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Phases in water octamer: molecular point of view

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Abstract. Results of modeling of phases and phase transition in the water octamer with TIP4P interaction potential from molecular point of view are presented. In the study the molecular dynamics method was applied. The advantage of using the dynamical characteristics of individual molecules in the cluster is shown, particularly, the distribution of the potential energy, to identify the phase of the cluster. The criteria for solid like and liquid like phases in the octamer are suggested and the connection isomer's structures with dynamics are discussed. The role of different types of H-bonds (DDA- and DAA-type) in dynamical characteristics of the cluster is clarified.

Key words: water clusters, structural transformation, isomerization, melting, molecular dynamics simulation, microcanonical ensemble.

INTRODUCTION

The understanding of occurrence of phase transitions in small clusters of water molecules is widely discussed during last few decades as it is important for specialists in numerous fields of chemistry, physics and environmental sciences. Phase transitions in water clusters cannot be recognized by caloric curves behavior alone, as in van der Waals clusters [1]. Those transitions associated with the restructuring of the H-bond network. It raises the question about “the quantum of restructuring” – the minimal water cluster that can undergo phase transition. At present the dominating opinion declares the octamer (H₂O)₈ in this role [2–7]. The existence of an energy gap separating the low-lying minimum or possibly a small number of low-lying minima and a large number of higher-lying minima is a necessary condition for a cluster system to display a well-defined melting transition. From this point of view, the water octamer is suitable object to detect a phase transition. Several computational experiments have predicted that the global energy minimum configuration for the water octamer corresponds, in fact, to two, S₄ and D_{2d}, cubic-like isomers which are practically isoenergetic [8–16]. Other isomers of (H₂O)₈ with non-cubic structure are realized at quite high total energy of the cluster. It gives some possibilities for the researches to separate the phases and to study solid-liquid phase transitions of these aggregates in computer simulations. The water octamer also has another source of interest since it has emerged as a building block for larger clusters of water molecules [3].

Criteria which are used for studying phase changes in water clusters can be grouped into three correlating types: structural, energetic and thermodynamic. The most popular and

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widely used parameter to indicate the structural changes in clusters is the Lindemann index [17]. This parameter measures the fluctuations in length of intermolecular bonds and usually calculated by the molecular dynamics method. The value of Lindemann index close to 0.1 serves as a threshold of phase transformation in clusters [1]. Another criterion uses the structural order parameter such as the ratio between the largest and the smallest moments of inertia of the cluster [12]. Growing values in dipole moment with increase of the temperature also used as a mark of phase changes [18]. It has been found that in general, the dipole moment of the cluster increases significantly as the cluster melts, suggesting that it could be used to distinguish the solidlike and liquidlike phases.

The energetic approach was applied to study phase coexistence in water clusters by analyzing short-time average of the total kinetic energy [3]. The bimodal profile of the histogram of the temporally averaged kinetic energy of octamers serves as the indicator of solid-liquid phase transition.

From thermodynamic point of view, computer simulations have shown that these aggregates undergo solid-liquid phase transitions in a thermal range spanning, roughly, the 150 K–220 K intervals [4, 15, and 18]. The presence of a pronounced peak in the curves of heat capacity versus temperature is also taken as an indicator of a phase change in cluster. At the same time the authors mentioned that isomerization can also give rise to peaks in the heat capacity curves. It can happen when cluster has several solidlike isomers that are energetically accessible, but the transitions between them, if occur, are a sudden transition between solidlike structures. A further increase of temperature is needed to move the cluster in liquid state, where the structural changes happen in a continuously.

Recently a new classification method of phase transitions in finite systems has been suggested [19]. This method is based on calculation of the microcanonical entropy and its energetic derivative. The method is universal, but numerically demanding. Thermodynamic quantity (internal energy and specific heat) as continuous function of temperature was suggested to define phase transition in water clusters [20]. In this paper the correlation between specific heat peaks and bimodal potential energy distribution are taken as a mark of phase transition in the water octamer. Temperature dependence of structural properties and thermodynamic behavior of water clusters have been studied by the Monte Carlo method using Wang–Landau sampling.

It is necessary to stress, that at the moment we do not have experimental evidence of phase changes in water clusters. Existing experimental results restricted by transitions with the participation of protonated water clusters [21].

