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Isomers of water molecules' dimer

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Abstract

Possible equilibrium configurations of 2 water dimers, satisfying the symmetry conditions, are considered. Energy of water dimers and one of the transition state are calculated. Cell complex for water dimers, representing the route of optimal rearrangement of water dimers, is built.

Keywords: dimers, molecular orbitals, equilibrium and saddle-point configurations, cell complex

Рассмотрены возможные равновесные расположения двух молекул воды, удовлетворяющие условиям симметрии. Рассчитаны энергии димеров и одного из переходных состояний. Построен клеточный комплекс для димеров воды, отражающий маршрут оптимальных перестроек димеров.

Ключевые слова: димеры, молекулярные орбитали, равновесные и седловые конфигурации, клеточный комплекс

Introduction

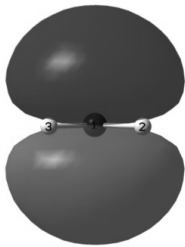
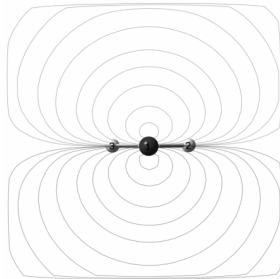
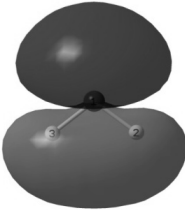
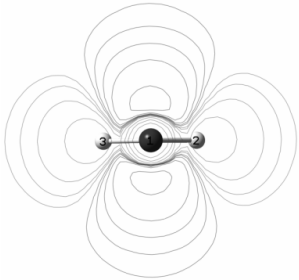
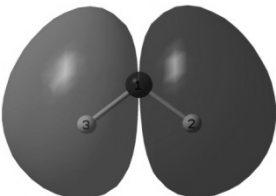
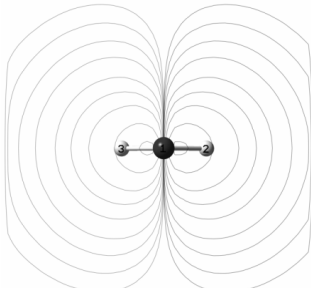
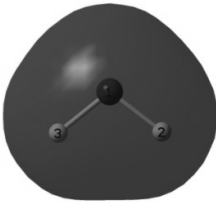
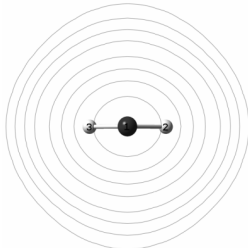
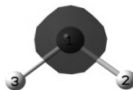
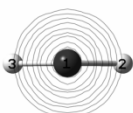
Water differs from other liquids by a number of the physical properties, in particular, by the heat capacity, many times exceeding thermal capacities of other liquids, and by rather low viscosity [1-3]. The aim of this work is to determine the nature of the anomalously high heat capacity and low viscosity by considering the specifics of the interaction between water molecules. The reason for a such situation lies in a specificity of interaction between molecules and molecular structure of a liquid. It is not necessarily to consider multimolecular systems for establishing this specificity, as it can be seen in the simplest molecular clusters, namely, dimers.

Experimental

The structure of the isolated water molecule was investigated experimentally and theoretically by computer simulation and is now well known. The water molecule has C_{2v} symmetry. It is possible to consider, that out of ten electrons in a chemical bonding dominate by six forming three three-center orbitals. One of them is a linear combination of the valence s-orbital of oxygen and two s-orbitals of the hydrogen atoms (№ 2 in Table 1). Two other molecular orbitals are linear combinations of p-orbitals of oxygen and s-orbitals of hydrogen (№ 3 and № 4 in Table 1). Orbital № 5 is a p-orbital of oxygen, oriented perpendicular to the plane of the molecule. Two electrons with opposite spins, forming a lone pair, are located at this orbital. Finding orbitals and their energies in this study were made using computer calculations with the RHF method in the 6-31G (d) basis.

Computer calculations of equilibrium water dimers were carried out by a number of researchers. In this study similar calculations of various isomers of the water dimer, classified according to their point symmetry, were done and routes of optimal rearrangement on the basis of representations of cell complexes were showed [4].

Table 1. Orbitals of the water molecule

Shape of MO	Contour	Energy, eV
№5 		-13.538014779 0.162825022
№4 		-15.496880138 -0.291134373
№3 		-19.21924582 -0.152457262
№2 		-36.461602214 -0.044110217
№1 		-559.48380684 0.037962619

The selection of possible dimers was carried out taking in account the binding conditions of the hydrogen atoms with the neighboring molecule of oxygen's atom. According to other authors, this arrangement of atoms is the most typically in the structure of liquid water. [1]

Dimer with the highest bond energy is represented in Figure 1.

