E5-2005-102

D. V. Denisov, S. Yu. Kulikovsky, D. I. Popov,
V. N. Samoilov

ON POSSIBILITY OF ACHIEVING SUPERCONDUCTIVITY IN WATER

Submitted to International Scientific Congress on Bioelectrography

Денисов Д. В. и др. E5-2005-102

О возможности генерации сверхпроводящего состояния воды

Изложены размышления о возможности получения свойств идеальной электропроводности воды. Вода рассматривается как сложная надмолекулярная структура, в которой возможно образование цепочечных кластеров. Перестройка структуры таких кластеров приводит к переносу заряда, который может быть интерпретирован как электронная проводимость без сопротивления в цепочке связей.

Работа выполнена в Научном центре прикладных исследований ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 2005

Denisov D. V. et al. E5-2005-102

On Possibility of Achieving Superconductivity in Water

Speculations on the possibility of achieving ideal electric conductivity of water are given in this paper. The water is considered to be a complex molecular structure where the formation of band clusters is probable. The structural change in such clusters leads to the charge transfer, which can be regarded as a special case of electron conduction without resistance in the cluster.

The investigation has been performed at the Scientific Center of Applied Research, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna, 2005

INTRODUCTION

Let us consider the structure of water at the mesoscopic level. At this level it is possible to study not separate atoms or molecules but their spatial organization — clusters, which are structures formed by several atoms or molecules. Yet this is not a macroscopic approach since clusters define molecular structure of the matter.

The viewpoint that the structure of a molecule completely defines the property of water (as any other liquid), and that molecules are uniformly distributed performing Brownian motion had been generally accepted for a long time. However, now more and more publications, both theoretical and experimental [1, 2], consider water as a complex cluster molecular structure. Moreover, the orthodox approach doesn't give the correct result on some occasions. It turned out that the water has structural «memory», which is the result of cluster's structure [2]. While molecule H_2O defines the main physical, chemical and biological properties, the cluster structure determines other subproperties that can be detected by molecular spectroscopy. A vast quantity of experimental studies [2, 3, 4, 7] led to several attempts to describe the water structure theoretically at the mesoscopic level. However, the question how to define the «structure of liquid» is still unanswered [5].

1. WATER CLUSTERS

It is well known that the formation of H_2O molecule requires two electrons from $2p$ shells of the oxygen. Two electrons that are left on the $2p$ shell and two on the $2s$ shell create pairs and are chemically inactive. However, there is proof [7] that electron shells $2s$ and $2p$ create hybrid shells so that four unpaired electrons can create hydrogen bonds with water molecules (Fig. 1).

It's worth noting that the bonding orbital between oxygen and hydrogen in H_2O is occupied by one electron from oxygen and one electron from hydrogen. Unoccupied shells, which are antibonding orbitals of oxygen and hydrogen from the neighboring molecules, can be occupied by those four electrons. Each hydrogen atom can create a bond with one antibonding orbital, i. e. with two oxygen electrons. Therefore, four hybridized electrons can establish chemical bonds with two hydrogen atoms, further called «hydrogen» bond. This bond based on antibonding orbital is less stable than covalent bond, therefore, the mechanism of bonding of two neighboring water molecules can be different from chemical bonds inside the water molecule. Further, we adhere to notion that hydrogen

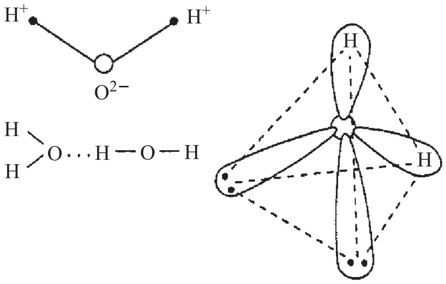

Fig. 1. Configuration of electron clouds of oxygen in water molecule [2]

bonds are weaker than covalent bonds but strong enough to create a metastable structure.

