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Fluctuation theory of hydrogen bonding applied to vibration spectra of HOD molecules in liquid water. II. Infrared spectra: contour shape, integrated intensity, temperature dependence

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The infrared spectra of HOD molecules in liquid water are calculated at constant density over the temperature range of 10 to 400°C from the statistical distributions of the vibration frequencies of water OH-groups determined previously from the experimental Raman spectra. Their shape and position are extrapolated over a wider temperature range. The dependence of contour shape and integrated intensity of the IR band on the frequency of its maximum, the first moment of a statistical contour and temperature are described numerically and analytically. Calculations are in qualitative agreement with all available experimental material and fitted quantitatively at a density of water of ~1 g cm⁻³. The success of the proposed model applied to infrared spectra supports once more the continuum treatment of liquid water structure.

1. Introduction

The modern approach to understand the origin of very broad width of the v_{OH} bands in hydrogen bonded complexes OH...B in a liquid phase is based on the statistical theory which postulates the anharmonic coupling between the OH and OH...B stretching modes (see the short impressive review in [1] and a more technical description in [2]). Intermolecular modes OH...B are considered as stochastic whose time dependence is suppressed. Therefore the band shape of the OH mode can be described as arising mainly from the statistical distribution of frequency v_{OH} shifts produced by different configurations $R_{OH\dots B}$ of the hydrogen bridge OH...B existing in the liquid. Each bridge configuration produces its own frequency of the O-H oscillator, the continuum for which forms a statistical contour P(v), describing the probability distribution of v_{OH} frequencies over the statistical ensemble. The statement on the predominant role of inhomogeneous spectral broadening is the key point of the fluctuation model of hydrogen bonding which was formulated, on a qualitative level, long ago in [3] and used repeatedly for the description of spectra of aqueous systems (see [4–10] and references cited in [4]). Computer

modelling also supports this statement since the reorganization time of a local environment in molecular dynamics greatly exceeds the period of OH vibrations which suppress the spectral diffusion (important in NMR spectra where the situation is opposite). Naturally, there are many situations where this model does not work (H-bonds in gas phase, in cyclic dimers, in ices, etc). For example, the OH-band is very narrow in ice crystals due to the absence of fluctuations, although H-bonds are much stronger in ice than in liquid water [11].

For spectroscopic purposes the theory must be able to convert the Boltzmann distribution of H-bridge configurations, $P(\mathbf{R}_{OH...B}) \sim \exp[-U(\mathbf{R}_{OH...B})/k_BT]$, into statistical contour P(v). For this purpose, Bratos [2] proposed to expand the potential energy $U(\mathbf{R}_{OH...B})$ and other functions determining the P(v) into a Taylor series around the energy minimum. However, for water this procedure is unsuitable since here the statistical contour P(v) which occurs is very different from a Gaussian shape. More constructive is the formalism suggested by Zhukovsky [6] who presents the statistical contour by itself through the Boltzmann distribution in the form

$$P(v,T) = Q^{-1}(T)W(v) \exp(-E(v)/k_{\rm B}T).$$
(1)

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Here E(v) is the energy of the H-bond configuration that corresponds to the OH stretching frequency v, W(v) is the statistical weight (degeneracy) of such configurations and $Q(T) = \int W(v) \exp(-E(v)/k_{\rm B}T) dv$ is the statistical integral. The central point of the Zhukovsky formalism is assertion that both the functions E(v) and $W(\nu)$ determining the dependence of the statistical probability on frequency are temperature independent which proves to be true by calculations over a wide temperature range [5, 7] if the density of water is unchanged. This fact allowed us to obtain numerical and analytical expressions for temperature invariants E(v) and W(v) for water density of 1 g cm^{-3} [8] from experimental Raman spectra of the diluted solution of molecules HOD in D₂O at several temperatures using a specially developed method for solving an inverse integral convolution problem [9]. Having the numeric model for $P(\nu)$ at any predetermined temperature we should like in this paper to describe the contour shapes of HOD molecules in *infrared* spectra.

The shape of the experimental spectral band is given by the expression

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

Here $\varphi(v - v')$ is the homogeneously broadened line of the particular OH (OD) oscillator with a frequency for its maximum v' and F(v)' is the intensity factor describing the dependence of the integrated intensity of this line for frequency v', i.e. finally the energy of the hydrogen bond in which this oscillator is involved. In the case of water, formula (2) can describe only spectra of the diluted solutions of molecules HOD in D₂O (or in H₂O), in which intra- and intermolecular coupling of OH (or OD) vibrations is excluded; this substantially complicates the spectra of either H₂O or D₂O molecules but has no relation to the statistics of hydrogen bonds.

