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Potential of hydrogen bond in water. Comparison of the theory with vibrational spectra and results of molecular dynamics simulations

Yuri Ya. Efimov^{a,*}, Yuri I. Naberukhin^{a,b}^a Institute of Chemical Kinetics & Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia^b Novosibirsk State University, Novosibirsk 630090, Russia

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ABSTRACT

Potential of hydrogen bond is the function which relates its energy to geometrical parameters of hydrogen bridge: its length $R(O \dots O)$ and angles between direction $O \dots O$ and OH group $[\varphi (H-O \dots O)]$ and/or lone pair of proton accepting oxygen atom $[\chi (-O \dots O)]$. Previously we have suggested an approach to design such potentials based on the approximate numerical solution of a reverse problem of the spectrum band shape in the frames of the fluctuation theory of hydrogen bonding. In the given work this method is applied to construction of the two-parameter potentials that depend on parameters $\{R(O \dots O), \varphi (H-O \dots O)\}$ or $\{\varphi (H-O \dots O), \chi (-O \dots O)\}$. Using them, the spectra of OH vibrations of HOD molecules in a liquid phase are calculated theoretically in good agreement with experiment in the temperature range up to 200 °C. Distributions of angles $P(\varphi, T)$, $P(\chi, T)$, and energies $P(E)$ are calculated also. The same distributions and spectra are independently calculated on the basis of the geometrical parameters of the hydrogen bridges obtained from molecular dynamics models of water. The shapes of the spectral contours and their temperature evolution calculated for computer models turned out to be similar to experimental ones only for the potential that includes the length of H-bond $R(O \dots O)$.

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1. Introduction

Hydrogen bonds play an important role in structure formation of various systems and also define a structure and unique properties of liquid water as a cradle of a life. Thus investigations of different aspects of H-bonding became the area of interests for the chemical scientific community. Main features of water and dilute aqueous solutions are defined by a three-dimensional network of hydrogen bonds between its molecules. The detailed information on the arrangement of this network can be obtained basically by methods of computer simulations. However in these methods the *total* potentials of intermolecular interactions are used in which the contribution of hydrogen bonds is not separated. Therefore we are obliged to define the existence or absence of H-bond between a pair of molecules on the basis of artificial criteria establishing allowable values for geometrical and/or energy parameters of hydrogen bridge $O-H \dots O$.

Meanwhile, vibrational spectra are very sensitive to hydrogen bonding. Frequency of the stretching vibration of OH group, ν_{OH} , decreases under the influence of H-bond relative to the non-perturbed value ν_u ; the shift $(\nu_u - \nu_{OH})$ being proportional to the

energy of H-bond as a first approximation [1]. This shift is much larger than small shift due to van der Waals interactions which is practically identical for all OH oscillators (in various molecules). Thus, the width and the shape of a stretching band are defined exclusively by hydrogen bonds, reflecting their variety (fluctuations). This reasoning is a basis of the fluctuation theory of hydrogen bonding [2–5] that specifies interdependence between energy of H-bond and frequency of involved oscillator $E(\nu)$ and also establishes a relation of $E(\nu)$ with the distribution of stretching vibrations $P(\nu)$.

So, we have two aspects in the description of ensemble of hydrogen bonds: (1) computer methods allow to evaluate a configuration of any hydrogen bridge $O-H \dots O$, i.e. distance $R(O \dots O)$ and angles $H-O \dots O$ and $-O \dots O$ on the basis of the total potential in which H-bond is not separated; (2) vibrational spectra allow to find the distribution of stretching frequencies $P(\nu)$ and distributions of corresponding energies of hydrogen bonds $P(E)$ for different temperatures. Combination of these aspects makes it possible to determine how energy of H-bond (or frequency ν_{OH}) must depend on the set of geometrical parameters of the hydrogen bridge $\{G\}$ in order to describe distributions of frequencies $P(\nu, T)$ obtained from experimental spectra of molecules HOD at different temperatures. Required expression $E(\{G\})$ we name the potential of H-bond.

We have offered in [6] the method for calculation of the potential of H-bond on a basis of both spectroscopic data and the known empirical correlations between spectra and the results of struc-

* Corresponding author. Fax: +7 383 330 73 50.

E-mail address: efimov@kinetics.nsc.ru (Y.Ya. Efimov).

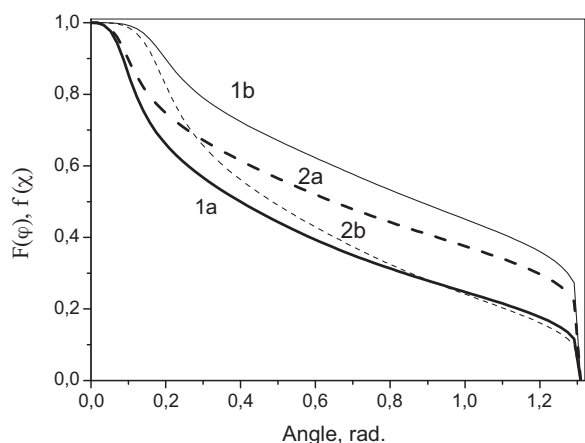


Fig. 1. Factors of weakening of hydrogen bond due to the bend of angles φ (thick curves 1a and 2a) and χ (curves 1b and 2b). Curves 1 correspond to a version 1: Eq. (5a), curves 2 correspond to a version 2: Eq. (5b). Angles φ and χ are in radians.

tural investigations. Two simplest possibilities were considered: the H-bond potential depends only on the length of the hydrogen bridge, $R_{O...O}$, or only on the angle of its bend φ ($H-O...O$). The assumption of one-parametrical potential of H-bond allowed us to find this potential strictly; however the obtained interrelations between geometrical parameters, frequency of the OH vibration and the energy of hydrogen bond have turned out to be in the evident contradiction with other known data. Hence, the one-parametrical description of the potential of H-bond is insufficient.

