

# Structural Changes in Water Clusters during Methane Adsorption

A. E. Galashev

*Institute of Industrial Ecology, Ural Branch, Russian Academy of Sciences,  
ul. Sof'i Kovalevskoi 20, Yekaterinburg, 620990 Russia  
e-mail: galashev@ecko.uran.ru*

Received August 20, 2013

**Abstract**—The structure of water clusters that have adsorbed from one to six methane molecules is studied by molecular dynamics simulation. Characteristic structural units of Voronoi and hybrid polyhedra are employed to reveal the structural changes resulting from the attachment of CH<sub>4</sub> molecules to the clusters. The most significant changes in topological properties are associated with variations in the number of faces of simplified polyhedra. A change is unambiguously detected in the small-angle peak intensity in the angular distribution of nearest geometrical neighbors determined with the use of the Voronoi polyhedra. The results of two different calculations of the number of hydrogen bonds in the clusters are compared, and the “nonsphericity” coefficients are calculated for the polyhedra.

**DOI:** 10.1134/S1061933X14030041

## INTRODUCTION

Water is a complex associated liquid that has a structure of a tetrahedral network of hydrogen-bonded molecules. Thermal motion of molecules causes spontaneous rearrangements of this network. Microvolumes (clusters) with relatively low thermal motion energy and increased degree of structural order of water molecules may be formed in the 3D network of hydrogen bonds due to fluctuations. At the same time, a lower level of structural ordering is observed in bulk water around the clusters.

Water clusters are present in the atmosphere along with the vapor phase. A large fraction of surface molecules capable of hydrogen bonding imparts a high adsorption ability to water clusters. They can absorb various molecules, such as O<sub>2</sub>, N<sub>2</sub>, Ar [1–4], CO<sub>2</sub>, CO, N<sub>2</sub>O, NO, NO<sub>2</sub> [5–11], CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub> [12–16], in the atmosphere. Spectral characteristics of systems of water clusters (including those containing CH<sub>4</sub> molecules) were discussed in [12].

Methane has a low solubility in water. Weak van der Waals interactions take place between water and methane molecules; no chemical compound is formed in this case. Under certain conditions (at an elevated pressure and low temperature), methane occurring in water forms a hydrate with the chemical formula CH<sub>4</sub> · 5.75H<sub>2</sub>O. The cubic structure (CS) of low-pressure CH<sub>4</sub> clathrate (CS-I), which consists of small and large cells in a ratio of 2 : 6, is transformed into CS-II (CH<sub>4</sub> · 5.76H<sub>2</sub>O) as methane concentration and pressure are increased (at  $p > 35$  MPa). Methane hydrate CS-II exists at pressures below  $\approx 0.6$  GP; at higher pressures, HS-III clathrate with a hexagonal structure (HS) is formed. The type of a clathrate structure is

determined by not only the temperature and pressure, but also the size of a guest molecule.

Different mechanisms have been hypothesized for the initial stage of methane hydrate formation [17–20]. Molecular dynamics simulation [21, 22] gave rise to an opinion that the formation of methane hydrate is controlled by the adsorption interaction between clusters formed in water and gas molecules. Hydrates cannot be formed via the interaction between water clusters and methane under atmospheric conditions, because water clusters in the atmosphere are relatively small (the number of molecules is  $N < 100$ ), cannot contain stable guest cells, and do not have a structure that would correspond to clathrates.

The physicochemical properties of water clusters are, in many respects, determined by their structure. A hydrocarbon molecule bonded to a cluster distorts the original network of hydrogen bonds. As the number of adsorbed molecules increases, the local changes in the network of hydrogen bonds may become global ones. Structural analysis of small objects can be carried out using the statistical geometry method [23] based on the construction of the Voronoi polyhedra (VPs).

In the case of a system with a limited number of degrees of freedom, VPs can be constructed only for its interior. However, even in this case, great changes in the VP shape can be expected, provided that the number of points of space partition is small. The emergence of the “boundary” effects (i.e., the effects caused by the lack of the points at the periphery) makes VPs rather elongated and greatly increases their volume. In the case of polyatomic molecules, atoms of one type may play the role of polyhedron centers, while atoms of another type may serve as their nearest neighbors that determine the polyhedron faces. For

example, in the case of water, it is advantageous to use oxygen atoms as the centers and select the nearest neighbors among hydrogen atoms. These hybrid polyhedra (HPs) are easier to construct, since the number of hydrogen atoms is twice as large as that of oxygen atoms. However, hybrid polyhedra are not Voronoi polyhedra, since they fail to densely fill all of the space occupied by molecules without voids and overlaps. VP faces determine the cyclic structures formed from oxygen atoms, while HP faces determine rings composed of hydrogen atoms.

In this study, we shall use a molecular dynamic model to consider the adsorption of CH<sub>4</sub> molecules on (H<sub>2</sub>O)<sub>50</sub> clusters, the changes in the cluster structure during successive attachment of methane molecules, and the extent to which the shape of the clusters is distorted during the adsorption.

### COMPUTER MODEL

Molecular dynamics simulation was based on the DC model of water [24] developed by modifying the TIP4P rigid four-site model. The selected geometry of an H<sub>2</sub>O molecule corresponded to its experimental parameters in a gas phase:  $r_{\text{OH}} = 0.09572$  nm and the angle between the OH bonds of 104.5° [25]. Electric charges ( $q_{\text{H}} = 0.519e$  and  $q_{\text{O}} = -1.038e$ ) were located in the centers of H atoms and at point  $M$  lying in the bisector of the HOH angle at a distance of 0.0215 nm from the oxygen atom. The charge values and the position of point  $M$  were selected so as to reproduce the experimental values of the dipole and quadrupole moments [26, 27], as well as the calculated ab initio energy of a dimer and the characteristic distances in it [28]. Stabilization of the tetrahedral structure was, to a great extent, provided by the short-range Lennard-Jones (LD) interaction realized via the oxygen atoms. Moreover, point  $M$  was associated with polarizability  $\alpha_i$ , which was needed to calculate the nonadditive polarization energy

