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PACS 82.30.Rs

NATURE OF THE FREQUENCY SHIFT OF HYDROGEN VALENCE VIBRATIONS IN WATER MOLECULES

The physical nature of a frequency shift of hydrogen valence vibrations in a water molecule due to its interaction with neighbor molecules has been studied. Electrostatic forces connected with the multipole moments of molecules are supposed to give a dominating contribution to the intermolecular interaction. The frequency shift was calculated in the case where two neighbor molecules form a dimer. The obtained result is in qualitative agreement with the frequency shifts observed for water vapor, hexagonal ice, and liquid water, as well as for aqueous solutions of alcohols. This fact testifies to the electrostatic nature of H-bonds used to describe both the specific features of the intermolecular interaction in water and the macroscopic properties of the latter.

Keywords: frequency shift, hydrogen valence vibrations, electrostatic models of water molecule, dimer.

The work is devoted to the 80-th birthday anniversary of the outstanding Ukrainian physicist Galyna Oleksandrivna Puchkovska

1. Introduction

Longitudinal vibrations of the O–H complex in water molecules and their nearest homologs were studied in plenty of works carried out during a long-time interval [1–8]. Since those vibrations occur along the line of the chemical O–H bond, they are also often called valence vibrations. The frequency of those vibrations in an isolated water molecule amounts to $\omega_r \approx 3657$ cm^{-1}. If dimers and, in general, multimers of higher orders are formed, as well as if water changes its phase state, the indicated frequency considerably varies [4, 7]. Researches of the frequency shift are an important tool for testing the various electrostatic models of water molecules [9] and quantum-mechanical calculations for alcohol multimers [4].

Note that the frequency shift of valence vibrations in the O–H complex is observed not only for water molecules at the multimer formation or the phase state change, but also for alcohol molecules and in other cases. In particular, in work [3], it was shown that the O–H vibration frequency in the tert-butanol monomer C_4H_9-OH equals 4095 cm^{-1}, whereas the same frequency in the dimer $(C_4H_9-OH)_2$ decreases by 63 cm^{-1} and equals 4032 cm^{-1}.

It is conventionally considered that the frequency shift of longitudinal vibrations in the O–H complex results from the formation of a hydrogen bond with the energy $\varepsilon_{\rm H} \approx 10\, k_{\rm B}T_m$, where T_m is the ice melting temperature. However, the hydrogen bond concept invokes a lot of critical remarks [10–14]. On the one hand, the hydrogen bond is assumed to have a quantum-mechanical origin associated with a substantial overlapping of electron shells in the water molecule [15]. On the other hand, the thermodynamic and transport properties of water can be described quite satisfactorily with the help of intermolecular potentials [2, 9, 16–23]. The latter have the structure

$$\Phi(q_1,q_2) = \Phi_1^{(1)}(q_1) + \Phi_1^{(2)}(q_2) + \Phi_{\rm int}(q_1,q_2),$$

$$\Phi_{\rm int}(q_1,q_2) = \Phi_{\rm R}(q_1,q_2) + \Phi_{\rm D}(q_1,q_2) + \Phi_{\rm E}(q_1,q_2),$$

where q_1 and q_2 are the sets of coordinates that describe the spatial positions and orientations of water molecules; and the subscripts R, D, and E denote the repulsion, dispersion, and electrostatic components, respectively. The hydrogen bond does not arise here at all.

In work [24], it was shown that the hydrogen bond cannot be ignored completely, since, otherwise, there

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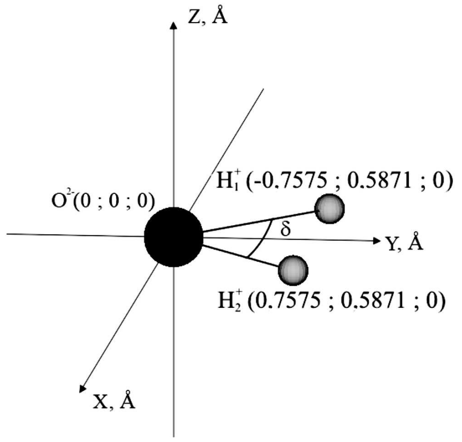

Fig. 1. Electrostatic model of water molecule (the coordinates of effective charges in Angström units are indicated in the parentheses)

emerges a difficult problem concerning the heat capacity of water. Namely, the latter is almost twice as high as the heat capacity of hydrogen sulfide, its nearest homolog. The solution of this paradox was presented in works [14, 24]. In particular, the interaction potential between two water molecules includes also the component $\Phi_{\rm H}(q_1,q_2)$ corresponding to the energy of the irreducible hydrogen bond. Hence,

$$\Phi_{\rm int}(q_1,q_2)=\Phi_{\rm R}(q_1,q_2)+$$

$$+\,\Phi_{\rm D}(q_1,q_2)+\Phi_{\rm E}(q_1,q_2)+\Phi_{\rm H}(q_1,q_2),$$

At the distances typical of a dimer,

$$|\Phi_{\rm H}(q_1,q_2)|\approx\frac{1}{5}|\Phi_{\rm E}(q_1,q_2)|,$$

i.e. the hydrogen bond is weak and can be taken into account in the framework of perturbation theory.

