Thermodynamic functions of liquid water calculated from the temperature evolution of the vibration spectrum contour

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Abstract

Configurational contributions of hydrogen bonds to thermodynamic properties of water (internal energy, entropy, and heat capacity) are calculated on the basis of statistical distributions of frequencies of the OH vibrations of liquid water, calculated earlier from the experimental Raman spectra in frameworks of the fluctuation theory of hydrogen bonding. Distributions of the energy of hydrogen bonds are determined. It is shown by comparison with computer experiments that previously established dependence of energy on frequency, $E(\nu)$, must be considered in this formalism as the effective energy of hydrogen bonding averaged over those configurations of hydrogen bridge O–H···O which lead to the given frequency ν in the vibrational spectrum. Contribution of van der Waals interactions not affecting the frequency shift to heat capacity is evaluated.

1. Introduction

According to the fluctuation concept of hydrogen bonding [1], wide bands in the vibrational spectra of OH oscillators of water reflect the equilibrium statistical distribution of geometrical configurations of the O–H···O hydrogen bridge caused by fluctuations in the local environment of various H_2O molecules in a liquid. Resulting distribution of frequencies of the stretching vibrations of OH groups can be written following to Zhukovsky [2] as a kind of Boltzmann distribution.

$$P(\nu, T) = Q^{-1}(T)\, W(\nu)\, \exp\left(-\frac{E(\nu)}{k_B T}\right). \qquad (1)$$

Here, $E(\nu)$ is supposed to be the energy of H-bond in which OH oscillator with the given frequency ν is involved and $W(\nu)$ is the statistical weight (degeneracy) of such configurations. There was suggested by Zhukovsky that both functions $E(\nu)$

and $W(\nu)$ do not depend on temperature. In [3], we have developed methods for practical determination of these functions on the basis of the temperature evolution of the contour shape of the experimental Raman spectra of HOD molecules diluted in D_2O. The numerical expressions for $E(\nu)$ and $W(\nu)$ have been found and occur to be really temperature invariant if density is constant. It has allowed us to calculate the shapes of contours in the Raman [3] and IR spectra [4] and to show that they agree fairly well with experimental ones at temperatures from 0 up to 200 °C. Moreover, essential distinctions between the form and position of these two types of spectra are described quantitatively.

Though the fluctuation theory of hydrogen bonding originally was advanced for treatment of spectral contours, it gives also in the natural way the thermodynamic information. That is possible because of the connection between the frequency of OH oscillator and the energy of hydrogen bond giving by the function $E(\nu)$. Therefore, distribution of frequencies $P(\nu,T)$ can be transformed to the distribution of energy (see Section 3), and thermodynamic functions can be calculated then by usual formulas of statistical physics. For average energy of hydrogen bonding in the whole ensemble

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of molecules takes place

$$< E(T) > = \int E(\nu) P(\nu, T) \mathrm{d}\nu = -\frac{\mathrm{d} \ln Q(T)}{\mathrm{d}\beta}, \qquad (2)$$

where $\beta = (k_B T)^{-1}$ and $Q(T)$ is the statistical integral

$$Q(T) = \int W(\nu) \exp\left(-\frac{E(\nu)}{(k_B T)}\right) \mathrm{d}\nu. \qquad (3)$$

The contributions of hydrogen bonding reflect the change of thermodynamic properties of water due to temperature re-organization of the network of hydrogen bonds and are usually called as the configurational contribution (see ref. [6], p. 174). The configurational contribution of H-bonds to internal energy of water twice exceeds average energy (2) since each molecule has two oscillator OH, i.e. twice represents itself as the donor of a proton in the network of hydrogen bonds: $U(T) = 2 <E(T)>$. The configurational contribution to the heat capacity is $C_v = \mathrm{d}U(T)/\mathrm{d}T$. Here, one must have in view the heat capacity at constant volume as it is shown that formula (1) works well only at constant density of a liquid.

