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Fluctuation theory of hydrogen bonding applied to vibration spectra of HOD molecules in liquid water. I. Raman spectra

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Statistical distributions of the frequencies of OH vibrations calculated from the experimental Raman spectra of HOD molecules over the temperature range of 10–200 °C using the recently developed deconvolution technique have been analysed in the framework of fluctuation theory of hydrogen bonding. Two temperature independent functions that are the basis of the Zhukovsky theory for describing the temperature transformation of frequency distribution functions of OH vibrations in a statistical ensemble of O—H···O bonds were established and analytically approximated. This made it possible to reconstruct the entire set of initial spectra and to extrapolate their forms to a wider temperature range. These results support the continuum model of liquid water structure.

1. Introduction

There are at present two main approaches to explain the origin of very wide band widths in the vibrational spectra of water. The first is based on the mixed (mixture) models of water that postulate that this liquid is represented by a finite set of species consisting of either associates of water molecules or the hydrogen bonds of different discrete configurations (strong, weak, very weak, broken, etc.). The observed spectral band is then a superposition of contours corresponding to these species. This method has the great disadvantage that it is almost impossible to assign theoretically the positions, widths and forms of spectral contours of each sort. Therefore in practice this method reduces the description of the broad band to its decomposition into components (typical examples are [1, 2]). This procedure is purely formal and cannot be considered of course as the theory of the form of spectral bands, especially as it leaves open the question of the origin of the large widths of component contours.

It is the continuum model of water that reveals the direct way to the constructive theory. It is based on the fluctuation concept of hydrogen bonding, according to which very broad bands in the vibrational spectra of water OH oscillators reflect a continual statistical distribution of geometrical configurations of the O—H···O hydrogen bridge inherent in liquids (unlike crystals) and caused by fluctuations in the local environment of different H_2O molecules. The cornerstone of the theory is the statistical contour $P(\nu)$ that describes the probability that an OH oscillator has the definite frequency ν in the continual ensemble of hydrogen bonds. Unfortunately, the present state of the liquid theory does not allow us to calculate $P(\nu)$ from first principles. However, other possibilities exist for developing a fluctuation theory.

In [3] we accepted $P(\nu)$ to be a Gaussian distribution, and showed that the fluctuation concept reproduces, at least qualitatively, the main features in the spectra of both liquid water and its complexes with organic bases. Rice *et al.* devoted a number of papers [4] to the construction of the different distributions of the continual model of hydrogen bonding in water, and in particular the water spectral contours [5], on the basis of some empirical and model information.

The decisive step in developing the formalism of the fluctuation theory as applied to spectral contours was made by Zhukovsky [6]. He put forward the hypothesis that the statistical contour is the Boltzmann function

$$P(\nu, T) = Q^{-1}(T)W(\nu)\exp(-E(\nu)/k_BT), \qquad (1)$$

where $Q(T) = \int W(\nu)\exp(-E(\nu)/k_BT)\,d\nu$ is the statistical integral. The central point of the Zhukovsky hypothesis is that both the functions determining the frequency dependence of the statistical contour, i.e., the H bond energy corresponding to the stretching frequency ν, $E(\nu)$, and the statistical degeneracy of such H bond configurations, $W(\nu)$, are temperature independent. It is difficult to prove this thesis theoretically. However, it is in agreement with a set of experimental facts [6–8]. The major condition for the temperature invariance of functions $E(\nu)$ and $W(\nu)$ is apparently

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the constancy of water density over the temperature range under study.

The description of water spectra should begin with HOD molecules, to exclude the coupling of OH oscillators that additionally complicates the spectra of H_2O molecules (this dynamic process has no relation to configuration statistics). Then the intensity of absorption (or scattering) by all OH (or OD) oscillators at frequency ν is given by the formula

$$I(\nu) = \int F(\nu')P(\nu')\varphi(\nu - \nu')\,\mathrm{d}\nu', \qquad (2)$$

where $F(\nu)$ is the intensity factor sharply increasing in the IR spectrum from the high to the low frequency wing but remaining practically unchanged along the band in the isotropic component of the Raman spectrum. It is the difference in the $F(\nu)$ functions that causes distinctions in the band shapes in the IR and Raman spectra. This fact makes it preferable to utilize Raman spectra for studying the statistics of hydrogen bond configurations.

In equation (2), $\varphi(\nu - \nu')$ is the spectral line (homogeneously broadened) of individual OH oscillators composing the inhomogeneously broadened band under study. Its centre at a frequency ν' is shifted further to low frequencies the stronger is the H bond in which this oscillator engages. If the absorption (scattering) lines of the individual oscillators are assumed to be infinitely narrow, i.e., for use in equation (2),

$$\varphi(\nu - \nu') = \delta(\nu - \nu'), \qquad (3)$$

then a simple relationship follows from equation (1) that the shape of the stretching band of HOD molecules should satisfy at two any temperatures T_1 and T_2

$$\ln\left(I(\nu,T_1)/I(\nu,T_2)\right) = C(T_1,T_2) + E(\nu)(1/T_1 - 1/T_2)/k_{\mathrm{B}}, \qquad (4)$$

where $C(T_1,T_2)$ is a frequency independent constant. As a first stage we may assume a linear relation between the H bond energy and the frequency of the Badger–Bauer type:

$$E(\nu) = -b(\nu_{\mathrm{u}} - \nu), \qquad (5)$$

where ν_{u} is the frequency of a free OH group not engaging in hydrogen bond. Then equation (4) acquires a unique ability to predict spectrum shape at any temperature from the experimental IR (or Raman) spectrum at only one temperature. On the other hand, this equation gives a recipe for calculating the functions $E(\nu)$ and then $W(\nu)$ from experimental spectra and reveals a new possibilities for applying fluctuation theory to real systems. This recipe has significant advantage in comparison with that of Bratos [9], who developed a general approach to contour description leading in essence to equation (1). However, he proposed determining the functions $E(\nu)$ and $W(\nu)$ by expanding them into Taylor series in the vicinity of the **energy function minimum**. This approach is not constructive for water spectra because the statistical contours here are far from a Gaussian distribution and are more likely of a bimodal character. Describing these modes separately would turn the Bratos formalism into a variant of the mixed model. The Zhukovsky recipe (equation (4)) provides a way to determine the basic functions $E(\nu)$ and $W(\nu)$ independently of their forms and the positions of the extrema.

