

The Role of Fermi and Darling–Dennison Resonances in the Formation of the Raman Spectra of Water and Water–Ethanol Solutions

I. V. Plastinin^{a, *}, S. A. Burikov^{a, b}, S. A. Dolenko^b, and T. A. Dolenko^{a, b}

^aMoscow State University, Moscow, 119991 Russia

^bSkobeltsyn Institute of Nuclear Physics, Moscow State University, Moscow, 119991 Russia

*e-mail: plastinin_ivan@mail.ru

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Abstract—Experimental studies show that Fermi and Darling–Dennison resonances make substantial contribution to the formation of Raman spectra of water and water–ethanol solutions. Based on the analysis of spectra with an optimization algorithm, constants of interactions W and contributions of Fermi resonance to Raman spectra of water and water–ethanol solutions are calculated at 25°C.

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INTRODUCTION

The Raman spectrum of liquid water is quite complex. It consists of a set of vibrational bands of different shapes and intensities that differ by orders of magnitude. The mechanisms of formation of the Raman spectrum of water [1] have yet to be determined. There is no model that adequately describes interactions in systems of bound molecules, and concepts of the vibrational resonances of water molecules, primarily Fermi and Darling–Dennison-type resonances, are unclear and contradictory.

Fermi-type resonance is the splitting of intramolecular vibration bands and the redistribution of intensities between the components of the doublet as a result of removal of accidental degeneration [2, 3]. Fermi resonance of the first type is most often encountered—the resonance between the fundamental of one vibration and the overtone of another [3]. In addition, resonances are possible in which overtones and combination frequencies are involved (i.e., Darling–Dennison resonances) [4, 5]. In this work, we investigated the Fermi resonance (FR) between the symmetric valence vibration and the overtone of the bending vibration of OH groups, and the Darling–Dennison resonance (DDR) between the first overtones of symmetric and asymmetric valence vibrations of OH groups.

The role of FR in water and aqueous solutions has yet to be established. There is disagreement among researchers regarding the contribution of FR to the formation of the Raman spectra of water and aqueous solutions. The authors of [5–10] believed the intensity of the Raman spectrum is transferred from vibrations

ν_1 to vibrations $2\nu_2$ as a result of FR between the overtone of bending vibrations $2\nu_2 \approx 3240 \text{ cm}^{-1}$ and symmetric valence vibrations ν_1 of water molecules. This energy transfer explains the presence of the intense low-frequency region of the valence band of the Raman spectrum of water near 3300 cm^{-1} . The authors of [11] argued that FR must be considered when explaining the nature of the valence band of the Raman spectrum of water, but its role is not too great. According to the authors of [12], however, calculations that consider the asymmetry of water molecules show that the contribution of FR to the valence band of the Raman spectrum of water is “unexpectedly large.” At the same time, it was proved in [13, 14] that FR has absolutely no effect on the formation of the valence band of the Raman spectrum of water.

Theoretical calculations of DDR in water indicate that it contributes substantially to the formation of the band in the region of $5900\text{--}7450 \text{ cm}^{-1}$ of the Raman spectrum of liquid water [5, 8, 9]. Nevertheless, the role of DDR in the formation of the band of $5900\text{--}7450 \text{ cm}^{-1}$ has yet to be studied experimentally.

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

FERMI RESONANCE

Figure 1 shows the scheme of FR. Here, ν_1 is the fundamental tone of one vibration, ν_2 is the funda-

mental tone of a second vibration, $2\nu_1$ is the overtone of the first vibration, Δ_0 is the frequency difference when there is no resonance, and Δ is the frequency difference when there is resonance.

