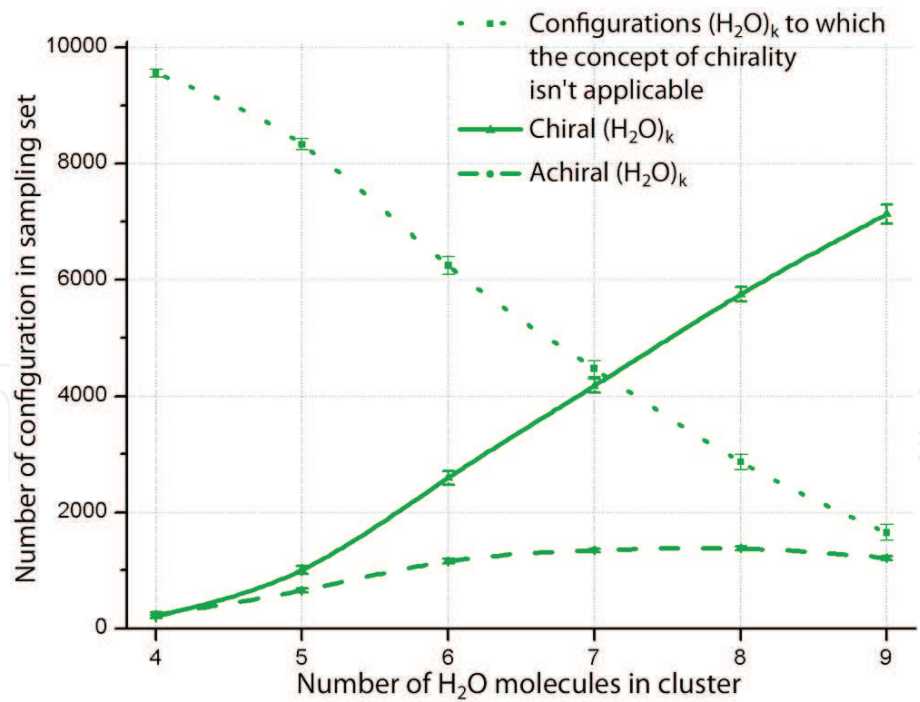


Figure 12.
Numbers of achiral and chiral configurations and configurations to which the concept of chirality is inapplicable as functions of number of water molecules for cluster $(H_2O)_k$ at temperature 300 K for 10,000 sampling set.

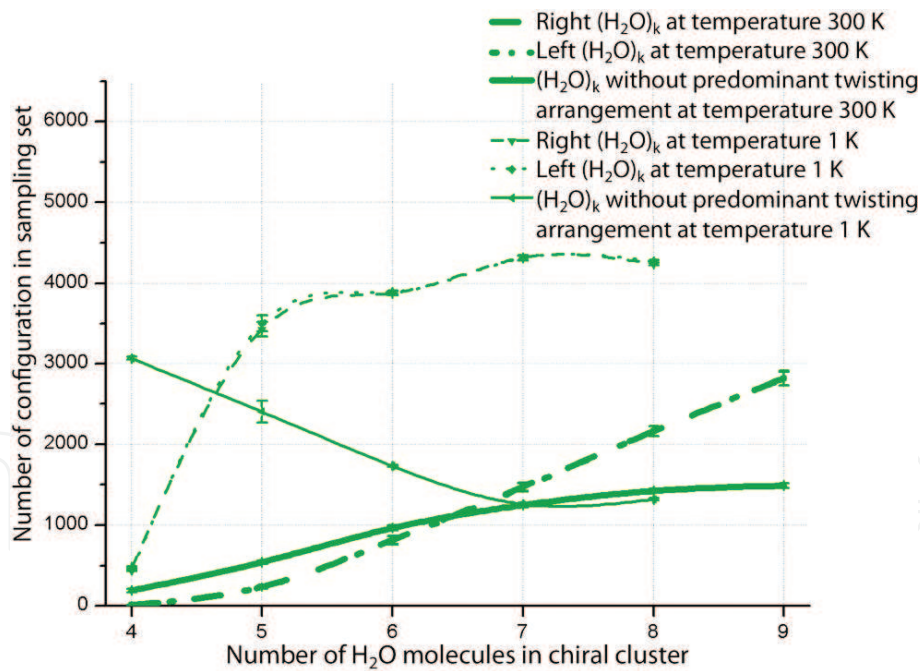


Figure 13.
Numbers of the right, left configurations and configurations without domination of one of the directions of twist as functions of number of water molecules for chiral cluster $(H_2O)_n$ at temperature 1 K and $(H_2O)_k$ at temperature 300 K for 10,000 sampling set.

2.2.3 Modification of chirality properties of water cluster $(H_2O)_n$ ($n \geq 10$) due to addition of ion K^+ or Na^+

Clusters $K^+(H_2O)_m$ and $Na^+(H_2O)_m$ with $m = 5 \div 10$ at temperature $T = 1$ K are obtained as in [24]. For each value m of clusters $K^+(H_2O)_m$ and $Na^+(H_2O)_m$, 20

10,000 sampling sets of configurations with random initial conditions are produced.