The simplifying assumption (3) makes it possible to recalculate band shapes rather well over the temperature range 10–80 °C [6, 7], but results in substantial overestimation of the intensity of the high frequency wings compared with experiment at higher temperatures [7]. The reason is a considerable contribution of the 'tails' of the homogeneously broadened contours $\varphi(\nu - \nu')$ composing the band. These tails, which do not correspond to any real oscillators in the statistical distribution $P(\nu,T)$ (that cannot have frequencies $\nu' > \nu_{\mathrm{u}}$), are exponentially strengthened by the Zhukovsky procedure (equations (1) and (4)) when recalculating a spectrum for higher temperatures. The only way to avoid this imperfection is to take into account the contribution of the $\varphi(\nu - \nu')$ contour.

Such an analysis was performed in [8] for the temperature transformation of the isotropic Raman spectrum. However, in that analysis is the problem, the inverse of equation (2), was not solved as a mathematical task, because the desired function $P(\nu)$ was found not by the direct solution of the integral equation (2) but by modelling it with the help of two Pearson distributions whose parameters were fitted to reach the best agreement with the experimental spectrum after the convolution (2) with the line contour of the individual oscillator $\varphi(\nu - \nu')$. This approach made it possible to ignore empirical relation (5) and to calculate independently the functions $E(\nu)$ and $W(\nu)$. As a result, taking into account the finite width of the individual oscillator line, we managed to achieve a much more precise description of the temperature evolution of the band of OH vibrations over the entire experimentally studied temperature range.

The next step in studying this problem was the paper of Georgiev *et al.* [10], which was the first to distinguish the contribution of the $F(\nu)$ intensity factor, basing on the IR spectra of HOD molecules isotopically diluted in D_2O. The authors numerically solved the inverse to the equation (2) problem on finding $P(\nu)$ for ten temperatures T from 22 °C to 86 °C. Equation (2) was deconvoluted with the help of the known techniques of direct and inverse Fourier transformations. Their statistical contours are very similar to those in [8] but differ in detail. The reasons may be as follows. The Fourier deconvolution method fails to provide the positive definite solution with a limited determination region (a break at frequency ν_u). Therefore, an additional limitation was applied in [10] to satisfy these two conditions: the final solution was of a form almost identical with that modelled by us [8] (the sum of two Pearson distributions, modified by polynomials). Further, there is some arbitrariness in the choice of the parameters of the Pearson distribution and convolving function $\varphi(\nu - \nu')$ in our earlier paper, and somewhat dramatic increase in the $\varphi(\nu - \nu')$ width with increasing temperature postulated in [10].

The purpose of this paper is to turn back to a stricter level of calculation, performed in [8] almost intuitively, and to construct a complete Zhukovsky model for liquid water with the analytical description of all the functions involved. This will make it possible to calculate the other water characteristics, i.e., contour shapes in IR spectra and configuration contributions of hydrogen bonds to thermodynamic functions.

2. Iterative deconvolution as a method for solving the inverse problem of integral convolution

A conventional method for solving the inverse problem of integral convolution of equation (2) type,

$$S(\nu) = \int_{\nu_1}^{\nu_2} P(\nu')\varphi(\nu - \nu')\,d\nu' \equiv \mathrm{Conv}\,(P(\nu)), \qquad (6)$$

i.e., determination of function $P(\nu) \equiv \mathrm{Deconv}\,(S(\nu))$ from the experimental $S(\nu)$ curve and known convolving function $\varphi(\nu - \nu')$ within the finite limits (ν_1, ν_2), is the inverse Fourier transform of the quotient from the division of the Fourier image of $S(\nu)$ by a Fourier image of $\varphi(\nu)$. However, in actual practice, this method fails to provide a positive definite solution and leads to oscillating components [12, 13]. It is a non-trivial problem to correctly exclude these demerits in the framework of a given method. We have developed a novel technique for solving the inverse problem to equation (2), described in detail in [11]. Its essence is the following.

As a zero approximation we take $P^0(\nu) = S(\nu)$, i.e., the experimental spectrum itself (which is already the convolution of the desired $P(\nu)$ with $\varphi(\nu)$), and convolve it once again with $\varphi(\nu)$. Then we calculate the misfit function $\delta^1(\nu)$ as a difference between the experimental $S(\nu)$ and the curve resulting from $P^0(\nu)$ convolution. Then $P^1(\nu) = P^0(\nu) + \delta^1(\nu)$ is taken as the first approximation for the statistical contour $P(\nu)$. In addition, we may correct it so that $P^1(\nu)$ should be everywhere non-negative and should be zero at high frequencies $\nu > \nu_u$. The first approximation is, as a rule, insufficient and the procedure can be repeated. After a few iterations (conventionally, about 5–10 times), the checking convolution of $P^i(\nu)$ with $\varphi(\nu)$ would be almost identical to the experimental spectrum. Further iterations result in negligible change in $S^i(\nu)$. It means that $P^i(\nu)$ may be considered as the achieved solution of the inverse problem (equation (6)).