The aim of the present paper is to calculate the configurational contributions to thermodynamics of water on the basis of the fluctuation concept of hydrogen bonding. The results are given in Section 2. In fact, they are the first successful attempt to obtain thermodynamic information for H-bonded liquids from the analysis of the spectrum band shape. Calculation of thermodynamic functions allow us also to consider some features of the formalism giving by the formula (1). The point is that the meaning of function $E(\nu)$ is not quite clear. On the one hand, it may be considered as a generalization of the known empirical Badger-Bauer correlation connecting position of a maximum of the stretching OH band with the averaged energy (enthalpy) of the whole assemblage of hydrogen bonds in a liquid. However, it is well known that the frequency of OH oscillator depends on the van der Waals interactions too (see, e.g. [5]). Therefore, $E(\nu)$ in the formula (1) has a sense of the effective H-bond energy (or energy of effective hydrogen bonding) determining the frequency of the OH oscillator that does not reduced to the pairwise contact. Comparison of our calculations with the computer experiments allows one to elucidate the sense of this effective interaction (Section 3).

2. Configurational contributions to thermodynamic functions

The configurational contribution to internal energy, $U(T)$, at any necessary temperature we determined by direct calculation of the integral (left part of the formula (2)) on the basis of functions $E(\nu)$ and $W(\nu)$, which were found in [3]. Calculations using the statistical integral $Q(T)$ (right part of the formula (2)) are much less precise since they consist of two steps and involve differentiation. Temperature dependence of $U(T)$ found is shown in Fig. 1 together with experimental
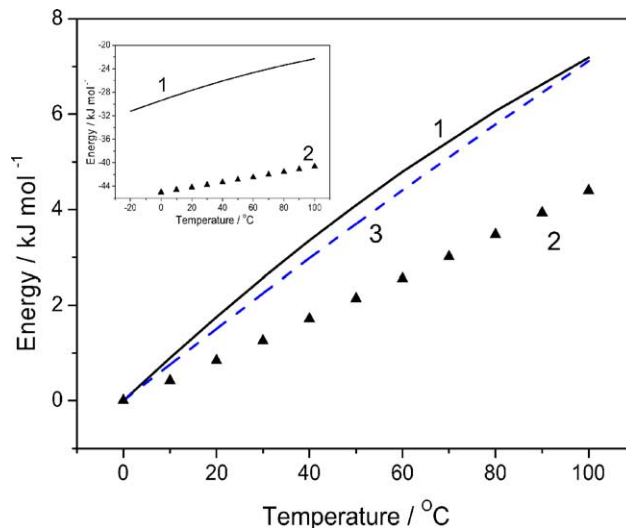

Fig. 1. Relative temperature dependence of internal energy. 1, The calculated configurational contribution to internal energy, $U(T)$; 2, the heat of vaporization of water, L, after [7]; 3, internal energy of water according to data of NIST [13]. At $T = 0\,^{\circ}\mathrm{C}$ all these three functions are maid equal to zero. Insert shows $U(T)$ and $L(T)$ in absolute units.

data. For the purpose of comparison all curves are put equal to zero at $T = 0\,^{\circ}\mathrm{C}$, whereas data in absolute units are depicted in insert. Calculation of the heat capacity through derivatives is also inconvenient, for it demands an analytical representation of all functions involved; therefore, we define it as $C_v(T) = U(T + 1/2) - U(T - 1/2)$, i.e. calculating a difference of energies in one degree. The temperature behaviour of the heat capacity is shown in Fig. 2.

