

## Methods for Measurements of Water Spectrum. Differential Non-equilibrium Energy Spectrum Method (DNES)

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### Abstract

In this review it is reported about the research on the structure of intermolecular water cyclic associates (clusters) with general formula  $(\text{H}_2\text{O})_n$  and their charged ionic clusters  $[\text{H}^+(\text{H}_2\text{O})_n]^+$  and  $[\text{OH}^-(\text{H}_2\text{O})_n]^-$  by means of computer modeling and spectroscopy methods as  $^1\text{H}$ -NMR, IR-spectroscopy, DNES, EXAFS-spectroscopy, X-Ray and neutrons diffraction. The computer calculation of polyhedral nanoclusters  $(\text{H}_2\text{O})_n$ , where  $n = 3-20$  are carried out. Based on this data the main structural mathematical models describing water structure (quasicrystalline, continuous, fractal, fractal-clathrate) have been examined and some important physical characteristics were obtained. The average energy of hydrogen bonding between  $\text{H}_2\text{O}$  molecules in the process of cluster formation was measured by the DNES method compiles  $-0.1067 \pm 0.0011$  eV. It was also shown that water clusters formed from  $\text{D}_2\text{O}$  were more stable, than those ones from  $\text{H}_2\text{O}$  due to isotopic effects of deuterium.

**Keywords:** hydrogen bond, water, structure, clusters.

### 1. Introduction

Water with its anomalous physical and chemical properties outranks all other natural substances on the Earth. The ancient philosophers considered water as the most important component of the matter. It performs a vital role in numerous biochemical and metabolic processes occurring in cells with participation of water, being a universal polar solvent for hydrophilic molecules having an affinity for water. Hydroxyl groups (-OH) in  $\text{H}_2\text{O}$  molecule, are polar and therefore hydrophilic. Moreover water act as a reagent for a big number of chemical reactions (hydrolysis, oxidation-reduction reactions). In chemical processes water due to its high ionizing ability possesses strong amphoteric properties, and can act both as an acid and a base in reactions of chemical exchange.

Modern science has confirmed the role of water as a universal life sustaining component, which defines the structure and properties of inorganic and organic objects, consisted from water.. The recent development of

molecular and structural-chemical concepts has enabled to clarify an explanation of ability of water molecules to form the short-lived hydrogen bonds with neighboring molecules and many other chemical substances to bond them into intermolecular associates. It has also become clear the role of bounded water in forming hydrated substances and their physicochemical conduct in aqueous solutions.

The great scientific and practical interest have the studies of a variety of specific supramolecular structures – cyclic water clusters described by general formula  $(\text{H}_2\text{O})_n$ , which may be calculated and studied with the help of modern numerical computing methods. The clusters are also important for studying the structure of water and hydration phenomena at molecular level since they form the basic building blocks of the hydrated substances. This paper deals with the mathematical modeling of the water structure and water associates.

## 2. Nature of Hydrogen Bond in Liquids and Crystals

The peculiarities of chemical structure of  $\text{H}_2\text{O}$  molecule and weak bonds caused by electrostatic forces and donor-acceptor interaction between hydrogen and oxygen atoms in  $\text{H}_2\text{O}$  molecules create favorable conditions for formation of directed intermolecular hydrogen bonds ( $\text{O}-\text{H}\cdots\text{O}$ ) with neighboring  $\text{H}_2\text{O}$  molecules, binding them into complex intermolecular associates which composition represented by general formula  $(\text{H}_2\text{O})_n$ , where  $n$  can vary from 3 to 50 (Keutsch & Saykally, 2011). The hydrogen bond – a form of association between the electronegative O oxygen atom and a H hydrogen atom, covalently bound to another electronegative O oxygen atom, is of vital importance in the chemistry of intermolecular interactions, based on weak electrostatic forces and donor-acceptor interactions with charge-transfer (Pauling, 1960). It results from interaction between electron-deficient H-atom of one  $\text{H}_2\text{O}$  molecule (hydrogen donor) and unshared electron pair of an electronegative O-atom (hydrogen acceptor) on the neighboring  $\text{H}_2\text{O}$  molecule; the structure of hydrogen bonding, therefore may be defined as  $\text{O}^{\cdot\cdot}\text{H}^+ - \text{O}^{\cdot\cdot}$ . As the result, the electron of the H-atom due to its relatively weak bond with the proton easily shifts to the electronegative O-atom. The O-atom with increased electronegativity becomes partly negatively charged –  $\delta^-$ , while the H-atom on the opposite side of the molecule becomes positively charged –  $\delta^+$  that leads to the polarization of  $\text{O} - \text{H}^+$  covalent bond. In this process the proton becomes almost bared, and due to the electrostatic attraction forces are provided good conditions for convergence of  $\text{O}\cdots\text{O}$  or  $\text{O}\cdots\text{H}$  atoms, leading to the chemical exchange of a proton in the reaction  $\text{O}-\text{H}\cdots\text{O} \leftrightarrow \text{O}\cdots\text{H}-\text{O}$ . Although this interaction is essentially compensated by mutual repulsion of the molecules' nuclei and electrons, the effect of the electrostatic forces and donor-acceptor interactions for  $\text{H}_2\text{O}$  molecule compiles 5–10 kcal per 1 mole of substance. It is explained by negligible small atomic radius of hydrogen and shortage of inner electron shells, which enables the neighboring  $\text{H}_2\text{O}$  molecule to approach the hydrogen atom of another molecule at very close distance without experiencing any strong electrostatic repulsion.

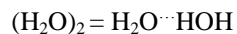
The  $\text{H}_2\text{O}$  molecule has four sites of hydrogen bonding – two uncompensated positive charges at hydrogen atoms and two negative charges at the oxygen atom. Their mutual disposition is characterized by direction from the centre of regular tetrahedron (nucleus of oxygen atom) towards its vertexes. This allows to one  $\text{H}_2\text{O}$  molecule in condensed state to form up to 4 classical hydrogen bonds, two of which are donor bonds and the other two – acceptor ones (taking into consideration bifurcate (“two-forked”) hydrogen bond – 5) (Pasichnyk *et al.*, 2008).

A hydrogen bond according to Bernal–Fowler rules (Bernal & Fowler, 1933) is characterized by the following parameters:

- a) an oxygen atom of each H<sub>2</sub>O molecule is bound with four neighboring hydrogen atoms: by covalent bonding with two own hydrogen atoms, and by hydrogen bonding – with two neighboring hydrogen atoms (as in the crystalline structure of ice); each hydrogen atom in its turn is bound with oxygen atom of neighbour H<sub>2</sub>O molecule.
- b) on the line of oxygen atom – there can be disposed only one proton H<sup>+</sup>;
- c) the proton, which takes part in hydrogen bonding situated between two oxygen atoms, therefore has two equilibrium positions: it can be located near its oxygen atom at approximate distance of 1 Å, and near the neighboring oxygen atom at the distance of 1.7 Å as well, hence both a usual dimer HO–H...OH<sub>2</sub> and an ion pair HO...H–OH<sub>2</sub> may be formed during hydrogen bonding, i.e. the hydrogen bond is part electrostatic (~90%) and part (~10%) covalent (Isaacs *et al.*, 2000). The state of “a proton near the neighboring oxygen” is typical for the interphase boundary, i.e. near water–solid body or water–gas surfaces.
- d) the hydrogen bonding of a triad O–H...O possess direction of the shorter O–H (→) covalent bond; the donor hydrogen bond tends to point directly at the acceptor electron pair (this direction means that the hydrogen atom being donated to the oxygen atom acceptor on another H<sub>2</sub>O molecule).

The most remarkable peculiarity of hydrogen bond consists in its relatively low strength; it is 5–10 times weaker than chemical covalent bond (Pimentel & McClellan, 1960). In respect of energy hydrogen bond has an intermediate position between covalent bonds and intermolecular van der Waals forces, based on dipole-dipole interactions, holding the neutral molecules together in gasses or liquefied or solidified gasses. Hydrogen bonding produces interatomic distances shorter than the sum of van der Waals radii, and usually involves a limited number of interaction partners. These characteristics become more substantial when acceptors bind H-atoms from more electronegative donors. Hydrogen bonds hold H<sub>2</sub>O molecules on 15% closer than if water was a simple liquid with van der Waals interactions. The hydrogen bond energy compiles 5–10 kcal/mole, while the energy of O–H covalent bonds in H<sub>2</sub>O molecule – 109 kcal/mole (Arunan *et al.*, 2011). The values of the average energy ( $\Delta E_{H...O}$ ) of hydrogen H...O-bonds between H<sub>2</sub>O molecules make up  $0.1067 \pm 0.0011$  eV (Antonov & Galabova, 1992). With fluctuations of water temperature the average energy of hydrogen H...O-bonds in of water molecule associates changes. That is why hydrogen bonds in liquid state are relatively weak and unstable: it is thought that they can easily form and disappear as the result of temperature fluctuations (Ignatov & Mosin, 2013a).