Two cases are possible: water molecule bonds with one neighboring molecule or with two molecules (Fig. 2). Figure 2, *a* shows a possible band structure; Fig. 2, *b* shows a volumetric structure. Volumetric structures can be different by their organization and properties. Experiments conducted 10 years ago [1] showed that at room temperature 50% of water molecules are water clusters like $(H_2O)_2$, $(H_2O)_4$, $(H_2O)_6$. Those structures were studied for stability [2] (Fig. 3). They have plane geometry except $(H_2O)_6$, which has 3D structure of hexagon (Fig. 4) and is the most stable of them all. As seen from Fig. 3, each of those structures has hydrogen atoms, which do not participate in the hydrogen bonding. Under certain conditions those clusters can create a bond with neighboring clusters or molecules, thus creating more complicated structures.

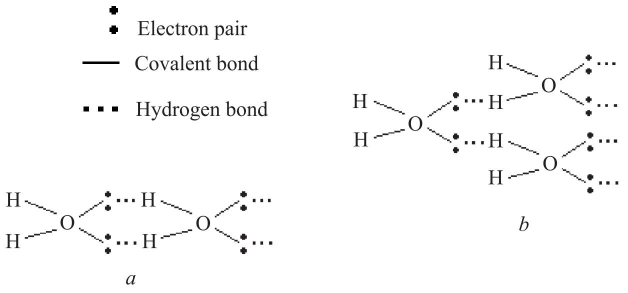

Fig. 2. Possible birth mechanisms of a cluster-like structure: a) band cluster, b) volumetric cluster

Let us consider a cluster nucleation process. Suppose that there exists a nucleus composed of several molecules. As it grows, it accepts more and more molecules of water. The difference in mass between a new cluster and a water molecule prevents the cluster from significant change in its energy. On the other hand, a water molecule can lose most of its kinetic energy at collision and, as a

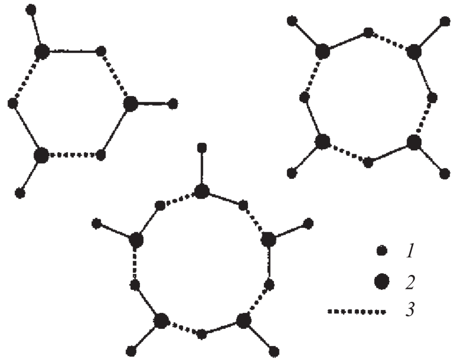

Fig. 3. Schematic structure of trimer, tetramer and pentamer — simple clusters of water molecules. *1* — hydrogen atom, *2* — oxygen atom, *3* — hydrogen bond

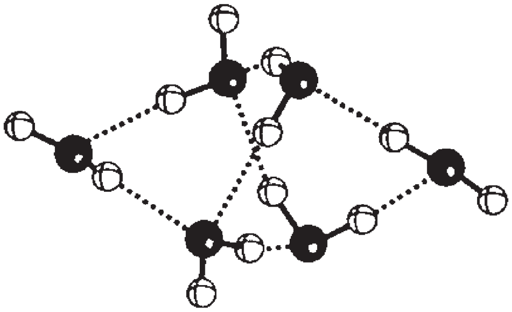

Fig. 4. Cellular-like equilibrium structure of hexamer $(H_2O)_6$ [4]

result, become a part of the cluster. This process continues until the surface and volume energies become equal; at this point the cluster reaches its equilibrium size and the growth stops. The type of atoms is the most important factor in this process. For example, the band cluster finds it more difficult to accept a new molecule than the volumetric cluster, which may also differ by structure and properties. However, the decisive factor for cluster dynamics is the external field. It can trigger growth of nuclei of a certain type, which results in appearance of one-type molecules in water. This, of course, leads to the appearance of certain properties. In other words, the value and structure of external field affects a certain property (via structure) of the water. This means that the property of water gives information on water structure, which, in turn, gives the information on the external field applied to the water. Moreover, the external field may not be necessarily applied at that moment; water preserves the cluster structure, which was formed under the influence of the external field, long enough. Therefore, the water clusters can be regarded as memory cells.