Figure 14 presents dependences of number of structural types on number of molecules in cluster with and without taking into account chirality for clusters $(\text{H}_2\text{O})_n$, $\text{K}^+(\text{H}_2\text{O})_m$, and $\text{Na}^+(\text{H}_2\text{O})_m$ at temperature $T = 1 \text{ K}$ for 10,000 sampling set. It follows that, as for a water cluster without impurity, increase of number of water molecules leads to increase of number of structural types in each sampling set.

Extrapolations for these curves are obtained using exponential dependence $y = ae^{bx}$. Parameters of extrapolation curves are listed in **Table 11**. It can be seen that the dependence of number of structural types in sampling set on number of water molecules in clusters $\text{K}^+(\text{H}_2\text{O})_m$ and $\text{Na}^+(\text{H}_2\text{O})_m$ at temperature 1 K is well correlated with exponential dependence.

Figure 15 shows dependences of numbers of chiral and achiral configurations in sampling set on number of molecules in clusters $(\text{H}_2\text{O})_n$, $\text{K}^+(\text{H}_2\text{O})_m$, and $\text{Na}^+(\text{H}_2\text{O})_m$ at 1 K. Number of chiral configuration increase with number of water molecules in cluster is not affected by addition of impurity particles. Number of achiral configurations in sampling set first increases up to seven water molecules contained in $\text{K}^+(\text{H}_2\text{O})_m$ cluster and up to eight water molecules contained in $\text{Na}^+(\text{H}_2\text{O})_m$ cluster and then begins to decrease.

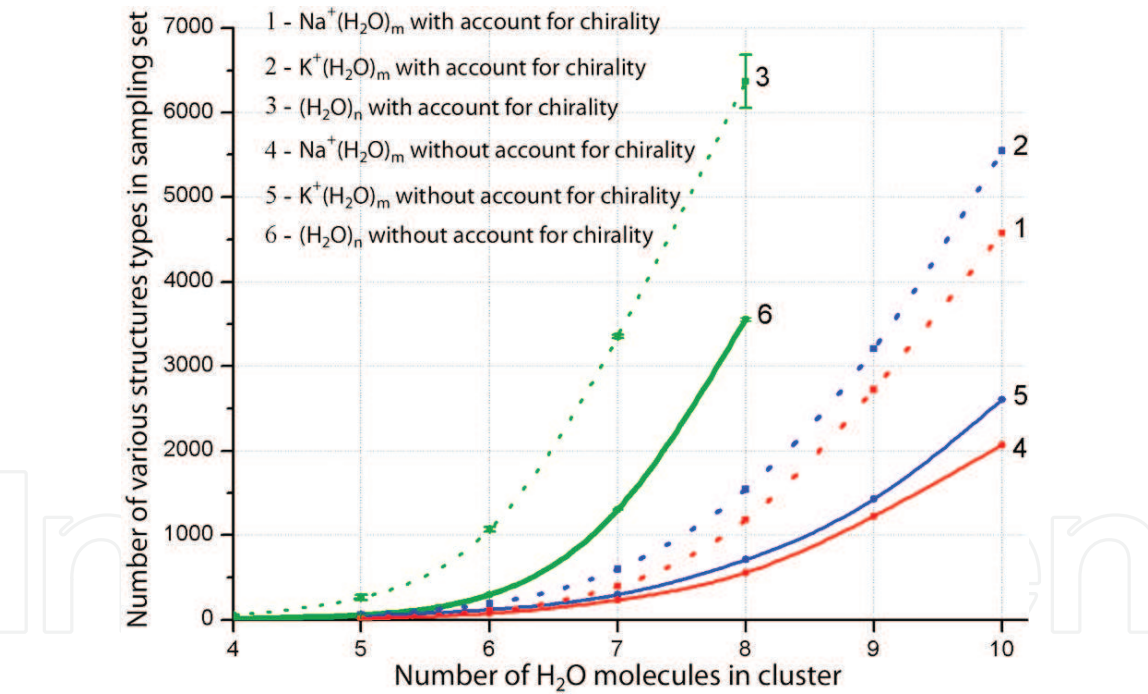


Figure 14. Number of types of structures as function of number of water molecules with and without taking into account chirality for clusters $(\text{H}_2\text{O})_n$, $\text{K}^+(\text{H}_2\text{O})_m$, and $\text{Na}^+(\text{H}_2\text{O})_m$ at temperature 1 K for 10,000 sampling set.