A quantum mechanical approach is needed for a complete description of intramolecular resonances [3]. Solving the problem of the interaction between two symmetric intramolecular vibrations of a water molecule with similar frequencies by means of perturbation theory [3, 15, 16], we obtain the expression for energies $E_{1,2}$ of two new vibrational states:

$$E_{1,2} = \frac{E_a + E_b \pm \sqrt{(E_a - E_b)^2 + 4W_{ab}^2}}{2}, \quad (1)$$

where E_a and E_b are the eigenvalues of unperturbed vibrational states a and b of the molecule, W_{ab} is the interaction operator of vibrations, and $(E_a - E_b) = \Delta_0$ is the natural splitting determined by the position of energy levels when there is no resonance. Equation (1) can be written as

$$E_{1,2} = \frac{E_a + E_b}{2} \pm (\Delta/2), \quad (2)$$

$$\text{where } \Delta = \sqrt{\Delta_0^2 + 4W_{ab}^2}.$$

Here, Δ is the total splitting as a result of resonance, which depends both on the matrix element of the interaction between two states $W_{ab} = W$ (this parameter is known as the interaction constant) and the value of Δ_0 . The resonance effect is thus completely determined by the value of W :

$$W = \frac{\sqrt{\Delta^2 - \Delta_0^2}}{2}. \quad (3)$$

Ratio R of the intensities of the components of a Fermi doublet is [16]

$$I_{\text{fund.t.}}/I_{\text{overtone}} = I_1/I_2 = (\Delta + \Delta_0)/(\Delta - \Delta_0) = R, \quad (4)$$

where $I_{\text{fund.t.}}$ is the intensity of the component corresponding to the fundamental tone of vibration, and I_{overtone} is the intensity of the component corresponding to the overtone.

There are still no accurate methods of calculating frequencies of bending and stretching vibrations for liquid water with and without resonant interaction.

DARLING–DENNISON RESONANCE

DDR in water is caused by possible interaction between overtones of the symmetrical ($2 \times 3330 \text{ cm}^{-1}$) and asymmetric ($2 \times 3430 \text{ cm}^{-1}$) stretching vibrations of OH groups. The third overtone of bending vibration ($4 \times 1650 \text{ cm}^{-1}$) and the combination of overtones of bending vibrations and symmetric stretching vibrations ($2 \times 1650 + 3330 \text{ cm}^{-1}$), hereinafter combination vibration, can contribute to the band of overtones

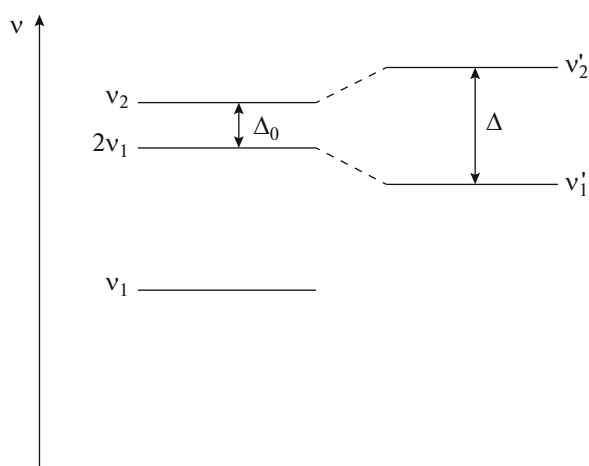


Fig. 1. Scheme of Fermi resonance.

($5900\text{--}7450 \text{ cm}^{-1}$). All of them can have the same symmetry, so they can perturb one another.

EXPERIMENTAL

Water and water–ethanol solutions with ethanol contents of 20 and 70 vol % were selected as our objects of study. Studies by many authors [17, 18] have shown that hydrogen bonds in the solution with an ethanol content of 20 vol % are much stronger than in water, and especially than in the solution with 70 vol % ethanol.

Deionized bidistilled water (electrical conductivity, $0.1 \mu\text{S cm}^{-1}$), 99.9% D_2O (Deutero GmbH), and 95% ethyl alcohol (Medhimprom OJSC) were used to prepare our samples.