We suppose that some uncertainty around description of phase transition in water clusters primary related to definition of phase of cluster and absence of complete set of parameters, of which change illustrates phase transitions. Usually solidlike behavior of water clusters is characterized by structural and dynamical features that do not differ substantially from those of polyatomic molecules: fluctuations of interparticle distances much smaller than their average values [12]. Liquidlike regime supposes the presence of intracluster diffusion. While the melting temperature of bulk phases is well-defined, the clusters conversion between solid-liquid structures takes place within the interval of temperatures, as it was noted above.

The present study is focused on the dynamical features of the phases of the water octamer from molecular point of view. In our approach we follow the dynamical characteristics of particular molecule of the cluster in order to get criteria of the phases. The article has Introduction and three parts: the second one describes the method and the models that we apply to extract the dynamical parameters of the system; the third part presents the results which illustrate the phases of the octamer, while the fourth part contains the final discussion of the results.

METHODS AND MODELS

In our study the microcanonical ensemble technique of molecular dynamics simulation is used to investigate the molecular features of octamer phases. The main reason to use this method is the possibility to follow the dynamical properties of cluster when it undergoes isomerization.

It has been already noted that water octamer has two isomers with close global minima particularly D_{2d} and S_4 symmetry structures, which dominate in the solidlike phase. In our study initial isomer of the octamer was taken as the S_4 cube-type.

Initial conditions were generated in a manner similar to applied previously in [22-24]. The changes in structures of water octamer are studied by solving the equations of motion with the following approach. Let the cluster consists of N_a atoms, which are described by the radii vectors $\mathbf{r}_i(t)$, momenta vectors $\mathbf{p}_i(t)$, and masses m_i , where $i = \overline{1, N_a}$, $t \in [0, t_0]$, t_0 is the running time of the trajectory. Then, the Hamiltonian of this system has the form:

$$H(\mathbf{p}_1(t), \dots, \mathbf{p}_{N_a}(t), \mathbf{r}_1(t), \dots, \mathbf{r}_{N_a}(t)) = \sum_{i=1}^{N_a} \frac{\mathbf{p}_i^2(t)}{2m_i} + U(\mathbf{r}_1(t), \dots, \mathbf{r}_{N_a}(t)), \quad (1)$$

where $U(\mathbf{r}_1(t), \dots, \mathbf{r}_{N_a}(t))$ is the potential energy of the interaction of particles in the cluster.

The system of the equations for the Hamiltonian (1) is solved using the difference scheme proposed by Verlet with the RATTLE algorithm to account of holonomic (rigid covalent) constraints [25].

The TIP4P potential is chosen because it has been proven its effectiveness in describing the interaction among water molecules in liquid water in the temperature about the range of melting ice. Since the work of Tsai and Jordan [26] this potential is applied to study the dynamical features of water clusters as it provides realistic description of potential energy surface of the clusters.

In our work we use the following dynamical criterion of hydrogen bond. The bond exists if the distance between oxygen and hydrogen atoms of different molecules does not exceed value: $r_{OH} \leq 2.6 \text{ \AA}$. The angle $\varphi_{O\dots OH}$ formed by the hydrogen atom of one molecule and the covalent OH-pair of other molecule do not exceed predetermined value: $120^\circ \leq \varphi_{O\dots OH} \leq 180^\circ$. The network of H-bonds in the cluster was analyzed using graph theory method [27]. The type of isomer was determined by identifying invariants with respect to the permutation of molecules in the matrix of H-bonds [28]. Cluster was considered broken up if any one of the listed above conditions is violated during the time $t > 5 \text{ ps}$.

The numerical experiment is conducted with the following parameters: a trajectory time length of $t_0 = 500 - 3000 \text{ ps}$, integration step with $\Delta t = 1 \text{ fs}$; conservation of the total energy within $\Delta E_{\text{tot}} = 10^{-3} \text{ eV}$. The threshold of isomerization of the cluster is identified using Lindemann index:

$$\delta(\text{OO}) = \frac{2}{N_m(N_m - 1)} \sum_{i < j}^{N_m} \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle}$$

where r_{ij} is the distance between the i -th and j -th oxygen atoms; N_m is the number of water molecules. As it was noted before it is accepted that cluster undergoes melting if Lindemann index exceeds the threshold value of $\delta(\text{OO}) = 0.1$. Each value of $\delta(\text{OO})$ is obtained after averaging over ten trajectories.

RESULTS AND DISCUSSIONS

In our work cubic structure of octamer (S_4 cube-type) is found to be the most stable and the value of the global potential energy is close to the previous studies of this system. We would like to note that even if the procedure followed in the present paper has provided reasonable structure, there is no guarantee that we have determined the configuration with the lowest energy. Figure 1a shows the structure of water octamer which is studied in present article. As one can see in figure 1a the molecules in the cluster are initially involved in formation of two types of H-bonds: with two donors and one acceptor (DDA) and two acceptors and one donor (DAA) H-bonds.