Another key feature of hydrogen bond consists in its cooperativity coupling. Hydrogen bonding leads to the formation of the next hydrogen bond and redistribution of electrons, which in its turn promotes the formation of the following hydrogen bond, which length increasing with distance. Cooperative hydrogen bonding increases the O–H bond length, at the same time causing a reduction in the H...O and O...O distances (Goryainov, 2012). The protons held by individual H<sub>2</sub>O molecules may switch partners in an ordered manner within hydrogen networks (Bartha *et al.*, 2003). As the result, aqueous solutions may undergo autoprotolysis, i.e. the H<sup>+</sup> proton is released from H<sub>2</sub>O molecule and then transferred and accepted by the neighboring H<sub>2</sub>O molecule resulting in formation of hydronium ions as H<sub>3</sub>O<sup>+</sup>, H<sub>5</sub>O<sub>2</sub><sup>+</sup>, H<sub>7</sub>O<sub>3</sub><sup>+</sup>, H<sub>9</sub>O<sub>4</sub><sup>+</sup>, etc. This leads to the fact, that water should be considered as associated liquid composed from a set of individual H<sub>2</sub>O molecules, linked together by hydrogen bonds and weak intermolecular van der Waals forces (Liu *et al.*, 1996). The simplest example of such associate can be a dimer of water:



The energy of the hydrogen bonding in the water dimer is 0.2 eV (~5 kcal/mol), which is larger than the energy of thermal motion of the molecules at the temperature of 300 K. Hydrogen bonds are easily disintegrated and re-formed through an interval of time, which makes water structure quite unstable and changeable (George, 1997). This process leads to structural inhomogeneity of water characterizing it as an associated heterogeneous two-phase liquid with short-range ordering, i.e. with regularity in mutual positioning of atoms and molecules, which reoccurs only at distances comparable to distances between initial atoms, i.e. the first  $\text{H}_2\text{O}$  layer. As it is known, a liquid in contrast to a solid body, is a dynamic system: its atoms, ions or molecules, keeping short-range order in mutual disposition, participate in thermal motion, the character of which is much more complicated than that of crystals. For example  $\text{H}_2\text{O}$  molecules in liquid state under normal conditions (1 atm, 22 °C) are quiet mobile and can oscillate around their rotation axes, as well as to perform the random and directed shifts. This enabled for some individual molecules due to cooperative interactions to “jump up” from one place to another in an elementary volume of water. Random motion of molecules in liquids causes continuous changes in the distances between them. The statistical character of ordered arrangement of molecules in liquids results in fluctuations – continuously occurring deviations not only from average density, but from average orientation as well, because molecules in liquids are capable to form groups, in which a particular orientation prevails. Thus, the smaller these deviations are, the more frequently they occur in liquids.

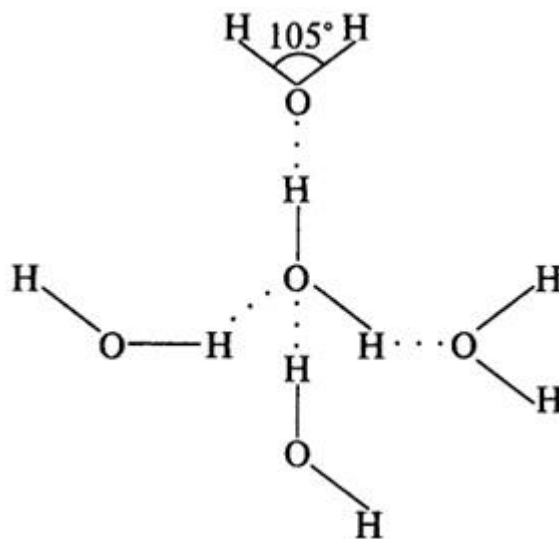


Figure 1. Hydrogen bonding between four individual  $\text{H}_2\text{O}$  molecules. It is shown the value of the angle between the covalent  $\text{H-O-H}$  bond in  $\text{H}_2\text{O}$  molecule.

The further important feature is that the hydrogen bonds are spatially oriented. As each  $\text{H}_2\text{O}$  molecule has four sites of hydrogen bond formation (two non-shared electron pairs at an oxygen atom and two uncompensated positive charges at a hydrogen atom), one  $\text{H}_2\text{O}$  molecule in a condensed state is capable to form hydrogen bonds with four  $\text{H}_2\text{O}$  molecules (two donor and two acceptor) (Figure 1), which results in

forming a tetrahedron crystal structure clearly observed in ice crystals.

At present time 14 crystalline modifications of ice are known, each of them has its own structure and a character of disposition of hydrogen atoms (Table). Crystals of all ice modifications are made up from H<sub>2</sub>O molecules, linked by hydrogen bonds into a 3D carcass, consisting of individual tetrahedrons, formed by four H<sub>2</sub>O molecules (Figure 2). In the crystalline structure of natural ice I<sub>h</sub> hydrogen bonds are oriented towards the tetrahedron apexes at strictly defined angles equal to 109°5' (in liquid water this angle is 104°5') (Mosin & Ignatov, 2013a). In ice structures I<sub>c</sub>, VII and VIII this tetrahedron is nearly the same as a regular 4 triangular tetrahedron. In ice structures II, III, V and VI the tetrahedrons are noticeably distorted. In ice structures VI, VII and VIII two intercrossing systems of hydrogen bonds are distinguished. In the centre of the tetrahedron is located an oxygen atom, at each of the two vertices – H-atom, which electron take part in formation of covalent bond with an electron pair of O-atom. The rest two vertices of the tetrahedron are occupied by two pairs of non -shared electrons of O-atom not participating in formation of molecular bonds.

Table. Ice Crystal modifications and their physical characteristics

Modification	Crystal structure	Hydrogen bond lengths, Å	Angles H–O–H in tetragonals, °
I <sub>h</sub>	Hexagonal	2.76	109.5
I <sub>c</sub>	Cubic	2.76	109.5
II	Trigonal	2.75–2.84	80–128
III	Tetragonal	2.76–2.8	87–141
IV	Rhombic	2.78–2.88	70.1–109
V	Monoclinic	2.76–2.87	84–135
VI	Tetragonal	2.79–2.82	76–128
VII	Cubic	2.86	109.5
VIII	Cubic	2.86	109.5
IX	Tetragonal	2.76–2.8	87–141
X	Cubic	2.78	109.5
XI	Hexagonal	4.50	90
XII	Tetragonal	4.01	90
XIII	Monoclinic	7.47	90–109.7
XIV	rhombic	4.08	90

Keys: I<sub>h</sub> – natural hexagonal ice; I<sub>c</sub> – cubic ice.

The carcasses of hydrogen bonds allocate H<sub>2</sub>O molecules in form of a spatial hexagon network with internal hollow hexagonal channels. In the nodes of this network O-atoms are orderly organized (crystalline state), forming regular hexagons, while H-atoms have various positions along the bonds (amorphous state). When ice melts, its network structure is destroyed: H<sub>2</sub>O molecules begin to fall down into the network hollows, resulting in a denser structure of the liquid – this explains why water is heavier than ice. The hydrogen bonding explains other anomalies of water (anomaly of temperature, pressure, density, viscosity,

fluidity etc. According to theoretical calculations, at the melting of the ice breaks about 15% of all hydrogen bonds (Mosin & Ignatov, 2011); by further heating to 40<sup>0</sup>C breaks down about half of hydrogen bonds in water associates. In the water vapor hydrogen bonds are absent.

The main difference between the structure of ice and water is more diffuse arrangement of the atoms in the lattice and disturbance of long-range order. Thermal oscillations (fluctuations) lead to bending and breaking of hydrogen bonds. Those out of the equilibrium positions H<sub>2</sub>O molecules fall into the adjacent structural voids and for a time held up there, as cavities correspond to the relative minimum of potential energy. This leads to an increase in the coordination number, and the formation of lattice defects. The coordination number (the number of nearest neighbors) varies from 4.4 at 1.5<sup>0</sup>C to 4.9 at 80<sup>0</sup>C.

