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New Aspects of Water Structure: Molecular Spectroscopy and Computer Simulation Analysis

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Abstract: An important feature of water molecule is ability to generate hydrogen bonds. The fact that the hydrogen bonds can be easily bent and switched over results in existence of hydrogen bond networks of different topology, that is justified by various modifications of crystal and amorphous ice. It is not surprising presence of a numerous amount of models for liquid water structure. In particular, there is an opinion that water consists of discrete types of associates: monomers, dimers, n-mers. As an argument for such "mixed" structure of water a fact is used that the contour of Raman spectrum changes essentially with temperature that is interpreted sometimes as a "swap" between various types of associates. Nevertheless it is naturally to suppose that water forms a unified set (continued network) of hydrogen bonds. Our work proves this idea. We are developing a concept of a continual structure of water. In frame of this concept we have explained non-trivial transformation of Raman and infrared contours shape. The formula obtained describes quantitatively the vibrational spectra of water in a wide interval of temperature. It means that it is not necessary to postulate discrete associates to explain the transformation of spectra. This result is a serious argument to speak on the water structure as a uniform three dimensional network of the hydrogen bonds

A spatial distribution of water molecules is studied by computer simulation. Having a network one can analyze structure of water in terms of topological and metrical network characteristics. Network analysis is a complementary to other methods of structure investigation, such as the method of correlation functions and the Voronoi-Delaunay approach. Topology and metric of the hydrogen bond network in water are very sensitive to temperature and pressure. The lowering of temperature and pressure results to more perfect tetrahedral arrangement. A spatial distribution of hydrogen bonds demonstrates a structure inhomogeneity. The regions where molecules have higher and lower tetrahedral order are organized in nano-scale regions, which turn fluently one into another.

Key Words: Structure of water, hydrogen bond, random tetrahedral network, Raman spectrum of water.

I. Introduction

An important feature of water molecule is an ability to generate hydrogen bonds with four neighbors. As a result water molecules form a four-coordinated network of the hydrogen bonds in a condensed state. Indeed, in the ice every water molecule has four equivalent hydrogen bonds with tetrahedral orientation. However there is a question: how are organized the hydrogen bonds in liquid state? Direct structural information to characterize a spatial distribution of the bonds is hard to obtain experimentally. Diffraction techniques^{1,2} offer only radial distribution functions for atoms. Vibrational spectra of the OH groups are very sensitive to formation of hydrogen bonds, however they give only statistical contour of the bond via frequency or energy^{3,4}. Recently a new complementary information about electronic properties of water was obtained by X-ray absorption spectroscopy (XAS)^{5,6,7}, but it does not advance us in understanding a spatial arrangement of the hydrogen bonds^{7,8}.

It is generally accepted that the hydrogen bonds play a fundamental role in the structure of liquid water, from melting up to critical temperature^{9,10}. A well-known model of the water structure is a continual network of the hydrogen bonds^{11,12}. Obviously, this network should not be like in ice. The hydrogen bonds can be easily bent, stretched and switched over. Therefore the network can have different topology and metrical distortion, what is justified by various modifications of crystal and amorphous ice^{13,14}. Nevertheless, the number of the nearest neighbors remains to be close to 4, what distinguishes water from simple liquids where this number is usually greater than 8. It is a cogent experimental fact. The integral over the first peak of the oxygen radial distribution function obtained from diffraction experiment shows that the coordination number is about 4.5¹. Numerous computer simulations of water confirms it. A majority of molecules have four neighbors, some molecules have 5 and rarely more neighbors^{15,16}.

Speaking about totally connected network of hydrogen bonds in liquid water one should answer a question: why water is liquid? It is not a trivial or scholastic question. The strength of a typical hydrogen bond is roughly 20 kJ/mol, a value much larger than kT . Hence one should expect water to behave like a stable (solid) network¹⁷. In contrast to this expectation the water molecules display a high mobility, comparable to molecules in non-hydrogen bonded liquids. Many people studied this problem^{16,18}. The answer was found: the hydrogen bonds in water are able to very fast switching to change topology of the network. It is an inherent physical property of the hydrogen bond resulting from its electronic properties. It is known, such switching takes a place also in ice. Additional contribution in diffusion and topology change in water are caused by bifurcated hydrogen bonds, which arise if a water molecule has more than four neighbors¹⁹. This phenomenon was studied in details by molecular dynamics method. It was shown the mobility of such molecules is higher than in average¹⁶. Thus, the continual network of hydrogen bonds is not in a contradiction with high mobility of water molecules and existence of liquid water.

