

MOLECULAR DYNAMICS SIMULATION OF THE STRUCTURE OF C6 ALKANES

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The models of hexane, 2,3-dimethylbutane, and cyclohexane are obtained by the method of classical molecular dynamics using the GROMACS software package. Two different force fields (the all-atom description and the approach of united atoms) are used. Radial distribution functions (RDFs) are calculated for the molecular centers of mass, and the shapes of Delaunay simplices are analyzed. It is shown that the most compact molecules (cyclohexane and 2,3-dimethylbutane) are located in the space as atoms in simple liquids. Thus, the structural distinctions between liquid cyclohexane and 2,3-dimethylbutane are the same as between simple liquids of the corresponding density.

Keywords: molecular dynamics, structure of simple liquids, molecular liquids, liquid alkanes.

INTRODUCTION

Saturated hydrocarbons (alkanes) represent a simple class of chemical compounds; at the same time, they have many interesting physical and chemical properties [1]. Their molecules demonstrate rather weak intermolecular interaction, but have various forms because of multiple isomers and conformers. Due to the absence of specific interactions, the geometrical features of molecules become more important; however, their role remains poorly studied up to now.

Among C6 alkanes, all hexane isomers are known to have approximately equal density. This value varies in the range from 0.645 g/cm³ to 0.657 g/cm³ at a room temperature, i.e. distinctions are less than 2%, whereas cyclohexane comes out of this interval by approximately 20% (0.774 g/cm³) [2]. Moreover, it has much higher viscosity, boiling and crystallization temperatures. There is no simple and clear explanation of such distinction till now; however there are the speculations based on features of the forms of molecules. Cyclohexane molecules have the *chair* conformation in a liquid. Everyday experience gives hints about the ability of such a form to promote denser packing, thus explaining the density of cyclohexane [2]. On the other hand, the cyclohexane molecule is often considered to be spherical. In this case, a distinction in the density of liquids is related to the complex form of the other C6 alkanes. However, it remains difficult to understand why the 2,3-dimethylbutane, whose molecule is as spherical as a cyclohexane molecule (Fig. 1), has nevertheless the density equal to the density of hexane?

It is known that cyclohexane and 2,3-dimethylbutane form a plastic crystal phase. Some other compact molecules also possess this property [3, 4]. Such liquids crystallize at first in a fcc or bcc structure with increasing temperature, and only then they transform into the normal crystal phase whose structure already depends on the form of molecules. The nature of a plastic crystal is still not understood in detail. Molecules in such crystals move in a complex way. It is considered that the neighboring molecules have arbitrary mutual orientations that change randomly. Thus, the molecules vibrate nearby the lattice sites and also actively participate in the translational diffusion motion [3]. Despite that, the crystalline texture peculiar

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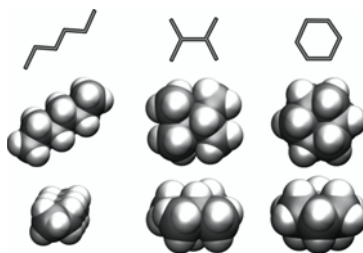


Fig. 1. Molecules of hexane, 2,3-dimethylbutane, and cyclohexane (from left to right). The topologies and van der Waals surfaces of molecules are shown in different projections. The hexane molecule is shown in the (*ttt*) conformation, the molecule of 2,3-dimethylbutane molecule is in the *trans*-conformation; see the text.

for packings of spherical atoms remains unchanged. However, if molecules are able to form a crystal structure as spherical particles, then this property should be manifested in a liquid, too. Indeed, their distant oscillations in the experimental radial distribution functions are similar to those for condensed noble gases, namely, beyond the intramolecular distances, regular oscillations are observed which smoothly decay with increasing r ; see, for example, [5-7].

In this work, we perform molecular dynamics simulation of liquid hexane, 2,3-dimethylbutane, and cyclohexane, and we also discuss to what extent the structure of these molecular liquids corresponds to the structure of simple liquids.

