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COMPUTER MODELING OF IONS H^+, H_3O^+, $H_5O_2^+$ TRANSPORT IN NANOSTRUCTURAL SUPERMOLECULES OF WATER

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Introduction.

It is known [1] that transport of a proton in various condensed states of water plays a key role in hydrogen conversion of energy. It is connected by that a proton – the basic agent of go-ahead carry of a charge in the water solutions used in fuel cells.

High mobility of the proton defines the unique go-ahead mechanism of "carry" of ions H_3O^+ and OH^-. At the same time, transport of cautions and anions is complicated by their capture in cellular nanostructures of the condensed phases of water. Mechanisms of transport of ions H_3O^+, $H_5O_2^+$, OH^- and go-ahead carry of the proton while are insufficiently investigated.

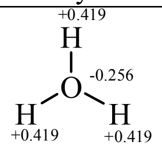
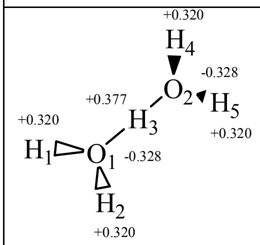
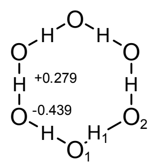
In the given work features of energetic barriers of transport of ions of water and go-ahead carry of the proton within the theory of quantum-field chemistry and methods of computer modeling [2] are studied.

Results and discussion

In quantum-field chemistry nanostructures of water (ice) are described by spatial circled net system of nanostructural supermolecules of water $(H_2O)_n$, which are bounded with intramolecular hydrogen bonds (O-H-O). Grids form a cellular structure of water nanoparticles. Walls of these cells have the form of a ring (O_6H_6). Six atoms of oxygen in it are connected by six hydrogen bonds. Transport of ions of water through cellular grids of water has as the basic limiting stage overcoming the barriers laying in a direction of an axis of a ring (O_6H_6) of a cell. Between walls of a cell and ions of water (H^+, H_3O^+, $H_5O_2^+$) forces of intermolecular adhesion operate.

Surfaces of potential energy of adhesion have been calculated by density functional method [2]. Distributions of electron charge density in particles undertook from calculations of ions of water and supermoleculare ring of water $(H_2O)_n$ by standard molecular orbital method in the minimal basis set (STO-3G). Results are shown in table 1.

Table 1. Parameters of ions of water

Ion system	Parameter	Value
	L(O-H),Å	0,99
	α(H-O-H), degrees	113,8
	L(O_1-H_1),Å	0,98
	L(O_1-H_3),Å	1,16
	α(H_1-O_1-H_2), degrees	107,5
	α(H_1-O_1-H_3), degrees	116,5
	α(O_1-H_3-O_2), degrees	178,7
	L(O_1-H_1),Å	1,03
	L(O_2-H_1),Å	1.80
	α(H-O_1-H_1), degrees	117,9
	α(O_1-H_1-O_2), degrees	177,8

On fig. 1 diagrams of the basic stages of passage cautions H_3O^+ and $H_5O_2^+$ through water ring and the basic intermolecular interactions for optimum geometry are shown.

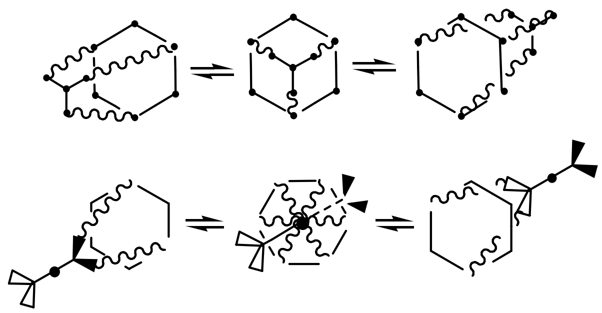


Fig. 1 Model of transition H_3O^+ and $H_5O_2^+$ through the circle (O_6H_6).

Potential curves of transport for H_3O^+ and $H_5O_2^+$ through a cyclic fragment are shown on Fig.2, 3.

