

On the interrelation between frequencies of stretching and bending vibrations in liquid water

Yu. Ya. Efimov *, Yu. I. Naberukhin

Institute of Chemical Kinetics and Combustion, RAS, Novosibirsk State University, Novosibirsk 630090, Russia

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Abstract

The problem is investigated whether the distributions of bending frequencies $P(\nu_{\text{bend}}, T)$ of H_2O molecules in the liquid could be calculated from statistical distributions $P(\nu_{\text{OH}}, T)$ of stretching frequencies on the basis of the empirical correlation established for their mean values. It is found that correlations of different kinds fail to reproduce real spectra. They result in a bending band that is too narrow and give rise to an Evans hole in the stretching band. This provides evidence of the strong intermolecular coupling of bending modes, which makes their frequencies statistically independent from stretching frequencies. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

There are two general approaches to understand the origin of very wide widths of OH stretching modes in systems with hydrogen bonding. The first concerns the anharmonic coupling of the high- and low-frequency modes (see overview in Ref. [1] and the last impressive development [2]). However, for water, it was found experimentally that satellite bands originating from such a coupling have a very low intensity [3,4]. This means that the anharmonic coupling in water is weak and therefore has no noticeable influence on the band shape. Indeed, as the form

of stretching band as its temperature transformation in both infrared and Raman spectra are described quite well within the framework of the fluctuation conception of hydrogen bonding [5–8], which is an alternative approach to the band broadening for hydrogen bonded species.

According to the fluctuation theory of hydrogen bonding [5–8], very wide bands in the vibrational spectra of water OH-oscillators reflect the statistical distribution of geometric configurations of a hydrogen bridge O–H...O. It is caused by the fluctuations of the local environment of the different H_2O molecules that are typical for liquids as compared to crystals. It is well known that there is a correspondence between stretching OH frequency, ν_{OH} , and energy of corresponding hydrogen bond E , e.g. of the type of the Badger–Bauer linear relation, $E = a + b\nu_{\text{OH}}$. This fact allows the

* Corresponding author. Tel.: +7-3832-332854; fax: +7-3832-342350.

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

Boltzmann statistics to be used for calculating the distribution $P(\nu_{\text{OH}})$ of the stretching frequencies of uncoupled OH oscillators [7]. However, the band in the stretching region of water is the result of coupling of two stretching OH vibrations and the bending overtone (Fermi resonance). Therefore, to calculate this contour, we have to know the distribution of the bending frequency $P(\nu_{\text{bend}})$, keeping in mind that $\nu_{2\text{bend}} \approx 2\nu_{\text{bend}}$.

Unfortunately, the bending frequency is sufficiently less sensitive to hydrogen bonding than the stretching, and the correlation between ν_{bend} and E is unknown. But some investigators have attempted to construct the correlation between stretching and bending frequencies. Thus, Falk [9] has found the interrelation between the mean frequency of stretching band of H_2O molecules and the peak frequency of their bending band in various crystalline hydrates and liquid complexes. The aim of the present article is to investigate whether this (or similar) interdependence could be used for the reconstruction of the $P(\nu_{\text{bend}})$ distribution starting from $P(\nu_{\text{OH}})$ distribution.

First of all, we verify the correspondence between experimental spectral contours and $P(\nu_{\text{bend}}, T)$ calculated on the basis of this correlation (and its modification). Then, we analyze the influence of such a correlation on the coupling of three intramolecular vibrations in the ensemble of H_2O molecules differently perturbed by hydrogen bonds due to fluctuations of local surroundings.

2. Calculation of the contour shape of bending vibrations of H_2O molecules in liquid water from the OH-frequency distribution

Analysing the behaviour of infrared spectra in the region of bending vibrations of different isotope modifications of water molecules in proton-accepting solvents and crystalline hydrates, Falk [9,10] has proposed the empirical correlation between the frequency of band maximum of ν_{bend} and the mean value of stretching frequencies

$$\langle \nu_{\text{OH}} \rangle = (\nu_s + \nu_{\text{as}})/2;$$

$$\nu_{\text{bend}} = 1590.6 + 0.2583 (3707 - \langle \nu_{\text{OH}} \rangle) \text{ cm}^{-1}. \quad (1)$$

Here, ν_s and ν_{as} are the frequencies of the band maxima of symmetric and antisymmetric vibrations of the OH-groups of H_2O molecule so that $\langle \nu_{\text{OH}} \rangle$ is the measure of the mean energy of two H-bonds involving a given molecule as a proton donor.

