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DIMERIZATION OF WATER MOLECULES. MODELING OF THE ATTRACTIVE PART OF THE INTERPARTICLE POTENTIAL IN THE MULTIPOLE APPROXIMATION

The work presents the detailed analysis of the water dimer properties. Their parameters are investigated on the basis of a multipole interaction potential extended up to the quadrupole–quadrupole and dipole–octupole terms. All main equilibrium parameters of the dimer are obtained: its geometry, ground-state energy, dipole and quadrupole moments, vibration frequencies, etc. They are thoroughly compared with those obtained in quantum chemical calculations and from spectroscopic data. The efficiency of the present model potentials is discussed. A new viewpoint on the nature of the hydrogen bond is presented. The results of studies are thoroughly compared with the spectroscopic and computer simulation data.

K e y w o r d s: water dimer, multipole interaction potential, dipole moment, quadrupole moment, hydrogen bond

1. Introduction

The main object of our research is the water dimer properties, which parameters are very sensitive to the type of intermolecular interaction. A water dimer is a closed system of two water molecules connected with the hydrogen bond. The equilibrium dimer configuration that corresponds to the minimum of the interaction energy is presented in Fig. 1. We will briefly discuss the main dimer parameters presented in Table 1 according to the quantum chemical calculations and experimental data. In [1], two types of dimers are studied: a "frozen" dimer, which has the distance between oxygen and hydrogen and the angle between O–H bonds fixed, and a "relaxed" dimer, where changes of the O–H length and the angle between bonds are allowed. In [2], a "frozen" dimer configuration was used to determine the H-bond energy and the dipole moment of a dimer (the intermolecular distance $r_{\rm OO}^{(0)}$ and the angle θ_0 were postulated). From the comparison of the quantum chemical results and the experimental ones, it follows that the optimum value of the ground-state energy of a water dimer is $\Phi_d \approx -(9 \div 10)k_{\rm B}T_m$, where $T_m = 273$ K is the melting temperature of ice, and is observed at $r_{\rm OO}^{(0)} = 2.98$ Å. The values of angle θ_0 and dimer dipole

moment D_d should be $\theta_0 = 50°$ and $D_d \approx 2.8\,$D, respectively.

This brief review of the dimer properties shows that, nowadays, there is no consistent approach to the problem of formation of dimers, as well as to the calculation of their equilibrium parameters. The biggest difficulty is related to the absence of a clear approach to the magnitude of characteristic contributions to the interaction energy.

In the present work, the water dimer properties are studied on the basis of a strictly defined potential that consists of: 1) literature-based dispersive and repulsive interaction and 2) multipole electrostatic interaction that is extrapolated to the overlapping region. Under the sufficient proximity of water molecules that leads to the overlap of the electron shells, it is necessary to use the quantum chemical calculations to determine the interaction energy. It was shown in [3] that the energy of a hydrogen bond itself does not exceed $\sim k_{\rm B}T_m$. The last circumstance is in agreement with the fact that the intramolecular distances in a water molecule change not more than by $(1 \div 3)\%$ [4, 5]. This means that we can neglect the contributions of hydrogen bonds to the interaction energy of two water molecules. For the first time, this fact had been understood in the works of Berendsen [6] and Barnes [7]. A critical review of the modern potentials, in which the existence of hydrogen bonds is ignored, is presented in [2]. In the same work, the

Table 1. **Characteristics of the equilibrium state of a water dimer according to different approaches**

	Specification	$r_{\mathrm{OO}}^{(0)}$, Å	θ_0, deg	E_d	D_d, D
[1]	Frozen dimer	2.954	19.3	−9.94	
	Relaxed dimer	2.896	20.5	−12.78	
[2]	6-31G	2.98	60	−10.69	2.2
	STO-3G	2.98	60	−9.39	1.72
	4-31G	2.98	60	−14.18	2.60
[9]		2.925	51.8	−9.11	
[10]				−10.32	
[11]	HF G-311G	2.814		−15.06	4.37
	HF G-311G++G(dp)	3.001		−8.85	3.45
	HF G-311G++G(3df, 3pd)	3.026		−7.37	2.88
	MP2 G-311G	2.797		−16.82	4.24
	MP2 G-311G++G(dp)	2.914		−11.21	3.30
	MP2 G-311G++G(3df, 3pd)	2.904		−9.79	2.68
	BLYP G-311G++G(dp)	2.927		−10.03	3.09
	BLYP G-311G++G(3df, 3pd)	2.944		−8.22	2.54
[12]					2.6
[13]		2.94			2.15
[4]	Exper.	2.976±0.004	57±10		
[5]	Exper.			−9.96±0.4	
[14]	Exper.				2.60

generalized Stillinger–David potential that eliminates its weaknesses and retains its positive features is presented. Let us mention the attempt in [8] to model the hydrogen bonds, but no results that deserve a significant attention are obtained. Specifically, the following aspects are studied in the present work: 1) the ground-state energy of a water dimer along with its dipole moment as functions of the intermolecular distance and the angles that define a relative orientation of molecules; 2) the influence of dimer's rotation on its ground-state energy and 3) vibration states of a water dimer. The possibility to use the electrostatic multipole potential for the description of attraction between water molecules in liquid water and the relations between the results obtained, computer simulations, and experimental data are discussed.