$$U_{\text{pol}}(\mathbf{R}_{1\dots N}) = -\frac{1}{2} \sum_i^N \mathbf{E}_i^0 \mathbf{d}_i^{\text{ind}}, \quad \mathbf{d}_i^{\text{ind}} = \alpha_i \mathbf{E}_i,$$

and the induced force acting on molecule  $k$  [29]

$$\begin{aligned} \mathbf{f}_k^{\text{ind}}(\mathbf{R}_{1\dots N}) &= -\nabla_k U_{\text{pol}} \\ &= \sum_{i=1}^N \mathbf{d}_i (\nabla_k \mathbf{E}_i^0) + \sum_{i \neq k}^N \nabla_k (\mathbf{d}_i \mathbf{T}_k), \end{aligned}$$

where  $\mathbf{R}_i$  is the radius vector of the  $M$  point in molecule  $i$ ,  $\mathbf{E}_i^0$  is the strength of the electric field generated by the fixed partial charges,  $\mathbf{E}_i$  is the strength of the field generated in the center of molecule  $i$  by both the charges and the interaction of the induced dipole moments with these charges, and  $\mathbf{d}_i^{\text{ind}}$  is the induced dipole moment of molecule  $i$ .

Dipole tensor  $T_{ij}$  is determined as

$$\mathbf{T}_{ij} = \frac{1}{4\pi\epsilon_v} \frac{1}{r_{ij}^3} \left[ \frac{3\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2} - 1 \right],$$

where  $\epsilon_v$  is the dielectric permittivity of vacuum.

Methane–methane atom–atomic interactions were represented by a sum of the LD and Coulomb contributions:

$$\Phi_{ij}(r) = \epsilon_{ij} \left[ \left( \frac{r_0}{r_{ij}} \right)^{12} - 2 \left( \frac{r_0}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}}.$$

The values of parameters  $\epsilon_{ij}$ ,  $r_0$ , and  $q_i$  for atoms H and C of a CH<sub>4</sub> molecule were taken to be 0.038 kcal/mol, 0.28525 nm, and 0.119 $e$  and 0.07382 kcal/mol, 0.43 nm, and  $-0.476e$ , respectively [30]. The parameters of the LD potential describing methane–water interactions were determined using the Berthelot–Lorentz formulas

$$\epsilon_{\text{aw}}^{(\text{LJ})} = \sqrt{\epsilon_{\text{a}}^{(\text{LJ})} \epsilon_{\text{w}}^{(\text{LJ})}}, \quad \sigma_{\text{aw}}^{(\text{LJ})} = \frac{\sigma_{\text{a}}^{(\text{LJ})} + \sigma_{\text{w}}^{(\text{LJ})}}{2},$$

where  $\epsilon_{\text{a}}^{(\text{LJ})}$ ,  $\epsilon_{\text{w}}^{(\text{LJ})}$  are the energy parameters, while  $\sigma_{\text{a}}^{(\text{LJ})}$ ,  $\sigma_{\text{w}}^{(\text{LJ})}$  are the geometry parameters of the potential for C and H atoms in a methane molecule and O atom in a water molecule, respectively.

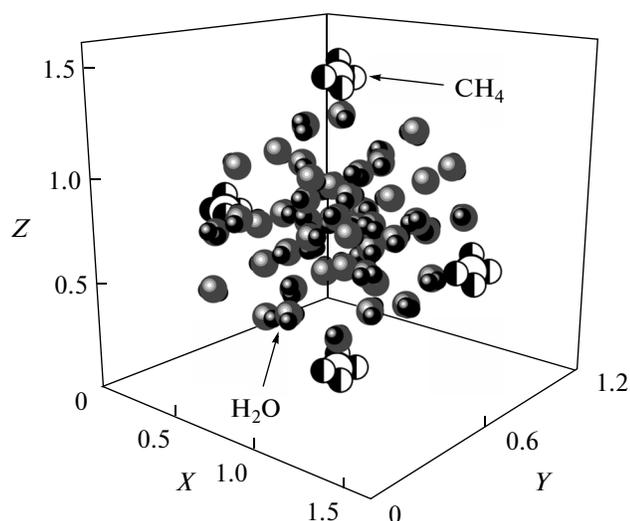
The methane molecule has the shape of a tetrahedron with the carbon atom located in the center and hydrogen atoms in the vertices. The HCH angle is equal to the tetrahedral angle of 109°. The interatomic distances in a CH<sub>4</sub> molecule are  $r_{\text{CH}} = 0.109$  nm and  $r_{\text{HH}} = 0.177$  nm. The nonpolar CH<sub>4</sub> molecule has a higher polarizability  $\alpha^p$  (2.6 Å<sup>3</sup>) than has the water molecule (1.49 Å<sup>3</sup>) [31].

Flexible molecular models were considered. Molecules were provided with flexibility via the procedure elaborated in terms of the Hamilton dynamics [32–34]: the deformation of a molecule was determined by

equilibrating total potential force  $\mathbf{f}(\mathbf{u}) = -\frac{\partial \Phi(\mathbf{r})}{\partial \mathbf{u}}$

with centrifugal force  $-\mu\omega^2$ , where  $\mu$  is the reduced mass,  $u$  is the distance between two atoms,  $\omega$  is the vibrational frequency, and  $\mathbf{r}$  determines the point at which the force is applied.

