Contribution of Fermi and Darling–Dennison resonances to the formation of Raman spectra of water and water–ethanol solutions

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As a result of the experimental study of water Raman spectra and water–ethanol solutions, it was established that Fermi resonance and Darling–Dennison resonance make significant contribution to the formation of Raman spectra. Basing on the analysis of the spectra using optimization algorithms, the coupling constants W and the contributions of Fermi resonance to spectra in water and aqueous ethanol solutions at various temperatures were calculated. The contribution of the resonance of Darling–Dennison to the formation of the spectra of solutions was analyzed. It was established that Fermi and Darling–Dennison resonances manifested stronger in a 20% solution of ethanol in water in comparison with pure water. These resonances weakened with increasing temperature. This effect was explained from the point of view of strength of hydrogen bonds. Copyright © 2017 John Wiley & Sons, Ltd.

Keywords: Fermi resonance; Darling–Dennison resonance; water–ethanol solutions; genetic algorithms

Introduction

Study of vibrational dynamics of liquid water molecules is extremely important for understanding many chemical and biological processes.[1,2] Dynamic properties of water in the cell reflect in great extent the state of cellular structures.[3] Water is involved in changing conformation of globular proteins[4], in molecular transport of charge and energy in biological tissues.[5]

Raman spectrum (RS) of the liquid water is very complicated. It consists of many vibrational bands with different shape and intensity caused by intra- and intermolecular interactions, resonances between different vibrations and overtones of vibrations, combination frequencies.[6] Still, the question about the mechanisms of formation of the RS of water remains open. There is no adequate model of the interactions of bounded molecules in water; concepts about role of anharmonic resonances in this model are ambiguous and contradictory. First, this applies to the resonances of the type of Fermi and Darling–Dennison.[6]

Resonance of Fermi type represents splitting bands of intramolecular vibrations and redistribution of intensities between components of doublet as a result of elimination of accidental degeneracy.[7,8] Fermi resonance of the first type between the fundamental tone of one vibration and the overtone of the other is most probable.[8] Resonances involving overtones and combination frequencies – Darling–Dennison resonances[9] – are also feasible. For study of vibrational dynamics of water molecules, Fermi resonance (FR) between the symmetric stretching vibration and the overtone of the bending vibrations of OH groups and Darling–Dennison resonance (DDR) between the first overtones of the symmetric and the antisymmetric stretching vibrations of OH groups are most interesting.

Currently, there are many theoretical calculations of the vibrational spectra of isolated molecules of water, showing the necessity of accounting the FR and DDR for the description of vibrational processes.[10–14] As a result of numerical calculation of vibrational spectra of water small structural fragments, the characteristics of the vibrational–rotational Hamiltonians and anharmonic resonances of Fermi and Darling–Dennison in small water associates were determined on the basis of solution of molecular Schrodinger equation in the framework of the density functional theory with hybrid functionals B3LYP, X3LYP.[15]

There are the results of experimental studies of anharmonic vibrational resonances in water, for example, by means of ultrafast time-resolved infrared spectroscopy.[16–21] The authors studied vibrational couplings and relaxation dynamics of bending and stretching vibrations in solutions of H_2O in D_2O by means of new ultrafast broadband mid-infrared light source.[11] It was established that stretching vibrations of HOD hydroxyl groups are in Fermi resonance with HOD bending vibrations. In addition, it was found that HOD is also anharmonically coupled with modes of D_2O. The OH oscillators with strong hydrogen bonds have tendency to relax through the bending mode; the oscillators with weak hydrogen bonds relax through other modes. The authors believe that they have experimentally demonstrated the existence of Fermi resonance between the stretching and bending vibrations of dilute HOD in D_2O (near 2200 cm^{-1}).

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Femtosecond dynamics of bending excitations of OH groups was investigated in the wavenumber range 1000–4000 cm^{-1} in the papers.[17–21] Bending vibrations of OH groups demonstrate that v = 1 stretching and v = 2 bending states are coupling by Fermi resonance. As a consequence, the v = 2 -> 3 and v = 1 -> 2 absorption bands of the bending vibration of OH groups are heavily broadened (more than 200 cm^{-1}).

All experiments with using ultrafast infrared spectroscopy have demonstrated a significant coupling of inter- and intramolecular vibrations of water in liquid phase. This capability of water to efficient dissipation of energy by means of ultrafast vibrational relaxation is very important for the stabilization of the reactive intermediates and for the result of water chemical reactions.

Thus, due to the energy transfer between vibrational modes, FR can affect the speed of breaking peptide bond.[22,23] It is known that water molecules take part in the breaking macroergic bond in the molecule ATP in the process of work of molecular motor F1-ATPase. The authors[24] assumed that due to the FR between the intra - and intermolecular vibrational modes of peptides, the coherent transfer of vibrational energy in α-helix can take place. There are few works in which FR is used to solve applied problems. For example, the authors[25] propose to determine the temperature of the biomaterial measuring the temperature of water contained in material using temperature dependence of the position, intensity and shape of the contours of the vibrations v_1 and $2v_2$.