2. Structure of the Interparticle Interaction Potential Between Water Molecules

The interparticle interaction potential is modeled with the expression

$$\Phi(r,\Omega) = \Phi_r(r,\Omega) + \Phi_D(r,\Omega) + \Phi_M(r,\Omega) + \Phi_{\mathrm{H}}(r,\Omega), \quad (1)$$

where $\Phi_r(r,\Omega)$ is the repulsive term, $\Phi_D(r,\Omega)$ describes the dispersive forces, $\Phi_M(r,\Omega)$ is a part of

the multipole expansion of the interaction energy between two water molecules, and $\Phi_{\mathrm{H}}(r,\Omega)$ is the irreducible contribution caused by the overlap of the electron shells of the water molecules (Ω is the set of angles that describe the orientation of water molecules). The reference to the multipole expansion for the interparticle interaction is supported by the following facts: 1) quantum chemical calculation of the multipole moments is a well-posed problem; 2) comparison of the different multipole contributions allows us to control the applicability of the multipole approximation for the electrostatic interaction. Due to the wide discussion of the parameters of dimers [4, 5, 9–13, 15–17], the last fact becomes stronger.

In the present work, the multipole contributions to the interparticle potential are considered up to the three-moment terms, i.e. up to the octupole-octupole effects:

$$\Phi_M(r) = \sum_{1 \le n,m \le 3} \frac{(-1)^n}{n!m!}(\hat{Q}_1^{(n)}\hat{Q}_2^{(m)}) : \hat{D}^{(n+m)}\frac{1}{r}. \quad (2)$$

Here, $\hat{Q}^{(k)}$ is the k-th multipole moment, whose components are defined as $\hat{Q}^{(k)} \Rightarrow \Rightarrow \sum_{1 \le i \le N} q_i x_{\alpha_1}^{(i)} x_{\alpha_2}^{(i)} ... x_{\alpha_k}^{(i)}$, $\hat{D}^{(k)} \Rightarrow \frac{\partial^k}{\partial x_{\alpha_1} \partial x_{\alpha_2} ... \partial x_{\alpha_k}}$ is the differential operator and (:) stands for the
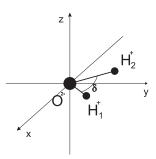
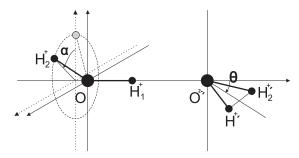**Fig. 1.** Molecular coordinate system

Fig. 2. Angles that define the orientation of molecules in LCS

sum over the indexes. The symbol $(\hat{Q}_1^{(n)}\hat{Q}_2^{(m)})$ is used to determine the Kronecker product of the matrices that correspond to the multipole moments, and r is the distance between oxygens. After all the necessary differentiations, we substitute: $r \Rightarrow \mathbf{r}_{\mathrm{OO}}$ and $x_\alpha \Rightarrow r_{\mathrm{OO}}\delta_{2\alpha}$, which corresponds to a selected dimer configuration. Multipole contributions include terms up to the dipole-octupole ones:

$$\Phi_M(r) = \Phi_{DD} + \Phi_{DQ} + \Phi_{QQ} + \Phi_{\mathrm{DO}} + ..., \qquad (3)$$

Table 2. **Components of the quadrupole moment of a water molecule in MCS**

	$Q_{XX}^{(0)}$, D Å	$Q_{YY}^{(0)}$, D Å	$Q_{ZZ}^{(0)}$, D Å
[1]	2.57	0.37	−2.94
[3]	2.34	0.43	−1.17
[13]	-0.09	−1.67	1.75
[18]	−0.07	−1.61	1.69
[23]	−0.19	−1.58	1.77
[24]	−0.07	−1.61	1.69
[25]	−0.55	−0.84	1.39
[26]	−0.07	−1.74	1.81

which take the form

$$\Phi_{DD} = \frac{1}{r_{\mathrm{OO}}^3}(\mathbf{d}^{(1)}\mathbf{d}^{(2)} - 3\mathbf{d}_2^{(1)}\mathbf{d}_2^{(2)}),$$

$$\Phi_{DQ} = -\frac{1}{2r_{\mathrm{OO}}^4}(6(d_\alpha^{(1)}Q_{2\alpha}^{(2)} + d_\alpha^{(2)}Q_{2\alpha}^{(1)}) -$$

$$- 15(d_2^{(1)}Q_{22}^{(2)} + d_2^{(1)}Q_{22}^{(2)})),$$

$$\Phi_{QQ} = \frac{3}{4r_{\mathrm{OO}}^5}(35Q_{22}^{(1)}Q_{22}^{(2)} - 20Q_{2\delta}^{(1)}Q_{2\delta}^{(2)} + 2Q_{\delta\gamma}^{(1)}Q_{\delta\gamma}^{(2)}),$$

$$\Phi_{\mathrm{DO}} = -\frac{3}{2r_{\mathrm{OO}}^5}(d_\alpha^{(1)}O_{\alpha\beta\beta}^{(2)} + d_\alpha^{(2)}O_{\alpha\beta\beta}^{(1)} +$$

$$+ 15(d_2^{(1)}O_{222}^{(2)} + d_2^{(2)}O_{222}^{(1)}) - 5(d_2^{(1)}O_{2\alpha\alpha}^{(2)} + d_2^{(1)}O_{2\alpha\alpha}^{(1)}) +$$

$$+ d_\alpha^{(1)}O_{\alpha22}^{(2)} + d_\alpha^{(2)}O_{\alpha22}^{(1)}).$$

The components of the dipole moment of a water molecule in the laboratory coordinate system (LCS) are given by the relations

$$\mathbf{d}^{(1)} = d(0, \cos(\delta/2 + \chi), \sin(\delta/2 + \chi)),$$

$$\mathbf{d}^{(2)} = d(0, \cos\theta, -\sin\theta),$$

where d is the absolute value of dipole moment of a water molecule, δ is the angle in the molecular coordinate system (MCS) that defines the positions of hydrogens. It is stated that the water molecule is oriented in MCS as in Fig. 2.