The general form of the procedure is $(i = 1, 2, \ldots)$

$$P^i(\nu) = \begin{cases} P^{i-1}(\nu) + \delta^i(\nu) & \text{if } P^i(\nu) \geqslant 0 \text{ and } \nu \leqslant \nu_u, \quad (7a) \\ 0 & \text{if } P^i(\nu) < 0 \text{ or } \nu > \nu_u. \quad (7b) \end{cases}$$

$$\delta^i(\nu) = S(\nu) - \mathrm{Conv}^{i-1}(\nu). \qquad (7c)$$

$$\mathrm{Conv}^i(\nu) = \int_{\nu_1}^{\nu_2} P^i(\nu')\varphi(\nu - \nu')\,d\nu'. \qquad (7d)$$

The initial condition is

$$P^0(\nu) = S(\nu). \qquad (8)$$

Note that two different limitations in equation (7*b*) may be used separately if, e.g., it is necessary either to provide the non-negativity of the desired $P(\nu)$ without limiting its definition area or, on the other hand, to set the definition area without requirements on the constancy of sign.

When applying this procedure to real spectral problems it is important to bear in mind that the exact form of $\varphi(\nu)$ function is, as a rule, unknown. What will be the result if the half-width of convoluting function $\varphi(\nu)$ is set incorrectly? Let us illustrate the problems arising. As the convolving function we take the Lorentzian

$$L(\nu - \nu') = 2H/\{\pi[H^2 + 4(\nu - \nu')^2]\}, \qquad (9)$$

with half-width $\Delta\varphi_{1/2} = H$. Figure 1 demonstrates the results of the deconvolution of the same experimental contour $S(\nu)$ using the Lorentzian with different values of $\Delta\varphi_{1/2} = (a)\ 25\,\mathrm{cm}^{-1}$ and $(b)\ 35\,\mathrm{cm}^{-1}$. It is seen that smaller value of the $\Delta\varphi_{1/2}$ causes a sharp peak at frequency ν_u (line 2 in figure 1(*a*)) whose intensity increases with increasing number of iterations trying to compensate (without any success) for the small deficit of intensity at the high frequency wing of checking convolution (line 1 compared with symbols in figure 1(*a*)). On the other hand, larger value of $\Delta\varphi_{1/2}$ leads to substantial narrowing of the desired $P(\nu)$ distribution (line 2 in figure 1(*b*)) so that it tends to zero at frequencies lower than ν_u. In this case, the intensity of the high frequency wing of the checking convolution (line 1 in figure 1(*b*)) slightly exceeds the experimental one (symbols). Only $\Delta\varphi_{1/2} = 30\,\mathrm{cm}^{-1}$ gives (after deconvolution of the $S(\nu)$) the $P(\nu)$ contour with the desired properties: it terminates at ν_u without an additional peak. Therefore

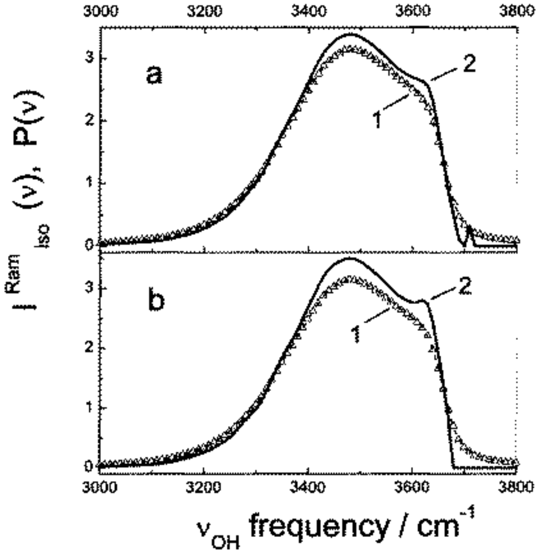


Figure 1. Deconvolution procedure and search for the correct half-width of the convolving Lorentzian function: symbols, experimental Raman spectrum $S(\nu)$ of HOD molecules at 50 °C [14]; line 2, result of deconvolution, $P(\nu) \equiv \mathrm{deconv}\,(S(\nu)$; line 1, its proving convolution with the same Lorentzian. Deconvolution by the Lorentzian of a half-width (*a*) $H = 25\,\mathrm{cm}^{-1}$, and (*b*) $\mathrm{H} = 35\,\mathrm{cm}^{-1}$. The number of iterations is 8. All calculations were performed using a set of discrete points separated by $10\,\mathrm{cm}^{-1}$. In particular, integration was substituted by summation.

it is $30\,\mathrm{cm}^{-1}$ precisely that we may consider the 'true' value for the half-width, $\Delta\varphi_{1/2}$. Thus our deconvolution procedure (combined with the physically reasonable requirements on the $P(\nu)$ shape) contains in itself some criterion for selecting a deconvolving function.

This conclusion was proved independently by a direct model calculation. First, we postulated the shape of the statistical distribution $P(\nu)$ tending to zero at $\nu = \nu_u$ and convoluted it with the Lorentzian with half-width H_0 to obtain the model 'experimental' spectrum $S(\nu)$. Then we subjected this spectrum to the deconvolution procedure stated above with various Lorentzian half-widths H. We found that a false peak at frequency ν_u (as in figure 1(*a*)) appeared always for $H < H_0$, and the deconvoluted contour vanished at frequencies smaller than ν_u (as in figure 1(*b*)) for $H > H_0$. These calculations were performed for several values of H_0 and H. The larger were H_0 and $|H - H_0|$ the larger were the features discussed.

3. Calculation of the statistical distribution of the frequencies of liquid water OH vibrations from Raman spectra

We used the isotropic component of the Raman spectra of HOD molecules diluted in D_2O, $I_\alpha(\nu)$, as initial data. At 10, 50 and 90 °C the Scherer *et al.* [14] spectra were used, and at 200 °C the Ratcliffe and Irish spectra [15], as all these were obtained almost at the same density $1\,\mathrm{g\,cm}^{-3}$. For our calculations, only the tabulated data are suitable to provide the proper accuracy. They are taken from [14], supplementary materials and from tables kindly donated by the authors of [15].