Type of dependence	a	b	Correlation coefficient
$\text{K}^+(\text{H}_2\text{O})_m$ without chirality at 1 K	3.34 ± 0.98	0.67 ± 0.03	0.98
$\text{Na}^+(\text{H}_2\text{O})_m$ without chirality at 1 K	3.02 ± 1.49	0.66 ± 0.05	0.99
$\text{K}^+(\text{H}_2\text{O})_m$ with chirality at 1 K	7.79 ± 3.56	0.66 ± 0.05	0.99
$\text{Na}^+(\text{H}_2\text{O})_m$ with chirality at 1 K	0.83 ± 0.25	0.78 ± 0.05	0.96

Table 11. Values of parameters of extrapolation curves.

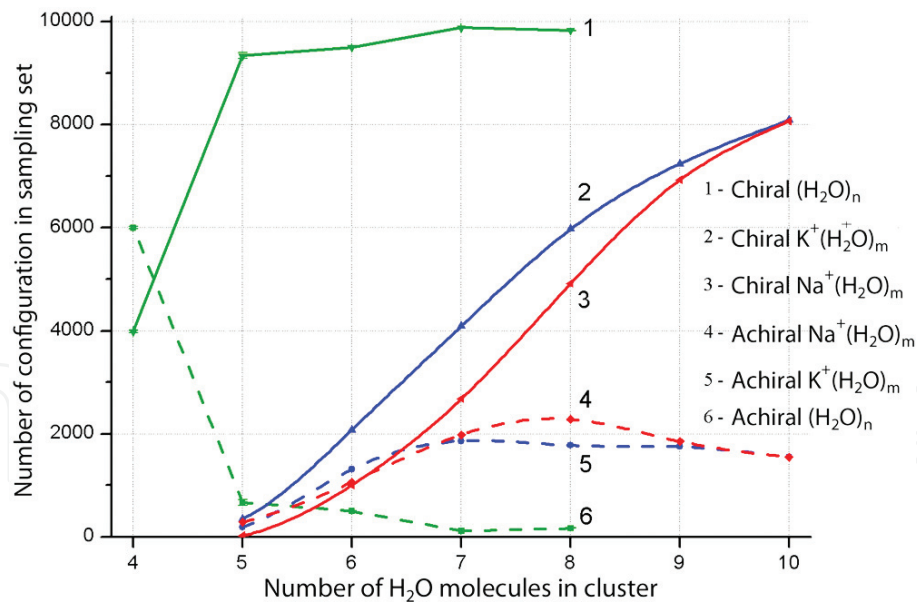


Figure 15.
Numbers of chiral and achiral configurations as functions of number of water molecules for clusters $(\text{H}_2\text{O})_n$, $\text{K}^+(\text{H}_2\text{O})_m$, and $\text{Na}^+(\text{H}_2\text{O})_m$, where $n = 4-8$ and $m = 5-10$ at temperature 1 K for 10,000 sampling set.

Figure 16 demonstrates dependences of number of the right, left configurations and configurations without domination of one of the directions of twist on number of water molecules for clusters $\text{K}^+(\text{H}_2\text{O})_m$ and $\text{Na}^+(\text{H}_2\text{O})_m$ at temperature 1 K for sampling set depending on m . Numbers of the right and left configurations for cluster $\text{K}^+(\text{H}_2\text{O})_m$ correlate with coefficient of correlation $r = 0.99982$ and for cluster $\text{Na}^+(\text{H}_2\text{O})_m$ with $r = 0.99998$. For larger values of m , the probability for a configuration to possess one of the directions of twist (either right or left) increases.

The situation becomes slightly different at temperature 300 K (see **Figure 17**). Numbers of the right and left configurations in sampling sets for clusters $\text{K}^+(\text{H}_2\text{O})_p$