The signal of the Raman spectrum was excited by an argon laser (wavelength, 488 nm; power, 350 mW) for recording in the region of $200\text{--}4000 \text{ cm}^{-1}$ and a diode laser (401 nm, 250 mW) for recording in the region of $5500\text{--}8000 \text{ cm}^{-1}$. The registration system included a monochromator (Acton; grating, 900 lines mm^{-1} ; focal length, 500 mm), and a CCD camera (JobinYvon, Synapse BIUV model). The practical spectral resolution was 2 cm^{-1} in the range of $2500\text{--}4000 \text{ cm}^{-1}$, and 25 cm^{-1} in the range of $5500\text{--}8000 \text{ cm}^{-1}$. The temperatures of the samples were controlled by a thermal stabilization system with an error of no more than 0.2°C .

Since only vibrations of the same symmetry participate in FR and DDR, we recorded polarized (I_{pol}) and depolarized (I_{dep}) Raman spectra of water and solutions in each experiment. Isotropic and anisotropic spectra were then calculated, in which symmetric and asymmetric vibrations were separated:

$$I_{\text{iso}} = I_{\text{pol}} - 4/3 I_{\text{dep}}, \quad I_{\text{aniso}} = 4/3 I_{\text{dep}}. \quad (5)$$

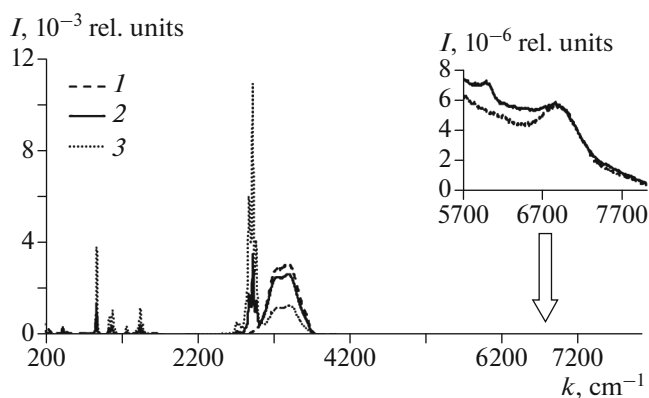


Fig. 2. Polarized Raman spectra of water (1) and water–ethanol solutions with ethanol contents of 20 (2) and 70 (3) vol % at 25°C; k is the wavenumber.

Figure 2 shows the experimental polarized Raman spectra of water and water–ethanol solutions at a temperature of 25°C. The vibrational bands of ethanol lie in the region of 500–1500 cm^{-1} ; the band with a maximum in the region of 1630 cm^{-1} is the bending band of water; the bands in the range of 2600–2900 cm^{-1} are caused by the stretching vibrations of the CH groups of ethanol; the bands in the range of 2900–3900 cm^{-1} are caused by valence vibrations of OH groups. In the region of 5900–7450 cm^{-1} , there is a band of overtones presumably caused by DDR.

CONTRIBUTION OF FR TO THE FORMATION OF THE VALENCE BANDS OF OH GROUPS

To determine the constant of FR interaction that characterizes its efficiency, we must find the values of frequency differences Δ_0 and Δ (formula (3)) between unperturbed and perturbed vibrational levels.

The frequencies of unperturbed vibrations were determined by the method proposed by the authors earlier [16]. The medium in which isolated OH groups were created (solutions of H_2O in D_2O with low concentrations of H_2O ($\approx 7\%$)) was simulated. Since there are no differences between symmetric and asymmetric valence O–H vibrations in such solutions, the isotropic and anisotropic valence bands of the OH groups coincide, and their frequency corresponds to that of the

unperturbed vibrations of OH-groups: $3433 \pm 3 \text{ cm}^{-1}$. This value agrees with the one obtained earlier: 3434 cm^{-1} [16].

The frequency of the bending vibrations of HOH is $1650 \pm 3 \text{ cm}^{-1}$. Due to the anharmonicity of the vibrations, however, the overtone frequency for OH groups is not exactly twice the frequency of the fundamental tone. Taking into account correction for the anharmonicity of vibrations of OH oscillators for the frequency of bending vibrations (17.04 cm^{-1} [19]), the unperturbed frequency of the overtone of the bending vibrations is $3283 \pm 6 \text{ cm}^{-1}$.