The statistical contour $P(\nu)$ is taken as a frequency distribution of the matrix element square of the polarizability tensor trace $\langle b^2 \rangle$ for a given vibration. Its relation to the experimental spectrum $I_\alpha(\nu)$ obeys the equation

$$I_\alpha(\nu) = \mathrm{Conv}\,[P(\nu)\psi(\nu)],$$

where $\psi(\nu) = (\nu - \nu_L)^4(1 - \exp(-h\nu/k_B T))^{-1}$ and ν_L is the excitation radiation frequency (the argon ion laser line, 4880 Å, in the papers cited). As the deconvolution function $\varphi(\nu)$, we used in [8] the Lorentzian with half-width $\Delta\varphi_{1/2} = 30\,\mathrm{cm}^{-1}$ (the same for all temperatures) corresponding to the IR spectrum of HOD molecules dissolved in CCl_4 at room temperature. (In nonpolar solvents, the water molecules exist as monomers taking no part in hydrogen bonds and being thus spectroscopically identical; therefore, the statistical distribution $P(\nu)$ reduces to the delta function and $S(\nu)$ reduces to $\varphi(\nu)$.) However, when deconvolving the IR spectra in the temperature range of 22–86 °C, Georgiev *et al.* [10] assumed that the half-width of convolving function $\varphi(\nu)$ increases with temperature according to

$$\Delta\varphi_{1/2} = 2712 \exp(\langle E_{HB} \rangle / k_B T), \tag{10}$$

where $\langle E_{HB} \rangle = -12.725\,\mathrm{kJ\,mol}^{-1}$ is the mean energy of hydrogen bonds in the ensemble. Over the temperature range studied by us this could lead to an increase in $\Delta\varphi_{1/2}$ from $10\,\mathrm{cm}^{-1}$ (10 °C) to $100\,\mathrm{cm}^{-1}$ (200 °C) that casts some doubt on our previous deconvolution results [8] with the temperature independent convolution function. Therefore, we performed trial calculations varying the $\Delta\varphi_{1/2}$ value analogously to that shown in figure 1, for experimental contours from 10 °C to 200 °C. More or less satisfactory results are obtainable, with reasonable variations of the background, if $27\,\mathrm{cm}^{-1} < \Delta\varphi_{1/2} < 33\,\mathrm{cm}^{-1}$ in all cases. The best results were recorded for $\Delta\varphi_{1/2} = 30\,\mathrm{cm}^{-1}$ (as figure 1 illustrates for 50 °C). This value will be used further for all temperatures. Note that the width of the homogeneously broadened contour $\varphi(\nu)$ depends on the relaxation processes common for any liquid rather than on hydrogen bonding. Besides, the resolution power of the spectrometer also contributes to it. Therefore, there is no obvious sense in relating the temperature dependence of the homogeneous width to the hydrogen bond energy, as assumed in expression (10).

Figure 2 shows the statistical frequency distributions $P(\nu, T)$ calculated by the above method from experimental spectra. The excellent quality of the solution of

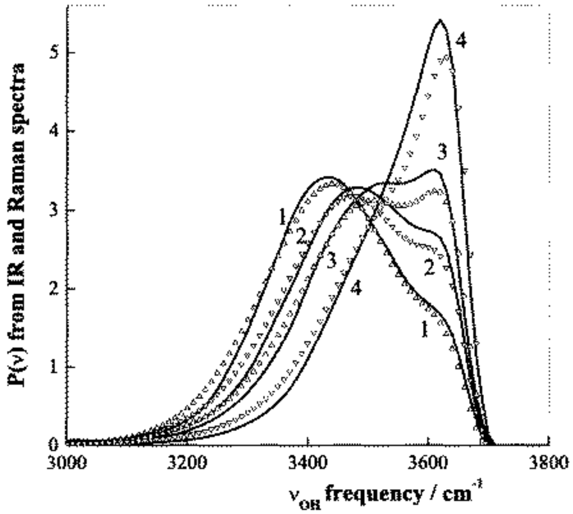


Figure 2. Statistical frequency distributions $P(\nu, T)$ of OH vibrations in liquid water: lines 1–4, calculated by us from experimental Raman spectra at 10, 50, 90, and 200 °C, respectively; symbols, similar statistical contours calculated according to [10] from IR spectra.

the inverse problem is confirmed by the results of checking convolutions $S(\nu, T)$ of the contours found $P(\nu, T)$, with the Lorentzian with a half-width of $30\,\mathrm{cm}^{-1}$. They coincide exactly with the experimental Raman spectra (even better than the symbols and lines in figure 1(*a*, *b*)). Figure 2 compares also our statistical contours with those constructed in [10] based on the IR spectra. Although there are some systematic differences, these two sets of statistical contours are, as a whole, in good agreement with one another at all temperatures. Such agreement is by no means trivial, because they were calculated on the basis of experimental IR and Raman spectra that differed strongly in the shape.

4. Calculation of the temperature invariants of Zhukovsky theory

Using statistical distributions $P(\nu, T_i)$ for four temperatures ($i = 1, \dots, 4$) we are able to calculate the two temperature independent functions $E(\nu)$ and $W(\nu)$ of Zhukovsky theory as follows. First, we calculate energy functions (to within the unknown constants C_{ij}) according to formula (4) from each pair of four statistical contours, $i < j = 2, 3, 4$:

$$E_{ij}(\nu) = k_B T_i T_j / (T_j - T_i) \ln [P(\nu, T_j)/P(\nu, T_i)]. \quad (11)$$

All the six curves obtained behave rather irregularly, evidently because of difficulties in the separation of the experimental contours of the HOD molecules against the background of bands of D_2O molecules prevailing in the solution. This leads to great relative errors in the remote contour wings (at $\nu > 3650\,\mathrm{cm}^{-1}$ and $\nu < 3200\,\mathrm{cm}^{-1}$). The curve $\langle E(\nu) \rangle$ averaged overall is more reliable and is shown in figure 3(*a*) by the dashed line 1.