The inconsistency is characteristic even of the approach made in works [9, 25] to the problem of the frequency shift of valence vibrations. The cited authors proposed one of the soft potentials describing both the intermolecular interaction and internal vibrations of water molecules. However, while calculating the frequency of valence hydrogen vibrations in a water dimer, a certain potential of the hydrogen bond is used. As a result, it was found that the vibration frequency of hydrogen $\rm H_1^+$ (see Fig. 2) in a standard dimer decreases by 300 $\rm cm^{-1}$, which is considered to prove the existence of a strong hydrogen bond between water molecules in the dimer. Note that this shift substantially exceeds the corresponding value obtained using the methods of IR and vibrational spectroscopy of water multimers in an argon matrix and the methods of absorption spectroscopy [7].

In this work, we give another evidence that irreducible hydrogen bonds are weak. We consistently calculated the frequency shift of longitudinal vibrations of the O–H complex in a water molecule that forms a dimer configuration with another water molecule. The calculations were carried out on the basis of the electrostatic model of soft water molecule proposed in work [2] and modified in work [9]. The interaction between water molecules was described with the help of the GSD potential [25]. We showed that the account of the electrostatic interaction between effective charges allows the experimentally observed frequency shift for hydrogen vibrations to be reproduced correctly at the qualitative level.

2. Electrostatic Models of Water Molecule and Dimer

In the initial Stillinger–David model and its generalized GSD version, the coordinates of three effective charges – an oxygen and two hydrogens – are considered variable, unlike the majority of models [17, 18, 21–23] widely applied in the literature in the last years. As a result, the indicated model allows minor modifications of water molecule parameters to occur under the influence of the nearest environment. Let us consider the main features of the interaction between effective charges in the GSD model.

2.1. Electrostatic model of water molecule

The model of isolated water molecule has a structure shown in Fig. 1. We use the potentials in the dimensionless form, i.e. the intermolecular interaction potential, as well as other combinations of constants that have the dimensionality of energy, are normalized by $k_{\rm B}T_m$, where $k_{\rm B}$ is the Boltzmann constant, and T_m the ice melting temperature. The corresponding renormalized quantities are tilded. In particular, $\tilde{\Phi}=\Phi/k_{\rm B}T_m$.

In accordance with the GSD potential [26], the energy $\tilde{\Phi}_1^1$ of the interaction between the hydrogens and the oxygen in a water molecule $\rm H_2^+{-}O_1^+{-}H_1^+$ (see Fig. 2) is written in the form

$$\tilde{\Phi}_1^{(1)}(\tilde{\mathbf{r}}_{\rm H_1},\tilde{\mathbf{r}}_{\rm H_2})=\tilde{\Phi}_{\rm R}^{(1)}+\tilde{\Phi}_{\rm C}^{(1)}+\tilde{\Phi}_{\rm Dq}^{(1)}. \qquad (1)$$

Here, various terms have the following sense:

– $\tilde{\Phi}_R^1$ is the potential of the hydrogen repulsion from the oxygen electron shell:

$$\tilde{\Phi}_{\rm R}^{(1)} = \tilde{b}_1 \left(\frac{e^{-\tilde{\rho}_1 \tilde{r}_{\rm H_1}}}{\tilde{r}_{\rm H_1}} + \frac{e^{-\tilde{\rho}_1 \tilde{r}_{\rm H_2}}}{\tilde{r}_{\rm H_2}} \right), \tag{2}$$

where $\tilde{b}_1 = b_1/k_{\rm B}T_m$, $\tilde{\rho}_1 = \rho\sigma$, and $\tilde{r}_{{\rm H}_k} = r_{{\rm H}_k}/\sigma$ are the amplitude and the reciprocal radius of repulsion forces between the oxygen and hydrogen atoms, and $\sigma = 2.98$ Å is the diameter of the oxygen atom;

– $\tilde{\Phi}_C^1$ is the potential of the direct Coulomb interaction between the effective charges in the water molecule:

$$\tilde{\Phi}_{\rm C}^{(1)} = \tilde{C}_1 \left(\frac{q_{\rm H_1} q_{\rm H_2}}{|\tilde{\mathbf{r}}_{\rm H_1} - \tilde{\mathbf{r}}_{\rm H_2}|} + \frac{q_{\rm O_1} q_{\rm H_1}}{\tilde{r}_{\rm H_1}} + \frac{q_{\rm O_1} q_{\rm H_2}}{\tilde{r}_{\rm H_2}} \right), \tag{3}$$

where $\tilde{C}_1 = C_1/\sigma = 205.59$ is the coefficient of conversion to dimensionless energy units ($k_{\rm B}T_m$), and the oxygen and hydrogen charges are measured in the electron charge units and equal $q_{\rm O_1} = -2.0$, $q_{\rm H_1} = q_{\rm H_2} = 1.0$;