CONSTRUCTION OF THE MODELS

We have simulated liquids using the GROMACS program package of classical molecular dynamics [8]. Two different force fields are used: OPLS-AA, the all-atom description taking into account both carbon and hydrogen atoms [9], and GROMOS96 — 45A3-UA, the approximation of united atoms in which each methyl group is represented by one atomic unit [10]. In the first case, the model of a liquid includes 1000 molecules, where each cyclohexane molecule is formed by 18 atoms (6 C and 12 H), and each molecule of non-cyclic analogues has 2 additional hydrogen atoms. In the second case (approach of united atoms), the model contains 2197 molecules. Here the molecule consists of exactly 6 atomic units representing CH_3 , CH_2 , or CH_1 groups. Calculations are made in both *NPT* ($T = 298.15$ K, $P = 1$ bar) and in *NVT* ensembles. The Berendsen thermostat is used (to equilibrate the system), and the Nose-Hoover thermostat is used to model in the equilibrium state. For a part of calculations the Bussi-Parrinello thermostat is used. It represents a modified version of the Berendsen thermostat, which is convenient for both the equilibration process and calculations in the equilibrated model. The equilibrium configurations of the models in a range from 1 ns to 5 ns are analyzed. The integration step is 2 fs in all cases. The stretching vibrations of atomic bond lengths between atoms are not taken into account.

Both force fields well reproduce the experimental densities of liquids. Especially good coincidence takes place for the potential of united atoms: better than 1%. It supports the results of the work [10], where this force field was optimized to describe the experimental densities of alkanes. The self-diffusion coefficients are calculated less accurately, but a good qualitative agreement is also achieved here. For cyclohexane we have obtained $D = 0.8 \cdot 10^{-9}$ m²/s, which is approximately 3 times smaller than that for 2,3-dimethylbutane ($2.9 \cdot 10^{-9}$ m²/s) and hexane ($3.3 \cdot 10^{-9}$ m²/s). Such a tendency is observed in the experiments too, where $D = 1.6 \cdot 10^{-9}$ m²/s, $3.8 \cdot 10^{-9}$ m²/s, and $4.1 \cdot 10^{-9}$ m²/s respectively at 25°C [2].

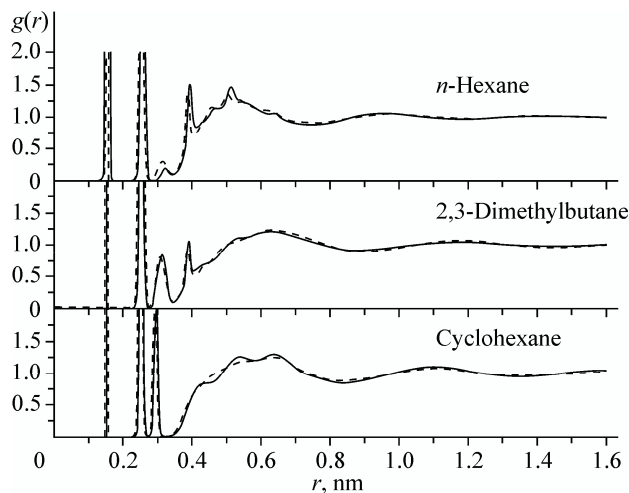


Fig. 2. Pair correlation functions of carbon atoms for hexane, 2,3-dimethylbutane, and cyclohexane. Solid curves are calculated with use of the all-atom force field; dashed curves correspond to the approach of united atoms.

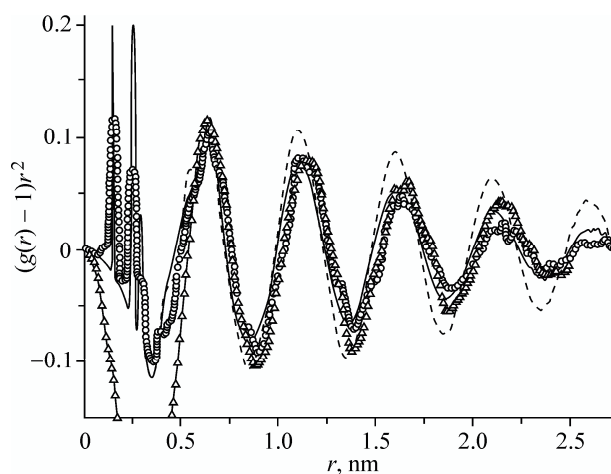


Fig. 3. Comparison of calculated (lines) and experimental (symbols) radial distribution functions for cyclohexane. Dash designates the all-atom force field; solid line corresponds to the united atoms approximation.