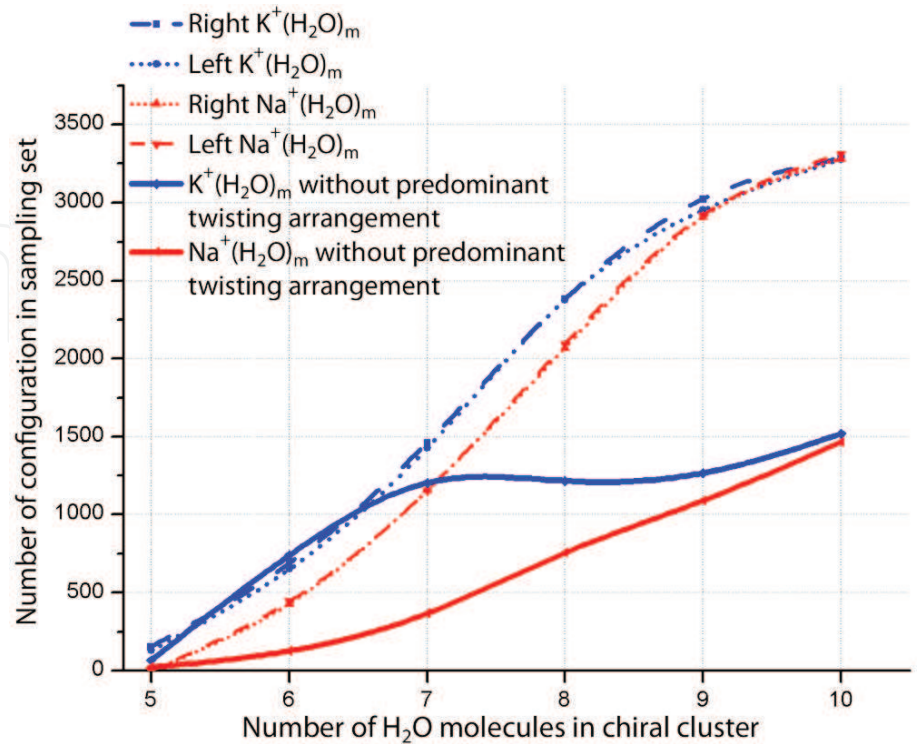


Figure 16.
Numbers of the right, left configurations and configurations without domination of one of the directions of twist as functions of number of water molecules for chiral clusters $\text{K}^+(\text{H}_2\text{O})_m$ and $\text{Na}^+(\text{H}_2\text{O})_m$, where $m = 5-10$, at temperature 1 K for 10,000 sampling set.

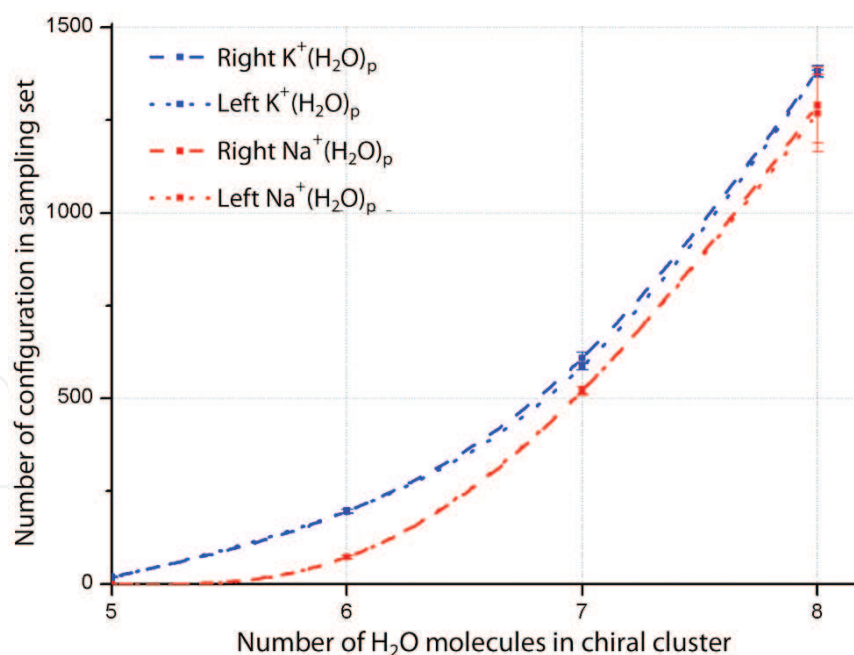


Figure 17.

Numbers of the right and left configurations as functions of number of water molecules for chiral clusters $K^+(H_2O)_p$ and $Na^+(H_2O)_p$, where $p = 5 \div 8$, at temperature 300 K for 10,000 sampling set.

and $Na^+(H_2O)_p$ ($p = 5 \div 8$) are equal. The difference in number of the right and left configurations in sampling sets for clusters with an impurity ion K^+ and Na^+ vanishes for clusters composed of eight or more water molecules.

Variation of chirality properties for clusters $(H_2O)_n$, $K^+(H_2O)_m$, and $Na^+(H_2O)_m$ ($n = 4 \div 8$, $m = 5 \div 10$) at temperature 1 K and for clusters $(H_2O)_k$, $K^+(H_2O)_p$, and $Na^+(H_2O)_p$ ($k = 4 \div 9$, $p = 5 \div 8$) at temperature 300 K with number of water molecules is studied. Twenty 10,000 sampling sets for each cluster are examined, obtained as in [21] using Monte Carlo method.

Figure 18 presents dependences of number of achiral configurations in sampling sets on number of water molecules for clusters $(H_2O)_n$ ($n = 4 \div 8$), $K^+(H_2O)_m$, and $Na^+(H_2O)_m$ ($m = 5 \div 10$) at temperature 1 K.

From **Figure 18**, it is possible to draw a conclusion that in clusters $K^+(H_2O)_m$ and $Na^+(H_2O)_m$ ($m = 5 \div 10$) at temperature 1 K the dependence of number of achiral configurations on number of water molecules has one maximum.

Figure 19 demonstrates the dependence of numbers of the right and left configurations on number of water molecules for clusters $(H_2O)_n$, $K^+(H_2O)_m$, and $Na^+(H_2O)_m$ ($n = 4 \div 8$, $m = 5 \div 10$) at temperature 1 K, whereas the results for clusters $(H_2O)_k$, $K^+(H_2O)_p$, and $Na^+(H_2O)_p$ ($k = 4 \div 9$, $p = 5 \div 8$) at temperature 300 K are shown in **Figure 20**. One can see that numbers of the right and left configurations in sampling set are equal within the accuracy; that is, clusters have no preferred direction of twist.