If this correlation is valid for every individual H_2O molecule in the statistical ensemble, it can be readily used to convert the distribution of stretching frequencies $P(\nu_{\text{OH}}, T)$ into the corresponding distribution $P(\nu_{\text{bend}}, T)$:

$$P(\nu_{\text{bend}}) = P[\nu_{\text{OH}}(\nu_{\text{bend}})] |d\nu_{\text{OH}}/d\nu_{\text{bend}}|. \quad (2)$$

In this formula, $\nu_{\text{OH}}(\nu_{\text{bend}})$ and $d\nu_{\text{OH}}/d\nu_{\text{bend}}$ can be taken from Eq. (1), substituting $\langle \nu_{\text{OH}} \rangle$ by ν_{OH} (then $|d\nu_{\text{OH}}/d\nu_{\text{bend}}| = 1/0.2583$). This implies that we consider the spectrum of HOD molecules where the intramolecular coupling of OH and OD vibrations is actually eliminated, and the OH band directly reflects the energy distribution of hydrogen bonds in the liquid at a given temperature [7,8].

The problem of extracting the statistical frequency distribution from experimental spectra has been studied in Ref. [11], and analytical expressions for $P(\nu_{\text{OH}}, T)$ are given in Ref. [12]. These distributions are displayed as dashed lines in Fig. 1 at 10 and 90 °C. Solid lines represent the frequency distributions of the bending overtone $P(\nu_{2\text{bend}})$ calculated from the above by Eqs. (1) and (2). (The use of $2\nu_{\text{bend}}$ instead of ν_{bend} in this figure illustrates the overlapping of frequency distributions involved in Fermi resonance without accounting for the anharmonicity. Transition to $P(\nu_{\text{bend}})$ can be readily performed by simple division of the frequency scale by 2).

As follows from the figure, the bimodal shape of calculated $P(\nu_{\text{bend}})$ contours have nothing in common with the experimental spectra of the bending band of H_2O molecules in both infrared [10,13] and Raman [14] spectra. The reason may lie in the fact that the correlation (Eq. (1)) uses the only one parameter—the half-sum of the frequencies of symmetric and antisymmetric vibrations of H_2O molecules. This implicitly assumes that the H_2O molecule is symmetric in a liquid and preserves the gas-phase symmetry C_{2v} . However it is hardly probable that two OH-

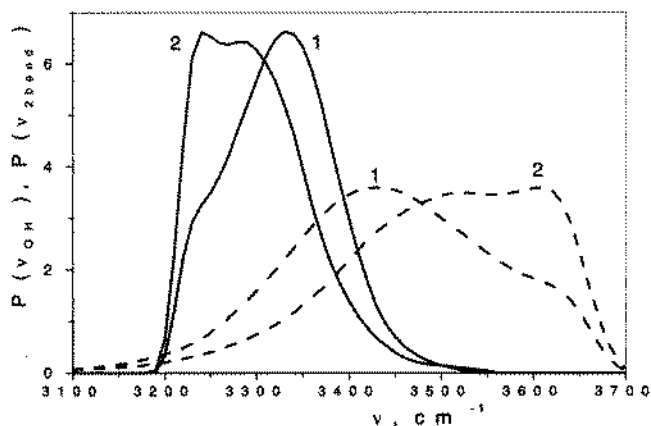


Fig. 1. Statistical frequency distributions of OH-oscillators in liquid water (dashed line) and the distributions of double frequencies of bending vibrations (solid line) calculated from them at 10 (curve 1) and 90 °C (curve 2) by Eqs. (1) and (2).

groups of one molecule in a liquid are simultaneously involved in the H-bonds of equal strength: most molecules are 'loaded' asymmetrically due to the fluctuations of local environment (Fig. 2).

If the correlation in question exists, it can be represented in general as $\nu_{\text{bend}} = \nu_{\text{bend}}(x, y)$ where, for simplicity, the partial (i.e. uncoupled) frequencies $\nu_{\text{OH}}^{(1)}$ and $\nu_{\text{OH}}^{(2)}$ are denoted by x and y , respectively. Thus, the distribution of bending vibration frequencies $z \equiv \nu_{\text{bend}}$ has the form:

$$P(z) = \iint_{z=z(x,y)} P(x, y) dx dy. \quad (3)$$

Integration is performed here over the set of points (x, y) corresponding to a given frequency z . A two-dimensional distribution $P(x, y) = P(x)P(y)$ determines the probability to find a molecule with $\nu_{\text{OH}}^{(1)} = x$ and $\nu_{\text{OH}}^{(2)} = y$. If the local surroundings of two hydroxyl groups of every H₂O molecule are independent, both $P(x)$ and $P(y)$ correspond to the same distribution $P(\nu_{\text{OH}}, T)$.