The last step in the derivation of $E(\nu)$ function is a natural constraint that for small frequency shifts it should reproduce the empirical Badger–Bauer correlation (equation (5)) and become zero with ν_{OH} tending to $\nu_u = 3707\,\mathrm{cm}^{-1}$. This function can be constructed using the expression ($x = \nu_u - \nu$)

$$E(x) = \frac{-bx}{1 + (A-1)^{-1}(x/x_m)^A}. \quad (12)$$

Two coefficients of this formula may be taken from experiment. The value of b is determined by the empirical Badger–Bauer correlation into which equation (12) transforms for small x. For water, we obtain $b = 14\,\mathrm{cal\,mol^{-1}\,cm} = 58.576\,\mathrm{J\,mol^{-1}\,cm}$. The optimum configuration of hydrogen bonds between water molecules is likely to be realized in ice at 0 K. Therefore, for the ν_m frequency corresponding to the minimum value of hydrogen bond energy E_{min} we assume the frequency of OH vibrations of HOD molecules in ice at 0 K. Extrapolating the data of [16] to $T = 0\,\mathrm{K}$, we obtain $\nu_m = 3264.7\,\mathrm{cm}^{-1}$. Coefficient A can be found by comparing formula (12) with $\langle E(\nu) \rangle$ and taking into account the relationship

$$A = [1 + E_{min}/(b x_m)]^{-1}, \quad (13)$$

where $x_m = \nu_u - \nu_m$.

We assumed $E_{min} = -22.0\,\mathrm{kJ\,mol^{-1}}$ (which gives $A = 6.629$). Figure 3(*a*) shows that, with such a choice, expression (12) provides a satisfactory approximation of $\langle E(\nu) \rangle$ if the frequency intervals corresponding to the uncertain wings of stretching band are neglected. The E_{min} value means the optimum energy of the hydrogen bond between water molecules, and a value of $-22\,\mathrm{kJ\,mol^{-1}}$ assumed by us is close to the H bond energy in ice of $-23.68\,\mathrm{kJ\,mol^{-1}}$ determined as half the sublimation energy of ice at 0 K [17]. Expression (12) was used in [8,10] with somewhat different parameter values.

Thus, we use equation (12) with the chosen parameters to describe the relationship between the H bond energy and the vibration frequency of the OH oscillator engaging in it. This function is depicted in figure 3(*a*) by the solid line 2. It is seen that, due to the presence of a minimum, this form of $E(\nu)$, in contrast to equation (5), leads to a double-valued dependence of ν on E. This should be considered as a fact unambiguously following from experiment. We plan to describe the consequences in a subsequent paper con-

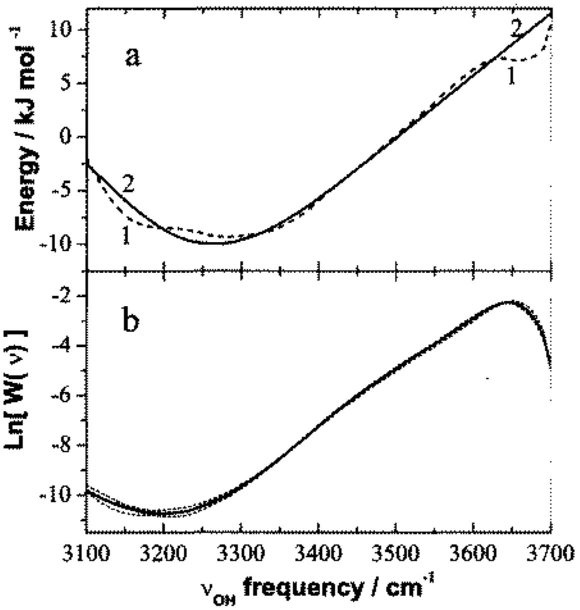


Figure 3. Construction of two invariant functions of Zhukovsky model. (*a*) Relationship between hydrogen bond energy and OH oscillator frequency: dashed line 1, average of $E_{ij}(\nu)$ curves calculated using expression (11) from all 6 pairs of statistical contours over the temperature range 10–200 °C; and solid line 2, approximation of energy function by equation (12) shifted by $+12\ \mathrm{kJ\,mol^{-1}}$. (*b*) Dependence of the function describing the state degeneracy of the OH oscillator frequency: dashed lines, $W_i(\nu)$ curves calculated using equations (14), (15) for 4 temperatures; and solid line, their mean, $W(\nu)$.

cerning the H bond energy distribution and thermodynamic functions.

Now we can determine the $W(\nu)$ function. To this end we first calculate four functions $W_i^*(\nu)$ on the basis of the defined $E(\nu)$ and four statistical contours $P(\nu, T_i)$:

$$W_i^*(\nu) = P(\nu, T_i)/\exp[-E(\nu)/(kT_i)]. \tag{14}$$

According to equation (1), these functions differ from the desired $W(\nu)$ by a factor $Q(T_i)$. The area normalized $W_i^*(\nu)$ curves

$$W_i(\nu) = W_i^*(\nu) \bigg/ \int_{\nu_o}^{\nu_u} W_i^*(\nu)\,\mathrm{d}\nu \tag{15}$$

almost coincide with one another, as shown in figure 3(*b*). This confirms Zhukovsky's hypothesis about the temperature invariance of the functions $E(\nu)$ and $W(\nu)$.