However, despite the great interest of specialists to the analysis of anharmonic resonances in liquid water, the contribution of the FR and DDR to the spectral Raman bands of water and aqueous solutions still remains unknown. First and foremost, it concerns the role of FR in the formation of water stretching band. One should note that according to the prevailing in the literature a few decades ago point of view, FR does not have any influence on the formation of water Raman stretching band.[26,27] The authors[28–35] suppose, that as a result of FR between the overtone of the bending vibration $2v_2 \approx 3240$ cm^{-1} and the fundamental tone of symmetric stretching vibrations v_1 of water molecules, pumping intensity of RS between vibrations v_1 and $2v_2$ occurs. Exactly, this energy exchange explains the presence of intense low-wavenumber region near 3300 cm^{-1} in the spectrum of water Raman stretching band. Authors[29] claim that FR should be taken into account for explanation of nature of water Raman stretching band, but its role is not so big. At the same time, according to theoretical calculations taking into account the asymmetry of water molecules, the authors[30] consider the contribution of FR to water Raman band as 'unexpectedly great'.

One should note that in our days the situation regarding consideration FR in water as a mechanism of Raman spectra formation remains contradictory. In the series of studies, for example, in[36–38] Fermi resonance is not taken into account in the study of Raman spectra. The authors claim that the intermolecular interactions break the symmetry of the vibrations so severely, that one should not consider symmetric and antisymmetric normal vibrations as a basis. Thus, according to the authors, one should not try to explain features of Raman spectra shape in terms of symmetric and antisymmetric vibrations. At the same time, the authors[39] showed that collective vibrations of water molecules in the condensed phase should partially retain their symmetry/antisymmetry. In the paper [41], where the structure of interfacial water was studied using vibrational sum-frequency generation [V-SFG]-spectroscopy, it was concluded that Fermi resonance contributes to the formation of vibrational spectra (although this contribution is smaller than the intermolecular interactions). Thus, the question of the role of Fermi

resonance in formation of water Raman spectra remains open. Earlier, the authors of this paper have carried out experimental studies of the contribution of the FR to the water Raman stretching band when its temperature changes from 20 to 99 °C and when the concentration of D_2O solutions and concentration of dissolved in water salts KI, KBr, KCl and KF changed.[33] The method of calculation of constants of interaction of Fermi resonance was proposed and implemented. It was found that intensity of component of Fermi-doublet is about 10% of intensity of low-wavenumber region of Raman stretching band of liquid water at the temperature 25 °C.[33] At the present, for liquid water, there are no accurate methods of calculation of the frequencies of bending and stretching vibrations in the presence and absence of resonance interaction.

Darling–Dennison resonance in water is caused by possible interaction of the overtones of the symmetric (2 × 3330 cm^{-1}) and the antisymmetric (2 × 3430 см$^{-1}$) stretching vibrations of OH groups. The third bending vibrations overtone (4 × 1650 cm^{-1}) and the combination of the bending vibrations overtones and the symmetric stretching vibrations (2 × 1650 cm^{-1} + 3330 cm^{-1}, further – the combination vibration) can give the contribution to the band of overtones (5900–7400 cm^{-1}). They can have the same symmetry, so they can 'disturb' each other.

Theoretical calculations of DDR in water testify the evidence of its significant contribution to the formation of band 5900–7450 cm^{-1} in RS of liquid water.[10,13–15] However, the studies, in which the role of DDR in the formation of the band 5900–7450 cm^{-1} was studied experimentally, are unknown for the authors of this paper. The spectra of the stretching vibrations overtone of H_2O and D_2O were studied in papers.[35–44] The authors noted a shift of the band towards high frequencies with increasing temperature (similarly to the corresponding shift of the band of stretching vibrations of fundamental tone), but they did not connect the process of formation of the band of overtones with resonance of Darling–Dennison.

The aim of this work was to study the role of the FR and DDR in the formation of Raman spectra of water and water–ethanol solutions and the dependence of the resonances contribution to the intensity of the spectra on the strength of hydrogen bonds in solutions.

Contribution of Fermi resonance to the formation of OH groups stretching bands

Method of determination of Fermi resonance coupling constants

Fermi resonance can take place only for vibration with the same symmetry [7]. In the case of liquid water, the intensive intermolecular interactions break the symmetry of the intramolecular vibrations and, according to some researchers, e.g.[37] one should not use a basis consisting of symmetric and antisymmetric vibrations. But one can mathematically resolve every vibration (including the vibration affected by strong intermolecular interactions) using basis of normal vibrations and specify the symmetric and antisymmetric vibrations. In this paper, such model, assuming the decomposition of vibrations using the basis of symmetric and antisymmetric vibrations, was used for the description of Fermi resonance in water.