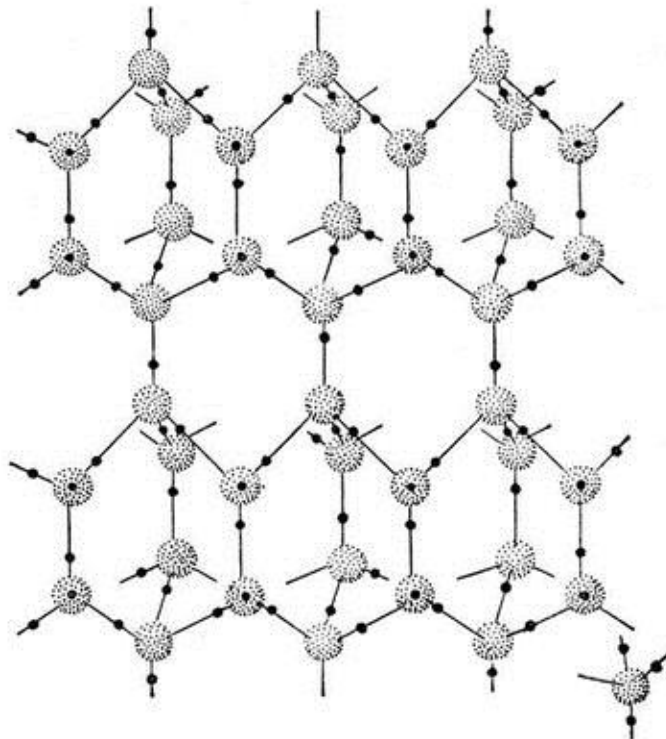
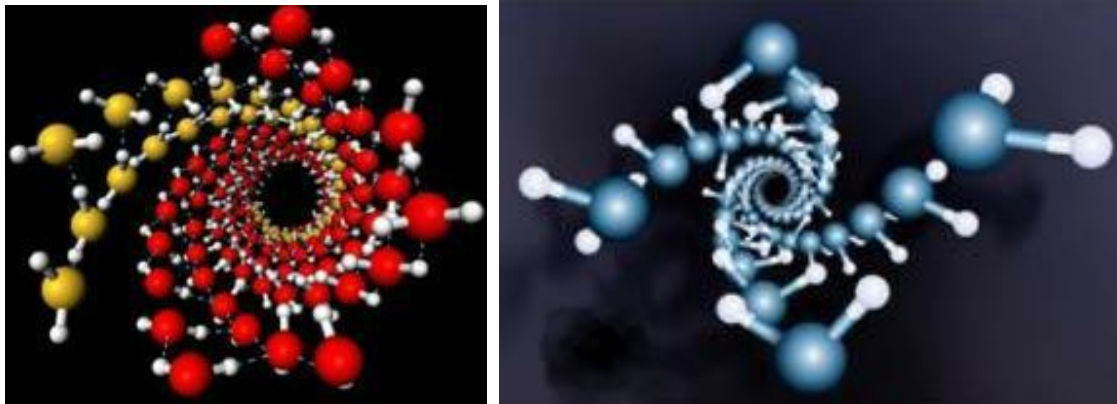


Figure 2. Hydrogen bonding in crystalline structure of natural ice I<sub>h</sub> under the temperature -10<sup>0</sup>C and pressure 1 atm. Grey balls – oxygen atoms, black balls – hydrogen atoms. On the right below shown the structural unit of crystalline ice structure.



a)

b)

Figure 3. Structures of water crystals in carbon nanotubes according to computer simulations (Bai *et al.*, 2006) (diameter of nanotubes 1.35–1.90 nm; pressure 10–40000 atm; temperature -23 °C): a) – a general view of the crystal structure of water in nanotubes, b) – the inner wall of the structure of water.

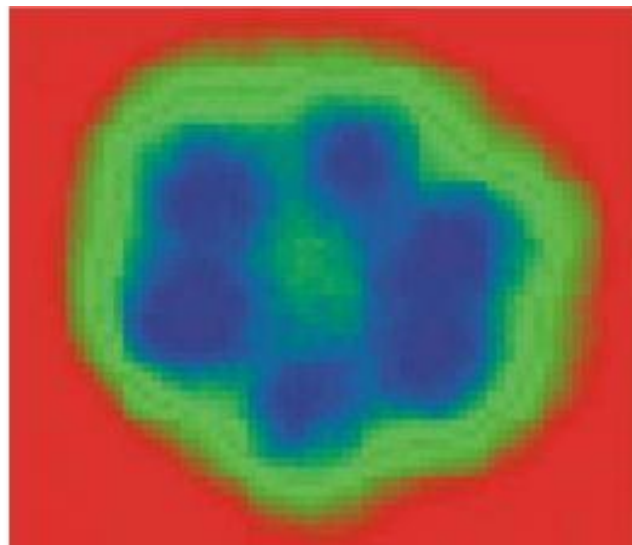


Figure 4. Image of hexamer nanocrystal of ice water (average size ~1 nm) by a scanning tunneling microscope after freezing water to 17 K on the hydrophobic metallic plates of Cu and Ag (Michaelides & Morgenstern, 2007).

Reports about evidence of existence of crystal structures in water have become more frequent in scientific literature nowadays (Michaelides & Morgenstern, 2007). As computer modeling showed, H<sub>2</sub>O molecules being placed in carbon nanotubes under high pressure and low temperatures formed crystalline nanostructures like DNA double helix (Bai *et al.*, 2006). In modeling experiment water got frozen inside carbon nanotubes with diameter 1.35–1.90 nm with pressure 10–40000 atm and temperature -23 °C. Hydrogen bonds in an ice crystal got distorted leading to the formation of a double-walled helix. The inner wall of this structure represents a four-fold twisted helix, while the outer consists of four double helices, resembling a helix of DNA molecule (Figure 3). While being frozen at 17 K on hydrophobic surfaces of Cu, Ag and their salts, water became crystallized into two-dimensional ice hexamer nanocrystal, consisting of

six attached together H<sub>2</sub>O molecules (Figure 4).

### 3. Structural Models of Water

There are several groups of models, describing structure of liquids – microcrystalline, quasicrystalline, continuous, fractal and fractal-clathrate models. The microcrystalline model of J. Bernal and P. Fowler suggests that water is a nonequilibrium 2-phase liquid containing groups of oriented molecules – microcrystals with several dozens or hundreds of molecules (Bernal & Fowler, 1933; Timothy & Zwier, 2004). Within each microcrystal in liquid a solid body ordering (long-range order) is strictly kept. As water is denser than ice, it is assumed that its molecules are allocated in a different way than in ice: like the atoms of silicon in mineral tridymite or in its more solid modification of quartz. The intermittent increase in water density from 0 to 3.98 °C and other anomalous properties of water was explained by the existence of tridymite component at low temperatures (Pople, 1951).

Quasicrystalline model by analogy with a quasicrystal, i.g. a structure that is ordered but not periodic (Nemukhin, 1996), suggests that relative disposition of particles in liquids is nearly the same as in crystals; deviation from regularity increases with the distance from the initial H<sub>2</sub>O molecule; far apart at longer distances there is no regularity in the disposition of H<sub>2</sub>O molecules. Each H<sub>2</sub>O molecule is surrounded by the four neighbouring ones, which are arranged around it in quite the same way, as they are in an ice crystal. However, in the second layer there appear deviations from regularity rapidly increasing with distance from the initial H<sub>2</sub>O molecule. Studies of X-ray scattering in liquids consisting of polyatomic molecules, revealed not only some regular arrangement of H<sub>2</sub>O molecules, but consistent pattern in mutual orientation of the molecules (Petkov *et al.*, 2012). This orientation becomes even more expressed for the polar molecules because of the hydrogen bonding effect.