The equations of molecular motion were solved by the fourth-order Gear method [35]. Time step  $\Delta t$  of integration was  $2 \times 10^{-17}$  s. In a preliminary molecular-dynamics calculation  $2 \times 10^6 \Delta t$  long, the equilibration was performed at  $T = 233$  K for a (H<sub>2</sub>O)<sub>20</sub> cluster free of impurity molecules. Configuration of the water cluster at the 40 ps time moment was subsequently used as the initial configuration to simulate the (CH<sub>4</sub>) <sub>$i$</sub> (H<sub>2</sub>O)<sub>50</sub> system,  $1 \leq i \leq 6$ . No more than six methane molecules were added to the water cluster by placing them, initially, into the areas accessible for



**Fig. 1.** Configuration of  $(\text{CH}_4)_4(\text{H}_2\text{O})_{50}$  cluster at the 50 ps time moment.

interatomic interactions. Each of the  $\text{CH}_4$  molecules being attached was initially placed into a position such that the shortest distance between the atoms of this molecule and the atoms of water molecules was at least 0.6 nm.  $\text{CH}_4$  molecule was placed in a coordinate axis originating from the center of mass of the  $(\text{H}_2\text{O})_{50}$  cluster; the initial orientation of the methane molecule was arbitrary. Cutoff radius  $r_c$  of all interactions in the model was 0.9 nm. If more than one  $\text{CH}_4$  molecule were attached to the water cluster, they were arranged pairwise in the axes of the Cartesian coordinate system (although, a pair could be incomplete). The coordinate axes were consecutively filled with  $\text{CH}_4$  molecules; i.e., if there were two methane molecules, they were placed in the same coordinate axis but on the opposite sides from the center of mass of the cluster. A newly formed system was equilibrated within a time interval of  $0.6 \times 10^6 \Delta t$ ; then, the desired physicochemical properties were calculated within a time interval of  $2.5 \times 10^6 \Delta t$ . Sonnenschein's scheme [36] for combined solution of the equations describing translational and rotational motion of molecules was used. This scheme is based on the Rodrigo–Hamilton parameters [37].

Detailed analysis of the cluster structure was based on constructing Voronoi polyhedra and hybrid polyhedra. The VPs and HPs were constructed around 40 oxygen atoms adjacent to the center of mass of a cluster every 1000 time steps. The polyhedra were constructed around oxygen atoms of water molecules; however, the centers of mass of  $\text{CH}_4$  molecules (for VPs) and hydrogen atoms of methane molecules (for HPs) could also serve as the neighbors specifying the faces.

The smallest water cluster (a dimer) had one hydrogen bond with an energy of about 15 kJ/mol [38]. The distance  $r_{\text{OH}}$  between a covalently bonded H atom and the nearest neighboring O atom that formed the hydrogen bond was approximately 0.2 nm. An interval of  $0.170 \leq r_{\text{OH}} \leq 0.245$  nm was assumed to correspond to the existence of a hydrogen bond [39]. The majority of hydrogen bonds were not perfectly linear (the OHO angle was  $\approx 160^\circ - 170^\circ$ ), while distance  $r_{\text{OO}}$  between neighboring oxygen atoms involved in hydrogen bonding was  $\sim 0.28$  nm [40]. The criterion  $r_{\text{OO}} < 0.32$  nm was also used to search for hydrogen bonds [41]. The hydrogen and oxygen components of the geometry criterion for determining a hydrogen bond are not equivalent. In this study, we attempt to determine the discrepancy between these estimates.

The uniformity of the distribution of the surrounding molecules with respect to the central one characterizes the “nonsphericity” of a polyhedron, which is determined by the following expression [23]:

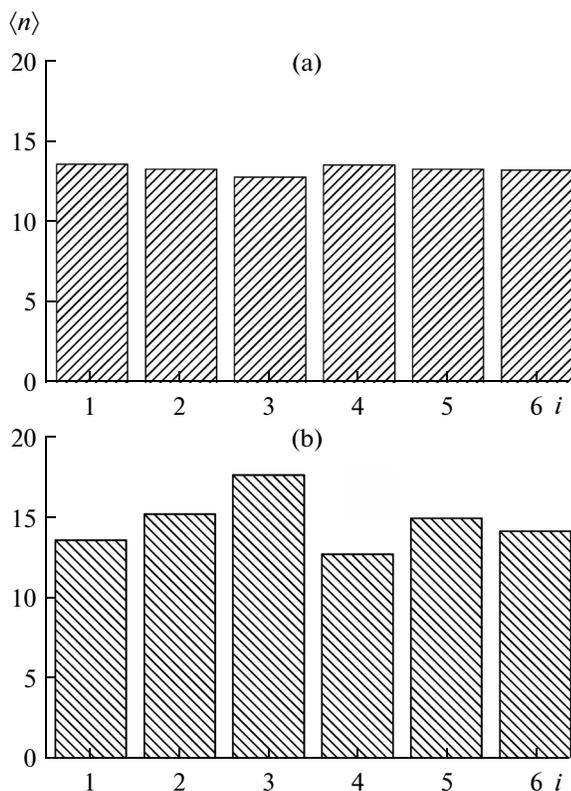
$$\eta = \frac{S^3}{36V^2\pi},$$

where  $S$  and  $V$  are the surface area and volume of the polyhedron, respectively. By definition,  $\eta$  is 1, 1.35, and 1.91 for a sphere, rhombic dodecahedron (VP of a face-centered cubic lattice), and cube (VP of a simple cubic lattice), respectively. For the VP of hexagonal ice, the nonsphericity is estimated as 2.25 [42], while, for an ideal tetrahedron, it is 3.31.

When constructing an HP, the hydrogen atoms belonging to the  $\text{H}_2\text{O}$  molecule, the oxygen atom of which played the role of the center of the polyhedron, were excluded from the nearest neighbors. In order to eliminate the small-scale thermal fluctuations, i.e., to analyze the averaged structure, rather small faces were excluded from polyhedra. This was performed by eliminating edges with lengths  $l < 0.5\bar{l}$ , where  $\bar{l}$  is the average length of a polyhedron edge. In many cases, the use of this procedure when constructing HPs allows one to eliminate double bonds between one molecule and an oxygen atom under consideration. Polyhedra with eliminated small edges are referred to as simplified ones.