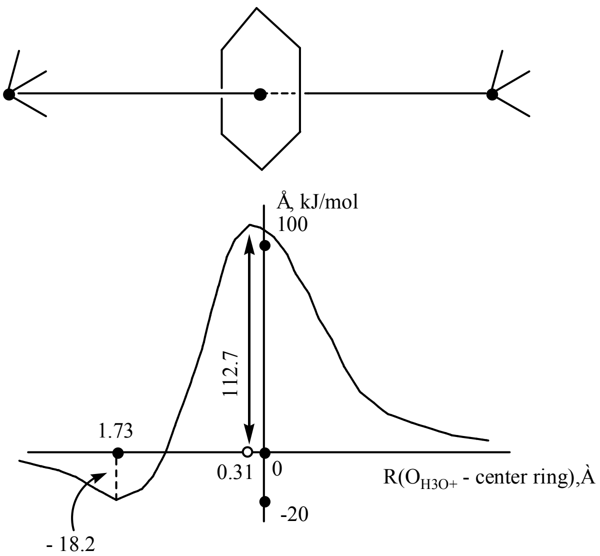


Fig. 2. Potential curve of passage of ion H_3O^+ through a cyclic fragment (O_6H_6).

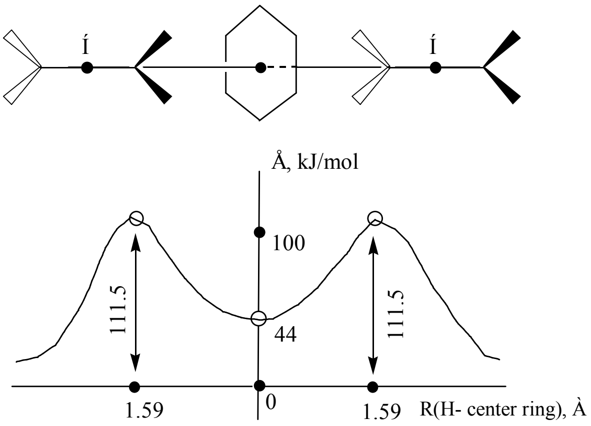


Fig. 3. Potential curve of passage of ion $H_5O_2^+$ through a cyclic fragment (O_6H_6).

In case of carry of a proton in the form of H_3O^+ through a cyclic fragment the high barrier (130 kJ/mol) is had. In case of carry of a proton in the form of $H_5O_2^+$ through a cyclic fragment it is had two barriers: a high external barrier (111 kJ/mole) and low internal barrier (67 kJ/mole). In the first case the barrier is connected with forces of pushing away of ion H_3O^+ from a ring at attempt to pass through it. In the second case one barrier is connected with forces of pushing away, and another with forces of an attraction of a proton to ions of oxygen. And the internal barrier is defining during carry of a proton in the form of $H_5O_2^+$. In a Fig. 4 it is shown a power surface of a barrier of passage H^+ through a ring (O_6H_6).

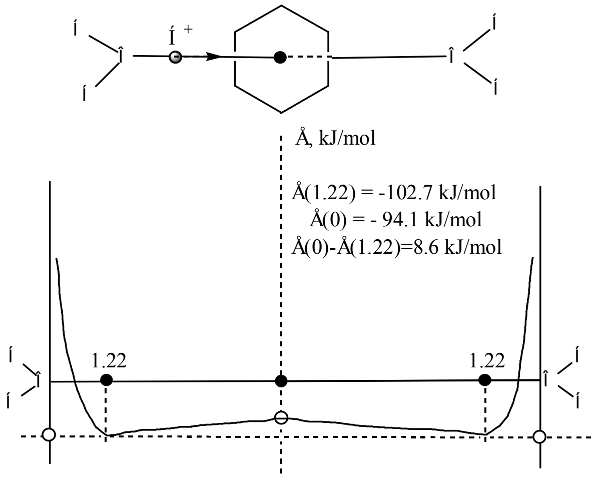


Fig. 4. Potential curve of passage H^+ through a cyclic fragment (O_6H_6).

The height of a barrier makes only 9 kJ/mole. The power barrier of transport of proton H^+ inside of the ordered supermolecules of water is much less than barriers of transport of ions H_3O^+, $H_5O_2^+$.

Conclusion

On the basis of the set abovementioned calculations clearly, that the power barrier of carry of a proton through ordered cellular nanostructure of water lays considerably below similar barriers of ions H_3O^+, $H_5O_2^+$. It also provides the effective go-ahead mechanism of carry of ions H_3O^+. The contribution of ion H_3O^+, $H_5O_2^+$ conduction to carry of charges inside of the ordered cells of supermolecules of water is small, as they are strong confined inside of cells of intramolecular hydrogen bounded water supermolecules $(H_2O)_n$. Transport of these ions can occur only on the areas laying outside of odered supermolecules of water.

References

1. Haile S.M. Materials for fuel cells. Materials Today 2003;(3):24-29.
1. Beznosyuk S.A. Modern quantum theory and computer simulation in nanotechnologies: Quantum topology approaches to kinematical and dynamical structures of self-assembling processes. Materials Science & Engineering C 2002;19 (1-2):369-372.