In contrary, many anomalies of water obtained with change of temperature and pressure are explained naturally by the network existence and the topology change. In particular, it is the strong deviation from the Arrhenius law at low temperature, existence of different phases of liquid and amorphous water (low dense LD and high dense HD)^{16,18,20,21}. All of them are explained by the fact that the network becomes more regular

at lowering temperature or pressure, i.e. where more molecules have a good (close to perfect) tetrahedral arrangement of its neighbors, what can result to an arrest of some molecules. On the other hand, increasing temperature (or pressure) causes additional bifurcated bonds, what enhances diffusion, see in details^{16,18}.

An objection to the hydrogen bond network was appeared recently from the results of the work⁶, where the XAS experiment data were interpreted as they demonstrate many broken hydrogen bonds in water. Using "electronic signatures" of hydrogen bonds, they concluded that only two hydrogen bonds belong to a water molecule. However, in this case water should has rather "a filamentous" structure instead of the tetrahedral network. Such a conclusion seems hasty. At first, the interpretation of the XAS experiment is not very simple. It is discussed now, should a pre-edge feature in the XAS spectra be really related with broken bonds?^{22,23}. The second, the electron signature of hydrogen bonds is not a sufficient characteristic for the hydrogen bond, as it discussed in⁸. Moreover, the structure of a molecular system is determined not only by energy of the bonds, but also by optimal arrangement of the molecules in space.

A really serious question about validity of the network concept lies in a field of vibrational spectroscopy. It concerns interpretation of shape transformation of the Raman and infrared spectra of the O-H group in water. The experiment demonstrates a swap of intensity from low frequencies to higher with temperature increase. Such transformation is explained usually be an existence of discrete aggregates of molecules (oscillators O-H) whose fractions are changed with temperature⁴. Therefore people working with the vibrational spectroscopy prefer water models with discrete associates of molecules: monomers, dimers, n-mers. The main reason to use such models is difficulty to explain temperature transformation of the vibrational spectra with temperature in frame of the concept of the continual network. In this paper we show a solution of this problem. We developed a theory describing the vibrational experiment on the base of the continual distribution of the hydrogen bonds without any discrete types of associates. In section II we demonstrate application of the theory both to Raman and infrared spectra of the O-H group in water in a broad temperature interval. In section III we discuss that such continual distribution of hydrogen bonds can be realized in space as a continual network.

II. Temperature transformation of Raman and infrared contours of O-H vibration in water.

The fact that hydrogen bonds can be easily bent and elongated results in existence of a statistical distribution of bonds in water. A numerous of configurations of the hydrogen bonds O-H...O is characterized by geometric parameters (such as a distance between the oxygen atoms $R_{O...O}$, distance between the oxygen and hydrogen R_{O-H} , angle of the bond $\angle OHO$), by energy E and by spectroscopic values (frequencies ν_{O-H} , $\nu_{O...O}$, intensities). Every characteristic from this set has its statistical distribution.

The basic characteristic of hydrogen bonding in water is a density probability function describing the bond energy distribution $P(E)$. This function depends on temperature. As it was shown in a paper³, a temperature dependence of this distribution can be described by a simple formula: $P(E, T) = W(E) \exp(-E/kT)$, which presents the Boltzmann distribution of the hydrogen bonds vs. temperature in the ensemble of

hydrogen bonds. Function $W(E)$ determines a degeneration of hydrogen bonds for a given energy (the same value of energy E is possible at different configurations, for different values of the geometrical parameters of the bond).

Because the energy of a given hydrogen bond correlates with the frequency of the O-H oscillator, a function $E(\nu)$ can be obtained. After that we can present the energy distribution of hydrogen bonds $P(E)$ in term of frequency: $P(E(\nu))$. It opens a way to work with vibrational spectra obtained experimentally. A mutual division of two spectra at two temperatures allows us to obtain functions $E(\nu)$ and $W(\nu)$ numerically^{3,24}.