It is known that the shape of the infrared band in the stretching region of HOD vibrations differs substantially from that of the isotropic component of the Raman spectrum considered in [8] (see figure 1). It is shifted relative to the latter toward lower frequencies and is unimodal at all investigated temperatures, i.e. has only one maximum without pronounced shoulders. As the temperature decreases, the integrated intensity of the band in the IR spectrum increases ten times from the value for gas to that for ice whereas in the Raman spectrum it remains almost unchanged. The goal of the present work is to account for these distinctions and to quantitatively describe the temperature evolution of the shape and the integrated intensity of the IR spectra of HOD molecules in liquid on the base of the distributions of OH oscillator frequencies calculated in [8]



Figure 1. Experimental spectra of OH vibrations of molecules HOD diluted in D₂O. Solid lines—isotropic Raman spectra at 10, 90°C [10] and 200°C [12] (from left to right); dashed lines—IR spectra at 10, 85°C [13] and 200°C [14] (from left to right). All curves are normalized at amximum to unity.

and with respect to the individual absorption ability of these oscillators described by the F(v) function.

2. Relations for integrated intensity of IR bands

The difference of the band shapes in the IR and Raman spectra is caused by a different form of function F(v) in formula (2). In the isotropic component of Raman spectra it is possible to accept F(v) = const.In the IR spectra the value of the intensity factor should increase with decreasing frequency ν_0 , i.e. with H-bond enhancement. This function cannot be calculated from first principles at present. It is impossible also to take it directly from experiment because experiment only gives the *integrated* intensity of a band in H-complexes with different strengths of hydrogen bond, but not the dependence of intensity on frequency in the statistical ensemble of oscillators for one type of H-complex. In such a situation it is reasonable to accept the simplest linear dependence for function F(v) in the form (assumed also in [7])

$$F(\nu) = \begin{cases} c[1 + k(\nu_0 - \nu)], & \nu < \nu_0, \\ c, & \nu > \nu_0, \nu_0 < \nu_u. \end{cases}$$
(3)

Here $v_u = 3707 \text{ cm}^{-1}$ is the frequency of the OH oscillator in vapour, which is a limiting value for the statistical distribution P(v) at high frequency side, v_0 is some frequency, which is still to be determined, and c = const. Taking into consideration F(v) we obtain the statistical distribution of IR absorption along the band in the form

$$P_{\rm IR}(\nu) = F(\nu)P(\nu) . \tag{4}$$

For comparison with experiment this distribution should be convoluted with the contour $\varphi(\nu - \nu')$ according to formula (2). To describe the Raman spectra this contour should be assumed to be Lorentzian with a half-width of 30 cm⁻¹, which is temperature independent up to 200°C [8].

Integrating (4) along a band with regard to (3) we derive the expression for the integrated intensity A of a band in the IR spectrum:

$$A/A_{\rm vap} = 1 + k(\nu_0 - \langle \nu_{\rm s} \rangle) + kD_1$$
. (5)

Here $A_{\text{vap}} = c$ is the integrated intensity of a line of a free OH-group (for water monomer in vapour) to which the statistical contour $P(\nu) = \delta(\nu - \nu_u)$ collapses at low density and $T \to \infty$, $\langle \nu_s \rangle$ is the first moment of the statistical contour $P(\nu)$,

$$\langle v_{\rm s} \rangle = \int_0^{v_{\rm u}} v P(v) \, \mathrm{d} v$$

and

$$D_1 = \int_{\nu_0}^{\nu_u} (\nu - \nu_0) P(\nu) \, \mathrm{d}\nu \,, \quad D_1 > 0.$$

The first moment of intensity distribution in the IR spectrum can be expressed analytically through parameters of statistical contour P(v):

$$\langle v_{\rm IR} \rangle = \frac{\int v P_{\rm IR}(v) \, \mathrm{d}v}{\int P_{\rm IR}(v) \, \mathrm{d}v} = \frac{A_{\rm vap}}{A} \left\{ (1 + kv_0) \langle v_{\rm s} \rangle - k M_2^{\rm (s)} - k \int_{v_0}^{v_{\rm u}} v(v_0 - v) P(v) \, \mathrm{d}v \right\}.$$