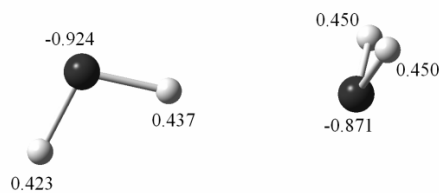
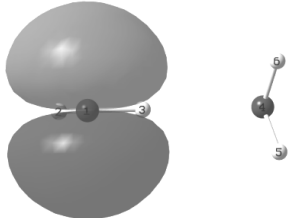
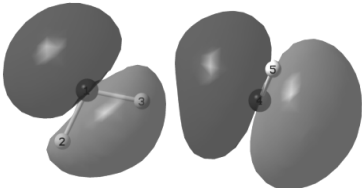
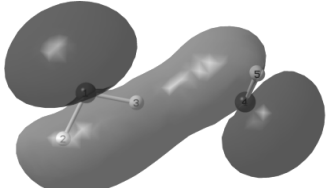
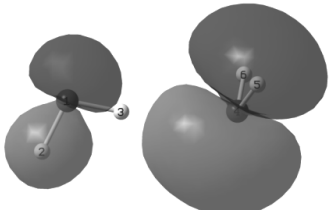
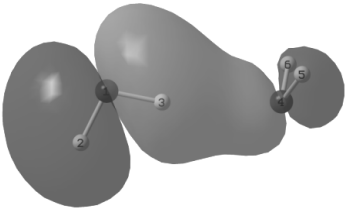
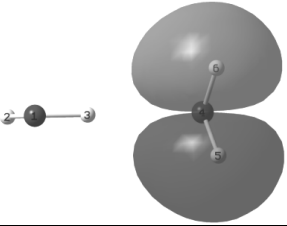
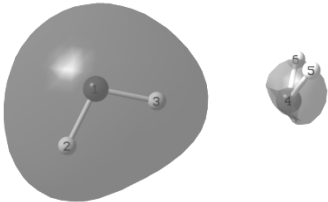
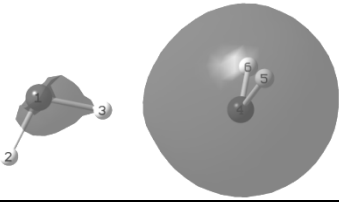




Fig. 1. The configuration of the dimer having the highest bond energy

It has C_s symmetry. To establish the nature of the chemical bonds between water molecules in this dimer the orbital analysis was carried out. The set of orbitals is presented in Table 2.

Table 2. Orbitals of the dimer which are shown in Fig. 1

<p>№10</p> 	<p>-12.802371583 eV</p>
<p>№9</p> 	<p>-14.110832954 eV</p>
<p>№8</p> 	<p>-14.935933479 eV</p>
<p>№7</p> 	<p>-16.34896117 eV</p>
<p>№6</p> 	<p>-18.612686276 eV</p>

<p style="text-align: center;">№5</p> 	-19.978262625 eV
<p style="text-align: center;">№4</p> 	-35.697342398 eV
<p style="text-align: center;">№3</p> 	-37.269972247 eV
<p style="text-align: center;">№2</p> 	-558.632615321 eV
<p style="text-align: center;">№1</p> 	-560.29703574 eV

The comparison of dimer orbitals with orbitals of water molecules shows that a set of orbitals of the dimer is decomposed into five orbital pairs, each pair is made of the same orbitals of water molecules according to the following scheme:

1→(1,2), 2→(3,4), 3→(5,6), 4→(7,8), 5→(9,10)

The first digit indicates the number of orbitals of water molecules, the number of dimer orbitals is shown in brackets. Formation of bonding and anti-bonding dimer molecular orbitals out of the same type of orbitals of water molecule and preservation of individual molecular orbitals in the dimer (dimer orbitals 1 and 2) were dominant motifs of genetic mechanism of dimer molecular orbitals formation. The water molecular orbital energy is shown in the right column of Table 1 (a top number). The lower number represents the difference between the total energy of the two orbitals of the dimer and the doubled energy orbitals of the water molecule, which is genetically related to these orbitals. Recent numbers indicate that the energy of first and fifth pairs of orbitals increases during the formation of the dimer of two water molecules. This means that these orbitals don't favour the formation of the dimer. Orbitals № 2, № 3, № 4 lead to a decrease in the energy of the system and ensure the stability of the dimer configuration. Orbital № 7 has the lowest energy among the three bonding molecular orbitals and it dominates the dimer formation. Table 2 shows that this orbital consists of molecular orbitals № 4. At this point one s-electron is transferred from the right molecule to the left molecule that becomes negatively charged. It is known, that such charge transfer is characteristic for the

ionic type of chemical bond, so it should be assumed, that the dominant bond of dimer, which is product of association of two water molecules, is an ionic bond. It should be noted that this implies that the two identical molecules may be electron donors or acceptors depending on their mutual arrangement.