Basing on the model of FR elaborated in[8,29,34] earlier, the authors of the this paper suggested the method of calculation of FR coupling constant[33] which characterizes its efficiency. In Fig. 1, the diagram of splitting intramolecular vibrations due to FR according to the model[8,29,34] is presented.
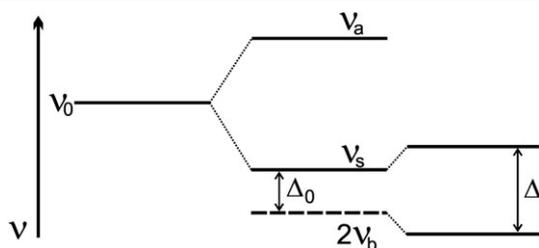
Figure 1. The diagram of Fermi resonance. ν_0 – unperturbed vibration, ν_s – symmetric vibration, νa antisymmetric vibration, $2\nu_b$ – bending vibration overtone; Δ_0 and Δ – difference between vibrational levels in the absence and presence of resonance.

Unperturbed stretching vibration with wavenumber ν_0 splits into symmetric ν_s and antisymmetric ν_a vibrations. The overtone of bending vibrations with wavenumber $2\nu_b$ lies not far from the symmetric stretching vibration, and if these vibrations have the same symmetry, FR between them can take place. The initial distance Δ between levels of symmetric stretching vibration and bending vibration overtone changes as a result of resonance, and it becomes equal to Δ. Complete description of the intramolecular resonances is provided only by quantum mechanical approach.[8] The main parameter characterizing FR is the so-called coupling constant W, which determines the position of the vibrational levels resulting from resonance. Solving the problem of the interaction of two symmetric intramolecular vibrations of water molecule with the close wavenumbers using the perturbation theory method [8,29,33], one can get the following expression which associates the value of coupling constants with values of wavenumber difference between components of Fermi doublet Δ and Δ in the absence and in the presence of resonance, respectively:

$$W = \frac{\sqrt{\Delta^2 - \Delta'^2}}{2} \qquad (1)$$

The ratio of intensities between the components of the Fermi doublet in this case will be equal to:

$$I_{fund.}/I_{over.} = I_1/I_2 = (\Delta + \Delta_0)/(\Delta - \Delta_0) \qquad (2)$$

where $I_{fund.}$ is the intensity of component corresponding to fundamental vibration, and $I_{over.}$ is the intensity of component corresponding to overtone.

Thus, for determination of FR coupling constant and ratio of intensities of the Fermi doublet components, it is necessary to find the values of frequency intervals Δ_0 and Δ (Eqn (1)) between unperturbed and perturbed vibrational levels.

Materials and methods

Objects of research

Studies of many authors[45–52] have demonstrated that due to hydrophobic hydration in water–ethanol solutions in the concentration range 20–25 vol.%, one can observe the self-organization of molecules and, as a result, the formation of clathrate-like structures. From literature data, it follows that with increasing concentration of ethanol from 0 to 20–25%, the hydrogen bonds in the solution are strengthened, and with further increasing concentration of ethanol up to pure ethanol, the hydrogen bonds became more weak in comparison with pure water. That is, the hydrogen bonds in solution with the concentration of ethanol 20 vol.% are stronger than

in water and much stronger than in solution with concentration of ethanol 70 vol.%. That is why water and water–ethanol solutions with concentration of ethanol 20 and 70 vol.% were chosen as solutions with different strength of hydrogen bonds.

For preparation of the samples, the deionized bidistilled water (with electroconductivity 0.1 µS/cm), 99.9% D_2O (Deutero GmbH) and ethanol with concentration 95% (Open Joint-stock Company 'Medchimprom') were used.

Laser Raman spectrometer

Excitation of Raman signal was performed by argon laser (wavelength 488 nm, power 350 mW) for registration of spectral bands in the region 200–4000 cm^{-1} and by diode laser (401 nm, 250 mW) for registration of spectra in the region 5500–8000 cm^{-1}. Laser radiation was linearly polarized. In the experiment, polarized and depolarized spectra were measured. System of registration consisted of monochromator (Acton, grating 900 grooves/mm, focal length 500 mm) and CCD camera (Horiba Jobin-Yvon, model Synapse BIUV). Practical spectral resolution was 2 cm^{-1} in the region 2500–4000 cm^{-1} and 10 cm^{-1} in the region 5500–8000 cm^{-1}. For regulation and control of the sample temperature, the special system of thermostabilization which allowed to control the temperature of the samples in the range from −5 to 92 °C with accuracy not worse than 0.2 °C was used. The samples were placed in a standard cuvette 10 × 10 × 40 mm with plug preventing evaporation.