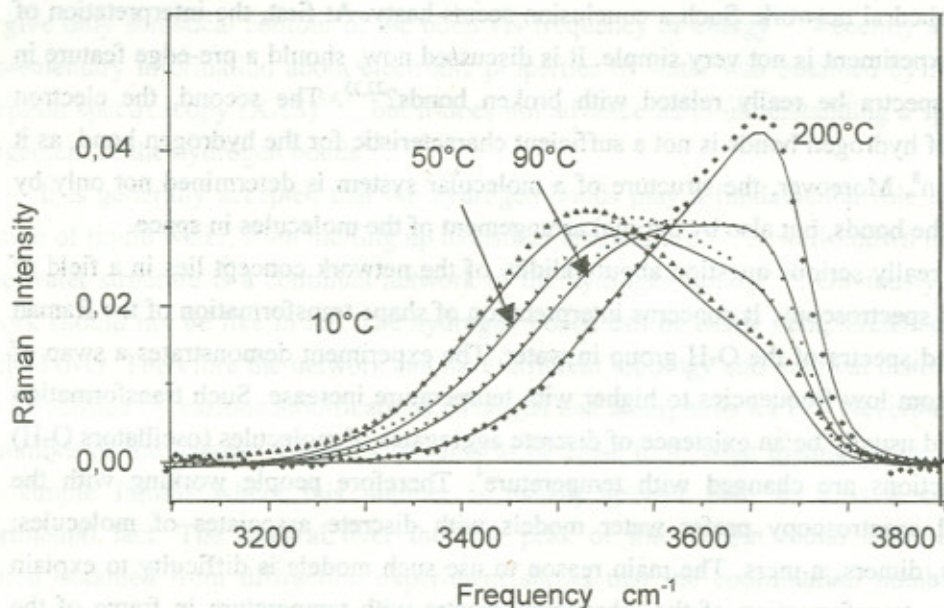


Fig.1. Raman intensity of the O-H group in water at different temperature. Symbols – experiment, lines – theory.

Having functions $P(E,T)$, $E(\nu)$ and $W(\nu)$ we are able to describe temperature evolution of the contour of O-H vibrations in water. The experimental spectrum $I(\nu, T)$ of the O-H vibrations in liquid water can be presented as a convolution of a continuum of narrow contours of the individual O-H groups $F(\nu)\varphi(\nu - \nu')$. As a result, the general formula for vibrational spectra is

$$I(\nu, T) = \int F(\nu') P(\nu', T) \varphi(\nu - \nu') d\nu'$$

At first we calculated the Raman contour for which the intensity factor $F(\nu)$ can be taken as a constant. Fig.1 demonstrates results for different temperatures, up to 200C at the density 1 g/cm³. One can see a very good fit of the theory with Raman experiment.

To calculate transformation of the infrared spectra is a more complex task. In this case not only frequency but also integrated intensity of the O-H oscillator depends on hydrogen bond energy. To take in to account the intensity factor $F(\nu)$ we used a known correlation between integrated intensity and peak frequency in a row of different systems with hydrogen bonds (not only aqueous). Fig.2 demonstrates experimental and predicted infrared spectra of water at different temperatures.