The values of components of the quadrupole and octupole moments, calculated in computer experiments or obtained experimentally are presented in Tables 2 and 3. The orders of magnitude for the multipole moments are:

$$d \sim 1\ \mathrm{D}, \quad Q \sim 10^{-8}\ \mathrm{D\cdot cm} \quad \text{and} \quad O \sim 10^{-16}\ \mathrm{D\cdot cm}^2.$$

Here, D equals 1 Debye – unit of dipole moments. In our opinion, the optimal values of components of the quadrupole moment of a water molecule are obtained in the computer experiment [13]. These values are in good accordance with the experimental data [18]. But the components of the quadrupole moment that correspond to the charge distribution in model potentials [1, 19–22] differ even by the sign (see Table 2). The same situation is also characteristic of the

octupole moments (see Table 3). The mutual coherence of different works is only observed in the values of dipole moment. This fact gives us the ground to conclude that most of the model potentials are unable to reproduce fine details of the intermolecular interaction. The transition between MCS and LCS is standard:

$$\mathbf{d}(\Omega) = R_\Omega \mathbf{d},$$

$$Q_{\alpha\beta}(\Omega) = R_\Omega Q_{\alpha\beta} R_\Omega^T,$$

$$O_{Y\alpha\beta}(\Omega) = R_\Omega O_{Y\alpha\beta} R_\Omega^T,$$

where R_Ω indicates the rotation matrix by the angle Ω: $\Omega = \alpha, \theta, \phi$ (α, θ, ϕ are the angles of rotation around the LCS axes, as given in Fig. 3)

For example, the rotation around the Oy axis is given by the direct and transposed matrices:

$$R_\alpha = \begin{pmatrix} \cos\alpha & 0 & \sin\alpha \\ 0 & 1 & 0 \\ -\sin\alpha & 0 & \cos\alpha \end{pmatrix}, \quad R_\alpha^T = \begin{pmatrix} \cos\alpha & 0 & -\sin\alpha \\ 0 & 1 & 0 \\ \sin\alpha & 0 & \cos\alpha \end{pmatrix}.$$

We note that the components of the quadrupole moment of a water molecule in [5, 15–20] were calculated with the use of the formula $\tilde{Q}_{\alpha\beta}^{(0)} = \frac{1}{2}\sum_i(3x_\alpha^{(1)}x_\beta^{(i)} - \mathbf{r}_i^2\delta_{\alpha\beta})$ that differs from our one by the multiplier $3/2$.

According to the selection of LCS (see Fig. 1), we can use only $O_{Y\alpha\beta}$ components of the octupole moment. By the same reason, as we use traceless quadrupole moments, we will use traceless octupole moments:

$$O_{Y\alpha\beta}^{(0)} = O_{Y\alpha\beta} - \frac{1}{3}O_Y\delta_{\alpha\beta},$$

where $O_Y = \sum_{\alpha=1}^{3} O_{Y\alpha\alpha}$ is the trace of the matrix $O_{Y\alpha\beta}$. From our point of view, the most convenient values of $O_{Y\alpha\beta}$ are obtained in [13] and [18], where the values of components of the octupole moments are almost the same.

The relative values of the multipole contributions of different orders to the interparticle potential are presented in Fig. 4. Here and below, we use the the dimensionless values for interaction energy $\Phi(r, \Omega) \rightarrow \tilde{\Phi}(r, \Omega)/k_B T_m$, where T_m is the crystallization temperature for liquid water. The curves in Fig. 4 correspond to the fixed value of angle χ, which is
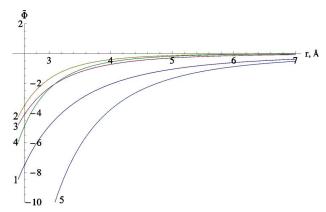

Fig. 3. Role of the corresponding contributions to the interparticle potential: *1* – dipole-dipole interaction, *2* – dipole-quadrupole, *3* – quadrupole-quadrupole, *4* – dipole-octupole, *5* – total multipole interaction
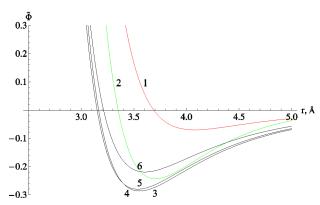

Fig. 4. The behavior of the sum of repulsive and dispersive terms for the Buckingham (*1*), Buckingham–Corner (*2*), SPC (*3*), SPC/E (*4*), TIPS (*5*), and TIP3P (*6*) potentials

supposed to equal $0.7°$ and does not depend on the distance between water molecules. The angle θ is a function of the intermolecular distance and was obtained from the minimum of the interaction energy at each value of r_{OO}. The total value of multipole contribution is shown by curve *5*. As we see, at a dis-

Table 3. **Components of the octupole moment of a water molecule**

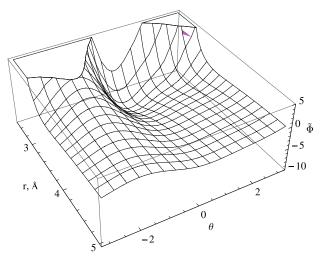|	$O_{YXX}^{(0)}$, D Å^2	$O_{YYY}^{(0)}$, D Å^2	$O_{YXX}^{(0)}$, D Å^2
[1]	1.91	0.30	–2.22
[13]	–1.29	–1.73	3.03
[18]	–1.33	–1.82	3.16

Fig. 5. Profile of the potential surface $\tilde{\Phi} = \Phi/k_\mathrm{B} T_m$ of the interaction of two water molecules (T_m is the temperature of melting for ice)

tance of 3 Å that is supposed to be the equilibrium for a water dimer, the depth of the total multipole interaction reaches -15.