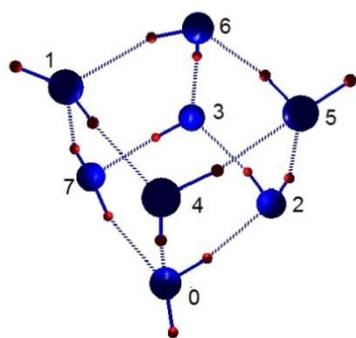


Fig. 1a. Water octamer at S_4 cube-type stable configuration;
N0, N1, N3, N5 molecules (DAA – H-bond);
N2, N4, N6, N7 molecules (DDA – H-bond).

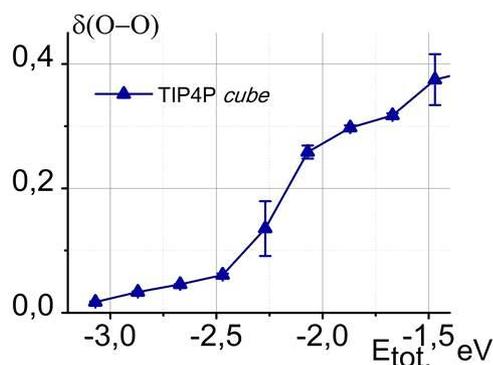


Fig. 1b. Lindemann index $\delta(OO)$ for S_4 cube-type water octamer with TIP4P potential (E_{tot} – total energy of the cluster).

Lindemann index $\delta(OO)$ (calculated to obtain the isomerization threshold is presented in figure 1b). The data presented in figure 1b include the isomers which contributions exceed 5% over the trajectory. The range of the total energy in figure 1b is taken from the global energy level to the threshold of cluster fragmentation. In the present study Lindemann index has been used to calculate the energy interval which belongs to solid or liquid phase of the cluster as it is suggested in the theory of clusters [1]. As it has being mentioned above we assume that cluster is in a solid state if Lindemann index is less than the threshold value of $\delta(OO) < 0.1$. According to the data presented in figure 1b, these criteria correspond to the values of the total energy $E_{tot} \leq -2.4$ eV.

Let us consider the dynamic characteristics of the solid phase of the cluster with $E_{tot} \leq -2.4$ eV and the liquid phase with $E_{tot} > -2.0$ eV. The following dynamic parameters have being calculated: the H-bond distance, the potential energy and H-bond numbers. They are shown in figure 2, figure 3 and figure 4 respectively.

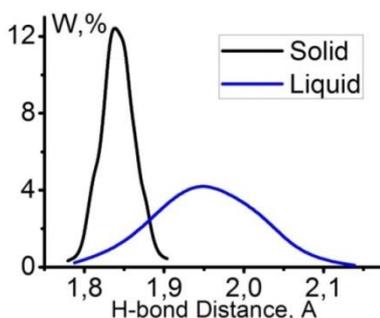


Fig. 2. Normalized H-bond distance distribution W (%). Solid phase ($E_{tot} = -2.86$ eV) (left). Liquid phase ($E_{tot} = -1.66$ eV) (right).

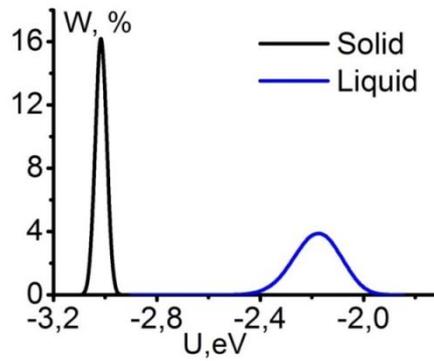


Fig. 3. Normalized cluster' potential energy U distribution W (%). Solid phase ($E_{tot} = -2.86$ eV) (left). Liquid phase ($E_{tot} = -1.66$ eV) (right).

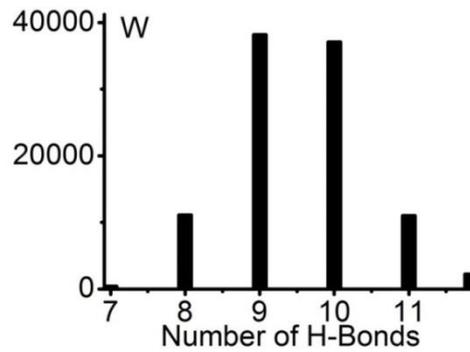


Fig. 4. H-bond numbers distribution (W). Liquid phase ($E_{tot} = -1.66$ eV); in solid phase ($E_{tot} = -2.86$ eV) we have 12 H-bond numbers.