Difference Δ_0 between undisturbed vibrational levels is thus $\Delta_0 = 3433 - 3283 = 150 \text{ cm}^{-1}$.

The frequencies of disturbed vibrations in the presence of FR were determined from experimentally obtained valence bands of the OH groups of water and water–ethanol solutions (Fig. 2). The isotropic valence bands were decomposed into components using the evolutionary search for a solution and method of a generalized reduced gradient that is implemented in the Solver add-in of Microsoft Excel [20]. The use of such powerful means of optimization does not require an a priori model of vibrational processes, which ensures less ambiguity in solving this incorrectly posed inverse problem [21]. It was found that the valence bands of OH groups of all our samples are described with good accuracy by four components of Gaussian shape (Fig. 3a, Table 1). Based on the existing model concepts about the structure of water [1, 6, 7, 15, 16], we may assume the isotropic valence band consists of the overtone of bending vibrations with C_{2v} symmetry (component 3), symmetric valence vibrations with C_{2v} symmetry (component 4), and symmetric valence vibrations of molecules with a different C_s symmetry that do not participate in FR (component 1). In addition, the spectrum contains vibrations of weakly bound molecules with C_{2v} symmetry (component 2) that appear in the region of 3645 cm^{-1} . They do not participate in the resonance, since their frequencies are too far from the overtone frequency of bending vibrations.

From physical considerations, two components of the isotropic valence band of OH groups (i.e., components 3 and 4) can therefore be interpreted as a Fermi doublet. Then we can determine difference Δ between

Table 1. Parameters of FR in water and water–ethanol solutions

| Sample | Position of decomposition components, cm^{-1} | | | | Δ_0, cm^{-1} | Δ, cm^{-1} | W, cm^{-1} | Contribution, % |
|-------------|--|--------------|--------------|--------------|----------------------------|--------------------------|---------------------|-----------------|
| | 1 | 2 | 3 | 4 | | | | |
| Water | 3217 ± 3 | 3618 ± 3 | 3210 ± 3 | 3410 ± 3 | 150 ± 4 | 200 ± 6 | 66 ± 4 | 14 ± 1 |
| 20% ethanol | 3263 ± 3 | 3621 ± 3 | 3211 ± 3 | 3449 ± 3 | 150 ± 4 | 238 ± 6 | 92 ± 5 | 23 ± 2 |
| 70% ethanol | 3021 ± 3 | 3634 ± 3 | 3230 ± 3 | 3423 ± 3 | 150 ± 4 | 193 ± 6 | 61 ± 4 | 12 ± 1 |

disturbed vibrational levels. For water, it is $\Delta = 3422 - 3214 = 208 \text{ cm}^{-1}$.

Considering our differences Δ_0 and Δ , the FR constant of interaction and the ratio of the intensities of the Fermi doublet are calculated using formulas (3) and (4), and then the FR contribution to the intensity of the valence band in %. The calculation results for all samples are given in Table 1.

Based on the obtained results, we can state that

- the contribution from the FR to the Raman spectrum of water and water–ethanol solutions is quite large, and it must be considered when explaining the mechanisms of the formation of Raman spectra;

- FR depends on the strength of hydrogen bonds in the sample. The effectiveness of FR increases in the following sequence: a solution with 70 vol % ethanol < water < a solution with 20 vol % ethanol. It can be explained by strength of hydrogen bonds in the samples. Stronger hydrogen bonds shift the frequencies of symmetric valence vibrations to the low-frequency region and bring them closer to the overtone of the bending vibrations. As a result, the FR contribution to the formation of the band grows (20% solution). In the 70% solution with weak hydrogen bonds, the frequency of symmetric valence vibrations is shifted to the high-frequency region and moves away from the position of the overtone of bending vibrations. W and the FR contribution to the formation of the spectrum are reduced in comparison with pure water and a 20% solution.