Kinetic theory of liquids proposed by Y.I. Frenkel, also called a “jump-wait” model, explains the structural properties of liquids by peculiarities of thermal motion of their molecules (Frenkel, 1975). The thermal motion of H<sub>2</sub>O molecules is characterized by two parameters: a period of oscillation of H<sub>2</sub>O molecule around an equilibrium position and a period of “settled life”, i.e. period of oscillation around one particular equilibrium position. Average time of “settled life” of a H<sub>2</sub>O molecule, within which H<sub>2</sub>O molecules keep unchanged equilibrium orientation is called relaxation time  $\tau$ :

$$\tau = \tau_0 \times e^{W/RT},$$

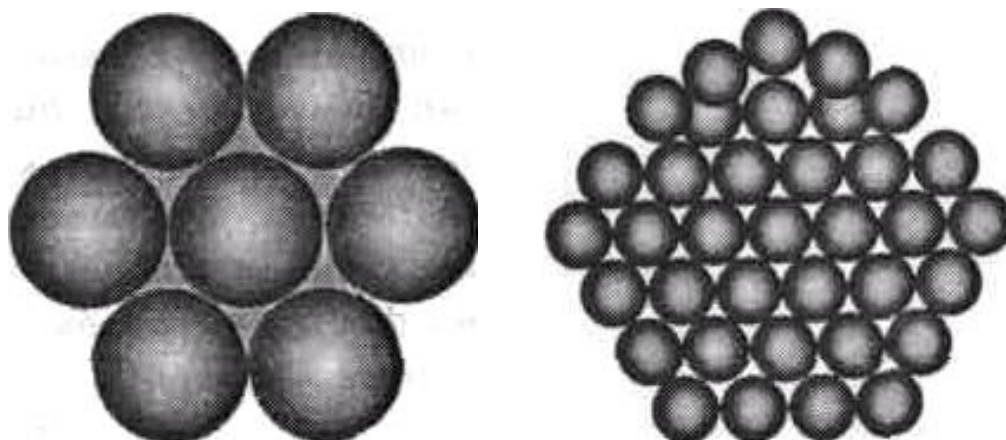
where  $\tau_0$  is an average period of oscillations of a H<sub>2</sub>O molecule around an equilibrium position (sec), W – a value of potential energy barrier, separating two neighboring equilibrium positions from each other (J), R – Boltzmann constant (J/K), T – absolute temperature (K).

According to calculations the relaxation time at room temperature makes up  $\sim 4.5 \cdot 10^{-12}$  sec, while the period of one oscillation of H<sub>2</sub>O molecules –  $10^{-12}$ – $10^{-13}$  sec. That is why each H<sub>2</sub>O molecule performs approximately 100 oscillations relative to the same equilibrium position before changing its place. Due to thermal fluctuations one H<sub>2</sub>O molecule within its “settled life” period of time oscillates around an equilibrium position, after then jumps up to new location and it continues to fluctuate up to the next jump.



Through these abrupt movements of molecules in liquids occurs diffusion, which, in contrast to the continuous diffusion in gases, called diffusion jump. With increase in temperature the period of “settled life” of  $H_2O$  molecules in a temporary state of equilibrium is reduced that brings the structure of water closer to a gas, in which translational and rotational motions of  $H_2O$  molecules prevail. Theoretical studies show that, along with the fluctuation of molecules surrounded by his neighbors and activation jumps in liquids occur flowing movement of molecules along with their immediate environment. In other words, being in oscillating state, the molecules in the liquid displaced each time by a certain distance (less than the interatomic distance), causing continuous diffusion. It is believed that in the liquefied inert gases and metals dominates continuous diffusion, while for associated liquids as water is more likely the jump diffusion mechanism. The thermal motion of  $H_2O$  molecules leads to continuous changes in distances between them, which cause fluctuations – continual deviations not only from the average density, but from the average orientation of the molecules as well, because  $H_2O$  molecules can form groups in which a certain orientation predominates. An attempt to change the water volume (even by small quantity) triggers the process of deformation of hydrogen bonds that fact may explain low water compressibility. Ice melting also causes weakening and deformation of hydrogen bonds, which makes water denser than ice. At the temperature  $3.98\text{ }^\circ\text{C}$  water acquires anomalous state, in which the quasicrystalline phase is maximally densified by filling up of ice carcass hollows with  $H_2O$  molecules. Further increase in temperature and energy of thermal motion of  $H_2O$  molecules leads to the gradual disintegration of associated water structures and to the partial rupture of hydrogen bonds with essential reduce of the “settled life” of each  $H_2O$  molecule in water associates.

The continuous and “fractal” models consider water as a complex dynamic system with a hydrogen network, forming the empty cavities and non-bonded  $H_2O$  molecules distributed within the network. The structure is based upon a dimensional carcasses of individual  $H_2O$  molecules, joined together into a multi-molecular associate similar to a clathrate having a configuration of a regular polyhedron (Samoilov, 1963). Stated geometrically, this model represents the packed spheres with varying degrees of packaging. Thus, the pentagonal packing of spheres, showed in Figure 5b, is denser, than the sphere packing model in Figure 5a (its density is 72%). Analogous structure has clathrate hydrates (gas clathrates) – crystalline water-based solids physically resembling ice, in which small non polar gas molecules are placed inside cavities of hydrogen bonded  $H_2O$  molecules.



a)

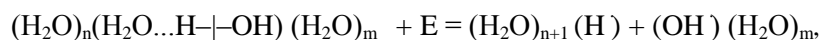
b)

Figure 5. The sphere (a) and the pentagonal (b) packing of balls representing H<sub>2</sub>O molecules in clusters.

In 1957 S. Frank and W. Wen proposed a model, postulating arbitrary formation of cyclic associates in water, which presumably had random groups of water associates – the “flickering clusters” with general formula (H<sub>2</sub>O)<sub>n</sub>, which are in a dynamic equilibrium with free H<sub>2</sub>O molecules (Henry et al., 1957). The hydrogen bonds between H<sub>2</sub>O molecules are in dynamic equilibrium; they are constantly broken and re-formed in new configurations within a certain time interval; these processes are occurred cooperatively within short-living associated groups of H<sub>2</sub>O molecules (clusters), which life spans are estimated from 10<sup>-10</sup> to 10<sup>-11</sup> sec.

Water associates evidently may have polymer structure, because hydrogen bond is on 10% partially covalent bond (Isaacs *et al.*, 2000). In 1990 G.A. Domrachev and D.A. Selivanovsky formulated a model of H<sub>2</sub>O-polimers based on the existence of mechanochemical reactions of ionization and dissociation of water in aqueous solutions (Domrachev & Selivanovsky, 1990). Water was thought as dynamically unstable quazi-polymer, composed of (H<sub>2</sub>O)<sub>n</sub> blocks with partially covalent by 10% hydrogen bonds, permitting at least to 10% of H<sub>2</sub>O molecules to comby in a sufficiently long-lived polymer associates. Similarly with mechanochemical reactions in polymers, in case of mechanical impact on water, the energy absorbed by water required for splitting up the H–OH bond, concentrates in a micro-scale area of the liquid water structure.

The splitting up reaction of the H–OH bond in water polymer associates is expressed by the following equation:



where E – the energy of the H–OH bond, 460 κJ/mole; the dot denotes an unpaired electron.

Splitting up of the H–OH bond is accompanied by formation of new disordered bonds between “fragments” of the initial molecules, leading to the formation of fluctuation areas with different density fluctuations that can be observed in aqueous solutions.

Another interesting physical phenomenon was discovered by A. Antonov in 2005 (Antonov, 2005). It was established experimentally that at evaporation of water droplet the contact angle θ decreases discretely to zero, whereas the diameter of the droplet changes insignificantly. By measuring this angle within a regular time intervals a functional dependence f(θ) can be determined, which is designated by the spectrum of the water state. For practical purposes by registering the spectrum of water state it is possible to obtain information about the averaged energy of hydrogen bonds in an aqueous sample. For this purpose the model of W. Luck is used, which consider water as an associated liquid, consisted of O–H...O–H groups (Luck *et al.*, 1980). The major part of these groups is designated by the energy of hydrogen bonds (-E), while the others are free (E = 0). The energy distribution function f(E) is measured in electron-volts (eV<sup>-1</sup>) and may be varied under the influence of various external factors on water as temperature and pressure.

For calculation of the function f(E) experimental dependence between the water surface tension (θ) and the energy of hydrogen bonds (E) is established:

$$f(E) = b \times f(0) / (1 + b \times E)^{1/2},$$

where  $b = 14.33 \text{ eV}^{-1}$

The energy of hydrogen bonds ( $E$ ) is measured in electron-volts (eV) and is designated by the spectrum of energy distribution. The water spectrum is characterized by a non-equilibrium process of water droplets evaporation, thus the term “non-equilibrium energy spectrum of water” (NES) is applied.

The difference  $\Delta f(E) = f(\text{samples of water}) - f(\text{control sample of water})$  is called the “differential non-equilibrium energy spectrum of water” (DNES).

DNES is a measure of changes in the structure of water as a result of external influences. The cumulative effect of all other factors is the same for the control sample of water and the water sample, which is under the influence of this impact.