The complete set of water dimers with an element of the point group symmetry is presented in Table 3.

Table 3. Stable isomers of water dimer

№1		-4136.945805565 C_s
№2		-4136.914047144 C_s
№3		-4136.888335096 C_{2h}
№4		-4136.878307697 C_s
№5		-4136.87695529 C_{2v}
№6		-4136.810760848 C_{2h}

The right column of the table contains the binding energy (eV), obtained by computing, and the symmetry of the dimer. The calculated frequencies of atom vibrations in each dimer are real. It means that all dimers in the table are in locally stable equilibrium.

Results and discussions

The reorganization of configurations, which arises at thermal motion, is the result of overcoming the potential barriers. The smallest of potential barriers achieved in the saddle configurations, which are characterized by that one of the natural frequencies which

is imaginary. Every such saddle configuration divides two metastable. Full set of equilibrium and saddle configurations can be presented in the form of the cell complex, reflecting the most probable routes of the dimer reorganization. The idea of a cell complex was formulated in [4] and was successfully used for other systems [5-7]. Numerical definition of a structure and characteristics of a cell complex of dimer calculations of the energy of saddle configurations were carried out by the pointwise calculation of energy and a range of frequencies near saddle configurations of a dimer. The received complex is represented in figure 2.

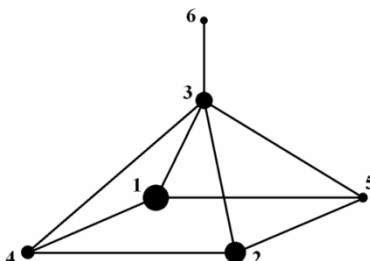


Fig. 2. Cell complex for set of water dimers

Circles in this figure show metastable states of a dimer, and their size reflects the binding energy of a dimer. Large radius of the circle corresponds to the lower value of the dimer energy. Each line in fig. 2 corresponds to a saddle configuration of dimer. Saddle configurations (1-4) and (1-5), as well as their wavefunctions shown below as an example.

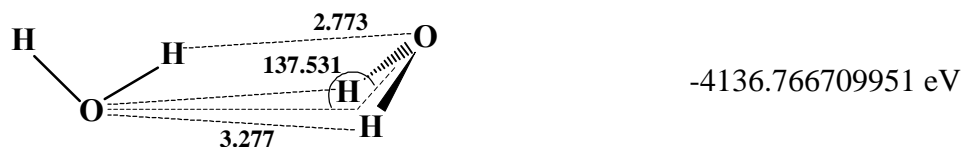
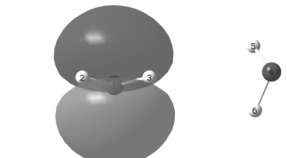
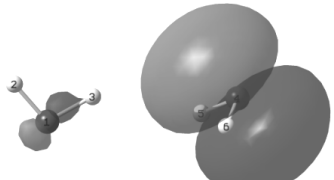


Fig. 3. Saddle configuration of the dimer (1-4)



Fig. 4. Saddle configuration of the dimer (1-5)

Table 4. Orbitals of the dimer, shown in Figure 3

<p style="text-align: center;">№10</p> 	-13.801096870 eV
<p style="text-align: center;">№9</p> 	-13.862278647 eV

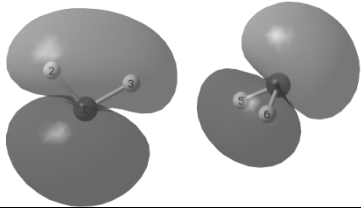
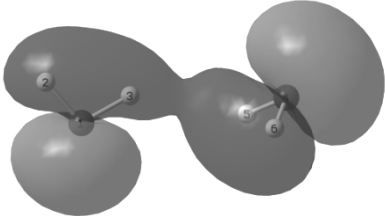
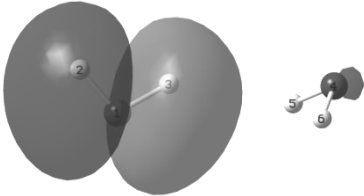
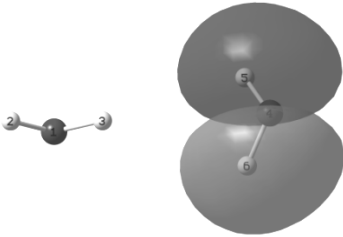
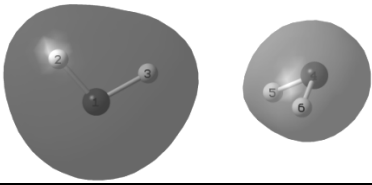
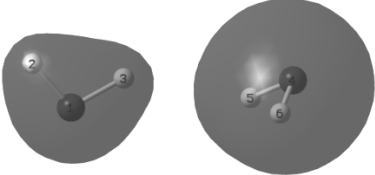