CONTRIBUTION OF DDR TO THE FORMATION OF THE RAMAN SPECTRUM OF OH GROUPS

The obtained isotropic Raman bands of water and a water–ethanol solution with an ethanol content of 20 vol % in the region of $5900\text{--}7450 \text{ cm}^{-1}$ were decomposed into four components of the Gaussian form (Fig. 3b). Unfortunately, the quality of the band of $5900\text{--}7450 \text{ cm}^{-1}$ of the solution with 70 vol % ethanol did not allow us to extract useful information from it. The positions of the resulting components 1–4 correspond to the third overtone of bending vibration $4\nu_{\text{def}}$, the combinations of the overtone of the bending vibration and symmetric valence vibration ($2\nu_{\text{def}} + \nu_{\text{sym}}$), the overtone of the symmetric valence vibration ($2\nu_{\text{sym}}$), and the overtone of the asymmetric valence vibration ($2\nu_{\text{asym}}$), respectively.

We can propose the following model of DDR as a result of the interaction between the above four components (Fig. 4). When interacting with one another, the levels of the first overtones of valence OH vibrations are shifted in opposite directions, and the frequency difference between them increases. As a result of two Fermi-type resonances between the combination vibration and each of the overtones of the valence

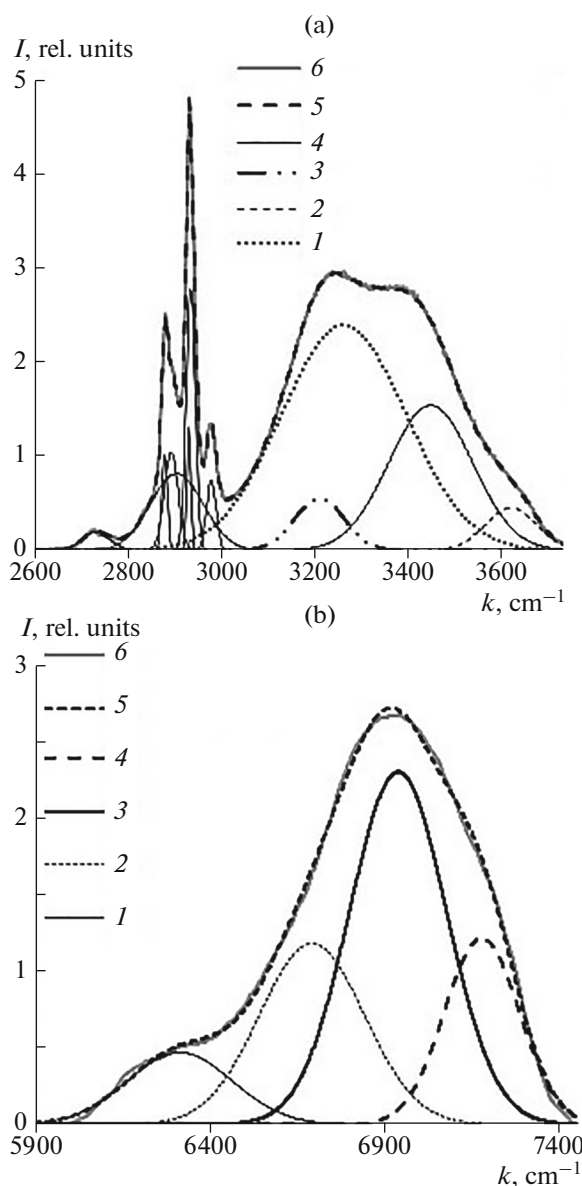


Fig. 3. Decomposition of the valence band (a) and the band of overtones (b) of vibrations of OH-groups of water–ethanol solution (20 vol % ethanol) into the contours of the Gaussian form. (1–4) components, (5) the sum of the components, (6) the original spectrum.

vibrations, levels of the overtones of valence vibrations are shifted up (the higher the level, the smaller the shifts), and the level of combination vibrations is shifted down. As a result of three Fermi-type resonances between each of the upper three vibrational states and the lower (Fig. 4), the upper three levels are shifted upward, and the fourth one is shifted down. In this model, we may therefore conclude that only the presence of DDR increases the frequency difference between the overtones of the valence vibrations, while the considered Fermi-type resonances reduces it (Fig. 4).