As in FR and DDR only vibrations with the same type of symmetry can take part, in the experiment, the polarized (I_{pol}) and depolarized (I_{dep}) Raman spectra of water and solutions were measured. Then, the isotropic and anisotropic spectra were calculated, in which the symmetric and antisymmetric vibrations were separated:

$$I_{iso} = I_{pol} - {}^4/_3 \times I_{dep}, \; I_{aniso} = {}^4/_3 \times I_{dep} \qquad (3)$$

Results and discussion

Experimental Raman spectra of water and water–ethanol solutions with concentrations 20 and 70 vol.% of ethanol were obtained in the following temperature ranges: from −4 to 92 °C (for water); from −5 to 85 °C (for 20% ethanol); from −5 to 75 °C (for 70% ethanol). In Fig. 2, one can see the obtained polarized Raman spectra of water and water–ethanol solutions at temperature 25 °C: in Fig. 2(a) – in the region of stretching vibrations (2500–4000 cm^{-1}), in Fig. 2(b) – in the region of stretching vibration overtones (5500–7500 cm^{-1}).

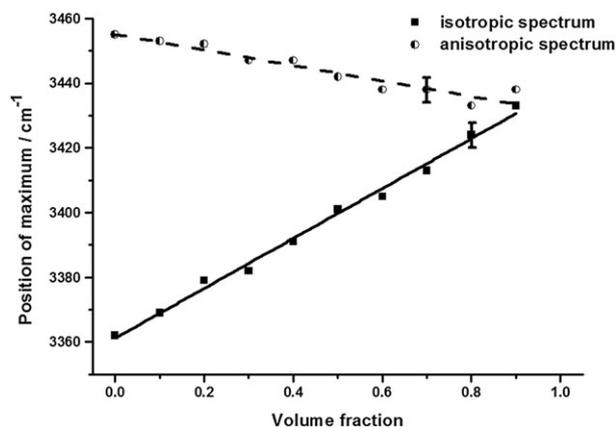*Determination of the interval of wavenumbers Δ_0 between the unperturbed vibrational levels*

The wavenumber of unperturbed vibrations of OH groups was determined by the method suggested by the authors earlier.[33] The media where there is no FR between vibrations of OH groups – solutions of H_2O in D_2O with small concentration of H_2O ($\approx$ 7%) – was prepared. At small concentrations of H_2O, the OH groups in solutions there are only HDO molecules surrounded by D_2O molecules. There are no the bending vibrations H—O—H, and therefore there is no FR. In addition, in isolated HOD molecules in D_2O, the differences between symmetric and antisymmetric stretching O—H vibrations disappear. That is why the isotropic and anisotropic stretching bands of such OH groups isolated from the other OH groups coincide.
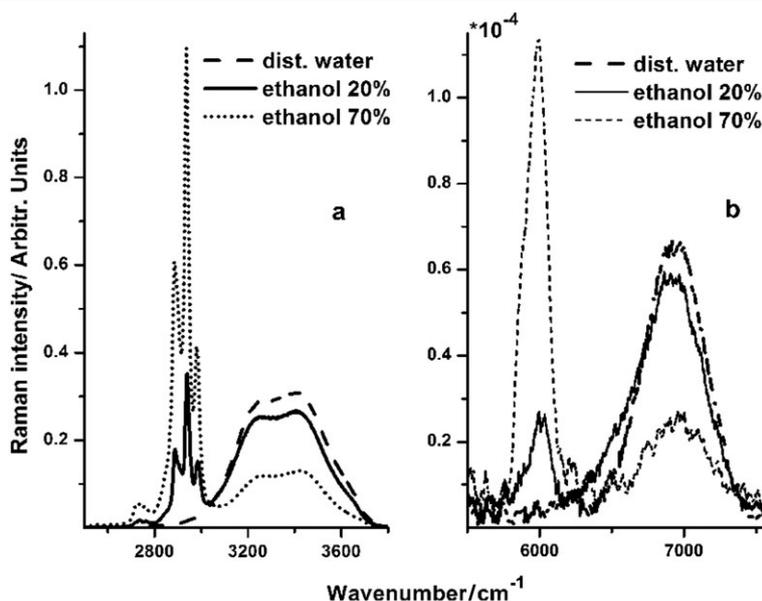
Figure 2. The polarized Raman spectra of water and water–ethanol solutions with ethanol concentration 20 and 70 vol.% at the temperature 25 °C in the spectral region 2000–4000 cm^{-1} (a) and 5500–7500 cm^{-1} (b).

For determination of the unperturbed OH vibrations, wavenumber of the dependencies of maximum position of the isotropic and anisotropic stretching bands of solutions of HDO on the concentration of H_2O in D_2O (Fig. 3) was obtained experimentally. When concentration of H_2O decreases, the maximums positions of spectra converge and become equal at concentration about 7% H_2O. The wavenumber of intersection of specified dependencies (Fig. 3), which equals to (3433 ± 3) cm^{-1}, was considered as unperturbed wavenumber of the OH groups stretching vibrations. The given value is in good agreement with the previously obtained value $(3434$ cm$^{-1})$.[33]

The wavenumber of bending vibrations HOH is equal to (1650 ± 3) cm^{-1}. However, the wavenumber of the OH groups overtone is not exactly equal to double wavenumber of the fundamental vibration due to anharmonicity of vibrations. Taking into account the correction for anharmonicity of the OH-oscillators vibrations for the wavenumber of bending vibrations -17.04 cm^{-1}, found in the study,[53] the wavenumber of the unperturbed bending vibration overtone is equal to (3283 ± 6) cm^{-1}.