The meaning of normalization (15) is transparent. Equation (1) shows that with $T \to \infty$, $P(\nu, T) \to Q^{-1}(T)W(\nu)$. Thus, the function describing the degeneracy of the hydrogen bridge configurations, giving rise to a given frequency ν, coincides in its form with the statistical contour at infinite temperature. It is clear because at $T \to \infty$ all possible configurations should have equal probabilities. To satisfy the obvious requirement

$$\int_{\nu_0}^{\nu_u} P(\nu)\,\mathrm{d}\nu = 1, \tag{16}$$

we should exclude the last uncertainty in the determination of function $W(\nu)$ assuming $Q(T \to \infty) = 1$. This gives normalization (15).

As invariant $W(\nu)$ function we take the average of four calculated $W_i(\nu)$ curves. Its logarithm is shown in figure 3(*b*) by the solid line. Any detailed form for function $W(\nu)$ is highly speculative and may be approximated analytically only with great difficulty. To calculate the form of the statistical distribution in detail the exact values of $W(\nu)$ should be used, as given in table 1.

For some purposes, however, it may be useful to employ the analytical representation of $W(\nu)$ function. In this case, the following complex dependence may be proposed (ν in $\mathrm{cm^{-1}}$):

$$W(\nu) = \exp[-\exp(|Y(\nu)|)], \tag{17}$$

$$\begin{aligned} Y(\nu) = {} & 1.55\exp\{-[(3735-\nu)/50]^2\} \\ & + 2.334\exp\{-|(\nu-3193)/440|^{2.3}\} \\ & - [(\nu-3603)/410] \\ & \times \exp\{-|(\nu-3603)/75|^{1.55}\} + 0.03. \end{aligned} \tag{18}$$

This representation allows one to determine, e.g., the frequencies of the statistical contour maximum at different temperatures. The Zhukovsky formalism may be used readily to find the condition for this maximum. Equating the frequency derivative of expression (1) to zero we obtain

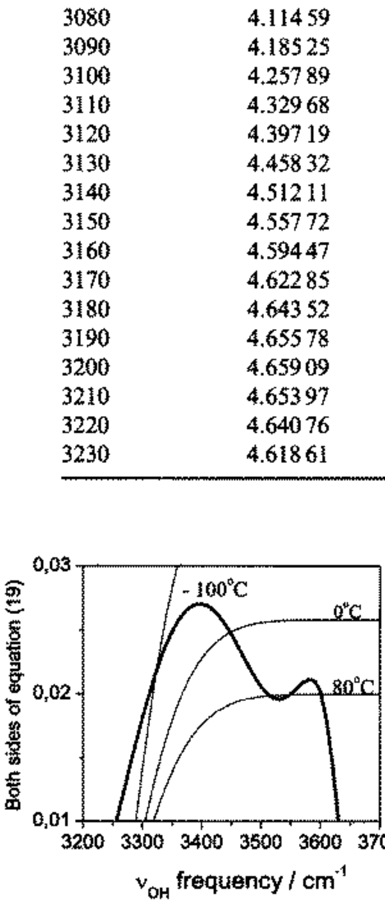
$$\frac{\mathrm{d}\ln W(\nu)}{\mathrm{d}\nu} = \frac{1}{kT}\frac{\mathrm{d}E(\nu)}{\mathrm{d}\nu}. \tag{19}$$

Figure 4 shows the curves corresponding to the functions on the right- and left-hand sides of this equation, the former being calculated by approximation (18). The intersection of these curves determines the position of the extremes of the statistical contour $P(\nu)$. It is seen that near 80 °C (more accurately, in the range 333–359 K) the contour should have three extremes (figure 4) that corresponds to a bimodal form of this contour.

The expansion of energy function (12) into a series near the $E_{\min}$ minimum is of the form

Table 1. Dependence of the degeneration function $W(\nu_{\rm OH})$ of hydrogen bond configurations corresponding to energy $E(\nu_{\rm OH})$ on the stretching frequency $\nu_{\rm OH}$ in a liquid water.

$\nu_{\rm OH}/{\rm cm}^{-1}$	$-\log_{10}(W)$	$\nu_{\rm OH}/{\rm cm}^{-1}$	$-\log_{10}(W)$	$\nu_{\rm OH}/{\rm cm}^{-1}$	$-\log_{10}(W)$
3000	3.66371	3240	4.58564	3480	2.32548
3010	3.72126	3250	4.54072	3490	2.23292
3020	3.78405	3260	4.48569	3500	2.14179
3030	3.84562	3270	4.42420	3510	2.05217
3040	3.89088	3280	4.35712	3520	1.96390
3050	3.93384	3290	4.28297	3530	1.87685
3060	3.98653	3300	4.20108	3540	1.79096
3070	4.04767	3310	4.11225	3550	1.70564
3080	4.11459	3320	4.01784	3560	1.61971
3090	4.18525	3330	3.91852	3570	1.53232
3100	4.25789	3340	3.81494	3580	1.44311
3110	4.32968	3350	3.70804	3590	1.35239
3120	4.39719	3360	3.59893	3600	1.26143
3130	4.45832	3370	3.48827	3610	1.17311
3140	4.51211	3380	3.37612	3620	1.09243
3150	4.55772	3390	3.26277	3630	1.02756
3160	4.59447	3400	3.14952	3640	0.98842
3170	4.62285	3410	3.03733	3650	0.98505
3180	4.64352	3420	2.92715	3660	1.02671
3190	4.65578	3430	2.82014	3670	1.12247
3200	4.65909	3440	2.71619	3680	1.28641
3210	4.65397	3450	2.61466	3690	1.55600
3220	4.64076	3460	2.51575	3700	2.09584
3230	4.61861	3470	2.41952	3707	infinity



ure 4. Mechanism of formation of statistical contour extreme: thick line, $d \ln W(\nu)/d\nu$ functions calculated by approximation (17); and thin lines, functions $(1/k_BT)\, dE(\nu)/d\nu$ at different temperatures.