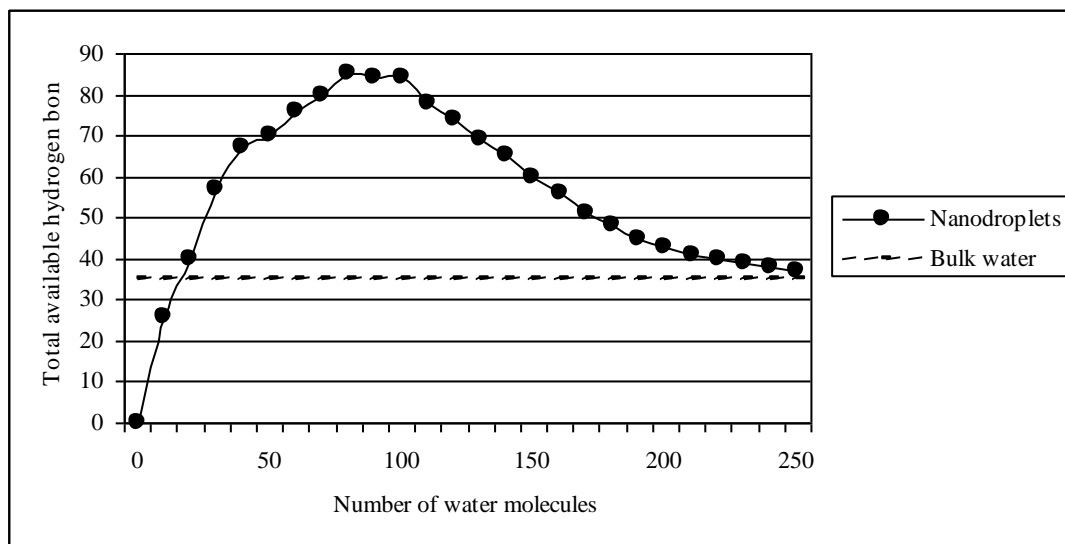


Figure 6. The total number of hydrogen bonds depending on the number of water molecules in clusters.

In 2005 R. Saykally (University of California, USA) calculated the possible number of hydrogen bonds and the stability of water clusters depending on the number of  $\text{H}_2\text{O}$  molecules (Figure 6) (Saykally, 2005). It was also estimated the possible number of hydrogen bonds (100) depending on the number of  $\text{H}_2\text{O}$  molecules (250) in clusters (Sykes, 2007). O. Loboda and O.V. Goncharuk provided data about the existence of icosahedral water clusters consisting of 280  $\text{H}_2\text{O}$  molecules with the average size up to 3 nm (Loboda & Goncharuk, 2010). The ordering of water molecules into associates corresponds to a decrease in the entropy (randomness), or decrease in the overall Gibbs energy ( $G = \Delta H - T\Delta S$ ). This means that the change in enthalpy  $\Delta H$  minus the change in entropy  $\Delta S$  (multiplied by the absolute temperature  $T$ ) is a negative value. These results are consistent with our data on research of NES spectrum of water on which it may make conclusion about the number of  $\text{H}_2\text{O}$  molecules in water clusters. NES spectrum of water has energy ranges from -0.08 to -0.14 eV (Figure 7). The spectral range lies in the middle infrared range from 8 to 14  $\mu\text{m}$  ("window" of the atmosphere transparency to electromagnetic radiation). Under these conditions, the relative stability of water clusters depends on external factors, primarily on the temperature.

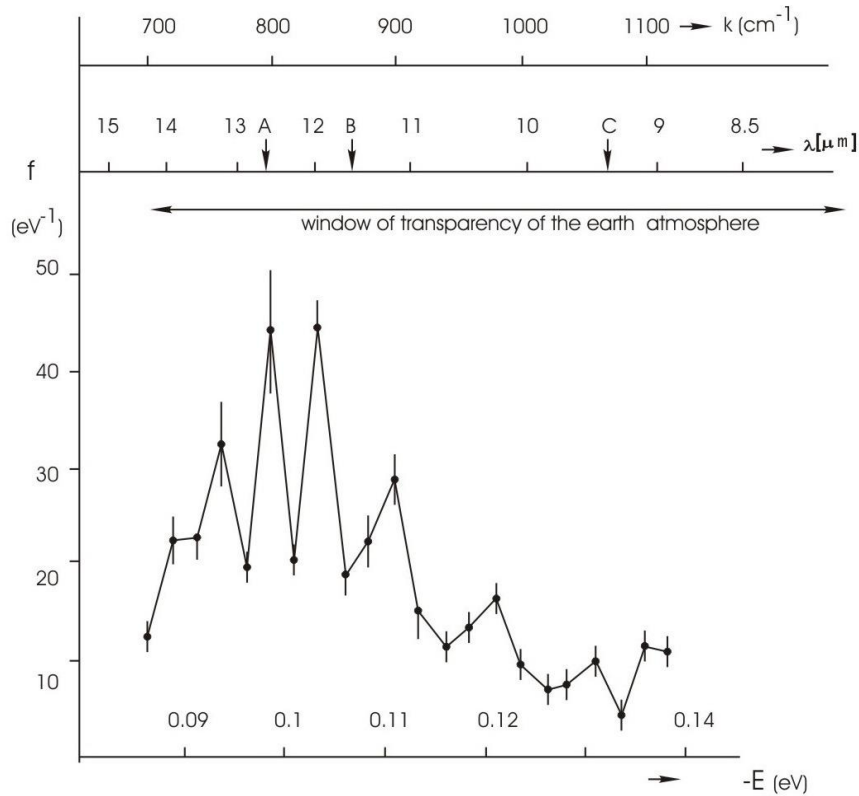


Figure 7. NES-spectrum of deionized water (chemical purity 99.99%, pH = 6.5–7.5, total mineralization 200 mg/l, electric conductivity 10  $\mu\text{S}/\text{cm}$ ). On the horizontal axis shows the energy of the H...O hydrogen bonds in the associates  $-E$  (eV). The vertical axis – energy distribution function  $-f$  ( $\text{eV}^{-1}$ ).  $k$  – the vibration frequency of the H–O–H atoms ( $\text{cm}^{-1}$ );  $\lambda$  – wavelength (mm).

It was shown that the  $\text{H}_2\text{O}$  molecules change their position in clusters depending on the energy of intermolecular H...O hydrogen bonds. The values of the average energy ( $E_{\text{H...O}}$ ) of hydrogen bonds between the  $\text{H}_2\text{O}$  molecules in the formation of cluster associates with formula  $(\text{H}_2\text{O})_n$  compile  $0.1067 \pm 0.0011$  eV. As the energy of hydrogen bonds between  $\text{H}_2\text{O}$  molecules increases up to  $-0.14$  eV, the cluster formation of water becomes “destructuring”. In this case, the energy redistribution between the individual  $\text{H}_2\text{O}$  molecules occurs (Figure 7).

All these data indicate that the water is a complex associated non-equilibrium liquid consisting of associative groups containing according to the present data, from 3 to 20 individual  $\text{H}_2\text{O}$  molecules (Tokmachev *et al.*, 2010). Associates can be perceived as unstable groups (dimers, trimers, tetramers, pentamers, hexamers etc.) in which  $\text{H}_2\text{O}$  molecules are linked by van der Waals forces, dipole-dipole and other charge-transfer interactions, including hydrogen bonding. At room temperature, the degree of association of  $\text{H}_2\text{O}$  molecules may vary from 2 to 6. In 1993 K. Jordan (USA) (Tsai & Jordan, 1993) calculated the possible structural modifications of small water clusters consisting of six  $\text{H}_2\text{O}$  molecules (Figure 8a–c). Subsequently, it was shown that  $\text{H}_2\text{O}$  molecules capable of hydrogen bonding by forming the structures representing topological 1D rings and 2D chains composed from numerous  $\text{H}_2\text{O}$  molecules. Interpreting the experimental data, they are considered as pretty stable elements of the structure. According

to computer simulations, clusters are able to interact with each other through the exposed protons on the outer surfaces of hydrogen bonds to form new clusters of more complex composition.

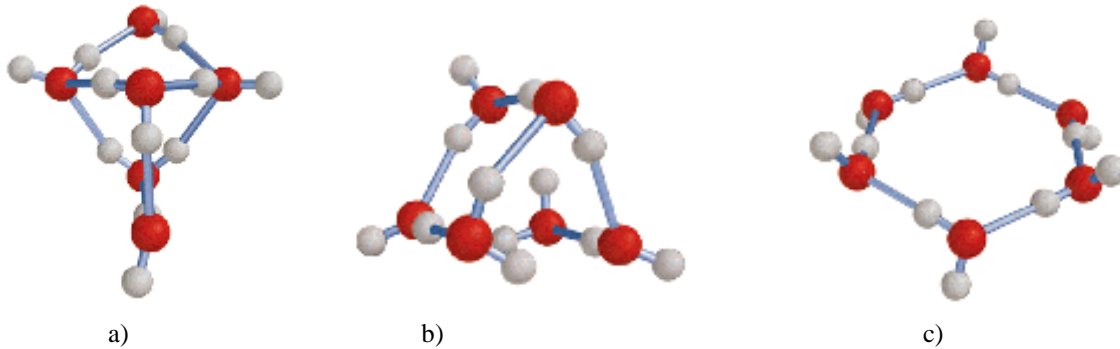


Figure 8. Calculation of small water cluster structures (a–c) with general formula  $(\text{H}_2\text{O})_n$ , where  $n = 6$  (Tsai & Jordan, 1993).