In [7] the developed method has been used for designing many-parameter potentials of hydrogen bond. The two cases were investigated in details, when the energy depends simultaneously on two geometrical parameters of the hydrogen bridge: either $R_{O...O}$ and $\varphi(H-O...O)$ or $\varphi(H-O...O)$ and $\chi(-O...O)$. Here we present more perfect variant of the solution for two-parametrical potentials and also compare the results following from it with experimental spectra and with data of computer simulations of water.

2. Theory: designing of multiparametric potentials of H-bond consistent with spectroscopic experiment

According to the fluctuation theory of hydrogen bonding, wide bands of stretching vibrations of water molecules in a liquid are a consequence of the statistical distribution of configurations of hydrogen bridges $O-H...O$ [3]. They differ from each other with geometrical parameters and energies of H-bonds that lead to various low-frequency shifts of the vibration frequencies of OH groups relative to non perturbed (without H-bonds) values [3,8]. In static approximation, the distribution of frequencies of these vibrations at a temperature T represents a statistical contour $P(\nu)$ that can be well described by Boltzmann's formula [2]:

$$P(\nu, T) \sim W(\nu) \exp \left[\frac{-E(\nu)}{k_B T} \right]. \tag{1}$$

Here $E(\nu)$ is the energy of the hydrogen bond corresponding to given frequency ν , and $W(\nu)$ is a degeneracy of states; the latter represents a fraction of configurations of the hydrogen bridges capable to give the frequency ν . Functions $W(\nu)$ and $E(\nu)$ do not depend on temperature and can be obtained from experimental vibrational spectra of molecules HOD diluted in D_2O (in order to exclude intra- and intermolecular couplings between different oscillators OH) as it was done in our works [3,5]. The idea of the approach offered in [6] consists in filling the phenomenological formula (1) by structural content. We want to express the energy of hydrogen bond

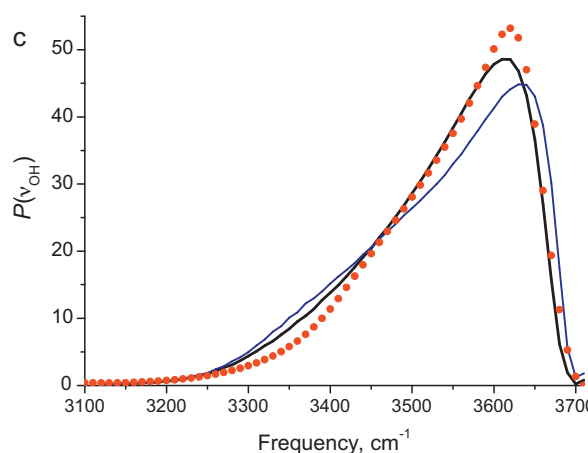
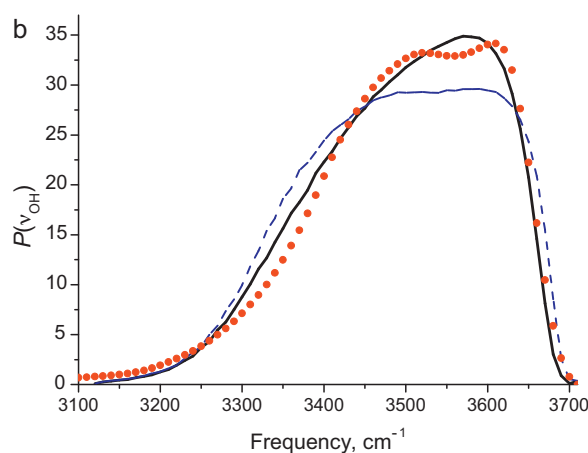
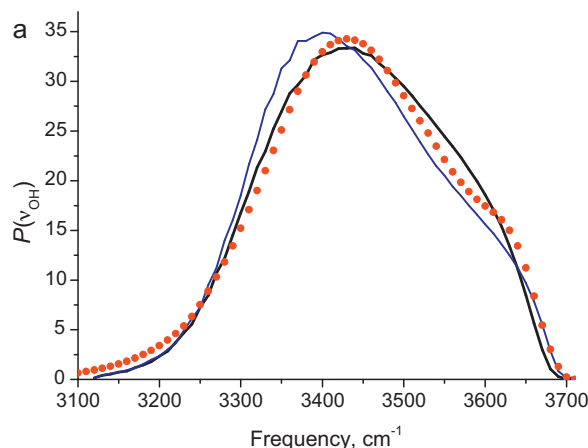


Fig. 2. Distributions of frequencies of stretching vibration of the HOD molecules (diluted in D_2O). Calculations according to the (φ, χ) -potential: thick lines correspond to variant 1 [formula (5a)], points – to variant 2 [formula (5b)]. Thin lines: statistical contours calculated from experimental spectra of isotropic component in Raman spectra in Ref. [5a]. (a) 10 °C, (b) 90 °C and (c) 200 °C.