One can see that the distributions of the H-bond distance (figure 2) and the potential energy of the cluster (figure 3) in general differ significantly for the solid and the liquid phases. To compare the results in figure 2 and figure 3 normalized forms are used. The unity of the normalization is the area under the curve of the distribution for solid phase of the clusters. One can see that the distribution of the H-bond distance in the liquid phase of the cluster is wider and shifts to higher values comparing to those in solid state. This result is natural as molecules' mobility in cluster increases with increase of the total energy. The data in figure 4 is consistent with the results in figure 3: decrease in the number of hydrogen bonds in the cluster leads to decrease of the modulus of the potential energy.

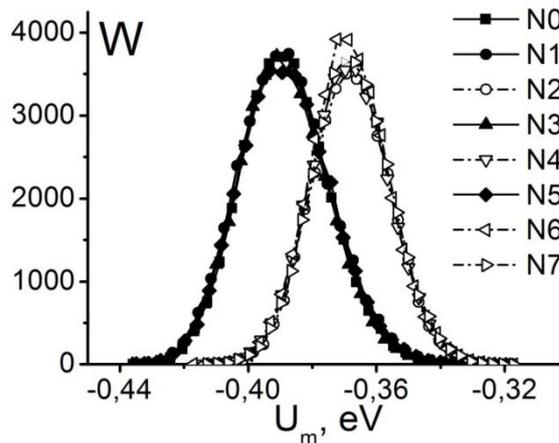


Fig. 5a. Molecule potential energy distribution. Solid phase ($E_{tot} = -2.86$ eV); N0, N1, N3, N5 molecule – DAA – H-bond; N2, N4, N6, N7 molecule – DDA – H-bond.

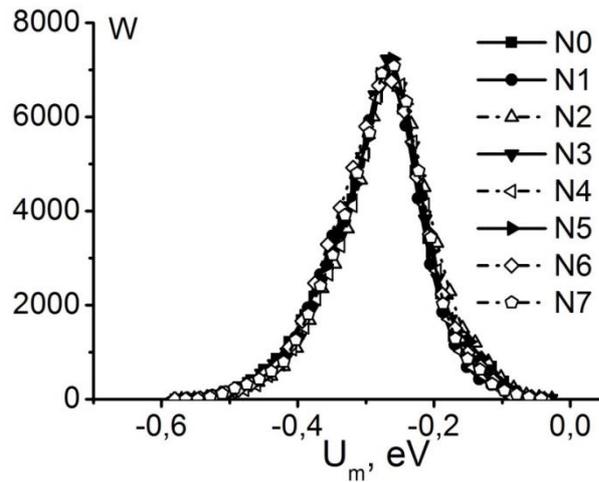


Fig. 5b. Molecule potential energy distribution. Liquid phase ($E_{\text{tot}} = -1.66$ eV).

The cluster phase can be determined by means of the distributions that are given in figure 5, where the potential energy for each molecule of the cluster in solid (figure 5a) and liquid (figure 5b) phases is presented. One can see that the distributions in figure 5a are grouped in two intervals of the potential energy: with bigger and smaller values.

If we compare the index of the molecule in figure 5a and its initial position in the cluster according to figure 1a one can notice that the distributions reflect different ways of formation of hydrogen bonds (DAA- and DDA-type). It means that the molecules in the solid phase move near equilibrium positions and have individual potential energy distribution according to the type of hydrogen bond. In the liquid phase of the cluster the molecules are equivalent in the dynamic characteristics, thereby they are dynamically indistinguishable (see figure 5b).