Calculations show that $U(T) = -27.66\,\mathrm{kJ\,mol}^{-1}$ at 293 K. Hence, the energy $-13.83\,\mathrm{kJ\,mol}^{-1}$ ($\sim 3.3\,\mathrm{kcal\,mol}^{-1}$) accounts for one H-bonded OH oscillator that corresponds to usual estimation of the average energy of hydrogen bonding in water [6]. This value, certainly, is less by module than the heat of evaporation, L, which is a measure of full energy of interaction between molecules of water and amounts to $44.2\,\mathrm{kJ\,mol}^{-1}$ at this temperature [7]. The value $[-L(T) - U(T)]/2$ represents, obviously, that part of internal energy (per one OH group) which does not influence the shift of its frequency. At 293 K, it is $-8.3\,\mathrm{kJ\,mol}^{-1}$.

The temperature trend of the calculated configurational contribution to energy, as Fig. 1 shows, is very close to that of the experimental internal energy at constant density of $1\,\mathrm{g\,cm}^{-3}$. However, distinctions between them, which are insignificant in scale of change of $U(T)$, result in essential difference in the behaviour of the heat capacity (see Fig. 2a). The calculated configurational contribution to the heat capacity changes much more strongly with temperature that is determined by larger curvature of the calculated dependence of $U(T)$ in comparison with experimental one. However, it is important that calculation reproduces a maximum in the temperature behaviour of the isochoric heat capacity, discovered recently for supercooled water (Fig. 2a); only in calculation it is situated at $-25\,^{\circ}\mathrm{C}$, and in experiment at $-5\,^{\circ}\mathrm{C}$.
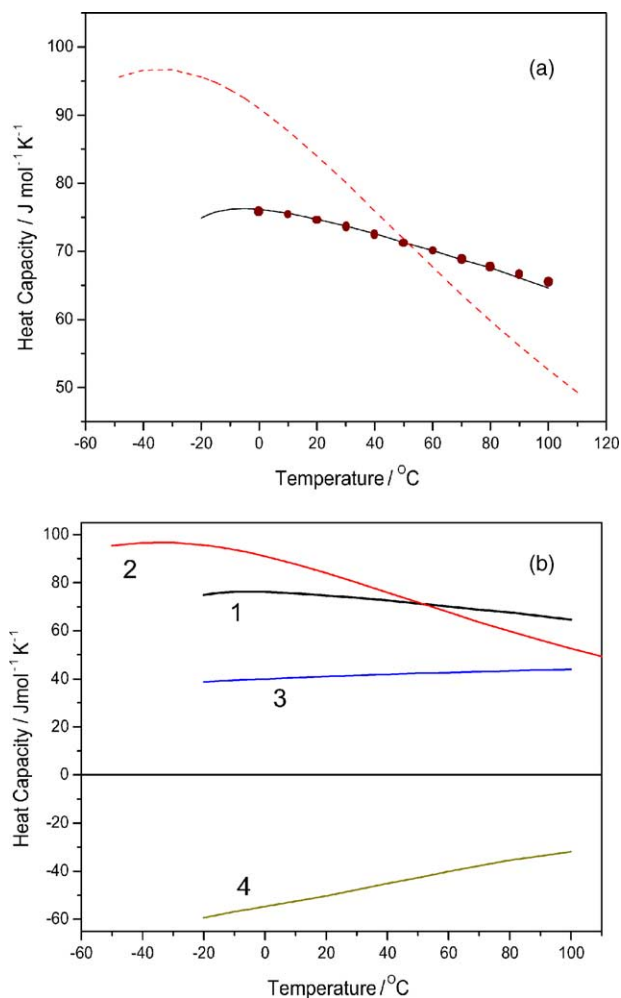
Fig. 2. Temperature dependence of the isochoric heat capacities C_v. (a) Solid line: experiment according to data [14,15] at $V = 18.04\,cm^3\,mol^{-1}$, points – data of NIST [13] at density of 1 g cm^{-3}. Dotted line: the configurational contribution of hydrogen bonding to the heat capacity. (b) Various contributions to the heat capacity. 1, Experiment; 2, the calculated configurational contribution of hydrogen bonding; 3, the vibrational heat capacity estimated as two Debye functions with characteristic frequencies of 192 and 583 cm^{-1} [8]; 4, the configurational contribution of the van der Waals interactions calculated as a difference between the experimental heat capacity (1) and theoretical contributions (2) and (3), see the formula (4).