E and its degeneracy W through geometrical parameters of the fragment $O-H...O$ which generate in a spectrum the given frequency ν . There are three parameters of the hydrogen bridge: its length $R_{O...O}$ and two angles φ ($H-O...O$) and χ ($-O...O$) between OH group and a lone pair of proton accepting oxygen atom with direction $O...O$ which mainly influence the frequency ν_{OH} . Thus, to solve the above problem we are to find such dependence of ν (and

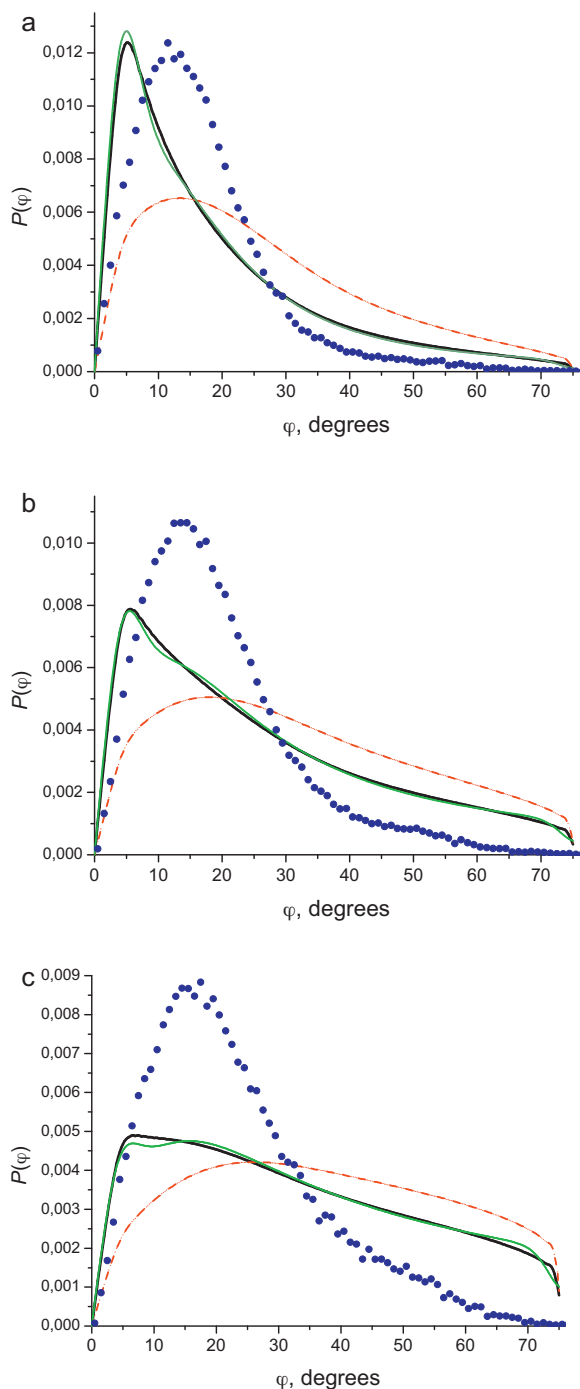


Fig. 3. Distribution functions of angles $P(\varphi)$ calculated according to the formula (7) using the (φ, χ) -potential in comparison with distributions obtained from molecular dynamics models. Thick lines: variant 1, thin dashes: variant 2, gray lines (practically coinciding with variant 1): calculations with the (R, φ) -potential; points: results of molecular dynamics. (a) 10 °C, (b) 90 °C and (c) 200 °C.

thereby E) on (R, φ, χ) which would describe the shape and temperature evolution of bands in experimental spectra according to the formula (1).

In [6] two elementary models have been considered, when the frequency ν_{OH} (and also energy of H-bond) depends on a single parameter: lengths of the bond R (how it was supposed in [9–11]), or its bend φ (as in [12,13]). In these models the task in view has unequivocal solutions: $\nu_{OH}(R)$, or $\nu_{OH}(\varphi)$ accordingly. However these formal solutions are physically unsatisfactory as they contradict the dependence of the frequency ν_{OH} and energy of H-bond on

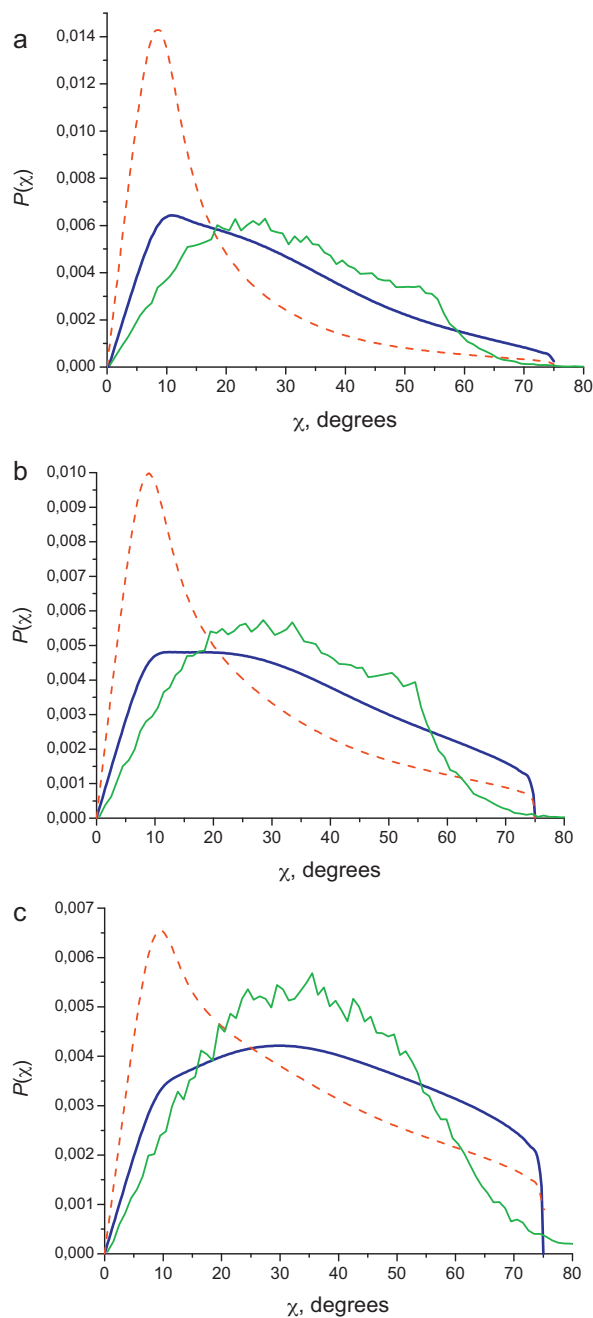


Fig. 4. Distribution functions of angles $P(\chi)$ calculated with (φ, χ) -potential. Thick lines: variant 1, dashes: variant 2; thin lines correspond to molecular dynamics results. (a) 10 °C, (b) 90 °C and (c) 200 °C.

the geometry of the hydrogen bridge that are known in a number of concrete cases.