The exact form of the functional dependence of $z(x, y)$ is unknown. The simplest improvement of correlation (Eq. (1)) preserving its validity for symmetric molecules ($x = y$) and holding for all the rest ($x \neq y$) is the hypothesis:

$$z = 1590.6 + 0.2583 (3707 - (x + y)/2) \text{ cm}^{-1}. \quad (4)$$

In this case, $(x + y)/2$ still reflects the mean

strength of two H-bonds perturbing OH-groups of a given molecule. Here, the frequencies x and y (and energies E_1 and E_2) are not equal in general, in contrast to Falk's formula (Eq. (1)) where uncoupled frequencies were implied to be equal. Since z depends now on the sum of two independent variables x and y , integration (Eq. (3)) can be performed by converting the distribution $P(x, y)$ into two-dimensional distribution $P(u, v)$ where $u = (x + y)/2$, $v = (x - y)/2$ and consequently $x = u + v$, $y = u - v$:

$$P(u, v) = P(x, y) \left| \partial(x, y) / \partial(u, v) \right| \\ = 2P(u + v)P(u - v). \quad (5)$$

Fig. 3 displays these distributions at two temperatures. Now, we can perform integration in Eq. (3) by the conventional integration of $P(u, v)$ surface over v at a fixed value of u , corresponding to the value $\nu_{\text{bend}} = z$ for which $P(z)$ is sought.

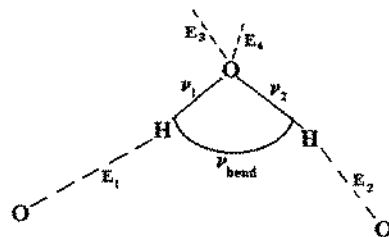


Fig. 2. Water molecule that forms two hydrogen bonds nonequivalent in geometry and energy which leads to the statistics of the frequencies of intramolecular vibrations.

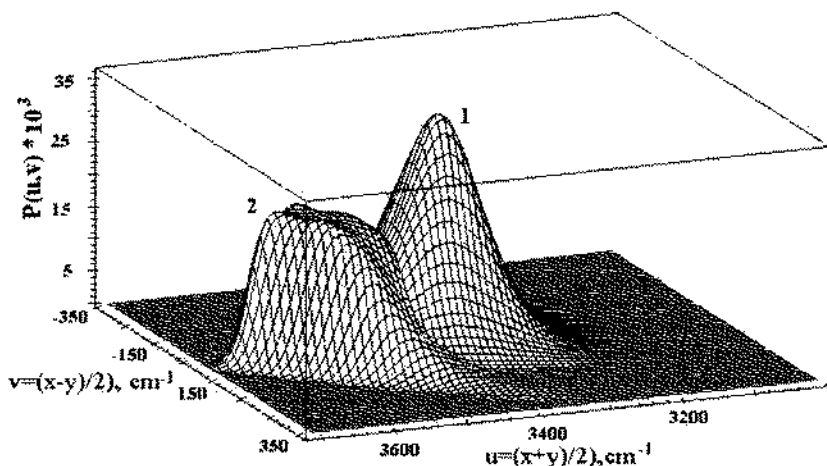


Fig. 3. Two-dimensional function of the density of probability to meet H_2O molecule in the liquid with a half-sum of OH-oscillator frequencies $u = (x + y)/2$ and their half-difference $v = (x - y)/2$ at -40°C (surface 1) and $+90^\circ\text{C}$ (surface 2).

The results of calculations at -40 , 10 , and 90°C are given in Fig. 4. For positive temperatures, the statistical contour $P(\nu_{\text{OH}})$ is taken directly from Ref. [11], and for supercooled water it is calculated by the procedure described in Refs. [8,12] which was verified over the range of at least 300°C . As compared with Fig. 1 the calculated contours are now unimodal and correspond in their form to the experimental contours [10,13,14]. Their temperature shift $(1677 - 1645)/130 = -0.24 \text{ cm}^{-1}/\text{K}$ is rather close to that obtained by Falk from experimental data [10] ($-0.18 \text{ cm}^{-1}/\text{K}$). However, the half-widths of these contours (43 , 51.5 and 48 cm^{-1} , respectively) are substantially smaller than those in infrared ($88 \pm 4 \text{ cm}^{-1}$) and especially in Raman ($120 \pm 15 \text{ cm}^{-1}$) spectra. The molecular dynamics calculations of the ν_{bend} band from the auto-correlator of proton velocity give an even greater value of about 300 cm^{-1} [15]. Thus, it must be accepted that the correlation of type (Eq. (1)), even with our modification (Eq. (4)), fails to give a quantitative description of the bending vibration band.