Fig. 2 shows that the calculated configurational heat capacity exceeds a full experimental heat capacity at low temperatures. It means that there is another contribution to the configurational heat capacity, reflecting temperature change of the energy of van der Waals interactions [$C_v(vdW)$], in addition to the contribution taken into account by our model describing changes with temperature of configurations of hydrogen bonding [C_v(H-bond)]. To compensate superfluous value of the C_v(H-bond) contribution, the $C_v(vdW)$ contribution should be negative. Thus, the negative van der Waals energy should be increased in absolute value with growth of temperature. This quite corresponds to usual idea that the network of hydrogen bonds in water becomes more deformed, less "open" with growth of temperature that results in increase

of the number of van der Waals contacts between molecules of water.

Thus, *three* contributions to the heat capacity of water exist, since to the two configurational contributions named earlier it is necessary to add vibrational contribution C_v(vib) caused by the excitation of intermolecular vibrations [6] (intramolecular vibrations at considered temperatures practically are not excited)

$$C_v = C_v(vib) + C_v(H\text{-bond}) + C_v(vdW). \qquad (4)$$

Following to Eisenberg and Kauzmann [6] we have estimated in [7] this vibrational contribution by means of two Debye functions with characteristic frequencies of 192 and 583 cm^{-1} (hindered translations and librations). Then, from Eq. (4) it is possible to calculate also $C_v(vdW)$. The temperature behaviour of all these contributions is shown in Fig. 2b. Hence, we must establish that in considered model of water there is a large negative contribution to the heat capacity from change of those van der Waals interactions, which do not influence the frequency of OH oscillators.

The temperature behaviour of the statistical integral (3) is more convenient to represent using function $S^*(T) = 2k_B \ln Q(T)$, which changes in much smaller limits than $Q(T)$. It is shown in Fig. 3 together with the configurational entropy calculated by usual thermodynamic relation $S(T) = S^*(T) + T dS^*/dT$. We see that calculated curve $S(T)$ as well as $U(T)$ has some larger curvature than experimental one.

It should be noted that in [7] and [8] configurational energy (and then other thermodynamic functions) was calculated simply as $\langle E(v) \rangle$ – without the 'two' factor, that meant treatment $\langle E(v) \rangle$ as energy of whole molecule of water in the given environment that most likely is no true.
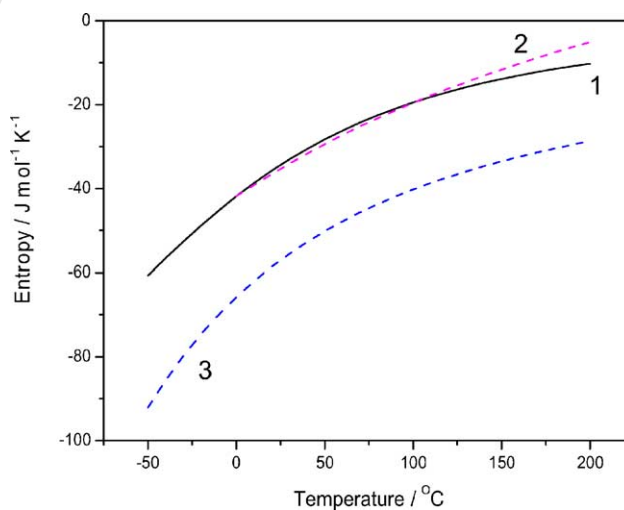