If the desired potential of hydrogen bond depends on several geometrical parameters then the search of dependence $\nu_{OH}(G)$ leads to the incorrect reverse problem whose solution demands special approaches and simplifying assumptions. In [7] an attempt of designing two-parameter potentials of hydrogen bond has been made when its energy depends on two geometrical parameters of the hydrogen bridge: either $\{R_{O...O}$ and φ (H–O...O) or $\{\varphi$ (H–O...O) and χ (–O...O) $\}$.

Calculation is based on two simplifying assumptions. First, it is postulated that the degeneracy $W(R, \varphi, \chi)$ is defined by purely geometrical probability for the proton-donor group O–H of one water molecule to meet a proton acceptor atom O of other molecule at

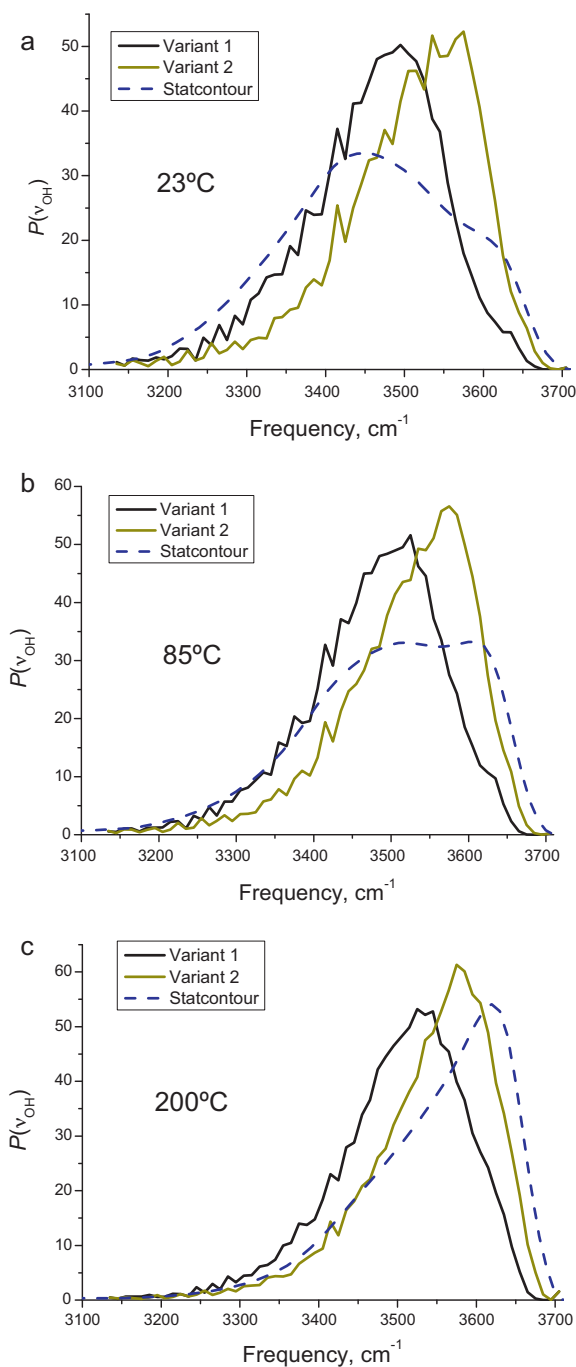


Fig. 5. Distributions of OH vibration frequencies of HOD molecules calculated on the base of the (φ, χ) -potential with (φ, χ) data set from molecular dynamics model of water. Thick lines: variant 1, thin lines: variant 2, dashes: statistical contours from Raman experiment [5a]. (a) 10 °C, (b) 90 °C and (c) 200 °C.

distance $R_{O \dots O}$ with the given angles φ and χ :

$$W(R, \varphi, \chi) = 4\pi R^2 \sin(\varphi) \sin(\chi). \quad (2)$$

Thus, the degeneracy of the given configuration of the hydrogen bridge does not depend on H-bond energy, as it must be. The latter defines the total probability of realization of such configuration for a temperature T by a multiplier $\exp[-E(R, \varphi, \chi)/k_B T]$, as well as in the formula (1).