We should consider the behavior of the Φ_DO term that describes the dipole-octupole interaction. From Fig. 4, it follows that the curves of Φ_DO and Φ_{QQ} cross at $r \sim r_*$, where $r_* \approx 3.2$ Å. This fact indicates the breaking of the multipole expansion. At the smaller distances, the electron shells begin to overlap, so it is the natural border for the usage of model electrostatic potentials.

3. Repulsive and Dispersive Interaction between Water Molecules

We will use the Buckingham–Corner [28], three-point SPC [19, 20], and TIPS [21, 22] potentials to describe the repulsion and dispersive effects between water molecules. In the Buckingham–Corner potential, the effects of repulsion and dispersive forces are described with the sum of pair contributions of the hydrogen–hydrogen, hydrogen–oxygen, and oxygen–oxygen types:

$$\tilde{\Phi}(r) = \tilde{B} e^{-\tilde{p}\left(\frac{r}{r_m}\right)} - \left(\frac{\tilde{A}_6}{r^6} + \frac{\tilde{A}_8}{r^8}\right) e^{-4\left(\frac{r}{r_m}-1\right)^3}, \quad (4)$$

where $\tilde{B} = (-\epsilon + (1+\beta)\frac{\tilde{A}_6}{r_m^6}) e^{-\tilde{p}}$, $\tilde{A}_6 = \frac{\tilde{\epsilon}\tilde{p} r_m^6}{\tilde{p}(1+\beta) - 8\beta - 6}$, $\tilde{A}_8 = \beta r_m^2 \tilde{A}_6$, $\beta = \frac{\tilde{A}_8 r_m^{-8}}{\tilde{A}_6 r_m^{-6}}$, ϵ is the potential well

depth, and r_m is the intermolecular distance at the minima of energy.

In the SPC and TIPS potentials, the dispersive and repulsive interactions inhere only in the electron shells of the oxygen atoms and are determined in the form similar to the Lennard-Jones potential:

$$\Phi_r^{(\mathrm{SPC})} = \frac{\tilde{B}_\mathrm{OO}}{r_\mathrm{OO}^{12}}, \quad \Phi_d^{(\mathrm{SPC})} = -\frac{\tilde{A}_\mathrm{OO}}{r_\mathrm{OO}^6}. \quad (5)$$

The comparative behavior of the repulsive and dispersive contributions to the Buckingham, Buckingham–Corner, SPC, TIPS, and TIP3P potentials is presented in Fig. 4.

As we can see, the minimum of the interaction energy is around $0.2 \div 0.3$, and its position is approximately at $(3.5 \div 3.6)$ Å. Curve *1* that corresponds to the Buckingham potential differs very much from the latter potentials. Of course, the simple comparison of the dispersive and repulsive curves is not enough to select the appropriate potential.

4. Ground State of a Dimer

In this section, we will present the results of studies of the ground state of a water dimer, based on potential (1), where we will ignore the contribution of the short-range H-bond potential. We will consider the positions of the oxygens and hydrogens in water molecule remain still for the ease of calculations. According to [16], such requirement leads to the error not more than $(1.5 \div 3)\%$. The ground state of a water dimer is identified with the minimum of the interaction energy of two water molecules oriented, as it is shown in Fig. 1. More specifically, the equilibrium distance $r_\mathrm{OO}^{(0)}$ between the oxygens and the angle θ_0 between the directions of unexcited dipole moments are found from the condition

$$r_\mathrm{OO}^{(0)}, \theta_0 \quad \leftrightarrow \quad \text{absolute min} \quad \Phi(\tilde{r}, \theta, \alpha = 0),$$

where Φ is the intermolecular interaction potential. It is considered to be a function of the dimensionless distance $\tilde{r} = r_\mathrm{OO}/r_\mathrm{OH}$, $r_\mathrm{OH} = 0.97$ Å is the length of the O–H bond, and the angle α describes the rotation around the H-bond (see Fig. 2).

The general view of the potential surface $\Phi(\tilde{r}, \theta)$ is presented in Fig. 5.

On the set of points of minimum for $\Phi(\tilde{r}, \theta)$, the angle θ_m is a function of $\tilde{r}$. Its dependence is presented in Fig. 6.

The radial dependence of the interaction energy at the angle θ_m corresponding to the absolute minimum is presented in Fig. 7.

It follows from Figs. 5–7 that the parameters presented in Table 4 correspond to the absolute minimum of the interaction energy.

One can see that the equilibrium parameters of a dimer are very sensitive to the selection of the form of repulsive and dispersive interactions. More precisely, these parameters depend on the law of decrease of the repulsive interaction. The depth of the potential well becomes bigger when the maximum of repulsion moves to the left (see Fig. 4). The position of the repulsive branch of the potential is a key factor that defines the equilibrium parameters of a water dimer. The value of the dipole moment of a water dimer is given by the formula

$$D_d = 2d_w \cos \frac{1}{2}(\theta_0 + (\delta/2 - \chi)). \tag{6}$$

The values given should be compared to the equilibrium values obtained from the computer simulations and experiments (see Table 1). As follows from Table 1, the intermolecular distance deviates from the literature data. Another important dependence is the dependence on the angle α of rotation around the H-bond (see Fig. 9). The variable α is an intradimer characteristic, so it is responsive for the rotation of molecules inside the dimer.

Another important characteristic of a dimer, which should be compared with other results [11, 12, 17], is the dependence on the angle θ corresponding to the transversal vibrations of H-bonds (see Chapter 4). It is presented in Fig. 8. We see that, in the region of the minimum, the dependence of the interaction potential has a slope. As a consequence, in different models of water, the deviations of the equilibrium value of θ can be huge. Moreover, the heat vibrations of the H-bond can influence the experimental values of the angle θ.