Fig. 3. Temperature dependence of entropy and statistical integral of water. 1, calculated configurational entropy; 2, experimental entropy of water at density of 1 g cm^{-3} [13] (at 0 °C it is maid equal to calculated one); 3, function $-S^*(T) = -2k_B \ln Q(T)$, $Q(T)$ is the statistical integral.
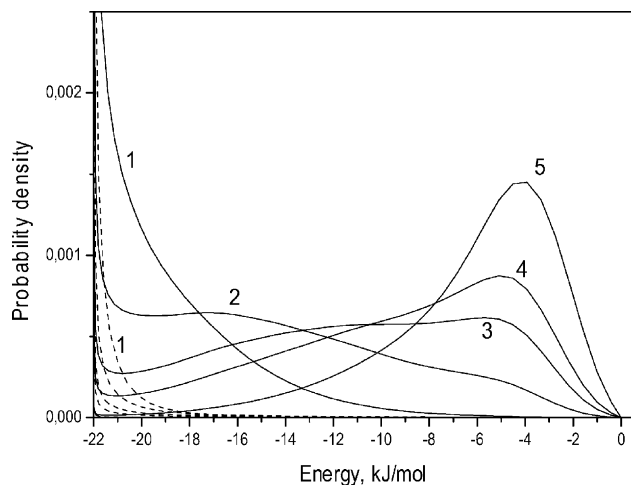
Fig. 4. Distribution of the effective energy of hydrogen bonding calculated at −100 (curves 1), 0 (2), 100 (3), 200 (4), and 1000 °C (5). Solid curves correspond to oscillators with $\nu > \nu_{min} = 3264.7\,\text{cm}^{-1}$, dotted curves to oscillators with $\nu < \nu_{min}$.

3. Distribution of energy of hydrogen bonds

It is easy to transform the distribution of the frequencies of OH oscillators, $P(\nu)$, into the distribution of energy of effective H-bonds in the statistical ensemble of water molecules

$$P(E, T) = P(\nu, T) \left| \frac{d\nu}{dE} \right| = \frac{P(\nu, T)}{|dE(\nu)/d\nu|} \qquad (5)$$

Derivative $dE(\nu)/d\nu$ may be calculated analytically as in [3] an explicit expression for function $E(\nu)$ is given. We shall remind that this function has a minimum at frequency $\nu_{min} = 3264.7\,\text{cm}^{-1}$ in which $E(\nu_{min}) = E_{min} = -22\,\text{kJ}\,\text{mol}^{-1}\,\text{bond}^{-1}$, that corresponds to optimal energy of the hydrogen bond (as in ice). In Fig. 4, distributions of energies for −100, 0, 100, 200, and 1000 °C are presented. They have somewhat unusual form. First, when energy tends to minimal value E_{min}, the distribution densities of energy tend to infinity what is caused by the vanishing derivative $dE(\nu)/d\nu$ in the point of minimum of the function $E(\nu)$. This infinity, certainly, does not result to divergences under calculation of any averaged over energy values since $\int P(E)dE = \int P(\nu)\,d\nu = 1$ follows from the normalization condition for $P(\nu)$. Second, each distribution $P(E,T)$ consists of two branches: one corresponds to OH oscillators with frequency of vibrations greater than ν_{min}, another with smaller (it is shown by a dotted line in Fig. 4). Despite an unusual form of distributions $P(E,T)$, their temperature transformation is quite clear. With growth of temperature the fraction of weak H-bonds increases and the fraction of strong ones decreases. Approximately at 50 °C probabilities of hydrogen bonds with energies from −20 up to −4 kJ mol^{-1} appear practically the same. At very high temperatures (and at constant density of ~1 g cm^{-3} to which all calculations concern) only weak hydrogen bonds in a vicinity −4 kJ mol^{-1} remain predominantly. It is obvious that at such big density they correspond to the extremely bent hydrogen bonds in deformed, but a continuous network.
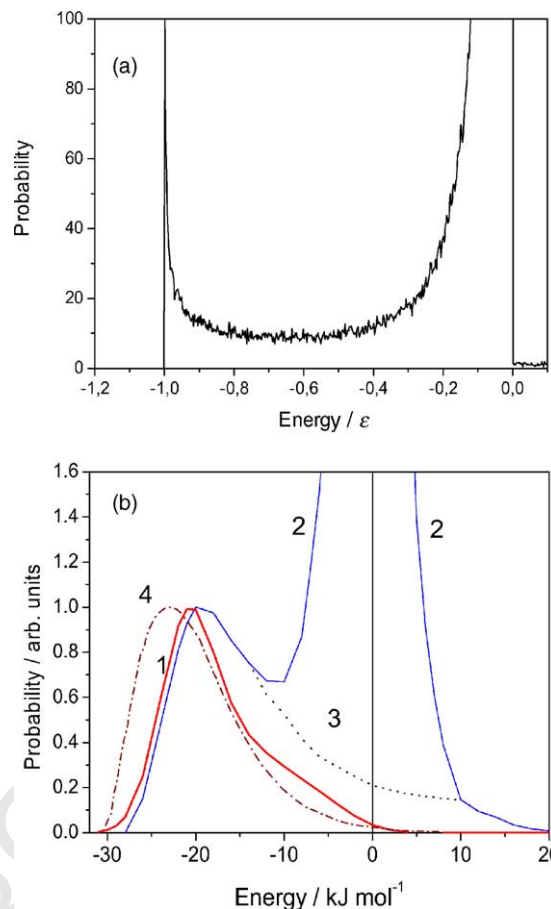