Secondly, it is accepted that influence of the hydrogen bond length R and both angles of its bends φ and χ on the low-frequency shift of frequency ν_{OH} relative to non perturbed (“monomeric”)

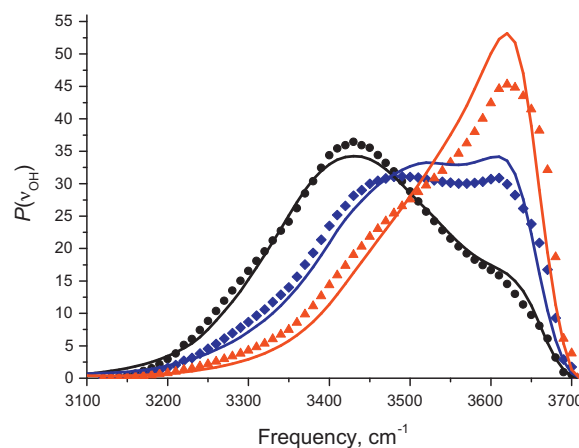


Fig. 6. Frequency distributions of stretching vibration of the HOD molecules (diluted in D_2O). Points represent calculation according to the (R, φ) -potential of hydrogen bonds by formula (9) with $\nu(R, \varphi)$ dependence under formulas (10)–(13). Circles: 23 °C, diamonds: 85 °C, and triangles: 200 °C. Lines are statistical contours calculated from experimental spectra of isotropic component in Raman spectra in [5a].

value $\nu_u = 3707 \text{ cm}^{-1}$ is multiplicative:

$$(\nu_u - \nu_{OH}) = \Phi(R) F(\varphi) f(\chi). \quad (3)$$

3. Results and discussion

3.1. Potential with two angles

Let the frequency ν_{OH} does not depend on the bond length R and is entirely defined by angles of its bend φ and χ that weaken H-bond (in the range from the minimum possible frequency for water $\nu_{\min} \approx 3120 \text{ cm}^{-1}$ for $\varphi = \chi = 0$ [3] up to $\nu_u = 3707 \text{ cm}^{-1}$ for the limiting value of any angle). Then it is possible to write down the relation:

$$(\nu_u - \nu_{OH}) = (\nu_u - \nu_{\min}) F(\varphi) f(\chi). \quad (4)$$

It is reasonable to consider that functions $F(\varphi)$ and $f(\chi)$ decrease monotonously from unit to zero with increasing a corresponding angle from zero (linear hydrogen bond) to the limit values φ_{\lim} or χ_{\lim} that leads to breakage of this bond. The lower and upper estimations of product $F(\varphi) \cdot f(\chi)$ were made in [7] under the assumption about symbiosis in the behavior of functions $F(\varphi)$ and $f(\chi)$. These two borders designated as $\Phi_1(\alpha)$ and $\Phi_2(\alpha)$ were presented in [7]. The optimum solution was searched numerically using a method of histogram integration (see lower); the best fitting to the function $W(\nu)$ in the formula (1) (known from the infrared experiments) was the criterion of the solution quality. In the given paper two variants are considered for search of functions $F(\varphi)$ and $f(\chi)$:

$$F(\varphi) = \Phi_1(\varphi)^a, \quad f(\chi) = \Phi_2(\chi)^b, \quad (5a)$$

$$F(\varphi) = \Phi_2(\varphi)^u, \quad f(\chi) = \Phi_1(\chi)^v. \quad (5b)$$

Limiting angles φ_{\lim} and χ_{\lim} have been set equal to 75 degrees: it influences only the scale of an axis of angles (see [7]) and can be modified if necessary. A procedure of histogram integration is as follows. We go over a lot of independent pairs of angles (φ, χ) , with equal small steps and with equal weights in the range $[0-75^\circ]$ each. Then the product $dW(\varphi, \chi) = \sin(\varphi) \cdot \sin(\chi)$ is calculated as the contribution of the given angle pair to a degeneracy of the states (2) that generates frequency ν_{OH} defined by formula (4) for the given pair of angles. The calculated quantity dW is added to the contents of the “box” (channel) of histogram (with width 10 cm^{-1}) that corresponds to a frequency $\nu_{OH} \pm 5 \text{ cm}^{-1}$. Thus, about 10^6 pairs of angles are analyzed, each of “boxes” being contained the sum of