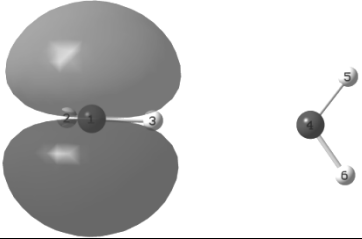
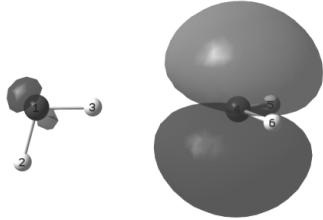
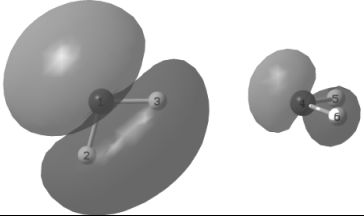
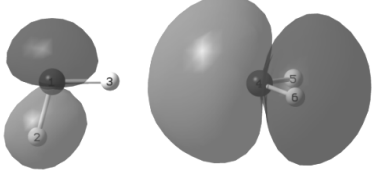
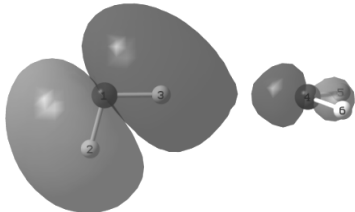
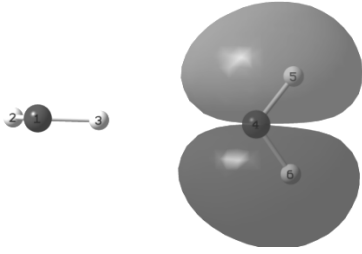
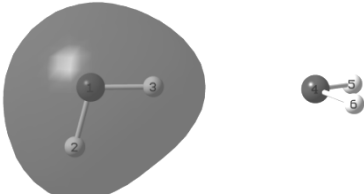
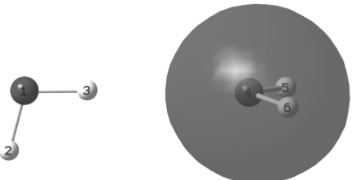


<p>№8</p> 	<p>-15.735686479 eV</p>
<p>№7</p> 	<p>-15.85740953 eV</p>
<p>№6</p> 	<p>-19.507867955 eV</p>
<p>№5</p> 	<p>-19.548622273 eV</p>
<p>№4</p> 	<p>-36.716500613 eV</p>
<p>№3</p> 	<p>-36.816522630 eV</p>
<p>№2</p> 	<p>-559.737934068 eV</p>
<p>№1</p> 	<p>-559.84770212 eV</p>

Table 5. Orbitals of the dimer, shown in Figure 4

<p style="text-align: center;">№10</p> 	-12.88765060 eV
<p style="text-align: center;">№9</p> 	-14.09374273 eV
<p style="text-align: center;">№8</p> 	-14.82750238 eV
<p style="text-align: center;">№7</p> 	-16.12757184 eV
<p style="text-align: center;">№6</p> 	-18.56686626 eV
<p style="text-align: center;">№5</p> 	-19.75210128 eV
<p style="text-align: center;">№4</p> 	-35.78836016 eV

<p style="text-align: center;">№3</p> 	-37.00362656 eV
<p style="text-align: center;">№2</p> 	-558.78616106 eV
<p style="text-align: center;">№1</p> 	-560.05156718 eV

The comparison of orbitals for initial configuration of the dimer and saddle configuration shows that orbitals for different energies undergo various changes. The most high-energy orbitals are the tenth and ninth, and also orbitals № 1-5 change a little in comparison with the eighth, seventh and sixth orbitals. Therefore, the dimer partial destruction of a chemical bond which is various for different orbitals is characteristic for a saddle configuration. More detailed picture of change of orbitals in the course of transition from a stable state to the saddle has to be received on the basis of consideration of a trajectory of transition that is planned for further researches.

Conclusions

The large number of metastable configurations with different energies can be the cause of high heat capacity of water and relatively low viscosity. The change in temperature causes a change in the structure of water forming more metastable states with higher energy, which is spent on the thermal energy source. In order to determine the energy density due to a change in the configuration of water molecules in a macroscopic sample, and further, the temperature dependence of the heat capacity should be addressed multibody problem in quantum and classical levels, which requires special modeling and comparing the results with the experimental laws. The similar situation develops for a viscous current. Under the influence of external stress there is a directed reorganization of water dimers, which is activated by thermal movement, thus number of various reorganizations with formation of the plastic deformation, coinciding in the direction with stress, is bigger. Flow hydrogen bonds switched eventually in the process of liquid, so the activation energy of viscous flow close to the energy of hydrogen bonds.

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