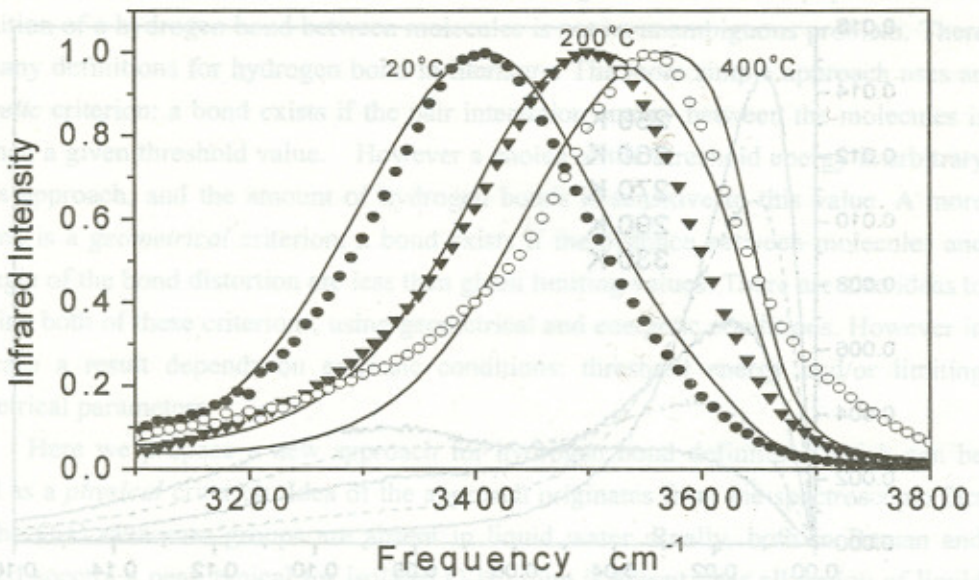


Fig.2. Normalized infrared intensity of the O-H group in water at different temperature. Symbols – experiment, lines – theory.

Thus, a full set of vibrational spectroscopy data is described on the base of the concept of the unified ensemble of hydrogen bonds. It means one does not need for any discrete associates of water molecules for interpretation of the contour transformation, as it often assumed.

III. Geometry of the hydrogen bond network

The network of the hydrogen bonds is very fruitful tool for structure investigations. Having the network one can study structure of water in terms of topological and metrical network characteristics. In particular, one can study statistics of rings or distribution of lengths and angles of the bonds on the constructed network. Network analysis is a complementary to other methods of structure investigation, such as the method of correlation functions, and the Voronoi-Delaunay approach, which is used for structure characterization of simple liquids, where there are no physical bonds between molecules.

In our works²⁵⁻²⁷ we studied the structure of liquid water in a wide temperature range from ambient conditions to supercooled region. Series of the molecular dynamic models contained 729 and 5832 molecules are used. The main attention was paid for studying a long distant correlation between molecules and intermolecular voids. It was obtained that water demonstrates *a structural inhomogeneity*. Earlier we obtained a spatial distribution of the Voronoi polyhedra with different volume is not homogeneous through a model. The polyhedra having larger volume ((and those whose volume is less then an average value) have a tendency to clustering. They reveal regions with lower and higher density in water. However, the obtained density difference is small (a few percent). It means that density inhomogeneity in water is not very pronounced. Another situation

takes place for more sensitive structure characteristics.

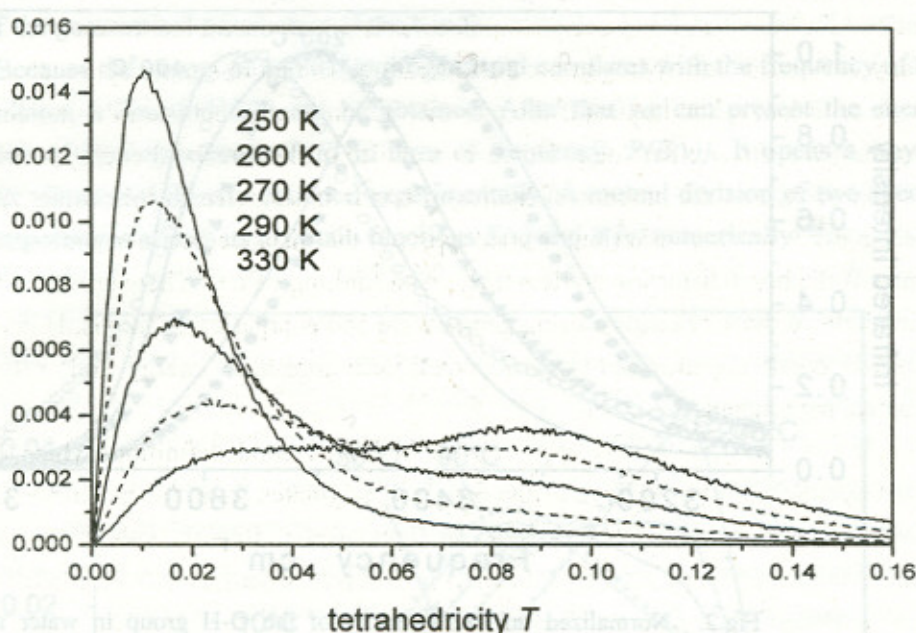


Fig.3. Tetrahedrity of the nearest neighbors of water molecules in liquid water for different temperatures at constant pressure.