RADIAL DISTRIBUTION FUNCTION (RDF)

Fig. 2 displays the pair correlation functions $g(r)$ of the investigated liquids calculated for carbon atoms (when the all-atom force field is used) and methyl groups (for the united atoms). Sufficiently well agreement of the structure of modeled liquids was obtained for different force fields.

Sharp peaks belong to the intramolecular distances. The nearest distance (between the covalently bonded carbon atoms) remains constant in the course of modeling. All peaks are broadened for longer distances because of the deformation of angles between the neighboring bonds and rotations around the bonds. Two first peaks, naturally, coincide for all liquids, while the subsequent intramolecular peaks are characteristic of the molecule. Cyclohexane has one additional distance (between the opposite carbon atoms in a ring); hexane demonstrates the multiple set of narrow peaks that correspond to distances between the remote carbon atoms of the molecule and depend on a molecule conformation.

The calculated RDFs are compared in Fig. 3 with the experimental ones obtained for cyclohexane by X-ray [6] and neutron [5] diffraction. Here the function $(g(r) - 1)r^2$ is presented which is commonly used in the diffraction analysis of liquids. This function better reveals the correlations with increasing r . It allows us to discuss some distinctions between the models obtained with use of different force fields. In the case of the all-atom force field, the distant oscillations decay more slowly than those in the model of united atoms; however, the positions of maxima coincide. These distinctions are almost not seen in the function $g(r)$ (Fig. 2). The model of united atoms (solid line in Fig. 3) even better fits the experimental data. So, our models made within the classical method of molecular dynamics well reproduce the structure of the studied liquids.

CONFORMATIONS OF MOLECULES

Rotations around the C–C chemical bond lead to the conformation transitions of molecules. We know that cyclohexane in a liquid is present mainly in the *chair* form; however, non-cyclic molecules are present in various conformations [11, 12]. In our molecular dynamics models, we see the same picture. Most often we observe the *ttt*, *ttg*, and *tgt* conformations in liquid hexane, in an amount of approximately 50%, 29%, and 11%. In [13] by means of quantum chemical calculations of the energy of different conformers, close estimations for a fraction of such conformations are obtained: 31%, 33%, and 16% respectively. The fractions of the other conformers are substantially smaller, which is found in

both our models and evaluated in [13]. We remind that *t* and *g* mean the *trans*- and *gauche*-positions around the given C–C bond.

Only two nonequivalent conformations are possible for 2,3-dimethylbutane: *trans*- and *gauche*- that differ in the rotation of a molecule around the middle C–C bond. The *trans*-conformation is planar (Fig. 1). In the case of the *gauche*-conformation, one methyl group is slightly raised above the molecule plane. According to our analysis, liquid 2,3-dimethylbutane consists of 77% of *gauche*-conformations. We have studied a rate of conformational equilibration and found that the equilibrium conformational composition of the liquid is reached in approximately 3-4 ns at room temperature if all molecules are in one conformation in the initial configuration.

RDF OF THE CENTERS OF MASS OF MOLECULES

To study the relative positions of molecules in our liquids we investigated the system of their centers of mass. The pair correlation functions $g(r)$ calculated for the centers of mass of molecules are shown in Fig. 4. For hexane this function has a broad first maximum and quickly decays. It is clear that for the elongated molecules the distance between the mass centers of the neighboring molecules significantly depends on their mutual orientation. However, for 2,3-dimethylbutane and cyclohexane these functions are similar to those characteristic for simple liquids, i.e. a sharp first peak with subsequently decaying oscillations. However, the curves for 2,3-dimethylbutane and cyclohexane are different, i.e. both liquids behave as simple ones but of different structures. The distant maxima of $g(r)$ decay with different rates and are regularly shifted, in spite of the fact that positions of the first peaks are slightly different. Such distinctions are peculiar to simple liquids when the density changes: since the size of atoms does not change, the first peak practically does not shift, and structural variations become apparent in subsequent oscillations.