It is necessary to mention that the most convenient dimer parameters to compare are: 1) the value of its dipole moment; 2) the values of components of the quadrupole moment and it average value, which is defined as $\bar{Q} = \frac{1}{3}(Q_{XX} + Q_{YY} + Q_{ZZ})$ (here, we use the components of the non-traceless quadrupole moment), and 3) the vibration frequencies of water dimer. According to (6), the experimental value of the dimer dipole moment allows us to control the
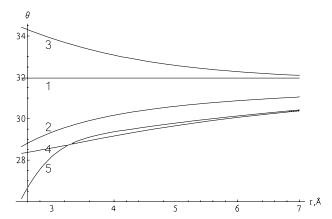

Fig. 6. Radial dependence of the angle θ_m (*5*). Angles α, β, and χ remain fixed and correspond to the absolute minimum configuration. Curves $1 - 4$ describe the dependence of θ_m in *DD*, *DQ*, *QQ*, and *DO* approximations, respectively
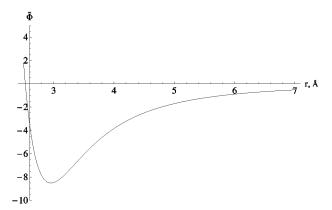

Fig. 7. Dependence of the interaction energy on the intermolecular distance in a dimer configuration

Table 4. **Equilibrium parameters of a water dimer for different interaction potentials**

	$r_{\rm OO}$	$E_d, k_{\rm B}T_m$	θ	χ	D_d, D
B	2.96	−8.5	28.03	0.75	2.8435
BC	2.89	−9.65	28.70	0	2.8148
SPC	2.72	−12.49	27.69	1.03	2.8143
SPC/E	2.72	−12.49	27.69	1.03	2.8143
TIPS	2.7	−12.66	27.61	1.14	2.8137
TIP3P	2.69	−12.90	27.60	1.16	2.8136

equilibrium values of the angle θ. The components of the quadrupole moment of a water dimer are connected with the components of the quadrupole mo-
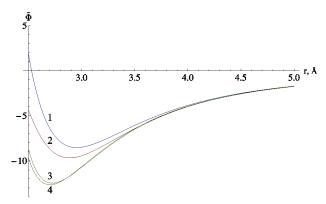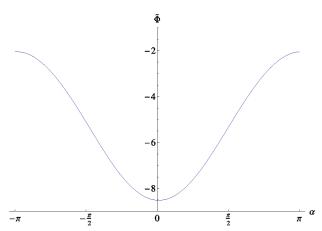
Fig. 8. Comparative behavior of the interaction potentials. (1) – B, (2) – BC, (3) – SPC, (4) – TIPS

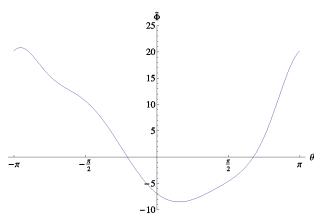**Fig. 9.** Dependence of the dimer energy on the angle of relative rotation around the H-bond

Fig. 10. Dependence of the interaction energy on the angle θ at $r_{\text{OO}} = 2.9757$ Å
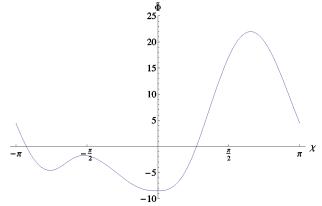

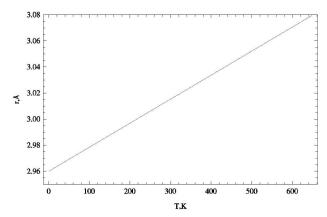**Fig. 11.** Dependence of the interaction energy on the angle χ

Fig. 12. Temperature dependence of the equilibrium distance between oxygen atoms in a water dimer
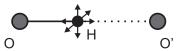

Fig. 13. Vibration modes of an H-bond

ment of an isolated water molecule by the relation

$$Q_{\alpha\beta}^{(d)} = Q_{\alpha\beta}^{(1)} + Q_{\alpha\beta}^{(2)} + \frac{1}{2}(R_\alpha(\mathbf{d}_2^{(w)} - \mathbf{d}_1^{(w)})_\beta +$$

$$+ R_\beta(\mathbf{d}_2^{(w)} - \mathbf{d}_1^{(w)})_\alpha), \tag{7}$$

where $R = r_{\text{OO}}^{(0)}$. The average value of quadrupole moment is

$$\bar{Q}_d = \bar{Q}_1 + \bar{Q}_2 + \frac{1}{3}d_w r_{\text{OO}}^{(0)}(\cos\theta - \cos\delta/2). \tag{8}$$

It is worth to mention that the components of the dipole and quadrupole moments can be easily calculated with the help of the methods of quantum

Table 5. **Frequencies of small oscillations**

	B		BC		SPC	TIPS
	"Frozen dimer"	Rotating dimer	"Frozen dimer"	Rotating dimer		
ω_1, cm^{-1}	175.12	166.23	182.51	164.20	63.14	68.91
ω_2, cm^{-1}	196.82	194.44	198.14	194.43	244.63	212.63
ω_3, cm^{-1}	391.83	385.63	400.87	386.73	246.00	247.64
ω_4, cm^{-1}	521.64	513.29	529.97	511.42	307.93	313.00

chemistry. Another surprising fact is the possibility of the existence of metastable states of water dimers. With the fixed angle θ that corresponds to a minimum, there is a possibility of the turn of another water molecule on a specific angle, that can be calculated studying the dependence of the interaction energy on angle χ.