Fig. 5. Distributions of pair energies of interactions. (a) The liquid consisted of Lennard-Jones particles (Monte Carlo technique, $N = 8000$, $\rho^* = 0.8$, $T^* = 0.5$). (b) Liquid water. 1, the distribution function of energy of effective hydrogen bonding $P(E,T)$ calculated by us at $T = 300$ K and convolved with Gaussian of half-widths 7 kJ mol^{-1}; 2, distribution function of pair energies from computer model after Fig. 16 from [11]; 3, the same as (2), but for water molecules with $R_{O\cdots O} < 3.6$ Å; 4, distribution of pair energies from computer model according to the "effective hydrogen-bond definition" proposed by D.L. Bergman, after Fig. 3 from [12].

When speaking about the unusual form of distributions $P(E,T)$ we mean that they are not similar to distributions of energies obtained in computer modeling of water (see, for example, [10–12]). Rahman and Stillinger, authors of the first work on computer modeling of water by the molecular dynamics technique [10], already marked that distribution of pair interaction energies of water molecules essentially differs from that for a liquid consisted of atoms interacting with Lennard-Jones potential $u_{LJ}(r) = \varepsilon[(r_0/r)^{12} - 2(r_0/r)^6]$. Distribution for Lennard-Jones system reveals a singularity when energy tends to the minimal value $-\varepsilon$ (see Fig. 5a), whereas for water in computer modeling no singularity is present here (Fig. 5b). In this respect, our distributions are similar to those for Lennard-Jones liquid, instead of water. This circumstance allows us to understand the probable sense of distributions $P(E,T)$.

Singularity in the Lennard-Jones system takes place because all particles interact with the same potential $u_{LJ}(r)$;

thus, the minimal energy for all pairs of molecules is identical $(-\varepsilon)$ and unequivocal connection between interparticle distance and pair energy exists. In water a situation must be different because the potential of hydrogen bonding (or the potential of full interaction in computer models) depends not only on distance between oxygen atoms, but also on mutual orientation of molecules. Therefore, each particular angular configuration of hydrogen bridge O–H···O determined by structure of the nearest environment must have their own minimum in the dependence of potential energy on distance $R_{O···O}$. As a result, the first singularity has to disappear. This consideration suggests that for comparison with computer experiment it is necessary to smear out our distributions $P(E,T)$ convolving them, for example, with a Gaussian, to account for van der Waals interactions. The result is shown in Fig. 5b. We see that the smeared distribution (Fig. 5b, curve 1) is very similar to the distribution of energy of hydrogen bonding which follows from computer experiments (Fig. 5b, curves 3 and 4). The half-width of the Gaussian, which is necessary for this purpose, is large enough: $7 \, \text{kJ mol}^{-1}$. This value is rather close to the mentioned above energy of van der Waals interactions which does not influence the frequency shift of OH oscillators, $-8.3 \, \text{kJ mol}^{-1}$. All this shows that the energy $E(\nu)$, appearing in the formalism used (1), has the meaning of the effective pair energy of hydrogen bond (created by multiparticle interaction) in which the variety of configurations of the hydrogen bridge is ignored (averaged).