It is interesting that the mean value obtained by us for the half-width, $\delta\nu_{\text{bend}}(1/2) \approx 48 \text{ cm}^{-1}$, closely corresponds to the half-width of the histogram of the $P(\nu_{\text{bend}})$ distribution of water molecules in 325 studied crystalline hydrates [9]. This allows us to conclude that the totality of the

realised configurations of H_2O molecule environments in all possible crystalline hydrates exhaustively describe the fluctuations of configurations realised in the liquid state.

Fig. 1 shows that the distributions of frequencies $P(\nu_{\text{OH}})$ and $P(\nu_{2\text{bend}})$ greatly overlap. Since the matrix elements of the coupling of two stretching oscillators with one another, $V = -5 \text{ cm}^{-1}$, and with the overtone of bending vibration, $W = 36 \text{ cm}^{-1}$ [5], are close by module, the importance of Fermi resonance in the formation of liquid water spectrum in the range of 3000 – 3700 cm^{-1} is indisputable. The result of the coupling of three oscillators depends on whether the (x, y, z) frequencies in the ensemble of H_2O

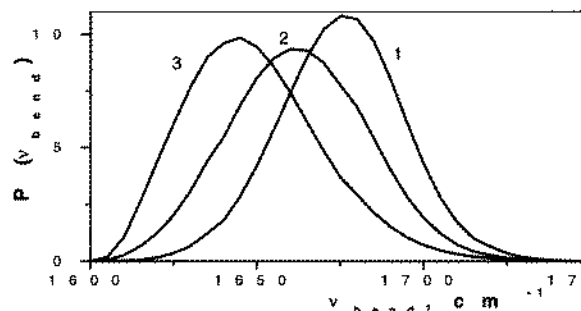


Fig. 4. Contours of bending vibrations calculated from Eq. (4) for -40°C (curve 1), 10°C (curve 2) and 90°C (curve 3).

molecules correlate, anticorrelate according to Eq. (4) or are independent of one another. In this paper, we consider the most prominent manifestations of anticorrelation (Eq. (4)) in the coupling of three vibrations for the ensemble of the fluctuationally perturbed water molecules.

3. Coupling between three intramolecular vibrations of H₂O molecules in the ensemble of fluctuationally perturbed ones

Calculations were carried out by the quantum-mechanical method of partial oscillators [16] as described in Ref. [5]. Let us consider the H₂O molecule accidentally perturbed by the fluctuations of local environment (Fig. 2). Let it have the frequencies $\nu_{\text{OH}}^{(1)} = x$, $\nu_{\text{OH}}^{(2)} = y$, $\nu_{\text{2bend}} = 2z$ as the partial frequencies of three interacting oscillators (i.e. frequencies *before* intramolecular coupling). Coupling of these three oscillators is the eigenvalue problem:

$$\mathbf{H}\psi = \mathbf{E}\psi \quad (6)$$

with Hamiltonian:

$$\mathbf{H} = \begin{bmatrix} x & V & W \\ V & y & W \\ W & W & 2z \end{bmatrix}. \quad (7)$$

The resulting frequencies ν_i ($i = 1, 2, 3$), being the eigenvalues of \mathbf{H} matrix, are the roots of the cubic equation:

$$\text{Det}(\mathbf{H} - \mathbf{E}\nu_i) = 0, \quad (8)$$

where \mathbf{E} is the unity matrix. The solution can be found in the simplest way by the Cardan formula in its trigonometric form. Solving Eq. (6) for the eigenfrequency ν_i , we determine the corresponding eigenfunction ψ_i , which is a linear combination of partial wave functions ψ_x , ψ_y , and ψ_{2z} . The contributions of ψ_x and ψ_y to i th vibration determines its intensity, which is different in infrared, Raman isotropic and anisotropic spectra (for details, see Ref. [5]). All three ν_1 , ν_2 , ν_3 frequencies calculated on the assumption of ‘anticorrelation’ (Eq. (4)) are shown in Fig. 5 in coordinates (x, y). It is seen that in the vicinity of 3300 cm^{-1} (by vertical)