In 2000 it was deciphered the structure of the trimer water, and in 2003 – tetramer, pentamer and the water hexamer (Wang & Jordan, 2003). Structures of water clusters with formula  $(\text{H}_2\text{O})_n$ , where  $n = 3–5$ , similar to the cage structure. Hexagonal structure with  $n = 6$ , consisting of six  $\text{H}_2\text{O}$  molecules at the hexagon vertices, is less stable than the cage structure. In the hexagon structure four  $\text{H}_2\text{O}$  molecules can be cross-linked by hydrogen bonds (Figure 9).

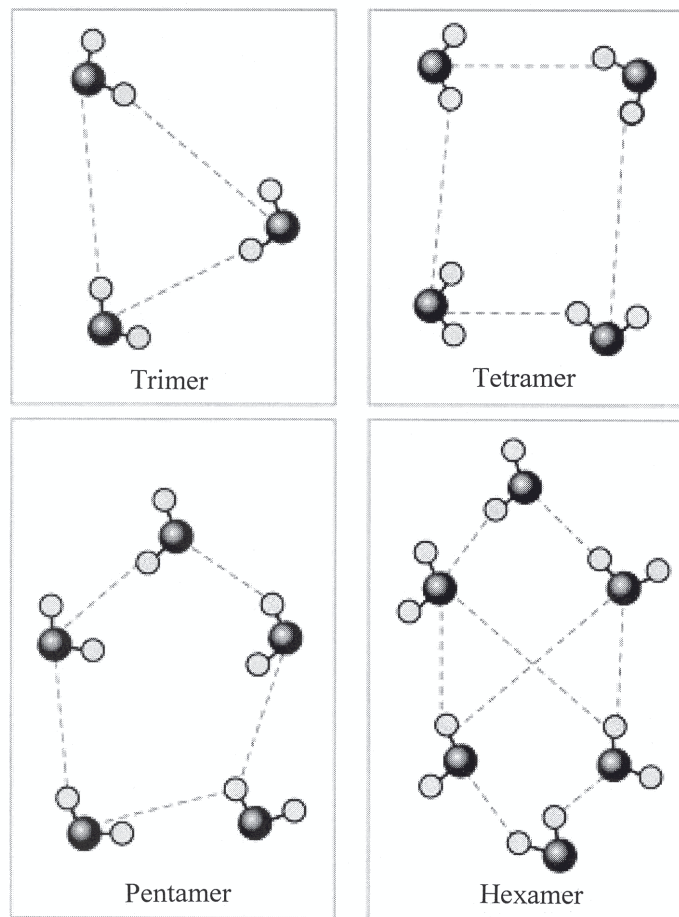


Figure 9. Cluster structure of a trimer, tetramer, pentamer and hexamer of water.

Quantum-chemical calculations of middle size clusters with the general formula  $(\text{H}_2\text{O})_n$ , where  $n = 6-20$ , have shown that the most stable structures are formed by the interaction of tetrameric and pentameric structures (Maheshwary *et al.*, 2001; Choi & Jordan, 2010). Thus the structures of  $(\text{H}_2\text{O})_n$ , where  $n = 8, 12, 16$ , and  $20$  are cubic, and structures  $(\text{H}_2\text{O})_n$  where  $n = 10$  and  $15$  – pentagons. Other structures with  $n = 9, 11, 13, 14, 17, 18$  and  $19$  evidently have a mixed composition. Large tetrahedron clusters as  $(\text{H}_2\text{O})_{196}$ ,  $(\text{H}_2\text{O})_{224}$ ,  $(\text{H}_2\text{O})_{252}$  (Figure 10) composed from the smaller ones formed a vertex of a  $(\text{H}_2\text{O})_{14}$  tetrahedron are also described (Chaplin, 2011).

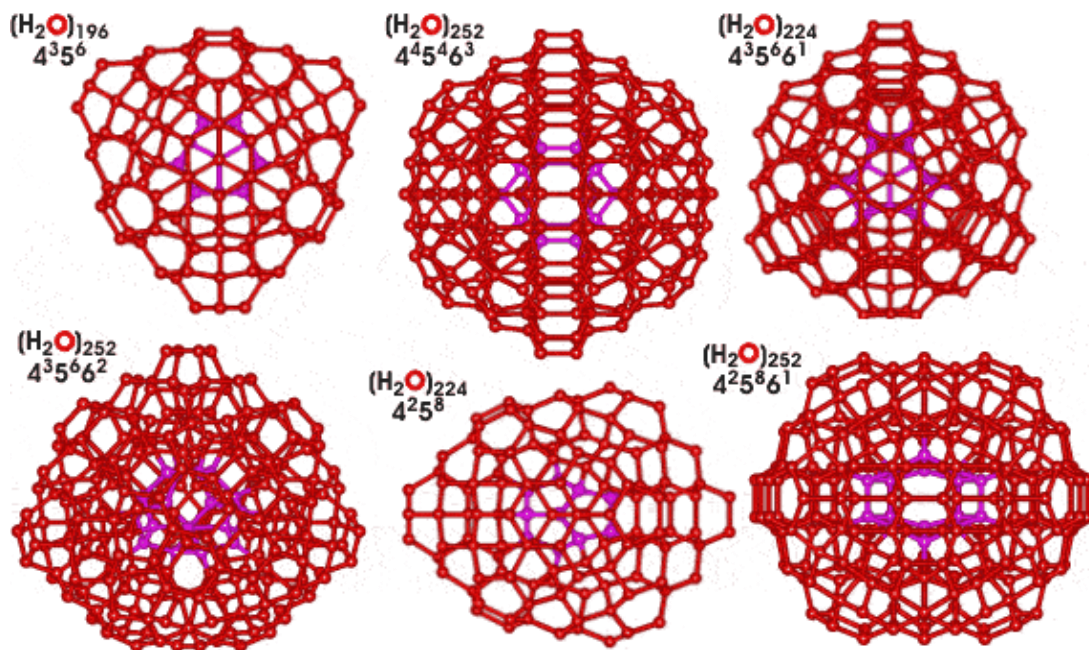


Figure 10. Tetrahedron water clusters  $(\text{H}_2\text{O})_n$  with different symmetry ( $n = 196, 224, 252$ ).

The clusters, evidently, may be rather stable under a certain conditions, and can be obtained in the isolated state within a very short interval of time. There is also a reason to believe that the charged ions stabilize the clusters. Therefore, the clusters can be divided into positively and negatively charged ionic clusters –  $[\text{H}^+(\text{H}_2\text{O})_n]^+$ ,  $[\text{OH}^-(\text{H}_2\text{O})_n]^-$ , and not having a charge – neutral clusters with general formula  $(\text{H}_2\text{O})_n$ . Clusters, containing 20 individual  $\text{H}_2\text{O}$  molecules and a proton in the form of hydronium ion  $\text{H}_3\text{O}^+$  (“magic” number) form the most stable ionic clusters  $[(\text{H}_2\text{O})_{20}\text{H}_3\text{O}]^+$  or  $[(\text{H}_2\text{O})_{21}\text{H}]^+$  (Figure 11) (Cui *et al.*, 2006). It is assumed that the stability of ionic clusters is due to the special clathrate structure in which 20  $\text{H}_2\text{O}$  molecules are formed 12 pentagonal dodecahedron, in which cavities is captured the  $\text{H}_3\text{O}^+$  ion. It is occurred because of all the clusters only the dodecahedron has a large cavities enough to accommodate a bulky  $\text{H}_3\text{O}^+$  ion. Subsequently, due to cooperative interactions  $\text{H}_3\text{O}^+$  is further able to move to the surface of the cluster and lose a proton  $\text{H}^+$  leading to the formation of hydronium ions like  $\text{H}_5\text{O}_2^+$ ,  $\text{H}_7\text{O}_3^+$ , and  $\text{H}_9\text{O}_4^+$ , fixed on the surface of the cluster. These data show the diversity of supposed water structures and the complexity of molecular interactions between the different water clusters, the nature of which we are only beginning to understand.