Agglomeration is possible even if two clusters collide, thus increasing in size. This process continues until the surface and volume energies equalize each other; this value depends on external fields, such as electric and magnetic fields, and temperature. The former controls the process of agglomeration, and the latter affects their stability. It is well known that the hydrogen bond is relatively weak; however, in simple ring clusters their symmetric structure reinforces the hydrogen bonds. Symmetry positively affects the strength of clusters and allows them to withstand temperatures close to the boiling point. In general, the bonds are nonsymmetric except for simple structures, and complex clusters can exist only in a narrow range of temperatures around room temperature. At higher temperatures, thermal fluctuations obliterate hydrogen bonds of complex molecular structures, leaving only simple clusters. When temperature decreases down to freezing point, the water tends to undergo the transformation into lowest energy state coinciding with the ideal crystalline structure of ice. Experiments [9] indicate that complex structures of size more than 100 Å can be detected only in a very narrow range of temperatures close to room temperature. Numerous studies of those structures are performed throughout the world; in particular, it has been shown that the structures can be formed in magnetic fields, react on different type of radiation and possess «memory».

2. ELECTRIC CONDUCTIVITY OF WATER

Due to the purpose of this paper, let us consider a simple band cluster (Fig. 5). Its structural organization possesses minimum information, but it has some properties, which are discussed here.

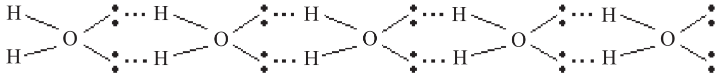

Fig. 5. The model of chain cluster of a water molecule

Suppose that we succeeded in removing one hydrogen ion from the left-end covalent bond. At that point we get one unsaturated bonding orbital. If we also block the removed ion, allowing only hydrogen bonding, then the hydrogen bond with the neighboring molecule becomes covalent (Fig. 6, *a*–*b*). This will happen only because the oxygen atom will never have three antibonding orbitals, and one of them will become bonding. Figure 6, *b* shows that the second oxygen atom has three hydrogen bonds, as the first atom previously had (counting from the left). In this case the second oxygen atom has the possibility of creating the chemical bond with either right or left neighboring molecule. In the first case we

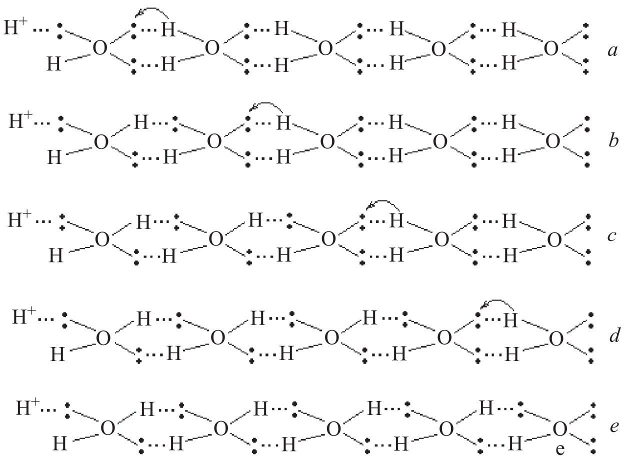

Fig. 6. The mechanism of electric conductivity of a water molecule

come back to the case in Fig. 6, *a*, and further compensation is impossible due to blockade of the removed hydrogen ion. In the latter case, we come to Fig. 6, *c*, and this process will repeat until we come to the last (utmost right) molecule in the chain (Fig. 6, *e*). At the end we gain one uncompensated electron at the right end of the band cluster. This electron together with the hydrogen ion at the left side creates the potential difference. Therefore, if this structure is connected to electric circuit, the electron can go to the circuit.

The difficulty in organizing this type of process is twofold. First, the technology of creating such band clusters is not available. Second, creating the blockade for the hydrogen atom seems not to be an easy task. If this is not done, then the reverse process would be possible, and the cluster comes to its initial state.