– $\tilde{\Phi}_{Dq}^1$ is the potential of the dipole-charge interaction between the dipole moment of oxygen and the effective charges of hydrogens:

$$\tilde{\Phi}_{\rm Dq}^{(1)} = \frac{\left(\tilde{\mathbf{d}}_{\rm O_1} \tilde{\mathbf{r}}_{\rm H_1}\right) q_{\rm H_1}}{\tilde{r}_{\rm H_1}^3} \left[1 - \tilde{L}(\tilde{r}_{\rm H_1})\right] + \\ + \frac{\left(\tilde{\mathbf{d}}_{\rm O_1} \tilde{\mathbf{r}}_{\rm H_2}\right) q_{\rm H_2}}{\tilde{r}_{\rm H_2}^3} \left[1 - \tilde{L}(\tilde{r}_{\rm H_2})\right], \tag{4}$$

where $\tilde{L}(\tilde{r}_{\rm H_1})$ is one of the screening functions, the explicit form of which is described in work [26]. Under the action of hydrogens, the dipole moment of oxygen in the water molecule acquires the value

$$\tilde{\mathbf{d}}_{\rm O_1} = -\tilde{\alpha} \left\{ \frac{\tilde{\mathbf{r}}_{\rm H_1} q_{\rm H_1}}{\tilde{r}_{\rm H_1}^3} \left[1 - \tilde{K}(\tilde{r}_{\rm H_1})\right] + \\ + \frac{\tilde{\mathbf{r}}_{\rm H_2} q_{\rm H_2}}{\tilde{r}_{\rm H_2}^3} \left[1 - \tilde{K}(\tilde{r}_{\rm H_2})\right] \right\}, \tag{5}$$

where $\tilde{\alpha}$ is the polarizability of oxygen, and $\tilde{K}(\tilde{r}_{\rm H_2})$ is another screening function [2,26]. The contribution of the dipole-charge interaction in Eq. (1) has the following structure:

$$\tilde{\Phi}_{\rm Dq}^{(1)} = -\tilde{\alpha}\tilde{C}_1 \Bigg[q_{\rm H_1} q_{\rm H_1} \frac{\left[1 - \tilde{K}(\tilde{r}_{\rm H_1})\right]\left[1 - \tilde{L}(\tilde{r}_{\rm H_1})\right]}{\tilde{r}_{\rm H_1}^6} \times \\ \times (\tilde{\mathbf{r}}_{\rm H_1}\tilde{\mathbf{r}}_{\rm H_1}) + q_{\rm H_1} q_{\rm H_2} \times \\ \times \frac{\left[1 - \tilde{K}(\tilde{r}_{\rm H_1})\right]\left[1 - \tilde{L}(\tilde{r}_{\rm H_2})\right] + \left[1 - \tilde{K}(\tilde{r}_{\rm H_2})\right]\left[1 - \tilde{L}(\tilde{r}_{\rm H_1})\right]}{\tilde{r}_{\rm H_1}^3 \tilde{r}_{\rm H_2}^3} \times \\ \times (\tilde{\mathbf{r}}_{\rm H_1}\tilde{\mathbf{r}}_{\rm H_2}) + q_{\rm H_2} q_{\rm H_2} \times \\ \times \frac{\left[1 - \tilde{K}(\tilde{r}_{\rm H_2})\right]\left[1 - \tilde{L}(\tilde{r}_{\rm H_2})\right]}{\tilde{r}_{\rm H_2}^6} (\tilde{\mathbf{r}}_{\rm H_2}\tilde{\mathbf{r}}_{\rm H_2}) \Bigg]. \tag{6}$$

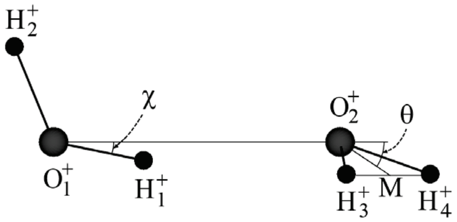

Fig. 2. Configuration of a linear dimer of two water molecules ($\chi = 3.76°$ and $\theta = 41.1°$ are the equilibrium angle values)

It differs from the expression presented in the work of Stillinger and David [2] by the coefficient $\frac{1}{2}$.

2.2. Interaction of two water molecules

If one water molecule turns out in the electric field of the other molecule, its internal energy changes by the magnitude of interaction energy:

$$\tilde{\Phi}_1^{(1)}(\tilde{\mathbf{r}}_{\rm H_1}, \tilde{\mathbf{r}}_{\rm H_2}) \to \tilde{\Phi}_2^{(1)}(\tilde{\mathbf{r}}_{\rm H_1}, \tilde{\mathbf{r}}_{\rm H_2}, \tilde{\mathbf{r}}_{\rm O_1H_3}, \tilde{\mathbf{r}}_{\rm O_1H_4}, \tilde{\mathbf{r}}_{\rm O_1O_2}) = \\ = \tilde{\Phi}_1^{(1)}(\tilde{\mathbf{r}}_{\rm H_1}, \tilde{\mathbf{r}}_{\rm H_2}) + \tilde{\Phi}_{\rm Int}, \tag{7}$$

where the term $\tilde{\Phi}_{\rm Int}$ looks like

$$\tilde{\Phi}_{\rm Int} = \tilde{\Phi}_{\rm R} + \tilde{\Phi}_{\rm D} + \tilde{\Phi}_{\rm E}. \tag{8}$$