## RESULTS OF CALCULATION

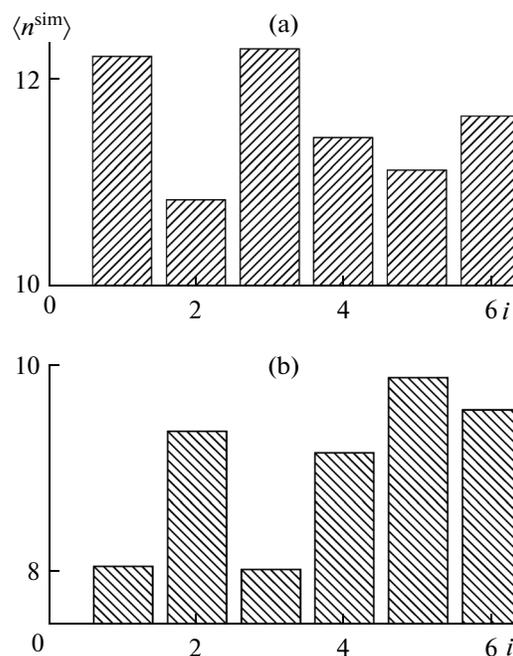
Figure 1 shows the configuration of a  $(\text{CH}_4)_4(\text{H}_2\text{O})_{50}$  cluster formed by the 50 ns time moment.  $\text{CH}_4$  molecules are in tight contact with  $\text{H}_2\text{O}$  molecules belonging to the cluster surface and have an orientation determined by the interactions with these water molecules. Since tetrahedral  $\text{CH}_4$  molecule carries external positive electric charges belonging to H atoms, tetrahedron vertices lie closer to the negatively charged oxygen atoms of the nearest water molecules. The situations, in which hydrogen atoms of a methane molecule are located near oxygen atoms of two or even



**Fig. 2.** The average number of faces in (a) Voronoi polyhedra and (b) hybrid polyhedra for  $(\text{H}_2\text{O})_{50}$  clusters that have adsorbed number  $i$  of  $\text{CH}_4$  molecules.

three  $\text{H}_2\text{O}$  molecules, are also possible. The symmetrical arrangement of hydrophobic methane molecules results in the densification of the water component of the cluster.

The common Voronoi polyhedra and hybrid polyhedra yield different statistical data for the average number of faces and sides in them. The  $\bar{n}_O$  and  $\bar{n}_H$  values characterize the numbers of geometrically neighboring oxygen and hydrogen atoms, respectively, for water molecules in clusters. In the latter case, the hydrogen atoms of a water molecule itself, the oxygen atom of which is located in the center of a VP, are not taken into account. Average number  $\bar{n}_O$  of faces in a VP is poorly sensitive to the addition of methane molecules to a water cluster (Fig. 2a). At  $1 \leq i \leq 6$ , the difference between the minimum and maximum  $\bar{n}_O$  values is  $<6.4\%$ . At the same time, the  $\bar{n}_H$  value significantly varies as  $\text{CH}_4$  molecules are adsorbed (Fig. 2b). When the number of methane molecules is varied in a range of  $1 \leq i \leq 6$ , the  $\bar{n}_H$  value changes within  $38.6\%$ . The difference in the stabilities of the  $\bar{n}_O$  and  $\bar{n}_H$  values attests to the conservatism of the distances between the oxygen atoms, which characterize a hydrogen bond, and the dynamic nature of the distances between oxygen and hydrogen atoms, which also characterize this

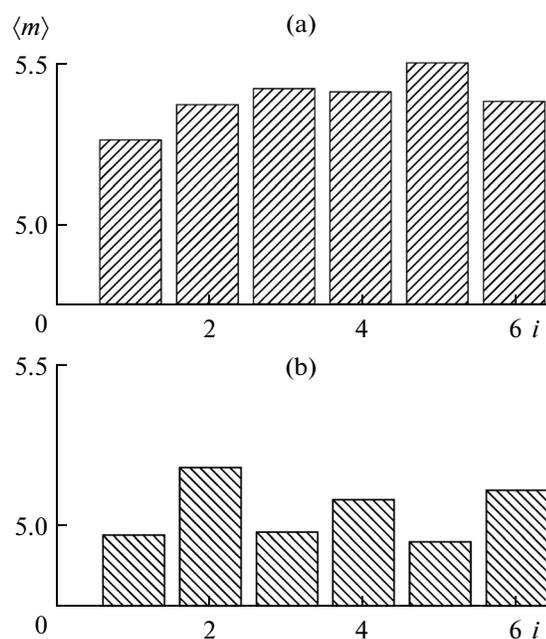


**Fig. 3.** The average number of faces in (a) simplified Voronoi polyhedra and (b) simplified hybrid polyhedra for  $(\text{H}_2\text{O})_{50}$  clusters that have adsorbed number  $i$  of  $\text{CH}_4$  molecules.

bond. The reason for the changes in the mobile component of the bond is the attachment of a  $\text{CH}_4$  molecule to the cluster. This attachment may cause both a change in the number of hydrogen bonds and their switching over.

The average number of faces in simplified VPs changes rather strongly (within  $13.4\%$ ) as number  $i$  of adsorbed  $\text{CH}_4$  molecules is varied from 1 to 6 (Fig. 3). For VPs, the  $\bar{n}_H^{\text{sim}}$  number has the smallest and largest values after a water cluster attaches two and three methane molecules, respectively. For simplified HPs, the  $\bar{n}_H^{\text{sim}}$  number varies within  $23.1\%$  ( $1 \leq i \leq 6$ ). A compensation character of  $\bar{n}_H^{\text{sim}}$  values with respect to  $\bar{n}_O^{\text{sim}}$  is observed for all  $i$  values. For example, the minimum  $\bar{n}_H^{\text{sim}}$  value is observed at  $i = 3$ , when  $\bar{n}_O^{\text{sim}}$  is maximum. The maximum  $\bar{n}_H^{\text{sim}}$  value is observed at  $i = 5$ , at which  $\bar{n}_O^{\text{sim}}$  has the second value. The mutually compensating behavior of the  $\bar{n}_O^{\text{sim}}$  and  $\bar{n}_H^{\text{sim}}$  values is caused by different signs of the electric charges carried by O and H atoms.