The process in Fig. 6, *a*–*e* shows that in reality it is not the electron that moves but the hydrogen bond. In other words (in Physics of the Solid State lingo), a defect in Fig. 6 is formed, which moves along the chain of water molecules with its subsequent relaxation. The defect on the right-hand side of Fig. 6, *e* is exactly the same as on the left-hand side of Fig. 6, *a*. It is evident that such a defect cannot exist for a long time on the right-hand side of this molecule. As a result, this electron will be given away by the molecule. If such a molecule is connected to electric circuit, we will gain a free electric charge carrier in that circuit.

Let us take a detailed look at Fig. 6. First, with every jump of the hydrogen bond, the water molecules have to modify their structure. If in Fig. 6, *a* all hydrogen atoms are oriented in one direction, then their direction completely changes by Fig. 6, *e*. In reality, such a change will likely be followed by the change in orientation and in bond angle of the water molecule. Both states (Fig. 6, a and e) have the same energy, but there is an energy barrier between them. To overcome the barrier, the utmost left molecule has to withstand sufficient deformation, otherwise, there will be no reaction in the chain.

The second change in this chain will be connected with the loss of the electron from the utmost right atoms in Fig. 6, e. After the loss of the electron, the forces on that atom become uncompensated, and lead to the change in the atomic configuration (most probably from sp-hybridization state to a more simple one). However, it is not known if the final state is energetically favorable. The initial energy of deformation by single hydrogen ion should be enough for the change in orientation of the water molecules, and restructuring the utmost right molecule, which loses the uncompensated electron. Even if this condition stands, the hydrogen bond should be sustained at the left molecule during all chain of these reactions. At no moment this bond can be changed to covalent. This problem can be solved by, for example, substituting the hydrogen ion by the atom of the alkaline metal, which is easier to control. Another solution would be creation of a special environment on the left side of the band-like cluster, where the hydrogen atoms ionize first and then enter in the reaction zone with the cluster.

It seems at first that the negative charge is generated on the right-hand side of the chain, however, this observation is erroneous. The charge is generated initially on the left-hand side of the chain, and afterwards is transferred to the right-hand side. Probably, the energy spent for charge generation will be greater than the energy gained from the charge acquisition on the opposite side of the cluster. It is possible that creation of the electron generators based on water clusters is energetically unprofitable. On the other hand, the charge is transferred along the chain without any energy loss. All one needs is to create the uncompensated deformation potential on one end of the cluster, sufficient for initiation of the process. In other words, the energy will be spent more efficiently in this process than in case of electron conduction in metals, especially at long distances.

Let us emphasize the analogy between the conduction in metals and conduction of water clusters. Firstly, it has to be stressed that the phenomenon in water clusters does not belong to superconductivity. Superconductivity is a collective phenomenon, pertinent to charges with integer spin and inherently connected with Bose condensation. In our case, only one electron that is transferred along the chain, possessing half-integer spin and no Bose condensation, can be thought of in this case. Secondly, the phenomenon of ideal conductivity is closer related to the described process. In the latter case, the charge carriers are electrons, which scatter neither on phonons nor on impurities, and this results in zero resistance. In our case, cluster is formed in such a way that it has no impurities. There is no scattering on phonons either, because it is not the electron that moves but the crystalline (cluster) lattice that reorganizes — the hydrogen bond moves. Finally, there is a potential difference between any two points in metal along the conduction path when current flows (electrons move). In our case, the deformation of cluster is just another method of creation of potential energy.

One of the characteristics of conduction process in water clusters is that only one electron can be transferred along the chain. What is important here is that this process can take place at room temperature. This possibility of the electric current conduction at room temperature without resistance pays off the energy spent in order to make it possible.

Now, let us take a look at one of the main problems — creation of stable water band clusters. The means of their creation can be both electric and electromagnetic fields. Magnetic field is used more for creation of circular clusters (Fig. 3), electric field can be used for creation of long band clusters.