The first contribution in Eq. (8), $\tilde{\Phi}_R$, is the potential of the hydrogen repulsion from the electron shells of oxygens. It is approximated by the Born exponential form, which coincides with a similar contribution in the MPM potential [9]:

$$\tilde{\Phi}_{\rm R} = \tilde{b}_1 \left[\sum_{i=1,2} \frac{e^{-\tilde{\rho}_1 \tilde{r}_{i{\rm O}_2}}}{\tilde{r}_{i{\rm O}_2}} + \sum_{j=1,2} \frac{e^{-\tilde{\rho}_1 \tilde{r}_{{\rm O}_1 j}}}{\tilde{r}_{{\rm O}_1 j}} \right] + \\ + \frac{\tilde{b}_2 e^{-\tilde{\rho}_2 \tilde{r}_{\rm O_1O_2}}}{\tilde{r}_{\rm O_1O_2}}. \tag{9}$$

Table 1. **Parameters of the GSD potential**

	$\tilde{L}_0$	$\tilde{L}_1$	$\tilde{L}_2$	$\tilde{L}_3$	$\tilde{L}_4$	$\tilde{b}_1$	$\tilde{\rho}_1$	$\tilde{b}_2$	$\tilde{\rho}_2$
GSD	8.8804	8.8804	8.1699	124.49	185.95	1064.7	7.656	42129.1	2.59

The second contribution in Eq. (8), $\tilde{\Phi}_{\rm D}$, defines the potential of the dispersion interaction between oxygens:

$$\tilde{\Phi}_{\rm D} = -\frac{\tilde{A}_{\rm O_1O_2}}{\tilde{r}^6_{\rm O_1O_2}}, \qquad (10)$$

It is similar to the dispersion part of the Lennard-Jones potential. The same form of the dispersion contribution is inherent to the SPC and SPC/E potentials [22] and to the TIPS and TIP3P ones [17].

The third contribution in Eq. (8), $\tilde{\Phi}_E$, defines the electrostatic interaction between oxygens and hydrogens in two water molecules:

$$\tilde{\Phi}_{\rm E} = \tilde{\Phi}_{\rm C} + \tilde{\Phi}_{\rm Dq} + \tilde{\Phi}_{\rm DD}, \qquad (11)$$

where the term

$$\tilde{\Phi}_{\rm C} = \tilde{C}_1 \left\{ \sum_{i,j=1,2} \frac{q_i q_j}{\tilde{r}_{ij}} + \right.$$
$$\left. + \left[\sum_{i=1,2} \frac{q_i q_{\rm O_2}}{\tilde{r}_{i\rm O_2}} + \sum_{j=1,2} \frac{q_{\rm O_1} q_j}{\tilde{r}_{{\rm O_1}j}} \right] + \frac{q_{\rm O_1} q_{\rm O_2}}{\tilde{r}_{\rm O_1O_2}} \right\} \qquad (12)$$

defines the direct Coulomb interaction between the effective charges of two water molecules and completely coincides with a similar contribution of the Coulomb interaction in the Stillinger–David potential.

Note that the electrostatic interaction between the effective charges, which simulate oxygens and hydrogens in the water molecules in a dimer, consists of two parts: (i) the interaction of the effective charges in molecule 1 with the dipole moment of molecule 2 and the interaction of the effective charges in water molecule 2 with the dipole moment of molecule 1, and (ii) the interaction of two dipole moments of the water molecules in the dimer. At distances between the molecules that considerably exceed the diameter of a water molecule, the interaction between the model charges of hydrogens and oxygens completely coincides with the interaction between the total dipole moments of water molecules.

The structure of the dipole-charge contribution $\tilde{\Phi}_{Dq}$ to the electrostatic interaction is the same as that of the Stillinger–David potential,

$$\tilde{\Phi}_{\rm Dq} = \frac{(\tilde{\mathbf{d}}_{\rm O_1}\tilde{\mathbf{r}}_{\rm O_1O_2})q_{\rm O_2}}{\tilde{r}^3_{\rm O_1O_2}}[1 - \tilde{L}(\tilde{r}_{\rm O_1O_2})] +$$
$$+ \frac{(\tilde{\mathbf{d}}_{\rm O_2}\tilde{\mathbf{r}}_{\rm O_1O_2})q_{\rm O_1}}{\tilde{r}^3_{\rm O_1O_2}}[1 - \tilde{L}(\tilde{r}_{\rm O_1O_2})] +$$
$$+ \left[\sum_{j=1,2} \frac{(\tilde{\mathbf{d}}_{\rm O_1}\tilde{\mathbf{r}}_{{\rm O_1}j})q_j}{\tilde{r}^3_{{\rm O_1}j}}[1 - \tilde{L}(\tilde{r}_{{\rm O_1}j})] + \right.$$
$$\left. + \sum_{i=1,2} \frac{(\tilde{\mathbf{d}}_{\rm O_2}\tilde{\mathbf{r}}_{{\rm O_2}i})q_i}{\tilde{r}^3_{{\rm O_2}i}}[1 - \tilde{L}(\tilde{r}_{{\rm O_2}i})] \right], \qquad (13)$$

where the subscripts i and j enumerate the hydrogen charges in water molecules 1 and 2, respectively; and $\tilde{\mathbf{d}}_{\rm O_1}$ and $\tilde{\mathbf{d}}_{\rm O_2}$ are the dipole moments of oxygens in the corresponding water molecules.