Thus, the interval of wavenumbers Δ_0 between unperturbed vibrational levels of OH is equal to $\Delta_0 = 3433 - 3283 = 150$ cm^{-1}.

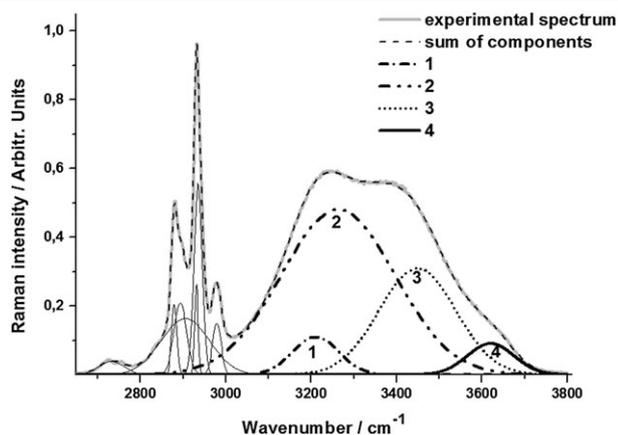*Determination of the interval of wavenumbers Δ between the perturbed vibrational levels*

The frequencies of perturbed vibrations in the presence of FR were determined from experimental stretching bands of OH groups of water and water–ethanol solutions (Fig. 1). Decomposition of the isotropic stretching bands of all samples in the investigated temperature range into components was performed using genetic algorithm (add-in 'GeneHunter' for Microsoft Excel from Ward Systems Group, Inc.[54]).

Genetic algorithm is one of optimization methods using approaches similar to natural selection in living nature. A set of values of chromosomes (the sought-for variables characterizing the solution, in our case, these are parameters of the Gaussian contours describing the experimental spectrum) represent an individual (a solution of the problem). The algorithm operates with a set of individuals (population) at the same time – it generates new solutions (individuals) by combining some individuals present in the population using selection of the fittest and such genetic operators as crossover and mutation. Genetic algorithms are less subject to sticking in local minima than traditional optimization algorithms, and they are good at solving high-dimensional optimization problems, being able to localize the optimal solution quickly.

Subsequent use of the generalized reduced gradient optimization algorithm (Generalized Reduced Gradient, GRG2, standard add-in 'Solver' for Microsoft Excel)[55] allowed us to determine the minimum of the residual functional more precisely. Application of these powerful optimization methods does not require any *a priori* model of vibrational processes, and therefore it provides the reduction of the ambiguity of the solution of this ill-posed inverse problem.[49]

It was obtained that the stretching bands of OH groups of all studied samples can be described with good accuracy by four components of Gaussian shape (Fig. 4). Parameters of decomposition are presented in Table S1 (Supporting Information). On the basis

Figure 3. Dependencies of the maximum position of the isotropic and anisotropic stretching bands of HDO solutions on the concentration of H_2O in D_2O.

Figure 4. Decomposition of the isotropic spectrum of OH groups stretching band of water–ethanol solution (20 vol.% of ethanol) into contours of Gaussian shape.

Figure 5. Dependencies of the coupling constant W on the temperature for all samples.

of existing model concepts about water structure,[6,11,12,33] one can assume that the isotropic stretching band consists of the bending vibrations overtone with C_{2v} symmetry (component 1), the symmetric stretching vibrations with symmetry C_{2v} (component 3) and the symmetric stretching vibrations of molecules with another symmetry C_s, not participating in FR (component 2). In addition, in the spectrum, there are vibrations of weakly bound molecules with symmetry C_{2v} (component 4), appearing in the region 3645 cm^{-1}. They do not participate in resonance, as their frequencies are too far from the wavenumber of the overtone of the bending vibrations.

Thus, according to the physical considerations, two components of the OH groups isotropic stretching band – components 1 and 3 – can be interpreted as Fermi doublet. In this case, one can find the interval of wavenumbers Δ between the perturbed vibrational levels.

With regard to obtained Δ_0 and Δ using expressions (1) and (2), the coupling constant of FR and the ratio of intensities of Fermi-doublet components can be calculated and then – the contribution of FR to the intensity of stretching band in percent.

Contribution of Fermi resonance to the formation of OH groups stretching band of water and water–ethanol solutions

For water at room temperature $\Delta_0 = 150$ cm^{-1} and $\Delta = 200$ cm^{-1}, By formulas (1) and (2), one can find FR coupling constant and estimate the contribution of FR to the intensity of stretching band in percent ×at room temperature: $W = 66$ cm^{-1}, $R = 7$ ($I_{over} \approx 14\%$ of I_{fund}).