The problem does not end here: several theoretical calculations show that band clusters have much less stable structure than simple volumetric structures like pentagons and hexagons. The latter can naturally exist for several days or even weeks, the lifetime of band clusters is much less. This decrease is mainly due to the fact that the lifetime of a simple hydrogen bond is very short, in symmetric volumetric structures the parameters of the stable covalent bonds and hydrogen bonds are averaged. The extended band clusters do not possess central symmetry (as well as large volumetric conglomerates with size more than 100 Å). Therefore, these clusters are subjected to destruction under the influence of thermal and other type of fluctuations.

Special conditions should be created for stability of water band clusters. One of those conditions is the operational temperature range, which coincides with the normal human life conditions (temperature less than 50°C). The second condition is creation of special supporting structure. Here is one more analogy to support the point.

At present time physics of nanostructures is full of publications on fullerenes C_{60} and other fullerene-like structures. It was discovered that compounds of fullerenes and some metals are high-temperature superconductors. An attempt was made to synthesize new compounds with even higher transition temperature, close to room temperature. At this point it was discovered that the maximum transition temperature would be accomplished by synthesizing the chains of the smallest possible fullerenes C_{20} [6]. It turned out that these chains are metastable. To solve this problem, it was suggested to pack the fullerenes in special nanotubes in order to preserve the structure of those chains and prevent them from destruction.

Such solution could be used in our case. In spite of some difference in size — the radius of water band cluster is 2 Å, the radius of fullerene chains is about 5 Å — it is possible to synthesize nanotubes that would sustain the stability of water clusters.

In case of fullerenes, the nanotubes are made of carbon, the same material the fullerenes are made of. We may speculate that the supporting structure could be made of volumetric clusters of water. However, this approach is questionable; any method that stabilize water clusters can be used here.

By any means, cluster structure of water molecules requires further research, however, even now we see new possibilities for application of water clusters, such as electrical energy transport with minimal loss.

In spite of aforementioned specifics, some theoretical and experimental facts [8] indicate that it is possible to create ideal conductivity in liquid water. This mechanism can possibly help to explain such effects as high-temperature superconductivity in biological structures (nerves). For such purposes it would be educational to create water clusters with given properties as thin films. Anyhow, water clusters in thin films would resemble superconductors based on polymers, which are synthesized in thin films.

REFERENCES

1. *Gabuda S. N.* Bonded water: facts and hypothesis. Novosibirsk: Nauka, 1982.
2. *Sapogin L. G., Kulikov I. V.* // Estestvoznanie. 1998. V. 3(4) (in Russian).
3. *Ponomarev O. A. et al.* // Biophysics. 2002. V. 47(3). P. 395.
4. *Lui K. et al.* // Nature. 1996. V. 381. P. 501.
5. *Martynov G. A.* Liquid structure — what is it? // Journal of structural chemistry. 2002. V. 43(3). P. 547–556.
6. *Miyamoto Y., Saito M.* Condensed phases of all-pentagon C_{20} cages as possible superconductors // Phys. Rev. B. 2001. V. 63. P. 161401R.
7. *Zatsepina G. N.* Physical properties and structure of water. M.: Moscow University, 1998.
8. *Polyak E. A.* Signs of superconductivity and superfluidity in liquid water // Hypothesis. 1992. V. 1. P. 20–33.
9. *Ponomarev O. A., Fesenko E. E.* // Biophysics. 2000. V. 45(3). P. 389.

Received on July 14, 2005.

Редактор *Н. С. Скокова*

Подписано в печать 20.10.2005.
Формат 60 × 90/16. Бумага офсетная. Печать офсетная.
Усл. печ. л. 0,68. Уч.-изд. л. 0,96. Тираж 315 экз. Заказ № 55069.

Издательский отдел Объединенного института ядерных исследований
141980, г. Дубна, Московская обл., ул. Жолио-Кюри, 6.
E-mail: publish@pds.jinr.ru
www.jinr.ru/publish/