Taking into account (5) and the connection between the second moment of statistical contour $M_2^{(s)}$ and its second *central* moment $M_{2\tilde{n}}^{(s)}$, $M_2(s) = M_{2\tilde{n}}(s) + \langle v_s \rangle^2$, we get

$$\langle \nu_{\rm IR} \rangle = \langle \nu_{\rm s} \rangle - \frac{k(M_{2c}^{\rm (s)} - D_2)}{1 + k(\nu_0 - \langle \nu_{\rm s} \rangle) + kD_1},\tag{6}$$

where

$$D_{2} = \int_{\nu_{0}}^{\nu_{u}} (\nu - \nu_{0})(\nu - \langle \nu_{s} \rangle) P(\nu) \, \mathrm{d}\nu, \quad D_{2} > 0$$

The coefficients k and v_0 in these formulas are to be found from a comparison with experiment. The IR contour shape appeared to be most sensitive to the choice of parameter v_0 while the value of k may be determined unambiguously from the temperature dependence of the integrated intensity, A.

3. Calculation of band shape and its temperature evolution

As an intrinsic (homogeneously broadened) contour $\varphi(\nu - \nu')$ we used, as in [8], a Lorentzian with a half-width of 30 cm⁻¹ for all temperatures. Such a choice provided good results for calculating Raman spectra [8] and agrees with the bandwidth of the IR spectrum of water in CCl₄ where H-bonds (and, consequently, their fluctuations) are absent. Moreover, artificial diminishing of this value to 20 cm⁻¹ or enlarging it up to 40 cm⁻¹ produces serious problems with reconstruction of experimental spectra during the deconvolution procedure [9] (see also [8]). The statistical contour for any temperature was calculated according to formula (1) using the invariant functions $E(\nu)$ and $W(\nu)$ found in [8].

In the literature there are few experimental data of high quality for IR spectra of HOD molecules in liquid water (H_2O and D_2O). We used tabulated spectra of Wyss and Falk [13] for 10, 35, 60 and 85°C and of Bondarenko et al. [14] for 20, 200 and 400°C. Parameters for the intensity factor in equation (3) were chosen using the Wyss and Falk spectra as these corresponded to a density of $\sim 1 \,\mathrm{g \, cm^{-3}}$ for which the theoretical model of the statistical contour was constructed and verified in [8]. The experiments of Bondarenko et al. were performed at a constant pressure of 1000 bar thus the density appreciably varied with temperature: it was 1.04, 0.92 and $0.69 \,\mathrm{g \, cm^{-3}}$ for the specified temperatures. For this reason it is possible to expect regular deviations of Bondarenko et al. spectra from our calculations.

To reproduce the Wyss and Falk contours it is absolutely necessary to take $v_0 < v_u$. If $v_0 = v_u$ is assumed, then in the contour at 85°C a shoulder appears at a frequency of about 3600 cm⁻¹. This shoulder is similar to that observed in the Raman spectra, but is absent in all experimental IR spectra. A reasonable agreement between calculation and experiment is achieved at $v_0 = 3670 \text{ cm}^{-1}$. A further decrease in v_0 gives no substantial improvement. The contour shape calculated is less sensitive to the value of factor k in formula (3). We used the value of k = 0.0913 cm which follows from the analysis of integrated intensities given in section 4.

The results of calculations involving these parameters are shown in figure 2. They fit quite well the experimental spectra of water under usual conditions (temperatures 10–85°C, density of ~1 g cm⁻³). For compressed water at a constant pressure of 1000 bar, we observe some discrepancy between calculation and experiment (figure 3). At 20°C (the density of 1.04 g cm⁻³) one can still speak about their agreement, but at 200°C (0.92 g cm⁻³) and 400°C (0.69 g cm⁻³) systematic differences are revealed: an excess intensity appears at frequencies near 3600 cm⁻¹ in calculated



Figure 2. A band of IR absorption of OH vibrations of molecules HOD diluted in D₂O at 10°C (1) and 85°C (2). Lines—calculation, circles—experiment by Wyss and Falk [13]. Spectra are normalized for height to unity.