One can be convinced that, unlike the Stillinger–David potential, the interaction potential $\tilde{\Phi}_{\rm GSD}$ has a correct asymptotics of the dipole-dipole interaction at distances that strongly exceed the size of a water molecule, $\tilde{\Phi}_{\rm GSD} \to \tilde{\Phi}_d(\tilde{\mathbf{d}}_1, \mathbf{d}_2)$, where $\tilde{\Phi}_d(\tilde{\mathbf{d}}_1, \tilde{\mathbf{d}}_2) = \frac{1}{\tilde{r}^3_{12}} \left[\left(\tilde{\mathbf{d}}_1 \tilde{\mathbf{d}}_1 \right) - \frac{3\left(\tilde{\mathbf{d}}_1\tilde{\mathbf{r}}_{12}\right)\left(\tilde{\mathbf{d}}_2\tilde{\mathbf{r}}_{21}\right)}{\tilde{r}^2_{12}} \right]$, and the dipole moment of molecule is a sum of the dipole moments of oxygen and hydrogens, $\tilde{\mathbf{d}} = \tilde{\mathbf{d}}_{\rm H} + \tilde{\mathbf{d}}_{\rm O}$. The values of the parameters in the GSD potential are quoted in Table 1.

Table 2 contains the equilibrium values of the energy $\tilde{\Phi}_d$ (see Fig. 2), the angles θ and χ, and the dipole moment D_d for the dimer calculated with the use of the GSD potential. The direct comparison testifies that they agree well with the results of quantum chemical calculations [27] and experimental data [28].

3. Behavior of the Vibration Frequencies of Hydrogens in a Water Molecule in Vapor, Water, and Ice

Let us discuss the shift of longitudinal (valence) vibration frequencies for the hydrogen $\rm H_1^+$ (see Fig. 2) that lies close to the line connecting the centers-of-mass of

Table 2. **Equilibrium values of the distance between the oxygens, the angles, the energy, and the dipole moment of a water dimer**

Parameters	$r_{\mathrm{O_1O_2}}$, Å	γ, deg	θ, deg	$\tilde{\Phi}_d$, Å	D_d, D
GSD	2.96	3.76	41.1	–8.01	2.54
Experiment	2.976 ± 0.004	-1 ± 10	57 ± 10	-9.96 ± 0.4	2.6

oxygen atoms in two neighbor water molecules forming a dimer. The corresponding vibration frequencies are determined according to the formula

$$\omega_{\|} \approx \sqrt{\frac{K_{rr}^{1}}{M_{\mathrm{Re}}}}, \tag{14}$$

where the force constant (in the dimensionless form) is defined in the standard manner:

$$\tilde{K}_{rr}^{(1)} = \left.\frac{\partial^2 \tilde{\Phi}_2^{(1)}}{\partial \tilde{r}_{\mathrm{H_1}}^2}\right|_{\tilde{r}'_{\mathrm{H_1}}}, \tag{15}$$

and the reduced mass of the oxygen–hydrogen system in the water molecule approximately equals

$$M_{\mathrm{Re}} \approx \frac{(M_{\mathrm{O}} + M_{\mathrm{H}})\, M_{\mathrm{H}}}{(M_{\mathrm{O}} + M_{\mathrm{H}}) + M_{\mathrm{H}}}. \tag{16}$$

The approximate character of formula (16) is explained by the fact that hydrogen H_2^+ (Fig. 2) is not located on the line connecting the centers-of-mass of oxygens. The second-order derivative in Eq. (15) is calculated at the point $\tilde{r}'_{\mathrm{H_1}}$ defined by the equation

$$\left.\frac{\partial\left(\tilde{\Phi}_1^{(1)}(\tilde{\mathbf{r}}_{\mathrm{H_1}}, \tilde{\mathbf{r}}_{\mathrm{H_2}}) + \tilde{\Phi}_{\mathrm{Int}}(\tilde{\mathbf{r}}_{\mathrm{O_1H_3}}, \tilde{\mathbf{r}}_{\mathrm{O_1H_4}}, \tilde{\mathbf{r}}_{\mathrm{O_1O_2}})\right)}{\partial \tilde{r}_{\mathrm{H_1}}}\right|_{\tilde{r}'_{\mathrm{H_1}}} = 0. \tag{17}$$

It should be noted that Eq. (17) gives rise to only an insignificant shift $\Delta\tilde{r}_{\mathrm{H_1}}$ in the equilibrium position of hydrogen H_1^+. Supposing that

$$\tilde{r}'_{\mathrm{H_1}} = \tilde{r}_{\mathrm{H_1}} + \Delta\tilde{r}_{\mathrm{H_1}}, \ \ |\Delta\tilde{r}_{\mathrm{H_1}}| \ll \tilde{r}_{\mathrm{H_1}},$$