It means that the contribution of the Fermi-doublet component relating to the overtone of bending vibrations constitutes 14% from the intensity of OH symmetric stretching vibrations at temperature 25 °C.

W and R at the other temperatures were calculated similarly. The obtained dependencies of calculated coupling constant W and the contribution of FR to the intensity of water Raman stretching band on temperature are presented in Fig. 5.

The coupling constants W and the contributions of FR to the intensity of OH groups Raman stretching band for water–ethanol solutions in studied temperature range were calculated using the method described above. The results are presented in Table 1 and in Fig. 5.
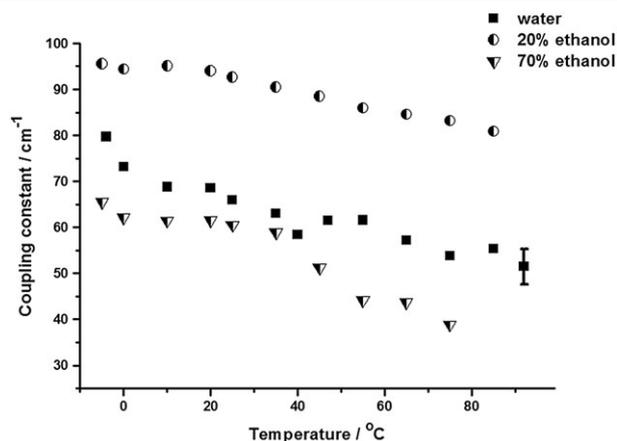
Table 1. The calculated coupling constants W and the contributions of FR to the intensity of stretching band of OH groups for water and water–ethanol solutions at temperature 25 °C

Sample	Δ_0, cm^{-1}	Δ, cm^{-1}	W, cm^{-1}	contribution, %
Water	150	200	66	14
20% ethanol	150	238	92	23
70% ethanol	150	193	61	13

As it can be seen in Fig. 5, for all samples, the coupling constant W and the contribution of FR to the intensity of stretching band significantly decrease with increase of temperature. This behavior of the characteristics can be explained by weakening hydrogen bonds with increasing temperature of water. As a result of this weakening, the wavenumber of OH groups stretching vibrations increases; stretching band shifts towards high frequencies. It leads to an increase of the interval of wavenumbers Δ between the overtone of bending vibration and the stretching vibrations.

The conclusion about the key role of the weakening of the hydrogen bonds in the change of RS correlates well with the results obtained by the authors[56] – according to their studies in solutions of linear alcohols the increase of temperature causes weakening and rearrangement of hydrogen bonds and the structure of the hydration shells of alcohol molecules becomes less ordered.

There is a significant correlation between the efficiency of FR and strength of hydrogen bonds in water and water–ethanol solutions. The coupling constant W and the contribution of the FR to the intensity of the stretching band increase in the samples with stronger hydrogen bond, i.e. in the row: solution with 70 vol.% of ethanol < water < solution with 20 vol.% of ethanol.

In the solution with 20% of ethanol, the more strong hydrogen bonds 'shift' the frequencies of symmetric stretching vibrations to low-wavenumber region and 'pull' them together with the overtone of bending vibrations: the contribution of FR to the formation of band increases. In 70% solution with weak hydrogen bonds, the wavenumber of symmetric stretching vibrations shifts to high-wavenumber region, and 'moves away' from the position of the overtone of bending vibration. W and the contribution of FR to the formation of the spectrum are reduced in comparison with pure water and 20% solution.
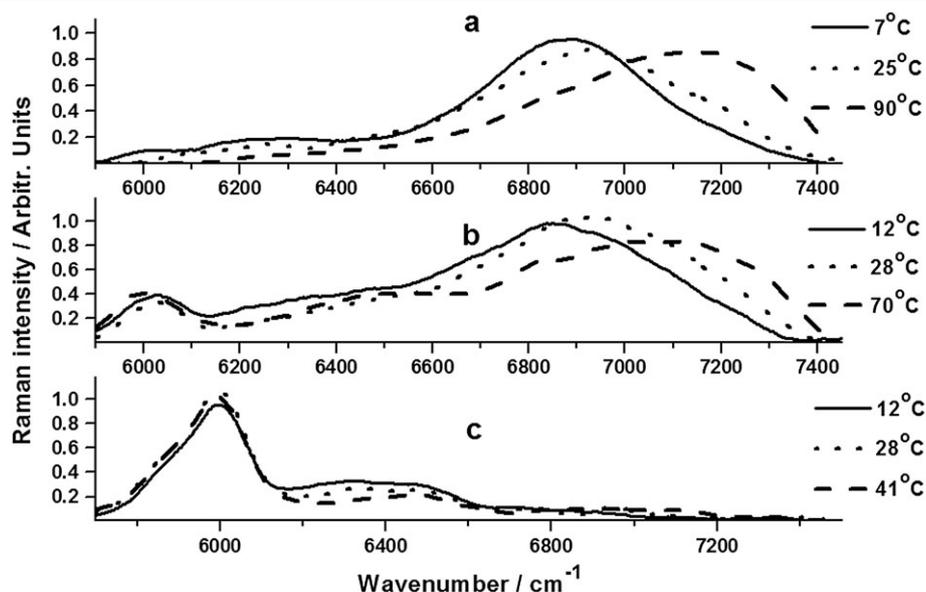
Figure 6. Isotropic spectral bands 5900–7450 cm^{-1} of water (a) and water–ethanol solutions with ethanol concentration 20% (b) and 70 vol.% (c) at different temperatures. Spectra were smoothed by 25 points.