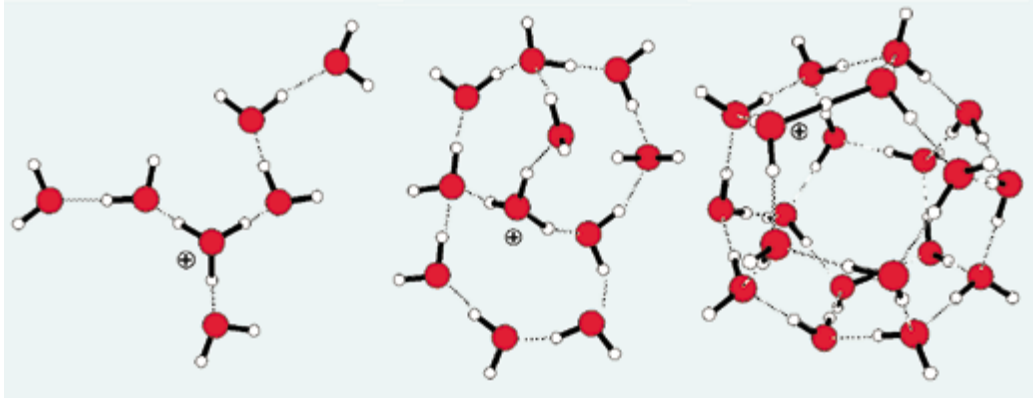


Figure 11. Formation of ionic clusters  $[(\text{H}_2\text{O})_{20}\text{H}_3\text{O}]^+$  or  $[(\text{H}_2\text{O})_{21}\text{H}]^+$  with captured hydronium ion  $\text{H}_3\text{O}^+$ .

It is reasonable that the structure of liquid water should be related to the structure of hexagonal ice, formed from  $\text{H}_2\text{O}$  tetrahedrons, which exist under atmospheric pressure. In the computer simulation  $\text{H}_2\text{O}$  tetrahedrons grouped together, to form a variety of 3D-spatial and 1D, 2D-planar structures, the most common of which is hexagonal structure where 6  $\text{H}_2\text{O}$  molecules (tetrahedrons) are combined into a ring. A similar type of structure is typical for ice  $\text{I}_h$  crystals. When ice melts, its hexagonal structure is destroyed, and a mixture of clusters consisting of tri-, tetra-, penta-, and hexamers of water and free  $\text{H}_2\text{O}$  molecules is formed. Structural studies of these clusters are significantly impeded, since the water is perceived as a mixture of different clusters that are in dynamic equilibrium with each other.

S. Zenin (Russia) calculated a cluster model based on a minimum "quantum" of water (Zenin, 1999), which is a 4 triangular tetrahedron composed of four 12 pentagonal dodecahedrons (Figure 12). The "quantum" consisted of 57  $\text{H}_2\text{O}$  molecules interacting with each other at the expense of free hydrogen bonds exposed on the surface. Of 57  $\text{H}_2\text{O}$  molecules in the "quantum" 17  $\text{H}_2\text{O}$  molecules compose tetrahedral completely hydrophobic, i.e. saturated with four hydrogen bonds in the central carcass, and four dodecahedra on the surface of each there are 10 centers for the formation of hydrogen bond (O-H or O). 16 "quanta" form a bigger cluster structure consisted from 912  $\text{H}_2\text{O}$  molecules similar to a tetrahedron.

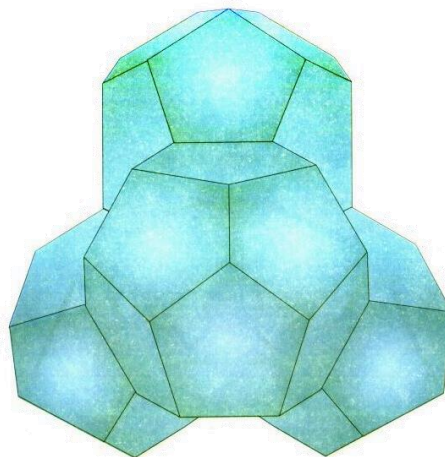


Figure 12. Model of water associate from 57  $\text{H}_2\text{O}$  molecules. Tetrahedron of four dodecahedron



(“quantum”) according to the model of S. Zenin (Zenin, 1999).

M. Chaplin (London South Bank University, UK) (Chaplin, 2011) calculated the water structure based on 20 triangular icosahedron (Figure 13). The structure is based on minimal tetrahedral water cluster, consisting of 14 H<sub>2</sub>O molecules. Arrangement of 20 of these 14-molecule structures forms an icosahedral network, consisting from 280 H<sub>2</sub>O molecules. Each 280-molecule in icosahedral contains several substructures with each H<sub>2</sub>O molecule involved in four hydrogen bonds; two as donor and two as acceptor. 13 overlapping icosahedra may form a more large cluster (tricontahedron) consisting from 1820 H<sub>2</sub>O molecules, which has twice more H<sub>2</sub>O molecules than in the previous model.

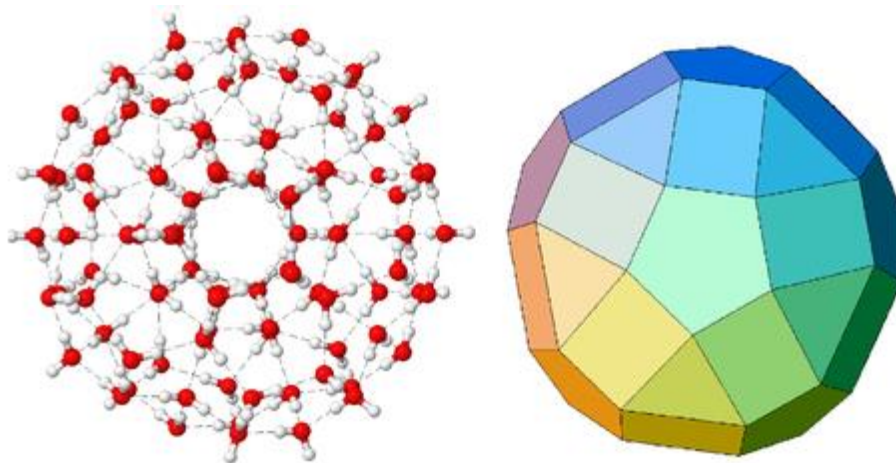


Figure 13. Icosahedron cluster based on 100 H<sub>2</sub>O molecules and the underlying structure.

#### 4. Methods of Studying of Water Clusters

Cluster structures in water calculated theoretically on computer were confirmed by <sup>1</sup>H-NMR, IR, Raman, Compton scattering, EXAFS-spectroscopy and X-ray diffraction (Ignatov, 2005; Mosin & Ignatov, 2011). Information obtained with using the modern detection methods corresponds to femtosecond time, i.e instantaneous dynamics of intermolecular interactions in the molecular scale. The presence of hydrogen bonding causes the noticeable effect on vibrational and <sup>1</sup>H-NMR spectra. In <sup>1</sup>H-NMR the chemical shift of the proton involved in the hydrogen bonding shifts about 0.01 ppm reducing strength of hydrogen bonding while the temperature is raised (Yamaguchi et al., 2001). Increased extent of hydrogen bonding within clusters results in a similar effect; the higher chemical shifts with greater cooperativity, the shorter hydrogen bonded O-H...O distances. <sup>1</sup>H peaks shift to greater ppm with increasing hydrogen bonding strength.

In IR-spectroscopy the characteristic vibration frequency bands containing hydrogen are reduced in spectra if hydrogen atom is included in the hydrogen bonding. Infrared absorption bands, such as OH-groups are much expanded when the hydrogen bond is formed, and their intensity increases. The main stretching band

in liquid water is shifted to a lower frequency ( $\nu_3$ ,  $3480\text{ cm}^{-1}$  and  $\nu_1$ ,  $3270\text{ cm}^{-1}$ ), while the bending frequency ( $\nu_2$ ,  $1640\text{ cm}^{-1}$ ) increased by hydrogen bonding (Ohno et al., 2005). Increased strength of hydrogen bonding shifts the stretch vibration to lower frequencies with greatly increased intensity in the infrared due to the increased dipoles. With raising the temperature the stretch vibrations shift to higher frequency, while the intramolecular vibrations shift to lower frequencies (Ignatov & Mosin, 2013b). Hydrogen bond energy lies in the range of 2.3 kcal/mole for the N–H...O-bonds up to 7.0 kcal/mol for the bonds with hydrogen fluoride F–H...F. The strength of the hydrogen bonding depends on the cooperative/anticooperative character of the surrounding hydrogen bonds with the strongest hydrogen bonds giving the lowest vibrational frequencies.