$$E(\nu) = E_{\rm min}\left[1 - \frac{A-1}{2x_{\rm m}^2}(\nu-\nu_{\rm m})^2 + \frac{(A-1)(A-5)}{6x_{\rm m}^3}(\nu-\nu_{\rm m})^3 + \cdots\right]. \quad (20)$$

h respect to equation (1), we find that at very low peratures, near 0 K, the statistical contour is the ussian distribution

$$P(\nu,T) \propto W(\nu_{\rm m}) \exp\left[-(\nu-\nu_{\rm m})2/2\sigma^2\right]$$

with dispersion $\sigma^2 = k_BTx_{\rm m}^2(A-1)^{-1}/|E_{\rm min}|$. For the statistical contour half-width, with our parameters, we tain

$$\Delta\nu_{1/2}({\rm cm}^{-1}) = 2.355\sigma = 8.535\sqrt{T({\rm K})}. \quad (21)$$

Indeed, the fluctuation concept of hydrogen bonding developed for the liquid state fails for ice. According to [16], the half-width of the stretching OH band of HOD molecules in polycrystalline ice Ih is almost temperature independent in the range 10–100 K, and amounts to 26–27 cm^{-1}. This width is much greater than that in the proton-ordered ices II and IX [18, 19], and results from proton disorder in Ih ice which is 'frozen in' the ice structure and is temperature independent. According to expression (21), this disorder corresponds to liquid fluctuations with a temperature of about 10 K.

5. Reconstruction of temperature dependence of the statistical contours and of stretching band shapes

Using Zhukovsky formalism, we may now reconstruct the entire set of experimental data. For comparison with experimental spectra, the calculated statistical contours $P(\nu,T)$ should be convolved according to equation (2)

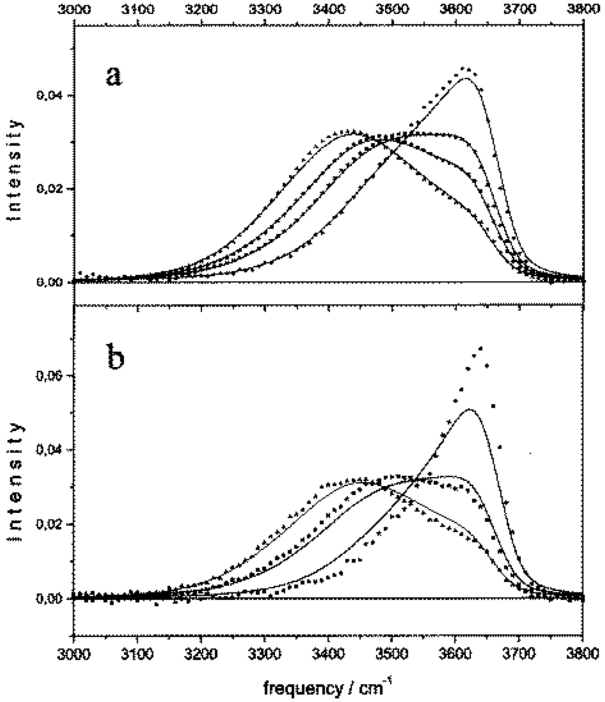


Figure 5. Comparison between the calculated and experimental isotropic Raman spectra of HOD molecules: solid lines, calculation based on the assumed model of statistical contours after their convolution with the Lorentzian of a half-width of 30 cm^{-1}; and dotted lines, experimental data. From left to right: (*a*) from [14] at 10, 50 and 90 °C and from [15] at 200 °C; and (*b*) from [15] at 25, 100 and 300 °C.

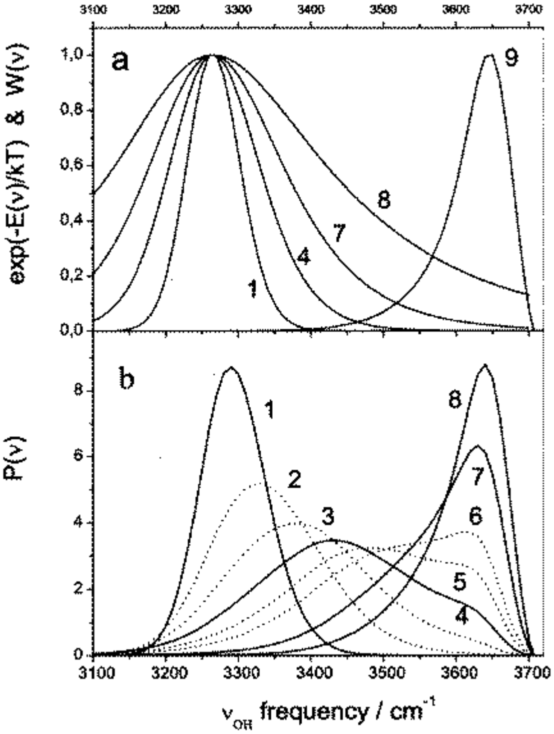


Figure 6. Origin of temperature evolution of a statistical contour and its extrapolation to a wider temperature range. (*a*) The mechanism of statistical contour formation: two cofactors determining the $P(\nu)$ shape according to equation (1), the Boltzmann exponent at $T = -173$, 0, 200, and 1000 °C (curves 1,4,7,8 at the left) and the function of state degeneracy $W(\nu)$ (curve 9 at the right). All curves are normalized in height to unity. (*b*) Statistical contours, being the product of above cofactors calculated for −173, −100, −50, 0, 50, 100, 200, and 1000 °C (curves 1–8, respectively). The contours are normalized in area to unity.