Figure 3. Comparison of experimental and calculated contours of the IR band of HOD molecules at high temperatures. Lines—calculation for OH vibrations at 20 (1), 200 (2) and 400°C (3). Symbols—experiment by Bondarenko *et al.* for OD vibrations of HOD molecules diluted in H₂O [14], at the same temperatures and constant pressure 1000 bar. For recalculation of the OH band from the OD band, the axis of frequencies for experimental spectra is stretched 1.36 times (the isotopic ratio for frequencies v_{OH}/v_{OD}).

spectra. It is impossible now to conclude whether this distinction is due to a change of density in the experiments or results from imperfection of the theory at high temperatures.

Figure 4 shows the temperature dependence of the OH band half-width. The figure demonstrates first of all a wide scatter in experimental data of different authors. For example, at T = 573 K, according to the data of Franck and Roth [15] for 1 g cm^{-3} , this half-width coincides with the data of Bondarenko *et al.*



Figure 4. Dependence of half-width of OH vibration band on temperature. A dashed line-calculation for the distribution $P_{IR}(v)$ (see the formula (4)). Solid linecalculation for a band taking account of homogeneous broadening (distribution $P_{IR}(v)$, convoluted with Lorentzian with a half-width of $30 \,\mathrm{cm}^{-1}$). Horizontal line segment on the right shows the asymptotic value of a half-width $(T = 10^5 \text{ K})$. Symbols—experiment. Full circles-the data of Franck and Roth for OD bands at constant density of 1 g cm^{-3} [15]; triangles—data of Bondarenko et al. for OD bands at constant pressure 1000 bar [14]; for recalculation of OH band from OD band the axis of frequency is stretched by a factor of 1.36. Diamonds at T = 297-300 K show the data for half-width of OH band from different authors, according to table 2 in [13].

referring to a density of $0.82 \,\mathrm{g \, cm^{-3}}$. Thus, the halfwidth seems to be density independent at constant temperature which is unreal and contradicts other data of former authors (see [15]). The half-widths obtained by different authors at room temperature (297-300 K) and listed in table 2 of [13] are also displayed in figure 4; they vary from 240 up to 265 cm^{-1} . Having in mind such a wide scatter of experimental data, it is useless to require complete agreement between calculation and experiment. Nevertheless, we may assert that calculations represent correctly a general tendency of the half-width temperature evolution and, first of all, the presence of a maximum at T = 300-400 K. Growth in the half-width at high temperatures in the experiments of Bondarenko et al. is probably caused by a strong decrease of the water density: at the last point (773 K) it was as small as 0.53 g cm^{-3} . It is possible, however, that growth in the half-width at T > 650 K is caused by an increase with temperature in a width of a homogeneously broadened contour $\varphi(\nu - \nu')$, which was considered constant in our calculations.

Figure 5 illustrates a general picture of the temperature transformation of the IR band of HOD water.



Figure 5. Calculated temperature evolution of OH band (convoluted with Lorentzian of the half-width of 30 cm^{-1}) at temperatures 150, 293, 373, 473, 573, 773 and 10^5 K (from left to right).

It correctly reflects the basic tendencies of the evolution of experimental spectra at increasing temperature, i.e. a monotonous shift toward high frequencies, broadening of the envelope up to $T \approx 100^{\circ}$ C and its narrowing at higher temperatures. As well as in the infrared experiment, there is no shoulder (all the more so for the second maximum) in the high-frequency wing of a band, in contrast to the isotropic component of the Raman spectrum (see figure 1). Certainly, for temperatures lower than -40° C (nowadays the achievable limit for supercooling of liquid water) the calculated spectra correspond to the hypothetical situation of a metastable liquid. However, at T = 100 K they are rather close to the experimental IR spectrum of the amorphous solid water detected in this temperature range [16]. The temperatures above 400°C are poorly investigated for dense water, and the appropriate curves on figure 5 may be considered as a prediction. It is worth noting that as the temperature increases, the spectra do not tend to those in the rarefied vapour (see figures 4 and 5). It means that at density $\sim 1 \,\mathrm{g \, cm^{-3}}$ a network of hydrogen bonds and a corresponding fluctuational ensemble of OH oscillators with a wide distribution of frequencies persists in water even at high temperatures (see also [8]).