2.2.4 Study of chirality properties of water shells of chiral impurities

Molecules L-valine, D-valine, L-glycerose, and D-glycerose and the smallest possible chiral cluster of water $(H_2O)_4$ are chosen as chiral objects to study ($(H_2O)_4$ is shown to be the most probable type of structure at 1 K (**Figure 21**)).

Water shells of specified thickness ($d = 4 \div 10$ Å with step 2 Å) are formed around each of the molecules L-valine, D-valine, L-glycerose, and D-glycerose and the right and left clusters $(H_2O)_4$. Each chiral object under consideration is situated in the center of water shell filled with molecules.

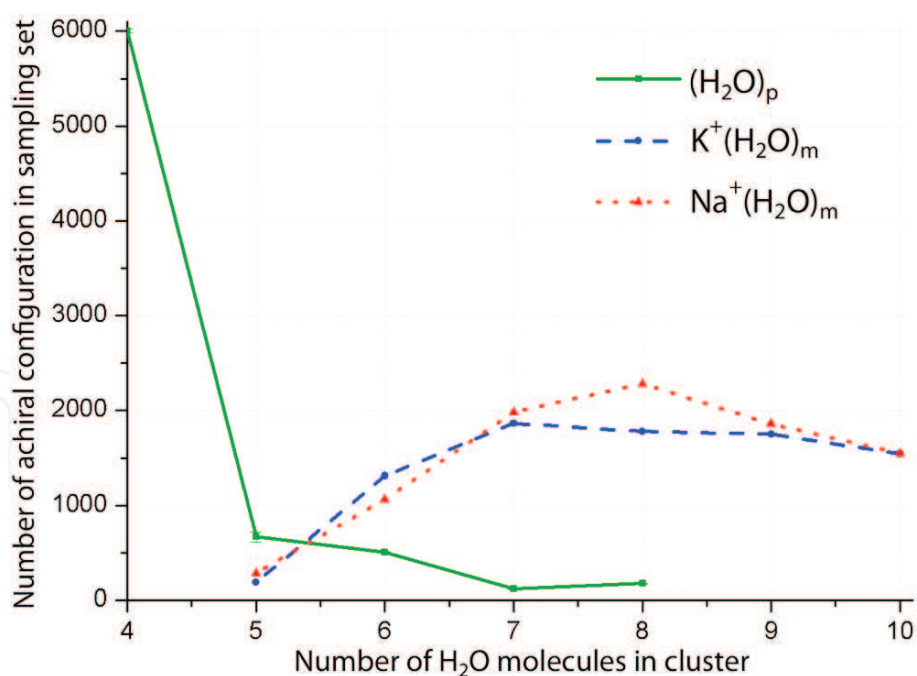


Figure 18.
Number of achiral configurations as function of number of water molecules for clusters $(\text{H}_2\text{O})_n$ ($n = 4 \div 8$), $\text{K}^+(\text{H}_2\text{O})_m$ and $\text{Na}^+(\text{H}_2\text{O})_m$ ($m = 5 \div 10$) at temperature 1 K.