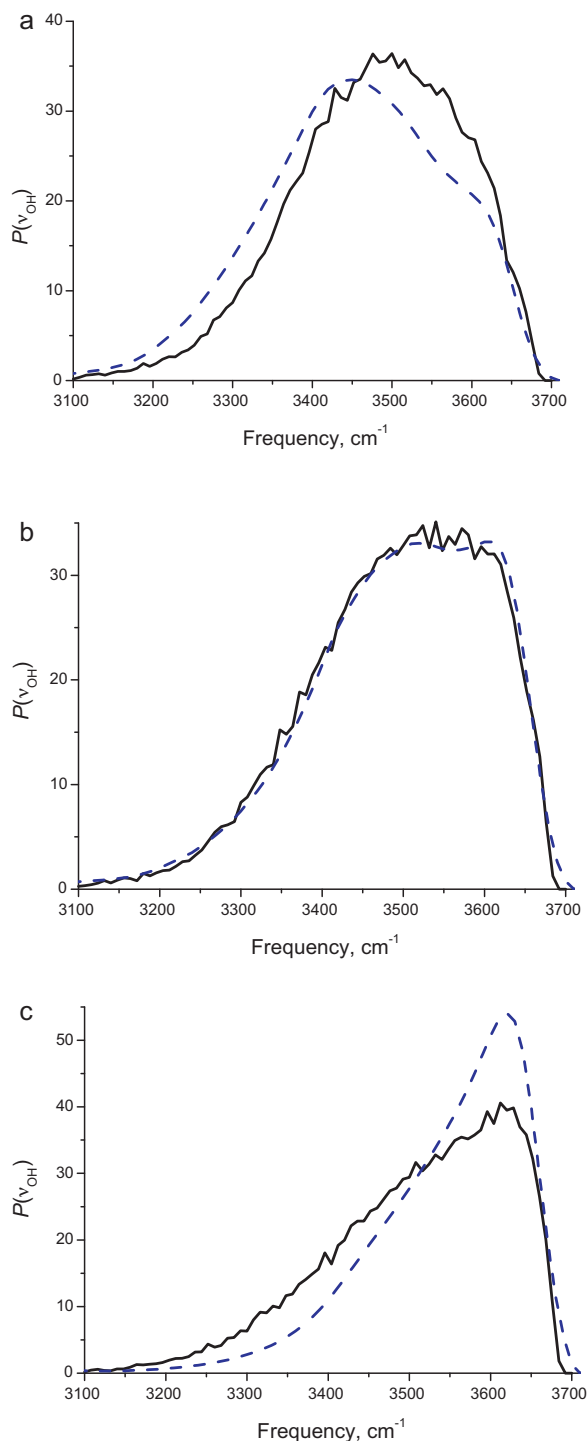


Fig. 7. Distributions of OH vibration frequencies of HOD molecules calculated on the base of the (R, φ) -potential by formula (9) with (R, φ) data from molecular dynamics model of water. (a) 23 °C, (b) 85 °C and (c) 200 °C. Solid lines – calculation; dashes – statistical contours obtained from experimental spectra.

contributions $dW(\varphi, \chi)$ only of those pairs which generate frequency $\nu_{\text{OH}} \pm 5 \text{ cm}^{-1}$. The best agreement of calculated function $W(\nu)$ with the experimental one has been found for the first variant at $a=0.67$, $b=0.42$ in the formula (5a), and for the second variant at $u=0.47$, $v=0.75$ in the formula (5b). In both cases the sum of powers in functions Φ_1 and Φ_2 is close to unit; that is clear as each of them approximates product $F(\varphi)f(\chi)$. The functions obtained are displayed in Fig. 1. Substitution (5) into (4) allows to connect fre-

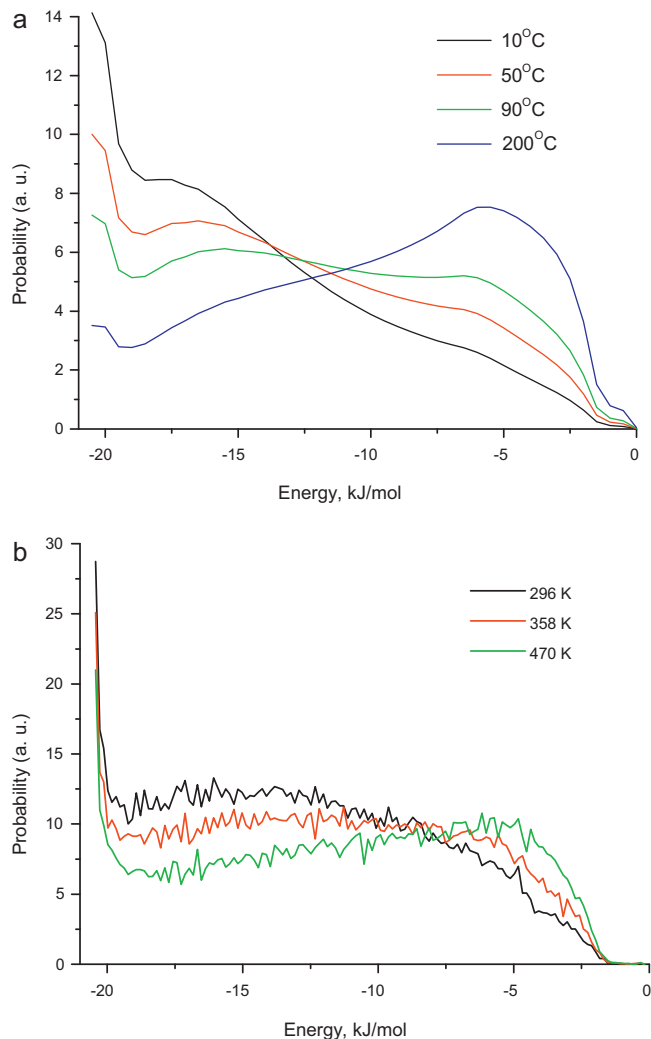


Fig. 8. Distribution functions of H bond energy (in arbitrary units) according to (R, φ) potential. (a) Calculations by the histogram integration method in the frames of the fluctuation theory; thick lines: 10 °C, dashes: 50 °C, dots: 90 °C, thin lines: 200 °C. (b) Calculations by the molecular dynamics models using the same potential of H-bond $E(R, \varphi)$; thick lines: 23 °C, dots: 85 °C, thin lines: 200 °C.

quency ν with angles φ and χ , i.e. solves a problem in the given formulation.

Test of the found solution by a method of histogram integration shows that reconstructed function $W(\nu)$ corresponds rather well to experimental one for both variants of the definition of functions $F(\varphi)$ and $f(\chi)$. Some small distinctions reflect the approximate character of the solution. In [7] other solution differing from given here has been given; that variant led to a little bit worst reconstruction of $W(\nu)$.

Spectra of OH vibrations of molecules HOD are calculated similarly to evaluation of the function $W(\nu)$. However, “boxes” of the histogram contain now not contributions of different pairs of angles to the degeneracy $dW(\varphi, \chi) = \sin(\varphi) \sin(\chi)$, but their products with the Boltzmann factor $\exp[-E(\varphi, \chi)/k_B T]$ (according to formula (1)) for the appropriate frequencies. The energy of hydrogen bond in a configuration (φ, χ) is approximated by the formula:

$$E(x) = -0.07x + 0.000104x^2 - 0.493 \times 10^{-6}x^3 + 0.1224 \times 10^{-8}x^4 - 0.828 \times 10^{-12}x^5 \quad (6)$$

found in [4]. Here $x = 3707 - \nu_{\text{OH}}$ (E in kJ/mol, ν_{OH} in cm^{-1}). Frequency ν_{OH} should be expressed therein through φ and χ by means of formulas (4) and (5).