The number of sides per face ( $\bar{m}_O$  and  $\bar{m}_H$ ) indicates the number of neighboring atoms that affect the establishment of the "contact" created by the O–O or O–H interaction. In the case of VPs, oxygen atoms control the O–O contact interaction, while the tight O–H interaction is ensured by the nearest hydrogen atoms. The attachment of from one to six  $\text{CH}_4$  molecules to a

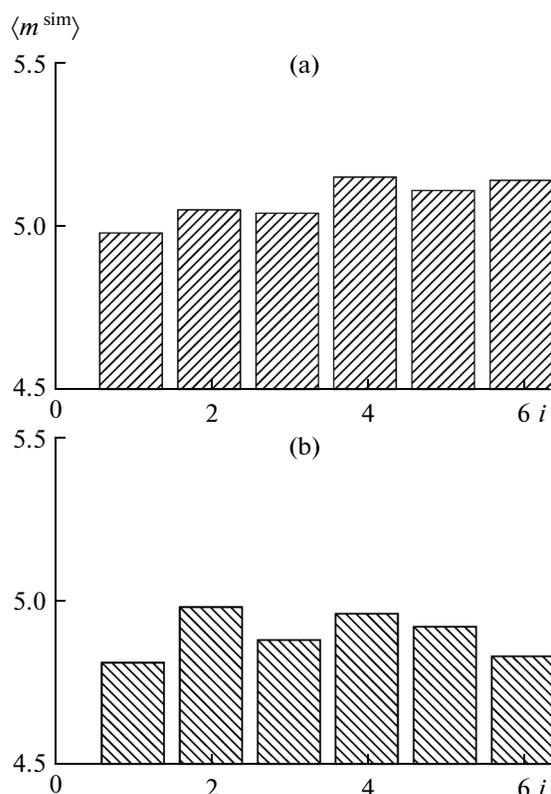


**Fig. 4.** The average number of sides in the faces of (a) Voronoi polyhedra and (b) hybrid polyhedra for  $(\text{H}_2\text{O})_{50}$  clusters that have adsorbed number  $i$  of  $\text{CH}_4$  molecules.

water cluster changes the  $\bar{m}_O$  value within 4.5%. The  $\bar{m}_H$  value can vary within nearly the same range (4.6%) (Fig. 4). Note that the maximum  $\bar{m}_O$  value and the minimum  $\bar{m}_H$  value are attained at  $i = 5$ . The  $\bar{m}_H$  values are always larger for even  $i$  values than those for odd ones. Contrariwise, with the exception of  $i = 1$ , the  $\bar{m}_O$  values for odd  $i$  are larger than those for the even ones. However, the difference in  $\bar{m}_O$  values at adjacent  $i$  can be negligible. Thus, at  $i > 1$ , the  $\bar{m}_O$  value is, to a certain extent, compensated by  $\bar{m}_H$  and vice versa. This compensation is explained by the fact that oxygen and hydrogen atoms are oppositely charged. However, the compensation cannot be complete or does not occur at all (at  $i = 1$ ) because of the different absolute magnitudes of the electric charges of O and H atoms.

As  $i$  is varied, the numbers of sides ( $\bar{m}_O^{\text{sim}}$  and  $\bar{m}_H^{\text{sim}}$ ) in the faces of simplified polyhedra vary more weakly than those of common polyhedra (Fig. 5). For example, the  $\bar{m}_O^{\text{sim}}$  value of VP varies within 3.4%, while variations in  $\bar{m}_H^{\text{sim}}$  for HP do not exceed 3.5%. At  $1 \leq i \leq 6$ ,  $\bar{m}_O^{\text{sim}}$  is close to 5. Hence, fifth-order rotation symmetry prevails in the framework structure (formed by oxygen atoms) of the clusters. This type of symmetry is inherent in the F structure [43] of a simple liquid [44].

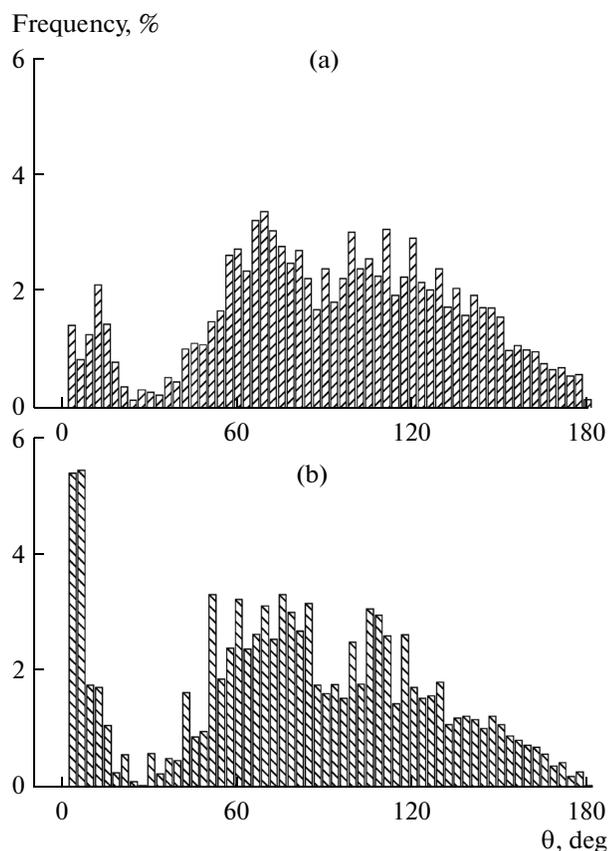
The changes in the spatial arrangement of molecules in a water cluster after one and six  $\text{CH}_4$  molecules have been adsorbed are illustrated in Fig. 6, in