$\Delta\tilde{r}_{\mathrm{H_1}}$ can be determined with the help of a simpler equation,

$$\tilde{K}_{rr}^{(1)}\Delta\tilde{r}_{\mathrm{H_1}} + \left.\boldsymbol{\nabla}_{\tilde{r}_{\mathrm{H_1}}}\tilde{\Phi}_{\mathrm{Int}}(\tilde{\mathbf{r}}_{\mathrm{O_1H_3}}, \tilde{\mathbf{r}}_{\mathrm{O_1H_4}}, \tilde{\mathbf{r}}_{\mathrm{O_1O_2}})\right|_{\tilde{r}_{\mathrm{H_1}} = \tilde{r}'_{\mathrm{H_1}}} = 0, \tag{18}$$

where $\tilde{K}_{rr}^{1}$ is the coefficient of elasticity for the bond between the hydrogen and the oxygen in the monomer.

Equation (18) acquires a very simple form in the case where the distance $\tilde{r}_{\mathrm{O_1O_2}}$ between the oxygens in the dimer largely exceeds the diameter of a water molecule. In this case, the potential $\tilde{\Phi}_{\mathrm{Int}}(\tilde{\mathbf{r}}_{\mathrm{O_1H_1}}, \tilde{\mathbf{r}}_{\mathrm{O_1H_2}}, \tilde{\mathbf{r}}_{\mathrm{O_1O_2}})$ looks like

$$\tilde{\Phi}_{\mathrm{Int}}(\tilde{\mathbf{r}}_{\mathrm{O_1H_1}}, \tilde{\mathbf{r}}_{\mathrm{O_1H_2}}, \tilde{\mathbf{r}}_{\mathrm{O_1O_2}}) = q_i\Big[\tilde{\Phi}_{\mathrm{Dq}}(\tilde{\mathbf{r}}_{\mathrm{H_1}}, \ldots) + \\ + \tilde{\Phi}_{\mathrm{Dq}}(\tilde{\mathbf{r}}_{\mathrm{H_2}}, \ldots) - 2\tilde{\Phi}_{\mathrm{Dq}}(\tilde{\mathbf{r}}_{\mathrm{O_1O_2}}, \ldots)\Big], \tag{19}$$

where

$$\tilde{\Phi}_{\mathrm{Dq}}(q_i, \tilde{\mathbf{d}}_{\mathrm{w2}}) = \frac{q_i\left(\tilde{\mathbf{d}}_{\mathrm{w2}}\tilde{\mathbf{r}}_{\mathrm{O_1O_2}}\right)}{\tilde{r}_{\mathrm{O_1O_2}}^3}$$

is the potential of the charge-dipole interaction of hydrogens and oxygen of molecule 1 with the electric field of molecule 2, which can be approximated as the field of a dipole. In further calculations, we used two approximations associated with the fact that the hydrogen is subjected not only to electric forces, but also to the repulsion forces from the oxygen electron shell. First, we adopt that only the hydrogen position $\tilde{\mathbf{r}}_{\mathrm{H_1}}$ is changed. In this case, Eqs. (18) and (19) yield

$$\Delta\tilde{\mathbf{r}}_{\mathrm{H_1}} = -\frac{1}{\tilde{K}_{rr}^{(1)}}\frac{q_i}{|\tilde{\mathbf{r}}_{\mathrm{O_1O_2}} + \tilde{\mathbf{r}}_{\mathrm{H_1}}|^5}\Big[\tilde{\mathbf{d}}_{w2}|\tilde{\mathbf{r}}_{\mathrm{O_1O_2}} + \tilde{\mathbf{r}}_{\mathrm{H_1}}|^2 - \\ - 3\left(\tilde{\mathbf{d}}_{w2}\,(\tilde{\mathbf{r}}_{\mathrm{O_1O_2}} + \tilde{\mathbf{r}}_{\mathrm{H_1}})\right)(\tilde{\mathbf{r}}_{\mathrm{O_1O_2}} + \tilde{\mathbf{r}}_{\mathrm{H_1}})\Big].$$

With a satisfactory accuracy, this formula can be rewritten in the scalar form

$$\Delta\tilde{r}_{\mathrm{H_1}} = \frac{2}{K_{rr}^{(1)}}\frac{q_i\tilde{d}_{w2}\cos\theta}{|\tilde{\mathbf{r}}_{\mathrm{O_1O_2}} - \tilde{\mathbf{r}}_{\mathrm{H_1}}|^3}, \tag{20}$$