For studying structure of water it is naturally to use a numerical measure for tetrahedral order of nearest neighbors. A measure *tetrahedrity*, T , proposed earlier for a shape characterization of the Delaunay simplexes²⁸ was applied successfully to water study¹⁵. It is defined for a water molecule as

$$T = \sum_{j \neq i} (l_i - l_j)^2 / 15 \langle l \rangle^2 ,$$

where l_i is a length of a i -th edge of a coordination tetrahedron, which is created by four nearest neighbor molecules, $\langle l \rangle$ is an average length of all six edges of this tetrahedron. For an ideal tetrahedral network (like in ice Ih) the measure $T=0$, and it increases with the distortion of the structure. Distributions of T measure for our models are shown in Fig.3. For ambient temperature the distribution is bimodal. It demonstrates two types of local surroundings. The peak for smaller T belongs to molecules with a good tetrahedral arrangement of the neighbors. Such molecules become dominated in supercooled water. The peak for higher T belongs to molecules with more distorted surroundings. Only a small fraction of molecules have a drastic distortion of the tetrahedral order. They belong to the far tail of the distribution (beyond the bounds of Fig.3).

We studied also a spatial distribution of molecules with good (and bad) tetrahedral surroundings. They are clustering in nano-scale regions of more (and less) tetrahedral structure. All these molecules are includes in to a single continuous hydrogen bond network.

IV. Remarks about definition of the hydrogen bond.

It is clear a hydrogen bond network is rather a geometrical than a physical notion. Definition of a hydrogen bond between molecules is not an unambiguous problem. There are many definitions for hydrogen bond in literature. The more simple approach uses an *energetic* criterion: a bond exists if the pair interaction energy between the molecules is less than a given threshold value. However a choice of the threshold energy is arbitrary in this approach, and the amount of hydrogen bonds is sensitive to this value. A more detailed is a *geometrical* criterion: a bond exists if the distance between molecules and the angle of the bond distortion are less than given limiting values. There are also ideas to combine both of these criterions, using geometrical and energetic conditions. However in any case a result depends on extrinsic conditions: threshold energy and/or limiting geometrical parameters.

Here we propose a new approach for hydrogen bond definition, which can be called as a *physical* criterion. Idea of the approach originates from the spectroscopic fact that the O-H monomer groups are absent in liquid water. Really, both in Raman and infrared spectra a peak typical for isolated O-H group is absent over all region of liquid and fluid water (to density up to 0.2 g/cm^3).

Thus, we can suppose that every O-H group should be connected by the hydrogen bond with an oxygen of a neighbor molecule. The problem comes to determine with which one. In the simplest case we can choose that neighbor molecule, whose interaction with a given molecule is maximal. If values of interaction energy with different neighbors are equal, it simply means bifurcated bonds, see above. Preference of this determination of hydrogen bonds is following. It does not use any a priori parameters (energetic or geometrical), and it reflects a real physical situation in water, where every proton of the O-H group is tightly situated among oxygen atoms of water molecules. If water is still dense, the proton interacts with some oxygen with inevitability.

V. Summary

We explained transformation of the Raman and infrared spectra of water in a wide interval of temperature on the base of the concept of a continual structure of water. This result is an additional argument to speak well of the water structure as a uniform three dimensional network of hydrogen bonds. Water molecules in this network have predominantly four nearest neighbors, but the other numbers of neighbors are also possible because of bifurcated hydrogen bonds. The topology and metric of this network are very sensitive to temperature and pressure. At lowering temperature and pressure it becomes more tetrahedral (more molecules have arrangement of the nearest neighbors close to perfect tetrahedral). Spatial distribution of hydrogen bonds demonstrates a structure inhomogeneity. The clusters of water molecules with higher and lower tetrahedral order are organized into nano-scale regions, which turn fluently one into another.

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