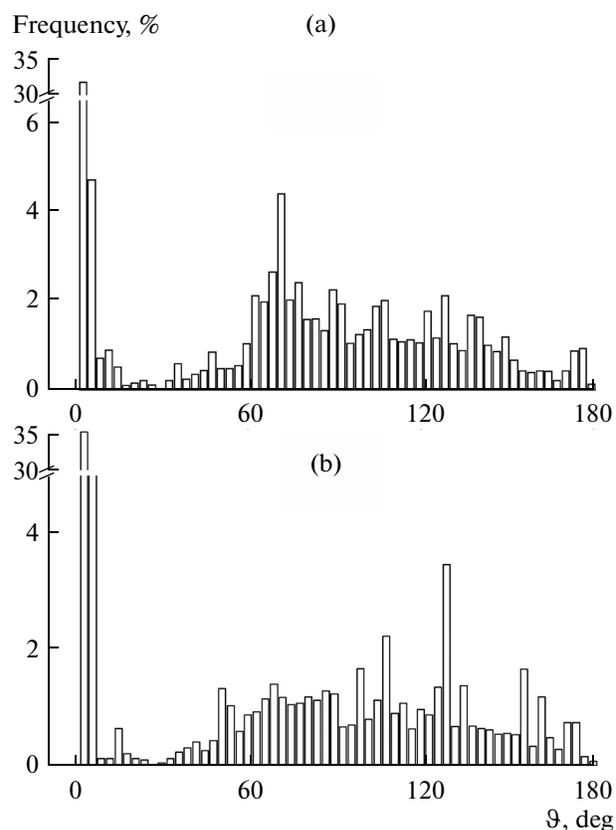
**Fig. 5.** The average number of sides in the faces of (a) simplified Voronoi polyhedra and (b) simplified hybrid polyhedra for  $(\text{H}_2\text{O})_{50}$  clusters that have adsorbed number  $i$  of  $\text{CH}_4$  molecules.

which the angular distribution ( $\theta$ -distribution) of oxygen atoms is shown. Three characteristic types of mutual orientation of O atoms may be distinguished after both one and six methane molecules are added to the cluster. In the former case, the groups of  $\theta$  angles correspond to the positions of  $12^\circ$ ,  $70^\circ$ , and  $110^\circ$ ; in the latter case, they correspond to positions of  $4^\circ$ ,  $68^\circ$ , and  $107^\circ$ . Thus, the strongest changes occur in the small-angle region of the spectrum. After six methane molecules have been attached, the strongest increase in maximum intensity (by a factor of 2.6) is observed in this spectral region. The peak at  $68^\circ$  has become more diffuse, while the peak at  $107^\circ$  has narrowed.

The angular distribution ( $\vartheta$ -distribution) resulting from the analysis of HPs, which refers to the  $\vartheta$  angles (HOH), characterizes the mutual arrangement of the nearest hydrogen atoms with respect to the central oxygen atom. The distribution of  $\vartheta$  angles changes much more weakly than the  $\vartheta$ -distribution does after  $\text{CH}_4$  molecules are added to a water cluster (Fig. 7). This especially concerns the small-angle region of the  $\theta$ -distribution. Regardless of the number of attached molecules, the rest of the spectrum is broad and continuous. The most intense peaks in this spectral region



**Fig. 6.** Angular distribution of the nearest geometrical neighbors preset using Voronoi polyhedra for  $(\text{H}_2\text{O})_{50}$  clusters that have adsorbed (a) one  $\text{CH}_4$  molecule and (b) six  $\text{CH}_4$  molecules.



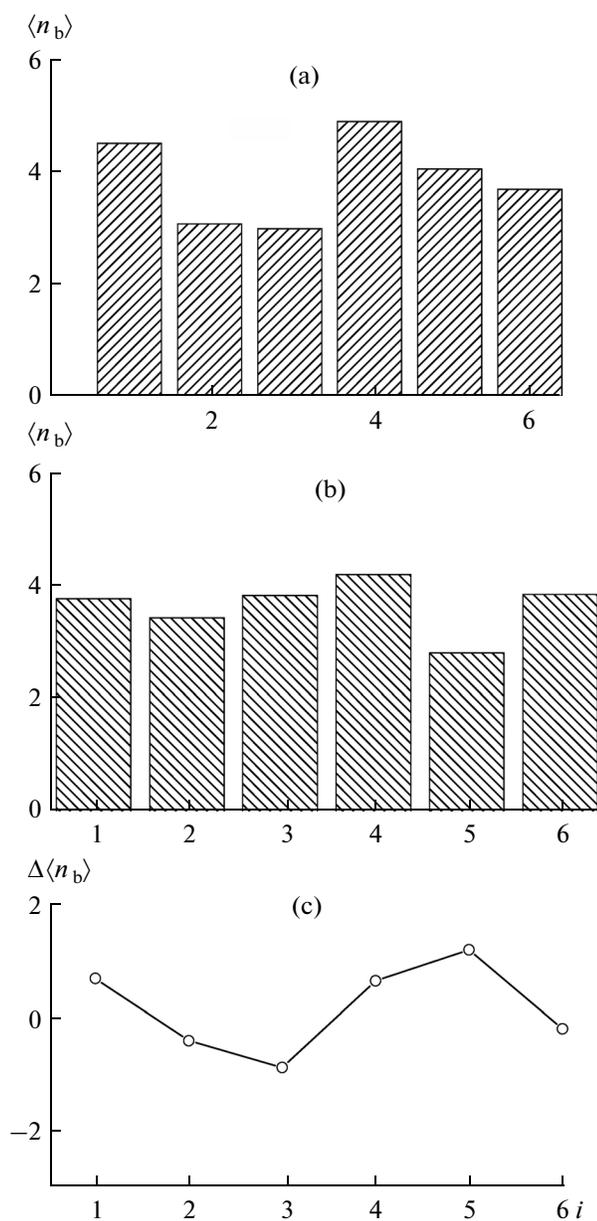
**Fig. 7.** Angular distribution of the nearest geometrical neighbors preset using hybrid polyhedra for  $(\text{H}_2\text{O})_{50}$  clusters that have adsorbed (a) one  $\text{CH}_4$  molecule and (b) six  $\text{CH}_4$  molecules.

are recorded at  $72^\circ$  and  $129^\circ$  after the first and sixth methane molecules are added to the water cluster, respectively. The changes observed in the  $\vartheta$ -spectrum most likely attest to labile orientation of hydrogen bonds.