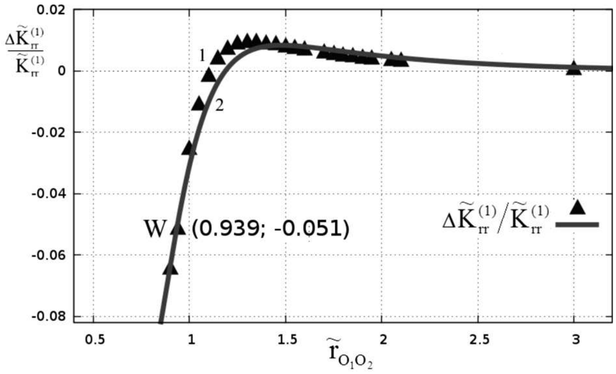

Fig. 3. Dependences of the relative force constant change on the distance $\tilde{r}_{O_1O_2}$ in the standard dimer calculated making allowance for the mutual adjustment of molecular orientations (triangles, *1*) and for the orientation of molecules as in Fig. 2 (solid curve, *2*)

Table 3. **Force constants for water molecules**

Constants	$\frac{\partial^2\tilde{\Phi}}{\partial\tilde{r}_1^2}$	$\frac{\partial^2\tilde{\Phi}}{\partial\theta^2}$	$\frac{\partial^2\tilde{\Phi}}{\partial\tilde{r}_1\partial\theta}$
GSD model	256.98	182.15	33.439
Experiment [2]	256.98	190.64	33.439

Table 4. **Frequencies of symmetric valence vibrations of hydrogens in a water molecule in vapor, liquid, and ice**

Source	Frequencies		
	ν_v, cm^{-1}	ν_w, cm^{-1}	ν_{Ice}, cm^{-1}
Experiment [1]	3657	3490	3200
Experiment [8]	3656.7	3280	
MSN-FP [8]	3656	3251	
SPC-FP [8]		3875	

where $F_1 = \frac{q_i\tilde{d}_{w2}\cos\theta}{|\tilde{\mathbf{r}}_{O_1O_2}-\tilde{\mathbf{r}}_{H_1}|^3}$ is the force that acts on the hydrogen with the coordinate $\tilde{\mathbf{r}}_{H_1}$. Second, we took into account that the electric field of the neighbor molecule also acts on the oxygen and the hydrogen connected with it in molecule 1. The approximate expression for the force acting on the oxygen of molecule 2 looks like $F_2 \approx -\frac{q_i\tilde{d}_{w2}\cos\theta}{\tilde{r}^3_{O_1O_2}}$. The sum δF_1 of the forces F_1 and F_2 equals

$$\delta F_1 \approx 3\frac{\tilde{d}_{H_1}\tilde{d}_{w2}\cos\theta}{\tilde{r}^4_{O_1O_2}},$$

This is the force that stretches the vector $\tilde{\mathbf{r}}_{H_1}$. As a result, we obtain the expression

$$\delta\tilde{r}_{H_1} \approx \frac{3}{\tilde{K}^{(1)}_{rr}}\frac{\tilde{d}_{H_1}\tilde{d}_{w2}\cos\theta}{\tilde{r}^4_{O_1O_2}}, \tag{21}$$

which differs from Eq. (20) by its functional dependence on the distance between the oxygens ($\delta\tilde{r}_{H_1}/\Delta\tilde{r}_{H_1} \sim 3\tilde{r}_{H_1}/\tilde{r}_{O_1O_2}$). However, at distances of several diameters of a water molecule, they are close by magnitude.

Taking into account that, by the order of magnitude, the elastic constant $\tilde{K}^1_{rr}$ can be evaluated as $\tilde{K}^1_{rr} \approx q_\mathrm{i}^2/\tilde{r}^3_\mathrm{H}$ in the framework of the electrostatic model, we obtain the estimate for the ratio $\delta\tilde{r}_{H_1}/\tilde{r}_{H_1}$:

$$\delta\tilde{r}_{H_1}/\tilde{r}_{H_1} \sim (\tilde{r}_{H_1}/\tilde{r}_{O_1O_2})^4 \leqslant 0.02.$$

Therefore, the shift can be neglected practically at all distances between the oxygens in the water dimer.

The values of force constants for the water molecule corresponding to the GSD potential are quoted in Table 3. For comparison, Table 3 also contains the relevant values determined experimentally.

The value of force constant $\tilde{K}^1_{rr}$ for symmetric valence vibrations in the equilibrium dimer configuration shown in Fig. 2 was calculated using formula (15). The relative variation of the constant, $\Delta\tilde{K}^1_{rr}/\tilde{K}^1_{rr}$, as a function of the distance between the oxygens in the dimer is plotted in Fig. 3. Point W in the plot with the coordinates $(0.939, -0.051)$ corresponds to the distance $r_{O_1O_2} = 2.8$ Å between the oxygens, which is typical of liquid water near the ternary point. The relative change of the constant of symmetric valence vibrations equals $\Delta\tilde{K}^1_{rr}/\tilde{K}^1_{rr} = -0.05$ at this point. Hence, the values of force constant for valence vibrations at the distance corresponding to the equilibrium state of a dimer and the distance between water molecules in liquid water differ from each other by 5%.

4. Discussion of the Results

The frequency shift of hydrogen valence vibrations in a water molecule depends on the phase state of water and can reaches a magnitude of several hundreds of inverse centimeters (Table 4). In this work, we suppose that the main contribution to the experimentally observed magnitude of frequency shift is made by the electrostatic forces connected with the multipole moments of water molecules.