Fig. 5 displays $g(r)$ for two Lennard-Jones liquids, calculated also by the method of molecular dynamics. Values of the parameter σ are identical for them, and the ϵ values are different to provide different densities of the liquids. One can see that for a less dense Lennard-Jones liquid, $g(r)$ decays faster and its oscillations are shifted in comparison to a more dense liquid. This behavior is similar to that in Fig. 4. Note that a similar behavior of $g(r)$ with changing density is also characteristic of rigid sphere packing [14].

Thus, we come to the conclusion that the distinction between the pair correlation functions for 2,3-dimethylbutane and cyclohexane shown in Fig. 4 is just the same as between simple liquids of different densities.

It should be noted that the values of $\sigma = 5.4 \text{ \AA}$, $\epsilon = 3.1 \text{ kJ/mol}$, and $\epsilon = 2.6 \text{ kJ/mol}$ are chosen to produce 12% of the density difference for liquids at normal temperature and pressure. The difference allows us to compare these Lennard-Jones liquids with our molecular ones. Recall that the observed inequality in the molar density of 2,3-dimethylbutane and cyclohexane is 20%. However, part of this difference may have a trivial reason due to a smaller size of a cyclohexane molecule, which results in that the same volume can accommodate a larger number of smaller molecules. We evaluated the distinction in the size of molecules by the difference in the first peak positions of the function $g(r)$ in Fig. 4, which gives no more than 2.5%. This scaling factor leads to a change in the density of about 8%. The densities of our liquids are discussed in more detail in [15, 16].

DELAUNAY SIMPLICES

For the analysis of a three-dimensional structure of our liquids we have used Delaunay simplices. Let us remind that a Delaunay simplex represents a tetrahedron with vertexes formed by four of the mutually nearest atoms. In our case, it is four centers of gravity of the molecules. The Delaunay simplices are in fact the elementary three-dimensional blocks that are convenient for the study of the structure of various systems [17].

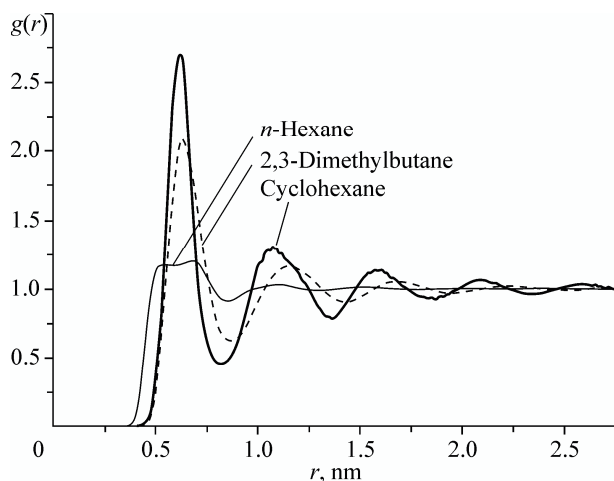


Fig. 4. Pair correlation functions for hexane, 2,3-dimethylbutane, and cyclohexane calculated for the mass centers of the molecules.

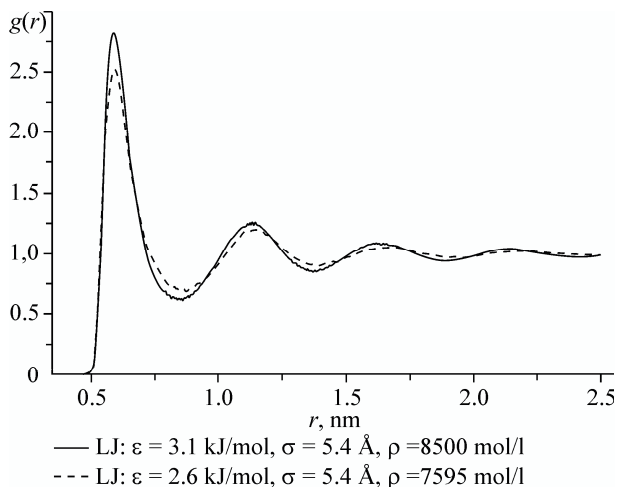


Fig. 5. Pair correlation function of a Lennard-Jones liquid for different densities. Less dense liquid has a shift of the distant maxima towards large r and decays faster.