Spectra calculated by this way are shown in Fig. 2. One can see that they rather well reproduce experimental spectra. This demonstrates a good quality of the (φ, χ) -potential for hydrogen bond designed by us. In calculated spectra, as well as in experiment, “Walrafen’s shoulder” nearby 3650 cm^{-1} is weak for $T = 10^\circ\text{C}$; for 90°C it reaches the intensity of a low-frequency maximum ($\approx 3500\text{ cm}^{-1}$), and for $T > 100^\circ\text{C}$ it becomes the dominating component. Within the frames of the given model this picture can be explained by sharp growth of the fraction of the bent hydrogen bonds with increasing temperature. The model also properly describes the behavior of spectra at negative temperatures: shift of the maximum toward lower frequencies, narrowing of the band and disappearance of the shoulder of “weak” H-bonds in super-cooled water.

At last, having modified the formula (1) of the fluctuation theory it is possible to calculate distribution function of angles φ and χ corresponding to the given potential, and also its temperature dependence:

$$P(\varphi, \chi, T) = Q^{-1}(T) \sin(\varphi) \sin(\chi) \exp \left[\frac{-E(\varphi, \chi)}{k_B T} \right] \quad (7)$$

Calculated distributions $P(\varphi, \chi)$ significantly broaden with increasing temperature, and in distribution of angles χ (orientations of lone-pairs) an obvious shoulder appears for large angles. Unfortunately, experimental data on pair distribution of these angles in liquid water are unknown to us.

Integration of the pair distribution function of angles $P(\varphi, \chi)$ over φ or χ gives one-dimensional distributions of angles $P(\chi)$ and $P(\varphi)$ that are shown in Figs. 3 and 4 together with the results of next Section 3.2. Though they do not reproduce well the distributions of the same angles obtained from computer models, but are much more similar to them than calculated in [6] on the basis of one-parametrical potential $E(\varphi)$.

In addition, we calculated the distributions of frequencies of the OH vibrations using the same (φ, χ) -potentials (formulas (4) and (5)) applied to a set of pairs angles (φ, χ) , which were taken from molecular dynamics models (see Appendix A). They rather poorly agree with the experiment (Fig. 5). For low temperatures the version 1 (formula (5a)), and for high temperatures the version 2 (formula (5b)) appears a little bit best.

3.2. Potential with the H-bond length and the angle of its bend

Let us consider now the second type of two-parametrical potentials. Let frequency ν_{OH} (and energy of H-bond) depends on the length of this bond $R = R_0 \dots_0$ and the angle φ . Then purely geometrical probability (without the accounting for a role of energy) to meet the oxygen atom of proton accepting molecule, located at a distance $R \pm dR/2$ and an angle $\varphi \pm d\varphi/2$ relative to OH group of proton donor molecule H_2O , is defined by differential of the area of conic section of a spherical layer:

$$W(R, \varphi) dR d\varphi = 4\pi R^2 \sin(\varphi) dR d\varphi. \quad (8)$$

Then the general formula (3) transforms to

$$(v_u - \nu_{\text{OH}}) = \Phi(R) F(\varphi). \quad (9)$$

As a radial dependence $\Phi(R)$ we used the empirical correlation found for ν_{OH} frequency in the spectra of crystalline hydrates, where hydrogen bonds are close to linear [14] (R in angstroms):

$$\Phi(R) = 2.222 \times 10^7 \exp(-3.925R). \quad (10)$$

The search for function $F(\varphi)$ is very complicated problem. In [7] the approximate solution is received in rather subtle way; it can be analytically approximated by the sum of two exponents

monotonously falling down to zero for big angles:

$$F_1(\varphi) = \exp(-0.3 - 1.25\varphi) + 0.26 \exp(-100\varphi^2), \quad (11)$$

(angle φ in radians). However, unlike curves $F(\varphi)$ and $F(\chi)$ in Fig. 1, this function does not vanish when φ tends to the limit value. As a result, the calculated distribution of angles $P(\varphi)$ does not become zero at φ_{lim} . To correct this shortcoming we multiply the angular factor of weakening of H-bond (11) by the function which does not deform its form in the basic area of values but sharply decreases close to φ_{lim} :

$$G(\varphi) = \exp \left[-\frac{\varphi}{1.29} \right]^{50}. \quad (12)$$

We use as $F(\varphi)$ in all further calculations the modified function:

$$F(\varphi) = F_1(\varphi) G(\varphi). \quad (13)$$

Substitution of formula (13) into (9) defines dependence of frequency ν_{OH} on the length of H-bond and the angle of its bend; subsequent use of formula (6) defines dependence of the energy of H-bond on these parameters. Verification of the found solution of a reverse problem by calculation of function $W(\nu)$ (i.e. a direct problem; the way of calculation is described above) confirms its quite good quality if $R_{\text{lim}} = 3.05 \text{ \AA}$. Such short limit means that excessive lengthening of hydrogen bond in liquid water results in its breakage with switching to new H-bond with more efficiently located partner. In crystalline hydrates or water dimers in gas phase such a possibility is absent and much lengthy (up to 3.5 \AA) and weaker H-bonds are found in experiments.

Fig. 6 shows the spectra calculated by formula (9) on the base of parameters (R, φ) from formulas (10)–(13) in comparison with experiment for three selected temperatures. We see that our approximate solution for (R, φ) -potential gives a quite satisfactory description of spectra.

Distributions of geometrical parameters of the hydrogen bond corresponding to the given model of potential are defined by the expression:

$$P(R, \varphi, T) = Q^{-1}(T) 4\pi R^2 \sin(\varphi) \exp \left[\frac{-E(R, \varphi)}{k_B T} \right], \quad (14)$$

where $Q(T)$ is the statistical integral normalizing distribution (14) at a temperature T .