Role of Darling–Dennison resonance in the formation of OH groups Raman spectrum

To study the contribution of DDR to the formation of OH groups RS, the isotropic and anisotropic bands were obtained experimentally in the region 5900–7450 cm^{-1} for water and water–ethanol solutions with concentrations of ethanol 20 and 70 vol.% in temperature range from 7 to 90 °C (for water) and from 0 to 80 °C (for 20% ethanol). In Fig. 6, one can see the obtained isotropic bands of all studied samples at different temperatures: the bands of the overtone of OH groups vibrations near 6800 cm^{-1} and the band of the overtone of CH-groups stretching vibrations near 5950 cm^{-1}. Unfortunately, the band of the overtone of OH groups vibrations in RS of solution with concentration 70 vol.% of ethanol was extremely weak, and it did not allow to get useful information from this band.

According to the accepted model of DDR,[44] the isotropic band of the overtone of the stretching O—H vibrations (5900–7450 cm^{-1}) consists of the overtones of the symmetric and antisymmetric stretching vibrations, the third bending vibrations overtone and combination of the bending vibrations overtone with symmetric stretching vibration. Therefore, the band of the overtone can be described by four components. In order to select the components participating in DDR, the obtained isotropic bands were decomposed into four components of Gaussian shape using the method of genetic algorithms (Fig. 7). The parameters of decomposition are presented in Table S2 (Supporting Information).

The positions of the obtained components 1,2,3,4 correspond to the third overtone of the bending vibrations $4\nu_b$, the combination of the overtone of the bending vibrations and symmetric stretching vibrations ($2\nu_b + \nu_s$), the overtone of the symmetric stretching vibrations ($2\nu_s$) and the overtone of antisymmetrical stretching vibrations ($2\nu_a$), respectively.

One can suggest the following model of DDR as a result of interaction of the obtained four components (Fig. 8). Due to the interaction between each other, the levels of the overtones of stretching OH vibrations shift in opposite directions, and the interval of wavenumbers between them increases.
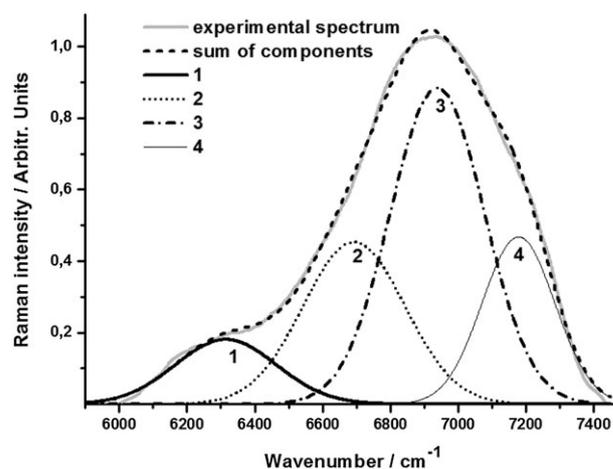
Figure 7. Decomposition of the isotropic spectrum of the stretching band overtone of OH groups vibrations of water–ethanol solution (20 vol.% ethanol) at the temperature 25 °C into contours of Gaussian shape.
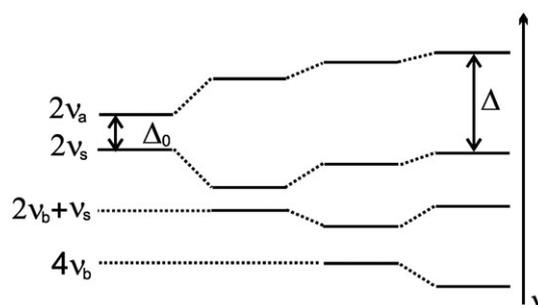
Figure 8. Diagram of interaction of the OH groups stretching vibrations overtones. $4\nu_b$ – third overtone of bending vibrations, $2\nu_s$ and $2\nu_a$ – overtones of symmetric and antisymmetric stretching vibrations, $2\nu_b + \nu_s$ combination of bending vibration overtone and symmetric stretching vibration; Δ_0 and Δ – difference between vibrational level in the absence and presence of resonance.
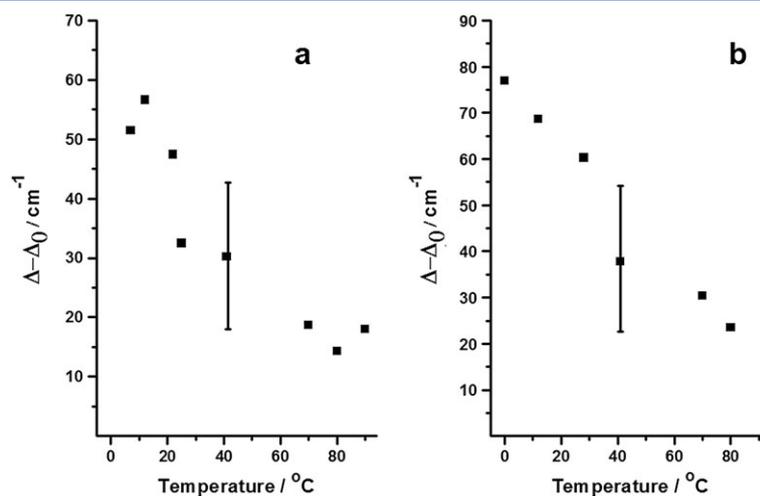
Figure 9. Dependencies of the broadening $(\Delta - \Delta_0)^{DDR}$ of band 5900–7450 cm^{-1} for water (a) and water–ethanol solution with ethanol concentration 20% (b) on the temperature.