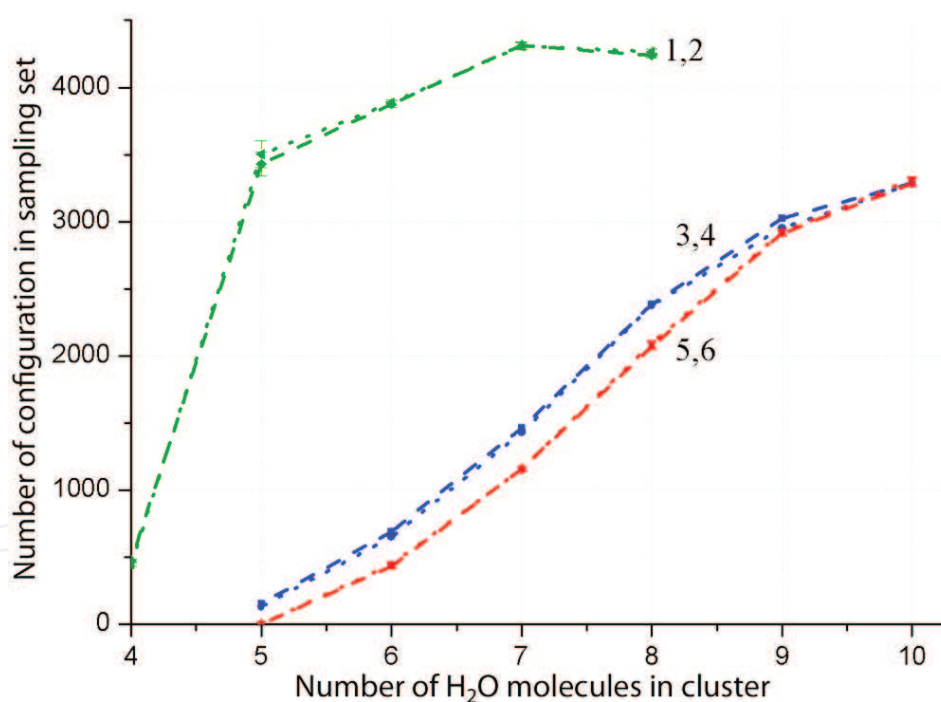


Figure 19.
Numbers of the right and left configurations of clusters in sampling set as functions of number of water molecules at temperature 1 K: 1, 2, $(\text{H}_2\text{O})_n$; 3, 4, $\text{K}^+(\text{H}_2\text{O})_n$; and 5, 6, $\text{Na}^+(\text{H}_2\text{O})_n$ ($n = 4 \div 8$, $m = 5 \div 10$). The dotted line represents right configurations, and points correspond to left configurations.

To create a sampling set of water shells, it is necessary to vary randomly the position of impurity structure. This was done using Gabedit software. A sampling set of 100 chiral molecules or structures with different positioning is created. The position of the impurity particle is fixed.

Next, these molecules are surrounded using the Solvate software with water molecules forming a layer of specified thickness. Thus, for each type of impurity, a sampling set of 100 structures or molecules with different positioning is created. Optimization of the obtained hydration shells is performed in Avogadro software

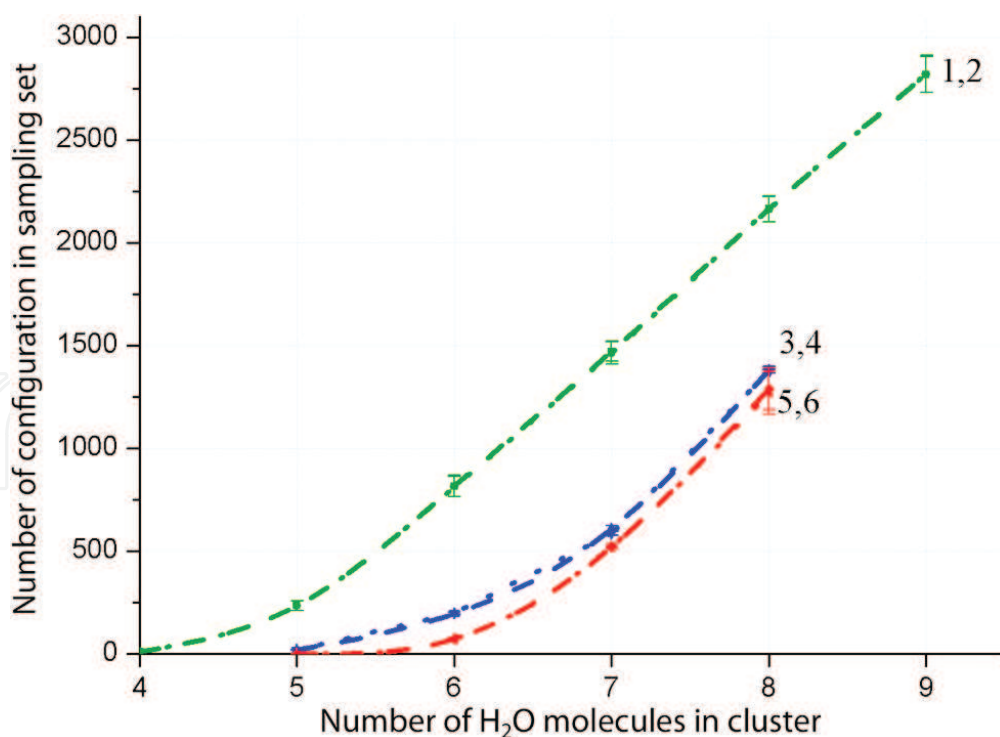


Figure 20.

Numbers of the right and left configurations of clusters in sampling set as functions of number of water molecules at temperature 300 K: 1, 2, $(\text{H}_2\text{O})_k$; 3, 4, $\text{K}^+(\text{H}_2\text{O})_p$; and 5, 6, $\text{Na}^+(\text{H}_2\text{O})_p$ ($k = 4 \div 9$, $p = 5 \div 8$). The dotted line represents right configurations, and points correspond to left configurations.