In X-ray absorption spectroscopy (EXAFS-spectroscopy) X-ray radiation excites the electrons of the inner shell of an oxygen atom in  $\text{H}_2\text{O}$  molecules and stipulates their transition onto unoccupied upper electronic levels in the molecules (Wernet *et al.*, 2004). Probability of electron transitions and characteristics of the absorption contour depends mostly on the molecular environment. This allows by varying the energy of the X-rays to study the distribution of associations for HOH...OH<sub>2</sub> bond judging on lengths and angles of the covalently bonded hydrogen atom in the molecule. EXAFS spectrum near the oxygen atom is also sensitive to hydrogen bonding. This method is used to obtain information about the molecular structure of water in the first coordination sphere. Since the time of excitation of electrons is much smaller than the vibrational motions in liquids, X-ray probe of the electronic structure provides information about the instantaneous changes of configurations of the water structure.

Diffraction techniques (X-ray and neutron diffraction) on liquid water allow to calculate the function of density radial distribution (O or H) and the probability of detection of  $\text{H}_2\text{O}$  molecules at a certain distance from a randomly chosen individual  $\text{H}_2\text{O}$  molecule (Tokushima *et al.*, 2008). This allows to detect the irregularities in water by constructing the radial distribution function, i.e. the distance between the atoms of O, H, and O–H in  $\text{H}_2\text{O}$  molecule and its nearest neighbors. Thus, the distribution of the distances between the oxygen atoms at a room temperature, gives three major peaks measured at 2.8, 4.5 and 6,7 Å. The first maximum corresponds to the distance to the nearest neighbor and its value is approximately equal to the length of the hydrogen bond. The second maximum is close to the average edge length of a tetrahedron, as  $\text{H}_2\text{O}$  molecules in the crystalline structure of ice I<sub>h</sub> arranged at the vertices of the tetrahedron allocated around the center of the molecule. The third peak, expressed very weakly, corresponds to the distance to the third and more distant neighboring  $\text{H}_2\text{O}$  molecules on the hydrogen network. In 1970 I.S. Andrianov and I.Z. Fisher calculated the distance up to the eighth of the neighboring  $\text{H}_2\text{O}$  molecule; the distance to the fifth the neighboring  $\text{H}_2\text{O}$  molecule turned out to be 3 Å, and to the sixth molecule – 3,1 Å. This allowed to draw conclusions about the geometry of hydrogen bonds and farther surroundings of  $\text{H}_2\text{O}$  molecules.

Another method for structural studies – neutron diffraction is similar to X-ray diffraction. However, because the neutron scattering lengths vary slightly among different atoms, this method is limited in the case of the isomorphous substitution of hydrogen atoms in  $\text{H}_2\text{O}$  molecule by deuterium (D). In practice generally operate with a crystal whose molecular structure is approximately defined by other methods. Then, it is measured the intensity of the neutron diffraction of this crystal. From these results, the Fourier transform is carried out; the measured neutron intensity and phase are using for calculation. Then, on the resultant Fourier map hydrogen and deuterium atoms are represented with much greater atomic weight than on the electron density map, as the contribution of these atoms in neutron scattering is essentially big. On

the resulting density map is determined the arrangement of hydrogen  $^1\text{H}$  (negative density) and deuterium D (positive density) atoms. A variation of the method consists in that the crystal of an ordinary protonated water ( $\text{H}_2\text{O}$ ) before measurements kept in 99.9 at.% of heavy water ( $\text{D}_2\text{O}$ ). In this case the neutron diffraction can not only establish the localization of the hydrogen atoms, as well as to identify those protons that can be exchanged by deuterium, that is particularly important for the study of isotopic (H–D) exchange. Such information in some cases may help confirm the correctness of the water structure established by other methods.

Clusters formed of  $\text{D}_2\text{O}$  are some more stable and resistant than those ones from  $\text{H}_2\text{O}$  due to isotopic effects of deuterium caused by 2-fold increasing nuclear mass of deuterium (molecular mass of  $\text{D}_2\text{O}$  is more by 11% than that of  $\text{H}_2\text{O}$ ). The structure of  $\text{D}_2\text{O}$  molecule is the same, as that of  $\text{H}_2\text{O}$ , with small distinction in values of lengths of covalent bonds.  $\text{D}_2\text{O}$  crystals have the same structure as a conventional ice  $\text{I}_h$ , the difference in unit cell size is very insignificant (0.1%). But they are heavy ( $0.982 \text{ g/cm}^3$  at  $0^\circ\text{C}$  over  $0.917 \text{ g/cm}^3$  for conventional ice).  $\text{D}_2\text{O}$  boils at  $101.44^\circ\text{C}$ , freezes at  $3.82^\circ\text{C}$ , has density at  $20^\circ\text{C}$   $1.105 \text{ g/cm}^3$ , and the maximum density occurs not at the  $3.89^\circ\text{C}$ , as for  $\text{H}_2\text{O}$ , but at  $11.2^\circ\text{C}$  ( $1.106 \text{ g/cm}^3$ ). The mobility of  $\text{D}_3\text{O}^+$  ion on 28.5% lower than that of  $\text{H}_3\text{O}^+$  ion and  $\text{OD}^-$  ion – 39.8% lower than that of  $\text{OH}^-$  ion, the constant of ionization of  $\text{D}_2\text{O}$  is less than the constant of ionization of  $\text{H}_2\text{O}$ , which means that  $\text{D}_2\text{O}$  has a bit more hydrophobic properties than  $\text{H}_2\text{O}$ . All these effects lead that the hydrogen bonds formed by deuterium atoms differ in strength and energy from ordinary hydrogen bonds (O–H length  $1.01 \text{ \AA}$ , O–D length  $0.98 \text{ \AA}$ , D–O–D angle  $106^\circ$ ). Commonly used molecular models use O–H lengths  $\sim 0.955 \text{ \AA}$  and  $1.00 \text{ \AA}$  and H–O–H angles from  $\sim 105.5^\circ$  to  $\sim 109.4^\circ$ . The substitution of H with D atom affects the stability and geometry of hydrogen bonds in apparently rather complex way and may, through the changes in the hydrogen bond zero-point vibrational energies, alter the conformational dynamics of hydrogen (deuterium)-bonded structures of associates. In general, isotopic effects stabilize hydrogen bond with participation of deuterium, resulting in somewhat greater stability of associates formed from  $\text{D}_2\text{O}$  molecules (Mosin & Ignatov, 2013b).

As a result of experiments on quasi-elastic neutron scattering was measured the most important parameter – the coefficient of self-diffusion of water at different temperatures and pressures. To analyse the self-diffusion coefficient on quasi-elastic neutron scattering, it is necessary to know the character of moving of molecules. If they move in accordance with the “jump-wait” model, then the “settled” life time (the time between jumps) of  $\text{H}_2\text{O}$  molecule compiles 3.2 ps. The newest methods of femtosecond laser spectroscopy allow to estimate the lifetime of the broken hydrogen bonds: a proton needs 200 fs to find a partner.

The studying the full details of the structure of associative elements in water can be made, considering all the parameters by computer simulation or numerical experiment. For this in a given space is chosen random ensemble of  $n$   $\text{H}_2\text{O}$  molecules and are optimal parameters – the energy of interatomic interactions, bond length, the arrangement of atoms and molecules, the most consistent with the diffraction data. Data thus obtained are then extrapolated to the actual water structure, and further used to calculate thermodynamic parameters. Data obtained by computer experiments, show that the nature of the thermal motion of the molecules in the liquids corresponds on the whole to a vibration of the individual  $\text{H}_2\text{O}$  molecules near the equilibrium centers, with occasional jumps up to the new position.

## 5. Conclusion

The experimental data obtained during the last years suggest that water is a complex dynamic associative system, consisting of tens and possibly hundreds individual H<sub>2</sub>O molecules binding by multiple intermolecular hydrogen bonds, being in a state of dynamic equilibrium. Up till now is scientifically proven the existence of associative water clusters with general formula (H<sub>2</sub>O)<sub>n</sub>, where n = 3–20. Although calculated structural models explain pretty well many anomalous properties of water and being in a good agreement with the experimental data on the diffraction of X-rays and neutrons, Raman, Compton scattering and EXAFS-spectroscopy, they are the most difficult to agree with the dynamic properties of water – flow, viscosity and short relaxation times, which are measured by picoseconds.

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