The basic result of our research consists in that the electrostatic forces really give rise to the frequency shift values that agree with experimental data by both the sign and the order of magnitude. For instance, according to Eq. (19), the frequency shift for valence vibrations equals

$$\Delta\omega \approx \frac{1}{1}\omega_0 \frac{\Delta\tilde{K}_{rr}^{(1)}}{\tilde{K}_{rr}^{(1)}},$$

where $\omega_0 \approx 3657$ cm^{-1} is the vibration frequency for an isolated water molecule. The relative increment of the elastic constant equals $\Delta\tilde{K}^1_{rr}/\tilde{K}^1_{rr} = -0.05$ at $r_{\mathrm{O_1O_2}} = 2.8$ Å, i.e. $\Delta\omega \approx -0.025\omega_0 = -91.43$ cm^{-1}. Hence, the frequency shift sign for the dimer coincides with the shift signs in liquid water and ice. The shear moduli are identical by the order of magnitude, but, nevertheless, they are appreciably different by the value. This circumstance has a simple qualitative interpretation. The total electric field acting on a water molecule in the liquid is, on the average, a little stronger than that acting from the neighbor molecule in the dimer. An insignificant increment of the electric field strength in the case of the liquid is associated with a weakly ordered arrangement of the centers-of-mass of the nearest neighbor molecules and their orientations. As a consequence, according to the superposition principle, only a weak enhancement of the electric field in the molecule takes place. The situation in ice is totally opposite.

Let us discuss a change of the elastic constant in the standard dimer (see Fig. 2) at $r_{\mathrm{O_1O_2}} = 2.85$ Å. It is at this distance that the oxygens of water molecules are arranged in the argon matrix. According to our calculations, the relative increment of the elastic constant, $\Delta\tilde{K}^1_{rr}/\tilde{K}^1_{rr}$, in the concerned dimer configuration amounts to -0.0443 at the fixed orientation of molecules as in the standard dimer and to -0.0432 if the molecules are allowed to adjust their orientations. Those variations in the elastic constant stimulate changes in the frequency of valence vibrations: to 3576 cm^{-1} in the former case and to 3578 cm^{-1} in the latter one. It should be noted that the relatively small value of orientational contribution is explained by the fact that the configuration of the system is in the interval where the energy of the repulsion between the molecules monotonically decreases. The frequency corresponding to experiments in the argon matrix [7] equals 3574 cm^{-1}. Therefore, we believe that it is possible to say about the complete coincidence of theoretical and experimental results. From our viewpoint, this is a sound argument in favor of the electrostatic nature of the frequency shift of valence vibrations.

It is very important that the explanation of the frequency shifts different by the magnitude is essentially based on the superposition principle, the application of which to sharply directed and saturated irreducible hydrogen bonds is impossible. For a more complete substantiation of this fact, we intend to consider the frequency shifts of valence vibrations in ice and liquid water in a separate work.

Not less important is the fact that, in rarefied vapor, one should expect a positive frequency shift, which directly follows from the behavior of the quantity $\Delta\tilde{K}^1_{rr}/\tilde{K}^1_{rr}$ depicted in Fig. 3. This fact is also qualitatively supported by experimental data [29] on the IR absorption in relatively rarefied water vapor.

We would like to express our deep respect to the late Galyna Oleksandrivna Puchkovska, who stimulated this work about 20 years ago. A delay in the solution of the formulated problem was connected with the absence of a suitable interaction potential between soft water molecules. Professor V.E. Pogorelov, who studied the shifts of valence vibrations in alcohols of the methanol series, permanently induced us to the solution of the formulated problem. Therefore, we consider Prof. G.O. Puchkovska and Prof. V.E. Pogorelov to be the principal authors of this paper. It is especially pleasant to mark this circumstance in connection with the 80-th anniversary of the birthday of unforgettable Galyna Oleksandrivna Puchkovska, which was in June this year. We are also sincerely grateful to Academician L.A. Bulavin for the comprehensive discussion of the results of this work at its various stages.

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Received 31.10.14.
Translated from Ukrainian by O.I. Voitenko

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ПРИРОДА ЗСУВУ ЧАСТОТИ ВАЛЕНТНИХ КОЛИВАНЬ ГІДРОГЕНІВ У МОЛЕКУЛАХ ВОДИ

Резюме

Робота присвячена дослідженню фізичної природи зсуву частот валентних коливань гідрогенів молекул води внаслідок її взаємодії з сусідніми молекулами. Приймається, що домінуючий внесок у міжмолекулярну взаємодію вноситься силами електростатичної природи, пов'язаними з існуванням мультипольних моментів молекул води. Розраховано величину зсуву частоти у випадку, коли дві сусідні молекули води утворюють димер. Отриманий результат якісно добре узгоджується з величиною зсувів частот, які спостерігаються у парі, льоді та рідкій воді, а також у водних розчинах спиртів [1–4]. Це свідчить про те, що водневі зв'язки, за допомогою яких намагаються відтворити специфіку міжмолекулярної взаємодії у воді, а також її макроскопічні властивості, формуються домінуючим чином силами електростатичної природи.