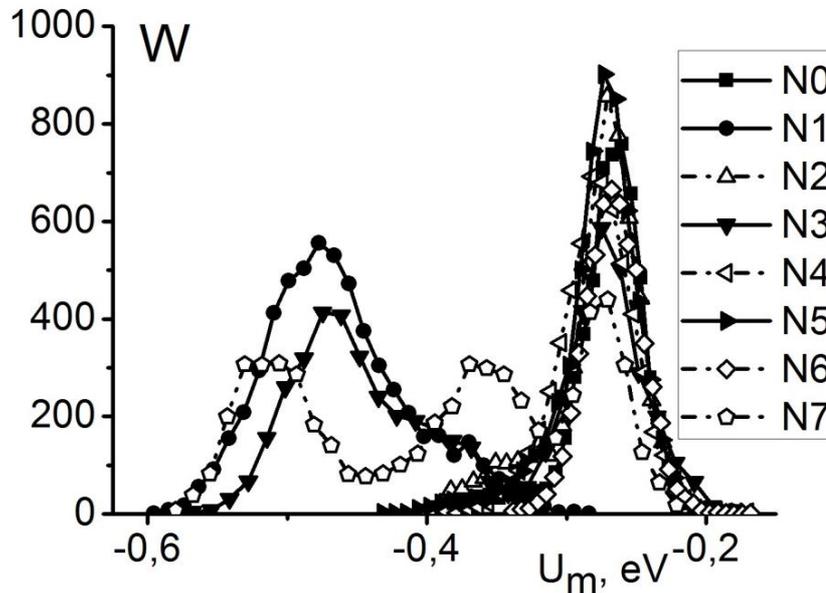


Fig. 6. Molecule potential energy distribution in intermediate energy interval ($E_{\text{tot}} = -2.26$ eV); time of the trajectory is 600 ps.

The question remains about dynamical characteristics of the cluster in the interval of energies between solid and liquid phases. To figure out the issue we present the potential energy distribution of each molecule in this energy interval (figure 6). One can see a few pronounced peaks in the distributions. Molecular dynamics visualization of H-bond net motion is allowed us reveal correlation between positions of the peaks in the distribution and the numbers of hydrogen bonds of each molecule. The peak with biggest value of potential

energy (around $U_m = -0.6$ eV) starts to grow when the molecule forms the maximal numbers of H-bonds (namely four H-bonds), but this is a very rare and a short-term event. The peak with the smallest value of the energy (around $U_m = -0.2$ eV) appears in the case of two H-bonds per molecule. It has been found that peaks in the distributions depend on the time of observation.

CONCLUSIONS

In this paper we have tried to answer the questions related to the dynamical characteristics of phases, structural changes and melting of water octamers. The main results of the work can be summarized as following. Water octamer constitutes stable (S_4 -cube-type) structure at a wide range of the total energy.

Concerning distributions of dynamical variables of octamer in general we can say that solid phase has 12 numbers of H-bonds and sharp peaks in the distributions of the potential energy and the H-bond distance. The results confirm that the dynamics of the cluster is carried out in the same potential well. Liquid phase of the cluster in common demonstrates expected dynamical characteristics. Distributions of the potential energy and the H-bond distance shifted to smaller value of the energy and bigger H-bond distance. It means that the cluster accesses to quite wide area of the potential energy surface and the number of H-bonds reduces.

The dynamical characteristics of molecules in the cluster in solid and liquid phases have principal differences that can be used as criteria of the phases in cluster. From molecule level a solid phase of the cluster can be characterized by specific distribution of potential energy, which reflects the molecule position in H-bond net. It is shown that the peaks in the molecular potential energy distribution are related to the type of H-bond (DAA- or DDA-type). In the liquid phase molecules show another dynamical behavior. All molecules in the liquid phase get identical potential energy distributions, what makes them indistinguishable. In case of intermediate energy values between solid and liquid phases the distributions of the molecule potential energy demonstrate multiple peaks behavior. Positions of the peaks depend upon the numbers of H-bonds of the molecule and on the time of observation.

Finally, concerning the phase changes in small water clusters we would like to underline that we have physically clear understanding of dynamics in extreme cases (namely in the solid and the liquid phase) and therefore we have clear criteria of the phases. Inevitable difficulties appear when we discuss the intermediate state of the cluster. First of all it is so because we deal with a finite system. It is not reasonable to search for the particular temperature or energy at which cluster undergoes phase change. Preliminary calculations on TIP4P water hexamer show that on molecule level hexamer demonstrates similar to octamer dynamics in solid, liquid phases and even in the intermediate region (the results now are in preparation for publication). Although the data on the dynamics of $(H_2O)_8$ contrast with the properties of $(H_2O)_6$ cluster where three distinct configurations with close energies are seen in solid phase of the cluster [29]. Therefore, multimodal distribution of temporal kinetic or potential energy per molecule, studied in [3] and [20] isn't a reliable proof of phase transition in the clusters. We can follow the scenario how the transformation occurs from molecule level, but still we have no reason for classifying the transformation as the phase transition.

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