As follows from Fig. 11, there are two local minima separated by the potential barrier. The depth of the second minimum is approximately $5k_{\mathrm{B}}T_m$, and its position corresponds to the reflection of a molecule relative to the xy plane.

5. Rotation of a Dimer

If a dimer is formed in the gas phase, its thermal motion consists of the translational, rotational, and vibration modes. It is clear that only rotations and vibrations influence the equilibrium parameters of a dimer. Let us mention that the experimental values of intermolecular distance [4, 5, 14] correspond to the rotating dimers. This circumstance is ignored in the computer experiments. In this section, we will consider only the rotational influence on the parameters of a dimer. The rotation of a dimer is followed by the emergence of centrifugal forces, which lead to the growth of the equilibrium distance between oxygens. Rotation takes place around two axes that are perpendicular to the OX axis. Both axes lie in the molecular planes. The growth of the distance between oxygens is determined by the equation

$$k(r - r_0) = m_0(\omega_1^2 + \omega_2^2)r, \qquad (9)$$

where the average frequencies of rotation can be estimated from the relations

$$\omega_1^2 = \frac{k_{\mathrm{B}}T}{I_1}, \quad \omega_2^2 = \frac{k_{\mathrm{B}}T}{I_2}.$$

The inertia moments I_1 and I_2 are equal to: $I_1 = 1.332 \times 10^{-33}$ g $\cdot$ cm^2, $I_2 = 1.219 \times 10^{-33}$ g $\cdot$ cm^2. The values of force constant k are calculated in the next chapter. But, regardless the calculations, the equilibrium distance grows linearly with the temperature. The rise of the equilibrium distance between oxygens is presented in Fig. 12.

As we can see, the distance between oxygens at the melting temperature increases approximately by 0.04 Å: from 2.96 Å to 3.00 Å. The ground-state energy decreases by 0.04. In a vicinity of the critical point, the equilibrium distance reaches 3.06 Å.

6. Small Oscillations of a Dimer

From the configuration of a dimer, it follows that the most characteristic types of small oscillations are: 1) longitudinal one connected with a change of the r_{OO} distance between the oxygens: $\tilde{r} = \frac{r_{\mathrm{OO}} - r_{\mathrm{OO}}^{(0)}}{r_{\mathrm{OH}}}$; 2) two transversal oscillations of the H-bond that are connected with small rotations around the x (by angle θ) and z (by angle ϕ) axes and 3) intradimer oscillations connected with a change of the relative orientation of water molecules during the rotation around H-bonds. Here, it is necessary to mention that the variables $\tilde{r}$ and θ are not independent and form a new pair of normal (hybrid) coordinates. Longitudinal and two transversal vibrations can also be interpreted as the oscillations of the H-bond (Fig. 13). We have to remember that dimers rotate; therefore, the spectra of small oscillations will change.

According to this, the Lagrange function for small oscillations of the dimer takes the form

$$L = \frac{1}{2} \sum_{1 \le i,j \le 4} m_{i,j} \dot{x}_i \dot{x}_j - \frac{1}{2} \sum_{1 \le i,j \le 4} K_{i,j} x_i x_j, \qquad (10)$$

where $x_i = (\tilde{r}, \theta, \phi, \alpha)$ are the generalized coordinates, and $\dot{x}_i = (\dot{\tilde{r}}, \dot{\theta}, \dot{\phi}, \dot{\alpha})$ are the generalized ve-

locities. It is easy to see that the mass tensor has a diagonal structure:

$$m_{11} = I_r, \quad m_{22} = I_\theta, \quad m_{33} = I_\phi, \quad m_{44} = I_\alpha,$$

where $I_r = \mu r_{\mathrm{OH}}^2$, $\mu = 1/2m_W$ is the reduced mass of a water molecule, $\tilde{I} = \frac{I_i^{(1)} I_i^{(2)}}{I_i^{(1)} + I_i^{(2)}}$ are the components of the reduced inertia moments, $i = \theta, \alpha$, and the superscripts number water molecules. In accordance with Fig. 1, the components of the inertia moment are:

$$I_\theta^{(1)} = 2m_{\mathrm{H}} r_{\mathrm{OH}}^2;$$

$$I_\theta^{(2)} = 2m_{\mathrm{H}} r_{\mathrm{OH}}^2 \cos^2 \delta/2;$$

$$I_\alpha^{(1)} = m_{\mathrm{H}} r_{\mathrm{OH}}^2 (1 + \cos^2 \delta);$$

$$I_\alpha^{(2)} = 2m_{\mathrm{H}} r_{\mathrm{OH}}^2 (1 - \cos^2 \delta/2 \cos^2 \theta)$$

and are equal to

$$I_r \approx 14.14 \times 10^{-46} \ \mathrm{g \cdot cm},$$

$$\tilde{I}_\theta \approx 0.83 \times 10^{-46} \ \mathrm{g \cdot cm},$$

$$\tilde{I}_\phi \approx 0.61 \times 10^{-46} \ \mathrm{g \cdot cm},$$

$$\tilde{I}_\alpha \approx 0.95 \times 10^{-46} \ \mathrm{g \cdot cm}.$$

The force constants k_{ij} are determined in a standard way: $k_{ij} = \frac{\partial^2 \Phi}{\partial x_i \partial x_j}|_{x_i=0}$. All the derivatives are calculated at a fixed value of angle χ. The frequencies of small oscillations are calculated in a standard way and are presented in Table 5 for the potential with repulsive and dispersive parts from the Buckingham and Buckingham–Corner potentials. Two first frequencies correspond to hybrid oscillations of the $\tilde{r}, \theta$-type. Their normal coordinates are (at $\chi = 0$):

$$u_1 = \frac{(k_{11} - I_r \omega_2^2)\tilde{r} + k_{12}\theta}{I_r(\omega_1^2 - \omega_2^2)(k_{22} - I_\theta \omega_1^2)} C_1 \exp(i\omega_1 t), \qquad (11)$$

$$u_2 = \frac{k_{12}\tilde{r} + (k_{22} - I_\theta \omega_1^2)\theta}{I_r(\omega_1^2 - \omega_2^2)(k_{22} - I_\theta \omega_1^2)} C_2 \exp(i\omega_2 t). \qquad (12)$$

Coefficients C_1 and C_2 are determined from the initial conditions. Thus, we can only speak about a single transversal oscillation of an H-bond, while the other one mixes with its longitudinal oscillation.