Figure 8 shows variations in number of hydrogen bonds  $\bar{n}_b$ , caused by the addition of  $\text{CH}_4$  molecules to a water cluster. Figures 8a and 8b characterize the hydrogen bonds via the distance between oxygen atoms and the O–H distance, respectively. It is seen that, according to both criteria, the greatest number of hydrogen bonds is formed when four methane molecules are attached to a water cluster. This is related to the symmetrical arrangement of  $\text{CH}_4$  molecules, which generates a 2D compression effect. The emergence of higher-order symmetry in a cluster due to the attachment of two additional  $\text{CH}_4$  molecules does not increase the specific number of H bonds because of a spatial rearrangement of cluster-composing water molecules. As methane molecules are attached, the specific number of bonds may vary within 63.7% in accordance with the oxygen-based criterion. At the same time, according to the hydrogen-based criterion,

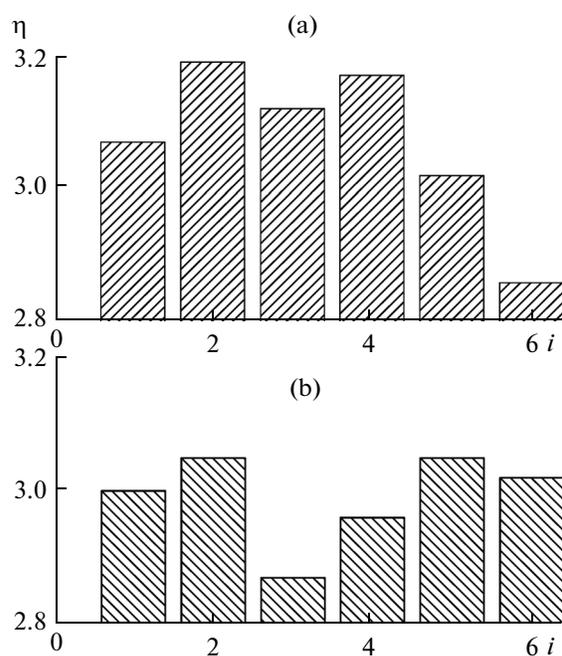
$\bar{n}_b$  varies within 49.1%. The former method for determining the number of hydrogen bonds (from the O–O distances) is rather rough, because a certain position of oxygen atom does not ensure a necessary orientation of H atoms of a corresponding  $\text{H}_2\text{O}$  molecule. The method of determining the number of hydrogen bonds with the help of HPs is more accurate. The difference in the  $n_b$  values obtained by these two methods is shown in Fig. 8c. It is clear that the value of  $\Delta\bar{n}_b = \bar{n}_b[\text{O}] - \bar{n}_b[\text{H}]$  may reverse its sign. It is negative at  $i = 2, 3$ , and 6 and positive in other cases. The determination of  $\bar{n}_b$  with the help of VPs may result in both over- or underestimation of this value by unity.

The cluster geometry is efficiently characterized by parameter of nonsphericity  $\eta$ . If the shape of a cluster is determined by the arrangement of oxygen atoms, the nonsphericity is especially high when two or four  $\text{CH}_4$  molecules have been attached (Fig. 9). In this case, the lowest value of the nonsphericity parameter is reached when a water cluster is uniformly surrounded by six  $\text{CH}_4$  molecules. If the nonsphericity is judged from the positions of hydrogen atoms, the situation is somewhat different. The maximum nonsphericity is,



**Fig. 8.** The average number of hydrogen bonds per  $\text{H}_2\text{O}$  molecule in water clusters that have adsorbed number  $i$  of  $\text{CH}_4$  molecules: (a) estimated using Voronoi polyhedra, (b) calculated using hybrid polyhedra, and (c) difference between calculations of  $\bar{n}_b$  using the former and latter methods.

in this case, attained at  $i = 2$  and  $5$ , while the minimum one is observed at  $i = 3$ . For both the oxygen- and hydrogen-based criteria, the value of  $\eta$  calculated at  $1 \leq i \leq 6$  lies in a range between 2.25 [42] for the VP of hexagonal ice and 3.31 for the packing of ideal tetrahedrons. The maximum fluctuations in the  $\eta$  value at  $1 \leq i \leq 6$  are as high as 11.5 and 6.3% according to the oxygen- and hydrogen-based criteria.



**Fig. 9.** Nonsphericity coefficient of (a) Voronoi polyhedra and (b) hybrid polyhedra for  $(\text{H}_2\text{O})_{50}$  clusters that have adsorbed number  $i$  of  $\text{CH}_4$  molecules.

## CONCLUSIONS

Molecular dynamics simulation has been used to study the structural changes in water clusters during methane adsorption. The structure of clusters has been studied in detail by constructing Voronoi polyhedra and hybrid polyhedra. The effect of small-scale thermal fluctuations on the structure of clusters has been eliminated with the use of the analysis of simplified polyhedra. The number of geometrical neighbors determined using both the common and simplified HPs undergoes noticeably greater changes during adsorption of methane molecules than this parameter determined by the analysis of corresponding VPs. The sensitivity to the structural changes, which is determined from the number of sides in polyhedron faces, is almost identical for VPs and HPs, including their simplified forms. A compensation relationship has been revealed between the number of geometrical neighbors determined using the simplified VPs and HPs and the number of sides in the faces for common VPs and HPs. The compensation relationship between the structural units is predetermined by different electric charges of oxygen and hydrogen atoms. Variations in the number of adsorbed methane molecules primarily affect the intensity of the small-angle peak in the angular distribution of geometric neighbors for VPs and have almost no effect on the intensity of the corresponding peak for HPs. Construction of PVs for an aqueous system yields a rough estimate for the number of hydrogen bonds. The  $\bar{n}_b$  value can be determined

more accurately from the data obtained from HPs. This method does not predict monotonous variations in the number of hydrogen bonds in a water cluster with increasing number of attached CH<sub>4</sub> molecules. The VP asymmetry of water clusters decreases at large numbers of adsorbed methane molecules ( $i = 5$  and  $6$ ). However, this is not observed in the case of HPs, in which the minimum asymmetry takes place at  $i = 3$ .

Thus, the adsorption of methane molecules by a water cluster causes a noticeable positional and orientational rearrangement of its structure. It is expected that this rearrangement will be detected by molecular spectroscopy.