Simple liquids (as well as rigid sphere packing) are known to have the Delaunay simplices in simple liquids whose shape is close to the shape of a regular tetrahedron, and the fraction of such simplices increases with increasing density [18, 19]. The same situation takes place for the simplices calculated for the mass centers of our molecules. Fig. 6 represents the T -distribution of simplices for our models. We remind that the T measure characterizes a deviation of the shape of the given simplex from the shape of a regular tetrahedron. A more regular shape of a simplex corresponds to smaller values of the T measure [17]. The number of such simplices in cyclohexane is approximately twice as large as in 2,3-dimethylbutane. There are good tetrahedral simplices in hexane too; however, their number is substantially less. It is caused by that the centers of gravity of hexane molecules are scattered in the space more chaotically than the centers of spherical particles (Fig. 4).

Fig. 7 shows the T -distributions for Lennard-Jones liquids presented in Fig. 5. One can see that the less dense liquid has the distribution identical to the distribution for 2,3-dimethylbutane. A more dense liquid also has a large fraction of tetrahedral simplices; however, it is less than in cyclohexane. The calculation for a more dense Lennard-Jones liquid improves the description of the T -distribution approaching it to cyclohexane. However, such a Lennard-Jones system should correspond to a non-equilibrium (glassy) state of the Lennard-Jones liquid. It is not surprising because we understand that the spatial location of our molecules is similar to the arrangement of spherical atoms; however, it does not mean at all that molecules should be identified with spheres.

In the work [14], we have analyzed the Delaunay simplices in packings of hard spheres. It has been shown that the T -distribution for packings of the hard spheres with the density (packing fraction) corresponding to 2,3-dimethylbutane and cyclohexane well coincides with the distributions in Fig. 7.

EQUIDENSE LIQUIDS

Direct confirmation of the fact that distinctions in the molecular forms of 2,3-dimethylbutane and cyclohexane are insignificant for the formation of the structure of a liquid can be given by a comparison of these liquids calculated with the same density. We can produce a model of liquid 2,3-dimethylbutane with the density of cyclohexane (0.773 g/cm^3) by increasing pressure. On the contrary, by decreasing pressure (and raising temperature) we can produce a model of cyclohexane with the density of normal 2,3-dimethylbutane (0.657 g/cm^3). It is difficult to make these experiments with real liquids, but it is possible to perform computer simulation. We have obtained that 2,3-dimethylbutane and cyclohexane have practically almost identical pair correlation functions and T -distributions of Delaunay simplices if their densities are equal.

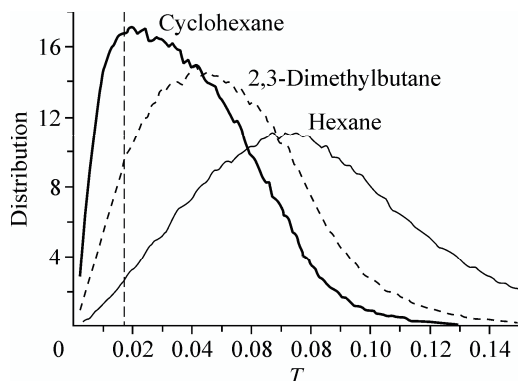


Fig. 6. T -distribution of the Delaunay simplices for molecular liquids (calculated for the mass centers of the molecules). Vertical line $T = 0.018$ separates the simplices belonging to the class of good tetrahedra.

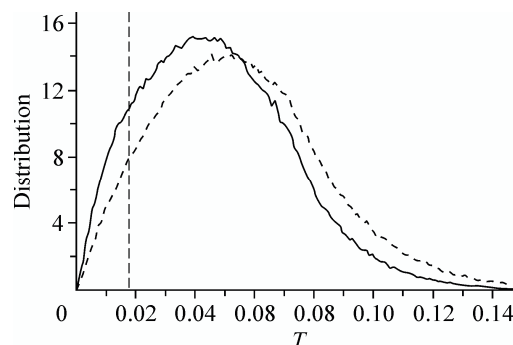


Fig. 7. T -distribution of the Delaunay simplices for Lennard-Jones liquids presented in Fig. 5.

CONCLUSIONS

The molecular dynamics models of liquid hexane, 2,3-dimethylbutane, and cyclohexane are obtained. Different force fields have been used: the all-atom one intended for modeling of organic and biological systems, and the approximation of united atoms, specialized for the description of liquid alkanes. It is noted that both force fields well reproduce the experimental density values of the modeled liquids and radial distribution functions.