One-dimensional distribution functions of angles φ have the form and temperature behavior practically coinciding with those calculated with potential $E(\varphi, \chi)$ in its first version (Fig. 3). It is a little unexpected as no efforts were made for coincidence of two essentially different solutions. Thus, obtained distributions $P(\varphi)$ are rather far from the distributions directly following from computer models (points in Fig. 3).

Distribution functions of bond lengths $P(R)$ obtained by the integration (14) over φ are much wider than those found in one-parametrical approach of potential $E(R)$ [6]. However they still cardinally differ from the experimental radial distribution functions of water by absence of a maximum of distribution. The reason is clear: the absence of repulsive (van der Waals) interactions in a radial part of our potential. It is a basic difference of our hydrogen bond potential from the total potentials of intermolecular interactions used in computer simulations. Not suitable for modeling the structure of a liquid, it is intended for the quantitative description of properties of separate hydrogen bonds and their systems in already created (with the total potential of interactions) computer models.

Distributions of OH vibration frequencies calculated by formulas (9)–(13) for the set of configurations (R, φ) in molecular dynamics models are shown in Fig. 7. They significantly better agree with the experiment than if pairs (φ, χ) are used with the (φ, χ) -potential (cf. Fig. 5). These pictures are, may be said, a main result (or goal) of this paper. They demonstrate that it is possible to construct such an

H-bond potential which give correct description of OH frequencies on the base of geometrical parameters of the H-bridge. They show also that the H-bond length R and the angle of its bend φ must be used as the principal parameters.

The method of histogram integration allows us to calculate the distribution of hydrogen bond energies at various temperatures in a way similar to calculations of functions $W(\nu)$ and $P(\nu, T)$. Fig. 8a shows that at low temperatures strong “ice-like” hydrogen bonds with energy nearby 20 kJ/mol prevail in water. The fraction of weaker H-bonds monotonously decreases with vanishing E (curve 1). At 200 °C the inverse situation takes place, and weak H-bonds with energy ≈ 6 kJ/mol dominate (curve 4). It is interesting that all energies from 6 to 20 kJ/mol are presented practically with equal weight at 90 °C (curve 3). A sharp maximum in the distribution $P(E)$ and break at -21 kJ/mol has no physical meaning. Termination at -21 kJ/mol reflects the absence of energies smaller than -21 kJ/mol in the used potential; infinite value of $P(E)$ at E_{\min} arises from $P(E) = P(\nu) / |\partial E / \partial \nu|$ because the $E(\nu)$ dependence in equation (6) has a minimum at E_{\min} where the derivative $|\partial E / \partial \nu|$ vanishes. However function $P(E)$ does not diverge; that is confirmed by the calculation over discrete intervals of energies E in a method of histogram integration.

Distributions of H-bond energies obtained from the set of O–H...O configurations in molecular dynamics models are presented in Fig. 8b. They qualitatively agree with calculations according to the fluctuation theory (Fig. 8a).

4. Conclusions

Two important problems have been solved in the paper:

1. We managed to find the quantitative dependence of H-bond energy on the geometrical parameters of hydrogen bridge O–H...O (the H-bond potential) that is consistent with the experimental band shape of water OH vibrations and their temperature evolution in the frames of the fluctuation theory of hydrogen bonding. It became possible due to extremely high sensitivity of the OH frequency on H-bond energy.
2. The designed H-bond potential allows us to calculate the distributions of OH frequencies on the base of geometrical parameters of the H-bridge found in the molecular dynamics models of water. This approach to calculation of the stretching OH frequencies is alternative to well known quantum mechanical procedures [17]. We show that spectra, calculated in such a manner, agree quite well with experimental spectra of HOD molecules dissolved in D₂O for temperatures from 10 up to 200 °C, if H-bond length $R(\text{O} \dots \text{O})$ and the angle of its bend $\text{H}-\text{O} \dots \text{O}$ are used as the principal parameters. The dependences found can be used also to evaluate H-bond energies and vibrational frequencies when basing on the results of the structural analysis (X-ray, neutrons).

We believe that results of this work (together with data of [6,7]) show that designing of potential of hydrogen bond on the basis of spectroscopic experiment is not a hopeless problem. The solutions

offered here can be considered as the very first approach which can be improved by refining of the made assumptions.

Acknowledgement

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Appendix A. Molecular dynamics computational details

We used molecular dynamics models for water consisting of $N = 3456$ molecules at different temperatures and density 1 g/cm^3 . Models were generated with the Poltev–Malenkov's potential of interaction [15,16] which is analogous to well-known three center SPC potential. All the characteristics considered below were averaged using ten independent models. According to the found solution for potential of hydrogen bond (see Sections 1 and 2), water molecules were considered as partners in H-bond if $R_{\text{O} \dots \text{O}} < 3.05 \text{ \AA}$. For each pair of molecules the geometrical parameters of the given H-bond were taken from the model. The angle χ necessary for calculations was found as follows. In a plane perpendicular to two O–H groups of proton-accepting water molecule and passing through bisector of the H–O–H angle we constructed directing vectors for two lone pairs with a tetrahedral angle between them. The angles between these vectors and a direction O...O: χ_1 and χ_2 were calculated, and the least of these angles gave value of χ for the given configuration of hydrogen bond.

Vibrational frequencies ν_{OH} were calculated for each O–H...O fragment using formulas of sections 1 or 2 and distributions of all parameters were constructed. Corresponding histograms were compared with results of theoretical calculations and also with the experimental spectra. In a similar way energies of hydrogen bonds were calculated and their distributions were constructed for various temperatures.

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