7. Discussion

From the qualitative point of view, the formation of dimers is related to the formation of a hydrogen bond between two water molecules. In this case, the ground-state energy of a dimer is identified with the energy of the H-bond. In our dimensionless units, it should be equal to –10. This estimate is confirmed by the quantum chemical calculations [9, 10, 16]. The close value of bonding energy ($\tilde{E}_d = -9.19$) is obtained, by using a generalized Stillinger–David potential [16]. However, the different approach is considered in the present work. It is supposed that the dimers are formed due to three well-defined types of interaction: repulsive, dispersive, and multipole electrostatic interactions. In our calculation, we restrict ourselves to all contributions up to the dipole-octupole ones. The extrapolation of the interaction to the overlapping region does not lead to any anomalous increase of the dipole-octupole interaction relative to other terms. This is the evidence of the legitimacy of using the described procedure of extrapolation on the distances up to $r_{\mathrm{OO}} = 3$ Å. The reliability of the results is confirmed by the fact that the values of quadrupole and octupole moments calculated in the computer experiments coincide with the experimental data. The optimal value of ground-state energy of a stationary dimer according to our calculations is $\tilde{E}_d = -9.65$ and is reached at the distance $r_{\mathrm{OO}}^{(0)} = 2.89$ Å. It is shown that the rotation of a dimer, which is quite natural in the gas phase, leads to an increase of the equilibrium distance by 0.04 Å. One more circumstance that can influence the experimental value of distance between oxygens is the excitation of longitudinal oscillations that correspond to the frequency ω_1. By the order of magnitude, the amplitude of oscillations of dimers is

$$|\Delta r| \approx \sqrt{\frac{k_{\mathrm{B}} T_m}{m \omega_{\parallel}^2}} \approx 0.1.$$

We see that the rotation and oscillations can change the distance between oxygens by 0.1 Å. This fact cannot be ignored. Another parameter of a dimer that can be controlled is the angle θ_0, which defines the equilibrium mutual orientation of the dipole moments of water molecules that form the dimer. This angle is directly connected with the values of dipole and quadrupole moments of a dimer, which can be cal-

culated with the help of quantum chemical methods or be obtained experimentally. In our work, the following values of the angle and dipole moment of a dimer correspond to the above interaction energy and the equilibrium distance: $\theta_0 = 28.7°$, $D_d = 2.81$ D. These values slightly differ from those obtained experimentally or calculated within the quantum chemical methods (see Table 1). In [11, 17], it was shown that quantum chemical calculations result in the dipole moment of a dimer $D_d = 2.6$ D. According to (6), this value corresponds to the angle $\theta_0 \approx 36°$. The value of θ_0 was also studied in [7, 8]. It was shown that, at $r_{OO} = 2.976$ Å, the angle θ_0 equals $57° \pm 10°$. From the spectroscopic experiments, it follows that the angle should be $51° \pm 20°$. Such a difference in the values of θ_0 is related to the sloping character of the dependence $\tilde{\Phi}(\theta)$ in a vicinity of the minimum, as it follows from Fig. 8. Vibrations and the rotation of a dimer also influence the value of θ_0:

$$|\Delta\theta| \approx \sqrt{\frac{k_B T_m}{I_\theta \omega^2}} \approx 2.6°.$$

The influence of the interaction of water molecules on the parameters of water molecules will affect, in some way, the equilibrium parameters of a dimer. It was demonstrated in [5] that the dipole moment of a water molecule increases by $1 \div 1.5\%$, when molecules approach it to a distance of 3 Å. So the growth of the dipole-dipole interaction will result in changes of the intermolecular distance and the interaction energy. The overlapping effects that manifest themselves at the distances smaller than 3 Å should not be considered because the relative shift of valence vibrations of a proton at the condensation does not exceed $1 \div 3\%$ [14]. But the existence of hydrogen bonds should not be neglected because they influence the value of heat capacity [29]. The weak overlapping of the electron shells shows itself in the tunneling of protons from one molecule to the other one along the hydrogen bond. But these effects are characteristic only at the superlow frequencies (~ 30 cm^{-1}). All these qualitative arguments allow us to state that the energy of the hydrogen bond itself does not exceed $k_B T_m$. The relatively small contribution of hydrogen bonds to the interaction potential was stated in the works by Dolgushin [30, 31]. He showed that the sharing indices of the electron density between water molecules under the influence of a neighbor molecule are less

than 3%. These results were confirmed by the later work by Fulton [32]. We mention that, in [6, 7], hydrogen bonds were ignored without any justification. In those works, it was shown that the interaction energy calculated with the potential consisting only of the classical electrostatic and repulsive interactions matches the quantum chemical result with sufficient accuracy. The multipole approximation allows us to easily build the averaged interaction potential between water molecules. It should be noted that certain limitations of the rigid multipole interaction will manifest themselves in the description of multimer properties, where multipartical effects take place. In particular, the equilibrium distance between oxygens reduces to $r_{OO} = 2.78$ Å in liquid water. The denial of the model of hydrogen bond as the specific donor-acceptor type of interaction finds its confirmation in another fact. The values of self-diffusion coefficients and shear viscosity for water have the same order of magnitude as those for the liquids that do not form hydrogen bonds. This fact indicates that the character of translational and rotational motions in these liquids is similar. It cannot be agreed with the existence of sharply directed hydrogen bonds with the interaction energy of $\sim 10 k_B T_m$. Our approach does not have such complexity. The electrostatic multipole interaction satisfies the superposition principle, so the total electric field formed by the randomly positioned and oriented water molecules is relatively small and does not affect critically the movement of water molecules.