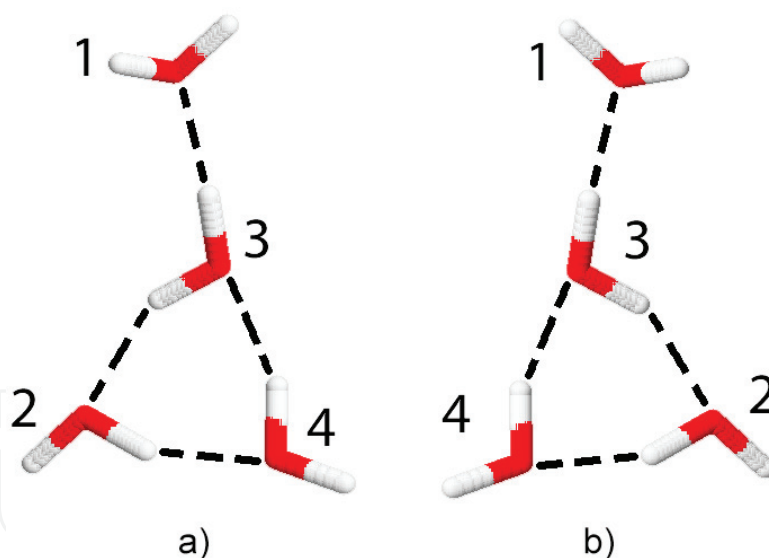


Figure 21.

(a) Left water cluster $(\text{H}_2\text{O})_4$. (b) Right water cluster $(\text{H}_2\text{O})_4$.

using the conjugate gradient method for potentials “MMFF94” up to $\Delta E \leq 10^{-5}$ kcal/mol. As a result, for each value of thickness of water shell and each studied chiral impurity, 100 configurations of H_2O molecules surrounding the impurity are obtained.

Next, using Avogadro software we removed the central chiral impurity particle from the system and analyzed chirality properties of the formed water shells.

Since the Solvate software can vary the position of water molecules within water shell of specified thickness, the analyzed water shells have different numbers of molecules. Values of number of water molecules belonging to water shell for various impurities and thickness values are given in **Table 12**.

Thickness of layer, Å	L-glycerose	D-glycerose	L-valine	D-valine	Left water cluster (H ₂ O) ₄	Right water cluster (H ₂ O) ₄
4	34 ± 1	34 ± 1	44 ± 1	44 ± 1	56 ± 1	57 ± 1
6	85 ± 1	83 ± 1	98 ± 2	100 ± 1	119 ± 1	122 ± 1
8	164 ± 1	162 ± 1	188 ± 2	186 ± 1	220 ± 2	219 ± 2
10	276 ± 2	274 ± 2	312 ± 2	311 ± 2	357 ± 3	356 ± 3
12	431 ± 3	428 ± 3	479 ± 3	478 ± 3	542 ± 5	542 ± 4
14	636 ± 3	635 ± 3	692 ± 5	696 ± 4	704 ± 3	695 ± 4

Table 12.
Number of water molecules in water shells.