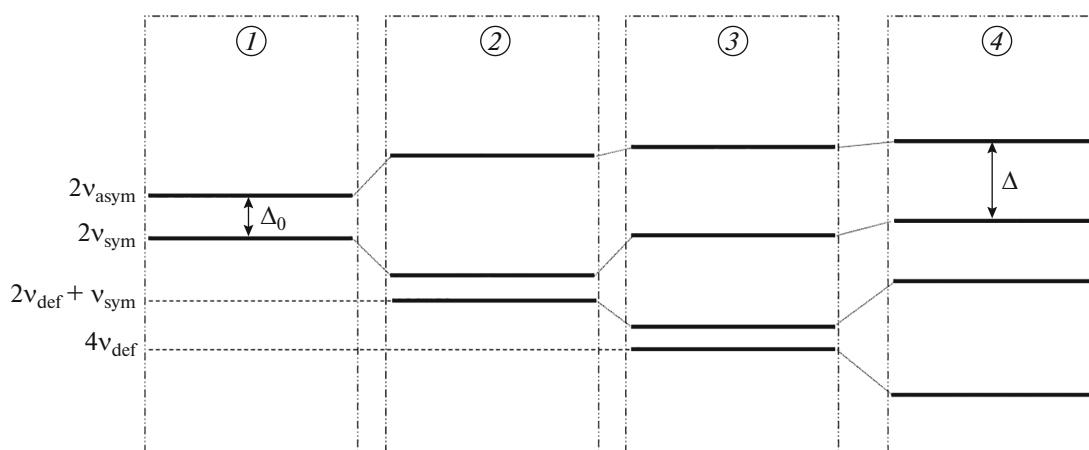


Fig. 4. Scheme of interaction between overtones of the vibrations of OH groups.

Frequency difference Δ_0 in the presence of DDR was determined as the difference between the positions of the centers of mass of the overtones of unperturbed symmetric and asymmetric valence bands—doubled positions of the centers of mass of isotropic and anisotropic valence bands. The position of the centers of mass was used in our calculations, since all symmetric valence vibrations of OH groups contribute only to the isotropic band, while asymmetric vibrations contribute only to the anisotropic band. Using the components obtained during the decomposition of the 5900–7450 cm^{-1} band, we calculated frequency difference Δ between the overtones of the disturbed symmetric and asymmetric valence vibrations.

We found that $\Delta - \Delta_0$ at a temperature of 25°C is 45 cm^{-1} for water; for 20% ethanol solution, it is 80 cm^{-1} (i.e., the band became wider). DDR thus makes a certain contribution to the intensity of the spectral band of 5900–7450 cm^{-1} belonging to water and water–ethanol solutions. In addition, stronger hydrogen bonds in the solution with 20 vol % ethanol correspond to the greater contribution of DDR to the specified band.

CONCLUSIONS

An experimental study of the role of FR and DDR in the formation of valence bands and the 5900–7450 cm^{-1} band of the OH groups of the Raman spectra of water and water–ethanol solutions with ethanol contents of 20 and 70 vol % at 25°C was performed.

Analysis of the valence bands of OH groups using optimization algorithms allowed to obtain quantitative estimates of the FR contribution to these bands: 14% for water, 23% for water–ethanol solutions with an ethanol content of 20 vol %, and 12% for water–ethanol solutions with an ethanol content of 70 vol %. It was established that the contribution of FR to the Raman spectra of water and water–ethanol solutions

is substantial and must be considered when explaining the mechanisms of the formation of Raman spectra. The FR depends on the strength of the hydrogen bonds in the sample: the stronger the hydrogen bonds in a solution, the greater the FR.

Analysis of the spectral band of 5900–7450 cm^{-1} of water and water–ethanol solutions with 20 vol % ethanol showed that DDR made a certain contribution to the intensity of this band. Stronger hydrogen bonds in the solution correspond to the greater contribution of DDR to the specified band.

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