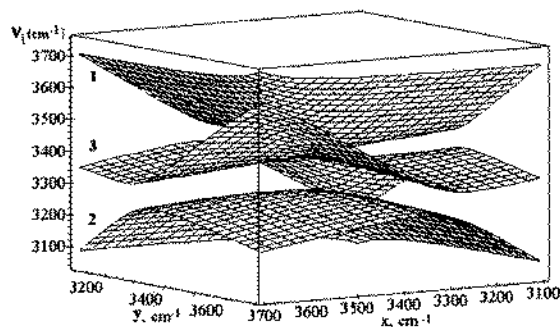


Fig. 5. Eigenfrequencies of three vibrations of H₂O molecule resulting from the intramolecular coupling of three oscillator with the initial (partial) frequencies $\nu_{\text{OH}}^{(1)} = x$, $\nu_{\text{OH}}^{(2)} = y$, $\nu_{\text{2bend}} = z$ when the correlation in Eq. (4) is applied. The calculation were performed by Eqs. (7) and (8). The digits indicate the vibration number.

in the range of at least 100 cm^{-1} , there are no frequencies except for a ‘leaf’ of the ν_3 surface at small values of x and y . It is similar to the well-known Evans hole [17], which reflects the total absence of vibrational states at the position of the overtone.

The results of calculations of intensities for the ensemble of 500 000 statistically disturbed H₂O molecules at 10°C using the algorithm [5] are displayed in Fig. 6. The upper part of the figure

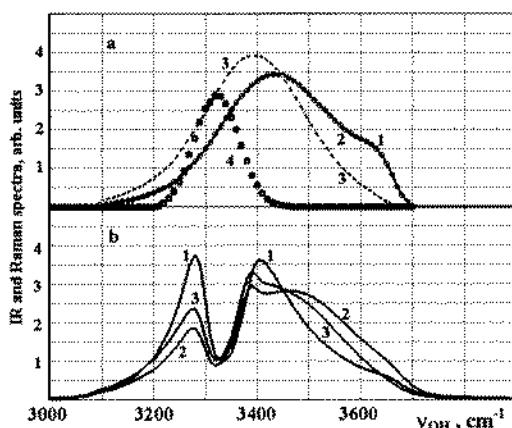


Fig. 6. Initial data (a) and the result of intramolecular coupling of three vibrations (b) at 10°C in the ensemble of 500 000 H₂O molecules differently perturbed by the fluctuations of local environment. 1: isotropic Raman; 2: anisotropic Raman; 3: infrared spectra; 4: distribution of bending overtone frequencies calculated using Eq. (4).

illustrates the initial data for the calculations. Curve 1 is the statistical distribution of OH-frequencies [11] derived from isotropic component of Raman spectrum of HOD molecules diluted in D₂O [18]. Curves 2 and 3 are calculated from curve 1 with account for the known dependence of intensity of individual oscillator on frequency (H-bond strength) in anisotropic Raman and infrared spectra, respectively. Curve 4 is the distribution of bending overtone frequencies generated in the process of calculations from $P(\nu_{\text{OH}})$ distributions using Eq. (4). Curves 1–3 in Fig. 6(b) are calculated Raman isotropic, Raman anisotropic and infrared spectra of H₂O molecules after convolution with the Lorentzian with the half-width of 30 cm⁻¹, which describes the homogeneous broadening [11]. We see a deep hole in all types of spectra in the vicinity of the bending overtone maximum. These contour shapes differ drastically from the real shape of stretching band where no evidence of such a hole has been observed.

4. Conclusions

Hence, the use of empirical correlation (Eq. (1)) and its modification (Eq. (4)) for reconstruction of the band form of bending vibrations shows that they fail to provide the correct result. It causes a bending contour that is too narrow and a deep Evans hole inside the stretching band. We see two ways out of this paradoxical situation (the two-structure interpretation of bending band as in Ref. [14] does not improve the situation because it is the special case of the fluctuation theory, which works with a continuous manifold of structures). Maybe the ν_{bend} frequency depends not only on the mean loading of a molecule $(\nu_{\text{OH}}^{(1)} + \nu_{\text{OH}}^{(2)})/2$, but on its asymmetry $(\nu_{\text{OH}}^{(1)} - \nu_{\text{OH}}^{(2)})$. But more probable is the assumption that there is the intermolecular coupling of bending vibrations of adjacent water molecules. Such a coupling, at first, broadens the bending contour in different phases

of water [19]. Then, it mixes the bending vibrations of many molecules to an extent that in each individual H₂O molecule, the partial frequencies of stretching and bending oscillators must be considered practically as independent.

Acknowledgements

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