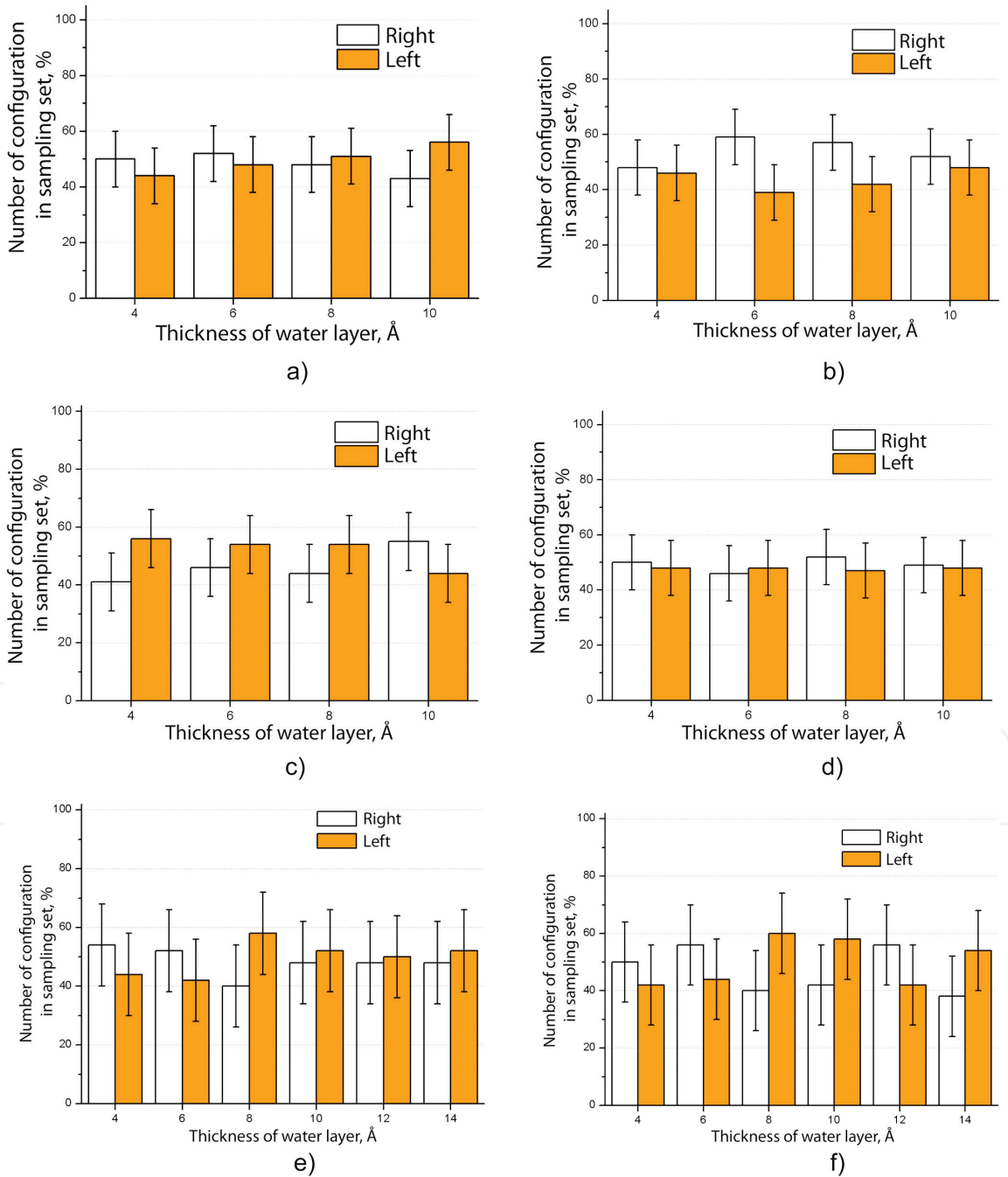


Figure 22.
Charts of numbers of the right and left configurations in sampling set for various thickness of water shell in system with a molecule: (a) D-glycerose, (b) L-glycerose, (c) D-valine, (d) L-valine, (e) left water cluster (H₂O)₄, and (f) right water cluster (H₂O)₄.

It is revealed that the molecules L-valine, D-valine, L-glycerose, and D-glycerose and chiral clusters $(\text{H}_2\text{O})_4$ with various values of thickness of water shell numbers of the right and left configurations in sampling set are equal (**Figure 22 (a)–(f)**). All configurations of water shells were chiral.

It should be noted that similar analysis has been conducted by us earlier in [25] for sampling set 50 (rather than 100, as in the present study) for each molecule L-valine, D-valine, L-glycerose, and D-glycerose and the right and left clusters $(\text{H}_2\text{O})_4$. This research indicated that for the aqueous system containing L-glycerose with 8 Å-thick water layer, the number of right-handed water shells in the sample is greater than that of left-handed ones. Also, for the system containing D-valine with 4 Å-thick water layer, the number of left-handed water shells in the sample was greater than that of right-handed shells. We recognize these results as wrong because the size of the sampling set was insufficient for obtaining statistically reliable result.

3. Conclusion

The conducted research leads to the following conclusions:

1. Addition to a small water cluster of an impurity ion K^+ or Na^+ changes its chirality properties, distribution of chiral and achiral configurations in sampling set, and number of structural types taking into account chirality.
2. Temperature affects distribution of chiral and achiral configurations in sampling set of small water clusters $(\text{H}_2\text{O})_n$ where $n = 4 \div 8$, but numbers of the right and left configurations in sampling set remain equal.
3. For clusters $\text{K}^+(\text{H}_2\text{O})_m$ and $\text{Na}^+(\text{H}_2\text{O})_m$ ($m = 5 \div 10$) at temperature 1 K, the dependence of number of achiral configurations on number of water molecules has one maximum (for $\text{K}^+(\text{H}_2\text{O})_m$ corresponding to eight water molecules, for $\text{Na}^+(\text{H}_2\text{O})_m$ corresponding to seven water molecules).
4. The number of types of chiral structures at temperature 1 K increases faster for cluster $(\text{H}_2\text{O})_n$ than for clusters of $\text{K}^+(\text{H}_2\text{O})_n$ and $\text{Na}^+(\text{H}_2\text{O})_n$ ($n = 5 \div 8$).
5. Achiral water configurations or configurations for which the concept of chirality is inapplicable exist in small water clusters. If the size of the condensed system is increased up to several dozens of water molecules, only chiral configurations are realized.
6. Clusters $(\text{H}_2\text{O})_n$, $\text{K}^+(\text{H}_2\text{O})_m$, and $\text{Na}^+(\text{H}_2\text{O})_m$ ($n = 4 \div 8$, $m = 5 \div 10$) at temperature 1 K and clusters $(\text{H}_2\text{O})_k$, $\text{K}^+(\text{H}_2\text{O})_p$ and $\text{Na}^+(\text{H}_2\text{O})_p$ ($k = 4 \div 9$, $p = 5 \div 8$) at temperature 300 K have equal numbers of the right and left configurations.
7. It is revealed that for water shell with thickness varied from 4 to 14 Å surrounding the molecule L-valine or D-valine, L-glycerose or D-glycerose, and the left or right water cluster $(\text{H}_2\text{O})_4$, there is no domination of the left or right configurations; that is, there is no preferred direction of twist.

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