## REFERENCES

- Galashev, A.E., Chukanov, V.N., and Galasheva, O.A., *Colloid J.*, 2006, vol. 68, p. 131.
- Novruzova, O.A., Chukanov, V.N., and Galashev, A.E., *Colloid J.*, 2006, vol. 68, p. 462.
- Novruzova, O.A., Galasheva, A.A., and Galashev, A.E., *Colloid J.*, 2007, vol. 69, p. 474.
- Novruzova, O.A., Galasheva, A.A., and Galashev, A.E., *Colloid J.*, 2007, vol. 69, p. 483.
- Galashev, A.E., Rakhmanova, O.R., and Chukanov, V.N., *Colloid J.*, 2005, vol. 67, p. 271.
- Galashev, A.E., Rakhmanova, O.R., and Chukanov, V.N., *Colloid J.*, 2005, vol. 67, p. 278.
- Galashev, A.E., Rakhmanova, O.R., and Chukanov, V.N., *Colloid J.*, 2005, vol. 67, p. 285.
- Galashev, A.E. and Rakhmanova, O.R., *Colloid J.*, 2009, vol. 71, p. 163.
- Galasheva, A.A., Rakhmanova, O.R., Novruzov, A.N., and Galashev, A.E., *Colloid J.*, 2007, vol. 69, p. 56.
- Galashev, A.E. and Rakhmanova, O.R., *Colloid J.*, 2009, vol. 71, p. 293.
- Galashev, A.E. and Rakhmanova, O.R., *Colloid J.*, 2010, vol. 72, p. 478.
- Galashev, A.E., *Colloid J.*, 2013, vol. 75, p. 253.
- Novruzov, A.N., Rakhmanova, O.R., Novruzova, O.A., and Galashev, A.E., *Russ. J. Gen. Chem.*, 2008, vol. 78, p. 73.
- Novruzov, A.N., Rakhmanova, O.R., and Galashev, A.E., *Colloid J.*, 2008, vol. 70, p. 55.
- Novruzov, A.N., Rakhmanova, O.R., and Galashev, A.E., *Colloid J.*, 2008, vol. 70, p. 64.
- Galashev, A.E., *Colloid J.*, 2013, vol. 75, p. 150.
- Sloan, E.D., *Nature* (London), 2003, vol. 426, p. 353.
- Sloan, E.D. and Koh, C.A., *Clathrate Hydrates of Natural Gases*, Boca Raton: CRC, 2008.
- Christiansen, R.L. and Sloan, E.D., *Ann. N. Y. Acad. Sci.*, 1994, vol. 715, p. 283.
- Radhakrishnan, R. and Trout, B.L., *J. Chem. Phys.*, 2002, vol. 117, p. 1786.
- Guo, G.J., Zhang, Y.G., Liu, C.J., and Li, K.H., *Phys. Chem. Chem. Phys.*, 2011, vol. 13, p. 12048.
- Walsh, M.R., Koh, C.A., Sloan, E.D., Sum, A.K., and Wu, D.T., *Science* (Washington, D. C.), 2009, vol. 326, p. 1095.
- Medvedev, N.N., *Metod Voronogo-Delone v issledovanii struktury nekristallicheskih sistem* (The Voronoi–Delone Method in the Investigation of Noncrystalline System Structure), Novosibirsk: Sib. Otd., Ross. Akad. Nauk, 2000.
- Dang, L.X. and Chang, T.-M., *J. Chem. Phys.*, 1997, vol. 106, p. 8149.
- Benedict, W.S., Gailar, N., and Plyler, E.K., *J. Chem. Phys.*, 1956, vol. 24, p. 1139.
- Xantheas, S., *J. Chem. Phys.*, 1996, vol. 104, p. 8821.
- Feller, D. and Dixon, D.A., *J. Phys. Chem.*, 1996, vol. 100, p. 2993.
- Smith, D.E. and Dang, L.X., *J. Chem. Phys.*, 1994, vol. 100, p. 3757.
- Ahlstrom, P., Wallqvist, A., Engstrom, S., and Jonsson, B., *Mol. Phys.*, 1989, vol. 68, p. 563.
- New, M.H. and Berne, B.J., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 7172.
- Spravochnik khimika. T. 1* (Chemist's Handbook), Nikol'skii, B.P., Ed., Leningrad: Khimiya, 1971, vol. 1.
- Lemberg, H.L. and Stillinger, F.H., *J. Chem. Phys.*, 1975, vol. 62, p. 1677.
- Rahman, A., Stillinger, F.H., and Lemberg, H.L., *J. Chem. Phys.*, 1975, vol. 63, p. 5223.
- Saint-Martin, H., Hess, B., and Berendsen, H.J.C., *J. Chem. Phys.*, 2004, vol. 120, p. 11133.
- Haile, J.M., *Molecular Dynamics Simulation. Elementary Methods*, New York: Wiley, 1992.
- Sonnenschein, R., *J. Comput. Phys.*, 1985, vol. 59, p. 347.
- Koshlyakov, V.N., *Zadachi dinamiki tverdogo tela i prikladnoi teorii giroskopov* (The Problems of Solid Body Dynamics and Applied Theory of Gyroscopes), Moscow: Nauka, 1985.
- Feyereisen, M.W., Feller, D., and Dixon, D.A., *J. Phys. Chem.*, 1996, vol. 100, p. 2993.
- Jeffrey, G.A. and Saenger, W., *Hydrogen Bonding in Biological Structures*, New York: Springer, 1991.
- Maheshwary, S., Patel, N., Sathyamurthy, N., Kulkarni, A.D., and Gadre, S.R., *J. Phys. Chem. A*, 2001, vol. 105, p. 10525.
- Gonzales, E.-Kh., Poltev, V.I., Teplukhin, A.V., and Malenkov, G.G., *Zh. Strukt. Khim.*, 1994, vol. 35, p. 113.
- Naido, K.J. and Kuttel, M., *J. Comput. Chem.*, 2001, vol. 22, p. 445.
- Medvedev, N.N., Voloshin, V.P., and Naberukhin, Yu.I., *Zh. Strukt. Khim.*, 1989, vol. 30, p. 98.
- Bernal, J. and King, S., in *Physics of Simple Liquids*, Temperley, H., Rowlinson, J., and Rushbrooke, G., Eds., Amsterdam: North-Holland, 1968.

Translated by D. Terpilovskaya