As a result of two Fermi type resonances between the combination vibrations and each of the stretching vibrations overtones, the levels of the stretching vibrations overtones shift up (the higher is the level, the lower is the shift) and the level of the combination vibration shifts down. Due to three resonances of the Fermi type between each of the three upper vibrational states and low that (Fig. 8) three upper levels shift up and the fourth that shift down. Thus, within the framework of this model, it can be concluded that only the presence of DDR leads to an increase of the interval of wavenumbers between the stretching vibrations overtones, whereas the considered Fermi type resonances lead to decrease of this interval (Fig. 8).

For all studied samples, the change of the band width of the overtones of OH groups stretching vibrations $(\Delta - \Delta_0)^{DDR}$ due to the interactions of vibrations by DDR type was calculated at different temperatures (Table S3 (Supporting Information)).

The interval of wavenumbers Δ_0 in the absence of DDR was determined as the difference between the positions of mass centers of the overtones of unperturbed symmetric and antisymmetric stretching bands – the doubled values of mass centers positions. For calculations, the positions of mass centers were used, as all symmetric stretching vibrations of OH groups give the contribution only to isotropic band and antisymmetric that give the contribution only to the anisotropic band. Using the parameters of components obtained by decomposition of the band 5900–7450 cm^{-1}, the interval of wavenumbers Δ between the overtones of perturbed symmetric and antisymmetric stretching vibrations was calculated.

The obtained temperature dependencies of the broadening $(\Delta - \Delta_0)^{DDR}$ are presented in Fig. 9.

Analysis of these dependencies (Fig. 9) leads to the conclusion that DDR reveals itself stronger in 20% solution of ethanol in water than in pure water. Taking into account the obtained temperature dependence, one can conclude that DDR reveals itself stronger in the solution with more strong hydrogen bonds.

Thus, the obtained results show that DDR provides the significant contribution to the formation of spectral band 5900–7450 cm^{-1} of water and water–ethanol solution. Moreover, the more strong hydrogen bonds in solution correspond to greater contribution of DDR to the specified band.

Conclusions

Experimental study of the role of FR and DDR to the formation of Raman spectra of water and water–ethanol solutions with ethanol concentration 20 vol.% and 70 vol.% in the temperature range from −5 °C up to 92 °C was carried out.

The following results were obtained:

1. Basing on the analysis of experimental Raman spectra with the help of optimization algorithms, the quantitative estimations of the FR contribution to stretching bands of OH groups for water and water–ethanol solutions were obtained. At temperature 25 °C, these values are the following: 14% for water, 23% for water–ethanol solution with ethanol concentration 20 vol.%, 13% for water–ethanol solution with ethanol concentration 70 vol.%.

   Thus, the contribution of FR to the OH groups stretching band of water and water–ethanol solutions is big enough, and it should be taken into account for explanation of the mechanisms of the Raman spectra formation.

2. Efficiency of FR depends on the strength of hydrogen bonds in the sample: more efficient FR corresponds to more strong hydrogen bond.

   2.1. FR coupling constant W is correlated with the strength of hydrogen bonds in the samples. The both parameters increase in the following row: solution with 70 vol.% of ethanol < water < solution with 20 vol.% of ethanol.

   2.2. For all samples, the FR coupling constant W and the FR contribution to the intensity of OH groups stretching band significantly decrease with increase of the temperature, i.e. with weakening hydrogen bonds.

3. The analysis of spectral band 5900–7450 cm^{-1} of water and water–ethanol solutions has been demonstrated that DDR gives the significant contribution to the formation of this band. The stronger hydrogen bonds correspond to the more significant contribution of DDR to the specified band.

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Supporting information

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