The second singularity in the Lennard-Jones liquid takes place at $E = 0$ (see Fig. 5a). Its origin is other than of the first one. It corresponds to a lot of molecules, which are removed from each other at large distances and as consequence are weakly interacted. Similar singularity is observed also in the molecular dynamics calculations of water (Fig. 5b, curve 2). However, there is an essential distinction. In computer modeling of water, one can construct the distribution of pair energies for molecules involved to "true" or "strict" hydrogen bonds only. Authors of work [11] did that taking into consideration molecules removed from each other no more than at distance $R_{\text{lim}} = 3.6 \, \text{Å}$. Bergman [12] used for this aim his own definition of the effective hydrogen bond. These recipes delete the singularity at zero energy from the distribution leaving only contributions of interactions of the nearest molecules such as hydrogen bonding (see curves 3 and 4 in Fig. 5b). It is remarkable that our curve 1 lies just between these two 'computer' estimations of distribution desired.

But in the Lennard-Jones liquid such a recipe accomplishes nothing. Since pair energy here is an unequivocal function of distance between atoms, introduction of the condition $R < R_{\text{lim}}$ simply limits distribution of energy by value $E = u_{LJ}(R_{\text{lim}})$. This distinction between Lennard-Jones liquid and water once again shows a role of mutual orientations between interacting water molecules: among the near molecules $(R < R_{\text{lim}})$ there are even repulsing ones (with positive pair energy of interaction) – obviously, because of unsuccessful mutual orientations. In our initial distributions $P(E,T)$ positive energies, certainly, are absent (Fig. 4) since the OH frequency is shifted by the "true" hydrogen bonding; positive energies appear only after smearing out $P(E,T)$ (see curve 1 in Fig. 5b).

4. Conclusion

In works [3,4] we have shown that fluctuation theory of hydrogen bonding well reproduces the form of contours of OH vibrations of molecules HOD both in the Raman and infrared spectra and their temperature evolution. It means that formalism based on it, including formula (1), correctly reflects essential properties of the ensemble of hydrogen bonds in water. This success has stimulated us to try to expand the area of applications of the abovementioned theory to other properties of liquid water. The calculation of configurational contributions to thermodynamic functions done here allows us, by comparison with experiment and computer simulations, to distinguish the role of hydrogen bonding and van der Waals interactions. On the other hand, the results obtained clarify some principal conceptions constituting the basis of the theory itself. It was implied previously that function $E(\nu)$ in the formula (1) is the energy of particular hydrogen bond in which individual OH oscillator is involved and which determines its frequency. Hence, it was postulated that pair energy of interaction of water molecules, which actually depends in the complex way on the equilibrium values of distance between molecules and their mutual orientation, may be replaced with one-parametrical dependence $E(\nu)$ and the appropriate distribution function $P(E,T)$. The successful reconstruction of spectral contours shows that this nontrivial hypothesis contains a rational grain. However, present results show that it is necessary to keep in mind that function $E(\nu)$ is only *effective* energy of hydrogen bonding specially adapted to the description of spectra. We believe that despite of the "effective" status of energy $E(\nu)$, further development of the fluctuation theory and, in particular, Zhukovsky's formula (1) opens new ways both for spectroscopy and thermodynamics of hydrogen bonded liquids. Occurrence of effective notions is typical for model theories. They, as a rule, do not follow from the first principles but, opening nontrivial laws, allow one to make useful theoretical generalizations.

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