It is shown that the radial distribution functions calculated for the mass centers of cyclohexane and 2,3-dimethylbutane molecules are similar to those of simple liquids, i.e. they have a clear first peak and the subsequent oscillations gradually decay with increasing r . The structural distinction between both liquids consists in that the distant maxima are regularly shifted and decay faster in 2,3-dimethylbutane than in cyclohexane. A similar distinction is characteristic of simple liquids with different densities.

The shape of Delaunay simplices calculated for the mass centers of molecules is analyzed. The distribution of simplices by the degree of closeness to the shape of a regular tetrahedron (T -distribution) appears to be the same as for simple liquids with the corresponding density.

By selecting special conditions (pressure and temperature), we have created the models of liquid cyclohexane with the density corresponding to that of normal 2,3-dimethylbutane, and, on the contrary, of 2,3-dimethylbutane with the density of cyclohexane. The structures of the liquids with equal densities are identical. It this means that the distinction in the forms of these molecules does not play a significant role in the formation of the structure of the liquid.

Thus, the cyclohexane and 2,3-dimethylbutane molecules in the liquid phase are located in the space as atoms in simple liquids. The structural distinction between both molecular liquids has the same nature as between the simple liquids with the corresponding density.

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REFERENCES

1. A. A. Petrov, *Chemistry of Alkanes* [in Russian], Nauka, Moscow (1974).
2. M. Iwahashi and Y. Kasahara, *J. Oleo Sci.*, **56**, No. 8, 443-448 (2007).
3. C. N. R. Rao, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **94**, No. 1, 181-199 (1985).
4. H. Farman, L. O'mard, J. C. Dore, and M.-C. Bellissent-Funel, *Mol. Phys.*, **73**, No. 4, 855-871 (1991).
5. H. Farman, J. C. Dore, M.-C. Bellissent-Funel, and D. G. Montague, *Mol. Phys.*, **61**, No. 3, 583-596 (1987).

6. L. Gontrani, F. Ramondo, G. Caracciolo, and R. Caminiti, *J. Mol. Liq.*, **139**, 23-28 (2008).
7. G. Temperli, J. Rowlinson, and J. Rushbrook (eds.), in: *Physics of Simple Liquids*, Mir, Moscow (1971).
8. D. van der Spoel, E. Lindahl, B. Hess, et al., *J. Comp. Chem.*, **26**, 1701-1718 (2005).
9. W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, *J. Am. Chem. Soc.*, **118**, 11225-11236 (1996).
10. D. Schuler, X. Daura, and W. F. van Gunsteren, *J. Comp. Chem.*, **22**, No. 11, 1205-1218 (2001).
11. H. L. Casal, P. W. Yang, and H. H. Mantsch, *Can. J. Chem.*, **64**, 1544-1548 (1986).
12. G. Venturi, F. Formisano, G. J. Cuello, et al., *J. Chem. Phys.*, **131**, 034508 (2009).
13. S. Tsuzuki, L. Schafer, H. Goto, et al., *J. Am. Chem. Soc.*, **113**, 4665-4671 (1991).
14. A. V. Anikeenko, A. V. Kim, and N. N. Medvedev, in: Proceed. "VI Internat. Symposium on Voronoi Diagrams in Science and Engineering," F. Anton (ed.), Technical University of Denmark (2009), pp. 271-277.
15. A. V. Anikeenko, A. V. Kim, and N. N. Medvedev, *Collection of Articles: Structure and Dynamics of Molecular Systems*, Yoshkar-Ola-Ufa-Kazan'-Moscow (2009), pp. 228 -231.
16. A. V. Anikeenko and N. N. Medvedev, *J. Struct. Chem.* (2011), in press.
17. N. N. Medvedev, *Voronoi-Delaunay Method for Non-Crystalline Structures* [in Russian], Siberian Division Russian Academy of Science, Novosibirsk (2000).
18. Yu. I. Naberukhin, V. P. Voloshin, and N. N. Medvedev, *Mol. Phys.*, **73**, No. 4, 917-936 (1991).
19. A. V. Anikeenko and N. N. Medvedev, *J. Struct. Chem.*, **50**, No.4, 761-768 (2009).