4. Temperature behaviour of integrated intensity

The formalism used in our calculations and proposed by Zhukovsky in the framework of the fluctuation theory of hydrogen bonding was developed for describing the contour of stretching OH bands. The formulas for integrated intensities given in section 2, develops this formalism further. A comparison between theoretical and experimental data on intensity can additionally verify the fluctuation concept independently of the contour shape description. Iogansen and Rosenberg [17] summarized all available, by then, experimental data of the integrated intensity of the IR bands of HOD molecules from vapour to ice over the temperature range 10 to 400 K including both the results of [13, 15] and their own data. All these data (except that for ice at 0 and 16 K) are described fairly well by a linear correlation of the Badger–Bauer type

$$A/A_{\rm vap} = 0.0829\Delta\nu - 5.2324$$
 ($R = 0.993$), (7)

where $\Delta v = v_u - v_{IR}^{max}$ and v_{IR}^{max} is the frequency of maximum of the IR band. As the intensity for OH vibration of HOD molecules in vapour we took half the sum of the integrated intensities of symmetric and antisymmetric stretching vibrations of the H₂O molecule from [18], $A_{vap} = 22.53 \text{ km mol}^{-1}$. Iogansen and Rosenberg [17], however, preferred to use the correlation

$$A^{1/2} = C_1 \Delta v^{1/2} + C_2$$
 (C₁ and C₂ are constants),

which they supposed to be universal (applicable to H-bonds of any type) and which readily describes the experiment on water with the correlation coefficient R = 0.998. The fluctuation theory cannot be applied for the description of all these data because the theoretical model of statistical contour $P(\nu)$, developed in [8] and used here, refers only to water at a constant density of 1 g cm^{-3} . The experimental data corresponding to this density are denoted in figures below with full circles.

Figure 6(*a*) summarizes all available information on the integrated intensity of the water IR band for different temperatures (per one OH oscillator). The data reported by Iogansen and Rosenberg [17], results by Bondarenko *et al.* [14], and also a single value for H₂O at T = 295 K from [19] are used here.

According to formula (5), integrated intensity should be a linear function of $v_0 - \langle v_s \rangle$ (D_1 can be neglected as its maximum value is only 0.6 cm^{-1} at 800 K). Figure 6(b) shows that this law is fulfilled quite well for the points corresponding to a density of 1 g cm^{-3} , if k = 0.0913 cmis accepted. Thus, we assume the following values for the intensity factor in expression (3): $v_0 = 3670 \,\mathrm{cm}^{-1}$, k = 0.0913 (see section 3). These values are very close to $v_0 = 3664.7 \text{ cm}^{-1}$ and k = 0.0934 cm obtained in [7] by other procedures. The fact that an increase in intensity of a particular OH oscillator is proportional, according to (3), not to the shift of its frequency relative to a vapour value $v_u = 3707 \text{ cm}^{-1}$ but to the shift relative to a smaller frequency $v_0 = 3670 \text{ cm}^{-1}$ indicates, probably, that the shift of frequency is determined not only by hydrogen bond strength, but also by van der Waals interactions. This is confirmed by interesting observations. The heats of evaporation of water from different solvents [19] as well as the integrated intensities of the



Figure 6. Dependence of the integrated intensity of IR absorption of OH vibration band of HOD molecules (*a*) on temperature and (*b*) on the first moment of the statistical distribution of frequencies $\langle v_s \rangle$. Symbols—experimental data: open circles at low temperatures and the big values $v_0 - \langle v_s \rangle$ correspond to ice [17], at T = 673 K and $v_0 - \langle v_s \rangle = 96$ cm⁻¹—to superheated vapour with different densities [17]; black circles [17] and an asterisk [19] a liquid at a density of ~1 g cm⁻³; triangles—a liquid at pressure 1000 bar [14]. Lines—results of calculation using formula (5). The first moment of the statistical contour $\langle v_s \rangle$ was found from distributions P(v) calculated for different temperatures on the basis of the model developed in [8].

methanol OH band in various solvents [21] are linearly dependent on the shift of the OH band frequency. However, the slope of this dependence is different for the solvents involved and not involved in hydrogen bonding; for the van der Waals solvents the slope is much smaller but not zero.

Let us consider the dependence of integrated intensity on temperature (figure 6(*a*)). The calculated straight line from figure 6(*b*) is transformed here to a curved line, whose asymptote at $T \rightarrow \infty$ is depicted by a horizontal line segment for T > 800 K. As well as in figure 6(*b*), the points related to a liquid phase at density of 1.04–0.96 g cm⁻³ (all full points and first four triangles on the left) are well described by this theoretical curve. The points for a density of 0.92 g cm⁻³ (a triangle at 473 K) and for 0.9 g cm⁻³ (the top circle at



Figure 7. Interrelation for frequency of maximum of the IR band of OH vibrations of molecules HOD, v_{IR} , (*a*) with temperature and (*b*) with integrated intensity. Designations of symbols are the same as in figure 6. Solid line—calculation. Dotted line shows behaviour of the first moment of distribution $P_{IR}(\nu)$; for this curve it is necessary to understand $\langle v_{IR} \rangle$ as v_{IR} on the axes (see formula (6)).