1. F.H. Stillinger and C.W. David, J. Chem. Phys. **69**, 1473 (1978).
2. H. Umeyama and K. Morokuma, J. Amer. Chem. Soc. **99**, 1316 (1977).
3. P.V. Makhlaichuk, M.P. Malomuzh, and I.V. Zhyganiuk, Ukr. Fiz. Zh. **57**, 113 (2012).
4. J. Odutola and T.R. Dyke, J. Chem. Phys. **72**, 5062 (1980).
5. Yu.M. Kessler and V.E. Petrenko, *Water: Structure, State, Solvation* (Nauka, Moscow, 2003) (in Russian).
6. H.J.C. Berendsen and G.A. van der Velde, in *Proceedings of the Workshop on Molecular Dynamics and Monte Carlo Calculations of Water*, edited by H.J.C. Berendsen (CECAM, Orsay, 1972), p. 63.
7. P. Barnes, J.L. Finney, J.D. Nicholas, and J.E. Quinn, Nature **282**, 459 (1979).
8. T. Ichiye and M. Tan, J. Chem. Phys. **124**, 134504 (2006).
9. M. Schütz, S. Brdarski, P.-O. Widmark, R. Lindh, and G. Karlström, J. Chem. Phys., **107**, 4597 (1997).
10. O. Matsuoka, E. Clementi, and M. Yoshimine, J. Chem. Phys. **64**, 1351 (1976).
11. K.B. Lipkovitz and D.B. Boyd, *Reviews in Computational Chemistry* (Wiley-VCH, New York, 1999).
12. H. Yu and W.F. Gunsteren, J. Chem. Phys. **121**, 9549 (2004).
13. P.L. Silvestrelli and M. Parrinello, J. Chem. Phys. **111**, 3572 (1999).
14. T.R. Dyke, K.M. Mack, and J.S. Muenter, J. Chem. Phys. **66**, 498 (1977).
15. H. Kistemacher, H. Popkie, E. Clementi, and R.O. Watts, J. Chem. Phys. **60**, 4455 (1974).
16. I.V. Zhyganiuk, Ukr. Fiz. Zh. **56**, 225 (2011).
17. *Spectral Manifestations of Intermolecular Interactions in Gases*, edited by Yu.S. Makushkin (Nauka, Novosibirsk, 1982) (in Russian).
18. J. Verhoeven and A. Dymanus, J. Chem. Phys. **52**, 3222 (1970).
19. H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, and J. Hermans, in *Intermolecular Forces*, edited by B. Pullman (Reidel, Dordrecht, 1981), p. 331.
20. H.J.C. Berendsen, J.R. Grigera, and T.P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).
21. W.L. Jorgensen, J. Am. Chem. Soc. **103**, 335 (1981).
22. W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, R.W. Impey, and M.L. Klein, J. Chem. Phys., **79**, 926 (1983).
23. S. Aung, R.M. Pitzer, and S.I. Chan, J. Chem. Phys. **49**, 2071 (1968).
24. J.F. Harrison, J. Chem. Phys. **47**, 2990 (1968).
25. D. Neumann and J.W. Moskowitz, J. Chem. Phys. **49**, 5 (1968).
26. J. Cipriani and B. Silvi, Mol. Phys. **45**, 259 (1982).
27. I.G. John, G.B. Bacskay, and N.S. Hush, Chem. Phys. **51**, (1980).
28. D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford Univ. Press, New York, 1969).
29. S.V. Lishchuk, N.P. Malomuzh, and P.V. Makhlaichuk, Phys. Lett. A **374**, 2084 (2010).
30. M. Dolgushin, *On a Universal Intermolecular Potential*, preprint ITP-77-83 (Inst. for Theor. Phys. of the NASU, Kiev, 1977) (in Russian).
31. M. Dolgushin and V. Pinchuk, *Theoretical Study of the Nature of Hydrogen Bond by Comparative Calculations*, preprint ITP-76-49R, (Inst. for Theor. Phys. of the NASU, Kiev, 1976) (in Russian).
32. R.L. Fulton and P. Perhacs, J. Phys. Chem. A **102**, 9001 (1998).

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ДИМЕРІЗАЦІЯ МОЛЕКУЛ ВОДИ.
МОДЕЛЮВАННЯ МІЖМОЛЕКУЛЯРНОЇ ВЗАЄМОДІЇ
НА ОСНОВІ МУЛЬТИПОЛЬНОГО ПОТЕНЦІАЛУ

Р е з ю м е

Робота присвячується детальному аналізу властивостей димерів води. Всі питання, пов'язані з цією проблемою, досліджуються на основі мультипольного потенціалу, подовженого до квадруполь-квадрупольного та диполь-октупольного внесків. Отримано значення всіх основних рівноважних параметрів димеру води: його геометричних характеристик, енергії основного стану, дипольного і квадрупольного моментів, частот коливальних станів тощо. Детально обговорюється адекватність модельних потенціалів міжмолекулярної взаємодії у воді. Пропонується новий погляд на природу водневого зв'язку. Результати дослідження ретельно зіставлено з даними спектроскопічних досліджень і комп'ютерних симуляцій.