with the Lorentzian of a half-width of 30 cm^{-1} used by us in the deconvolution procedure. The results are given in figure 5. It is seen that at 10, 50, 90 and 200 °C the initial spectra are reproduced well (figure 5(*a*)). The spectra of Ratcliffe and Irish at 25 °C and 100 °C are poorer (figure 5(*b*)) but, as a whole, quite satisfactory (the statistical spread in points in these spectra is much greater, according to the tables we have, than that in the data of Scherer *et al.* in figure 5(*a*)). Also only the spectrum at 300 °C in figure 5(b) is described inadequately by the fluctuation theory. Probably, this is due to the fact that experiments at this temperature were performed at a density of 0.718 g cm^{-3} [15], whereas all the other spectra and the $E(\nu)$ and $W(\nu)$ functions correspond to a density of about 1 g cm^{-3}. Thus, the fluctuation concept of hydrogen bonding is in good agreement with Raman experimental spectra of HOD molecules in a liquid at a 'normal' density over the temperature range 0–200 °C.

The Zhukovsky formalism can predict the temperature transformation of the statistical contour over a wider temperature range. Figure 6(*b*) shows such a transformation from −173 °C up to 1000 °C. High temperatures can correspond to a supercritical fluid and low temperatures to supercooled water and amorphous ice. When comparing these contours with experiment one must convolute them with the Lorentzian and remember that the density in an experiment would be constant at about 1 g cm^{-3}.

Figure 6(*a*) shows two cofactors of equation (1) whose product is $P(\nu)$. It is rather curious that at normal temperatures the major part of the frequency distribution is formed in the region of overlap of the wings, both the Boltzmann exponent and the function $W(\nu)$; only with the temperature approaching 0 K and infinity does $P(\nu)$ tend to this exponent and to $W(\nu)$, respectively. It is remarkable that at high temperatures statistical distribution does not show total disruption of the hydrogen bonds (no δ function at the frequency about ν_u). In fact, the high temperature contour (which is identical with $W(\nu)$) has the form of a sufficiently broad distribution with a maximum at about 3645 cm^{-1} (table 1) that may be assigned to the ensemble of weak, bent hydrogen bonds. This fact results, of course, from the high density of substance that gives no possibility for molecules to move apart even at high temperatures. These weak hydrogen bonds cannot by any means be considered in the framework of fluctuation theory as a separate species: they are an inseverable element of the single continuous distribution of H bond configurations in liquid water.

6. Conclusion

The main results of this study may be summarized as follows.

The novel deconvolution procedure is used to uniformly (not *ad hoc*) derive statistical distributions of vibration frequencies, $P(\nu, T)$, from a set of experimental spectra. The width of homogeneously broadened OH oscillator lines composing a wide Raman band was found to be independent of temperature up to 200 °C and equal to the width of the stretching line of a water molecule in inert solvent (with no H bonding). The reliability of the calculated contours $P(\nu, T)$ is justified by their similarity with those derived independently from IR spectra and also by the results of checking convolutions, $S(\nu, T)$, which exactly coincide with the experimental isotropic Raman spectra.

The problem of determining the $E(\nu)$ and $W(\nu)$ functions of the Zhukovsky formalism on the basis of statistical contours derived from the experimental spectra refers to a category of 'incorrect' inverse problems that do not have, from a mathematical viewpoint, the unique strict solution. The method proposed here gives one of the possible approximate solutions. However, this solution is adequate for our main purpose, i.e., to demonstrate the effective work of the developed formalism in calculating the shape of the contours of OH vibrations of HOD molecules over a wide temperature range.

The calculated $E(\nu)$ function has a minimum that leads to a double-valued dependence of the OH oscillator frequency ν on the H bond energy E, in contrast to the simple Badger–Bauer relation. As a result, the same value of E may be connected with two values of vibration frequency, less and greater than $\nu(E_{\min})$.

The function describing the degeneracy of the hydrogen bond configurations, $W(\nu)$, is identical with the statistical contour at infinite temperature. It reflects the fact that at $T \to \infty$ all possible geometries of O—H···O bridge should be equally probable, despite the differences in H bond energy. Even at very high temperatures there is no evidence of breakage of the hydrogen bond network. In fact, $P(\nu)$ conserves the form of a rather broad distribution near 3645 cm^{-1} instead of a sharp line at the free OH-group frequency. These (weak) hydrogen bonds are described by the same formulas as other (stronger) ones, and thus represent the integral element of a uniform continuous distribution of H bond configurations in liquid water. At temperatures somewhat lower than the boiling point the theoretical spectra should have three extremes that corresponds to a bimodal form of isotropic Raman experiments.

A quantitative description of both the shape and temperature transformation of the experimental spectra of HOD molecules in a liquid over the range 10–200 °C achieved in this paper on the basis of fluctuation theory proves that it is the continuum model that correctly describes water. However, the numerical values of the $E(\nu)$ and $W(\nu)$ functions obtained here are true only for water at a 'normal' density. It is planned to use these in further papers to describe the IR spectra and thermodynamics of hydrogen bonds in water. For other systems with hydrogen bonds (or water at another density), the configuration space for H bond geometries will differ from that for water at 1 $\mathrm{g\,cm}^{-3}$ and therefore the $E(\nu)$ and $W(\nu)$ functions may be changed. Unfortunately, at present they cannot be calculated theoretically, but may be reconstructed from empirical spectral data by the methods elaborated here. It would be very interesting to investigate the behaviour of the $E(\nu)$ and $W(\nu)$ functions under different situations; this may be done on the base of spectral experiments performed at various temperatures and under isochoric conditions.

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