673 K) are also situated in its vicinity. However, with a further decrease in density, the points deviate more and more from the theoretical curve (circles at 673 K correspond to density of $0.8-0.095 \,\mathrm{g \, cm^{-3}}$, and triangles at 523-773 K to a density of 0.877-0.528 g cm⁻³). Ice, certainly, should not be described by the fluctuation theory because the configuration of the hydrogen bridge is fixed here, thus a statistical contour collapses to a delta function. However, constructing the statistical contour in [8], we assumed that at T = 0 K only one optimal configuration of H-bonds corresponding to ice at T = 0 K should remain. Therefore the statistical contour frequency was set equal to the frequency of OH vibration in ice at T = 0 K (see figure 7(*a*)). The integrated intensity according to this logic seemed to be equal at T = 0 K to that in ice, too. This, however, is not the case (see figures 6(a) and (b)).

As far as the position of a band is concerned, the frequency of maximum absorption is recorded most easily by experiment. Conversely, this frequency is most difficult to calculate theoretically. One may calculate analytically only the first moment of the distribution $P_{\rm IR}(\nu)$ (see equation (6)). For the asymmetric band it does not coincide with the position of a maximum. In addition, its value changes after convolution with a contour $\varphi(\nu - \nu')$. Therefore the position of the band maximum was calculated numerically to within 1 cm^{-1} using cubic spline for the approximation of function W(v) tabulated in [8]. Figure 7(a) depicts the temperature dependence of the position of the IR band maximum and figure 7(b) shows its correlation with the integrated intensity. The calculated position of a band maximum for a density of $\sim 1 \,\mathrm{g \, cm^{-3}}$ fits the experiment somewhat worse than the calculated integrated intensity (compare figure 6). However, as a whole, the calculation provides a correct temperature evolution. The data for ice and a fluid of low density (open circles), certainly, are not described by the theory. Behaviour of the first moment and the frequency of maximum of the IR band at high temperatures are quite different which reflects contour asymmetry (see figures 3 and 5).

5. Conclusions

We believe that the above data indicate that the fluctuation model of hydrogen bonding describes well (qualitatively and quantitatively) the band shapes of HOD molecules in IR spectra and their temperature evolution. Since the theory also describes the Raman spectra over a wide temperature range [8] we may assert that the fluctuations of hydrogen bridge configurations do cause a large width of stretching bands for water and, probably, for other systems with hydrogen bonds of medium strength (alcohols, amines, etc.). We do not know at present any other theory where experimental spectra of water (IR and Raman) would be quantitatively reproduced even at one temperature. (Formal *decomposition* of a band into a set of contours supposedly constituting it, cannot be considered, certainly, as an explanation.) On the other hand, a successful description of band shapes in the vibration spectra of HOD water in the framework of the fluctuation concept of hydrogen bonding is a strong argument in favour of the continuum model of liquid water structure. The main characteristic of this model is the continuous network of H-bonds. Its spectroscopic manifestation is the OH-frequency distribution P(v)determined by the above-mentioned formula (1). The alternative mixture model of water, which introduces a finite number of discrete species (monomers, dimers, trimers etc., or other aggregates), is incapable of explaining and quantitatively describing even a small part of the known facts.

Some discrepancies between our results and experiment (even when considering density of about 1 g cm^{-3}) may be interpreted in two ways. On the one hand, there are evident imperfections in the theory. The linear frequency dependence for the intensity factor implied in equation (3) is, probably, too simplified. The width of a homogeneous contour $\varphi(\nu)$ is sure to increase somehow with temperature. Lastly, converting the experimental OD band of the HOD molecule into the OH band by a constant factor of 1.36, used by us in a few cases in addition to direct data in the OH-region, is not quite accurate because of the coupling of OH and OD vibrations through Fermi resonance with a bending overtone $2\nu_2$ [22]. On the other hand, there is no fair agreement among the experimental results of various authors; no information on the OH vibration contours at high temperatures and constant density is available. Therefore, further improvement of the theory can be made only on the basis of new systematic experimental data.

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