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Research Letter

The Role of Fermi Resonance in Formation of Valence Band of Water Raman Scattering

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The role of Fermi resonance in formation of valence band of water Raman scattering was investigated. Simultaneous measurement of characteristics of bending and valence bands of water in D_2O solutions, KBr and KCl and using genetic algorithms in conjunction with variation methods allowed increasing accuracy of estimation of Fermi resonance coupling constant and of Fermi resonance contribution into formation of water Raman valence band.

1. Introduction

Until now, mechanisms of formation of Raman valence band of water are not clarified. Many attempts (see, [1–6]) to determine contributions of intra- and intermolecular interactions and Fermi resonance (FR)—resonance between symmetric valence vibration ν_1 and overtone of bending vibration $2\nu_2$ of water molecule—did not lead to definite conclusions. Under FR energy transfers from vibration ν_1 to overtone $2\nu_2$ [1–6] occurs. This energy transfer can explain existence of the shoulder in low-frequency part (in the region $3300\,\text{cm}^{-1}$) of water Raman valence band. If authors of [6] account that FR role is not too great, that according to calculations in [4] the contribution of FR into water Raman valence band is unexpectedly great, and according to [7] FR does not influence the formation of water Raman valence band. Contradiction in the opinions about the role of FR in vibrational spectra of water is connected with absence of precise methods of calculating frequencies and intensities of intramolecular vibrations in spectra of liquids. Nevertheless, different models of FR are discussed in literature [2–5], and different methods of calculation of FR quantitative characteristics are suggested [1–9].

According to the generally received model [1–3, 5], the scheme of splitting of bands of intramolecular vibrations due to FR is presented in Figure 1. Valence vibrations of OH bond with "unperturbed" frequency ν^u are split into symmetric ν_s and antisymmetric ν_a components due to intramolecular interactions (V is the constant of intramolecular coupling). Due to intermolecular interactions, vibrations with frequencies ν_s, ν_a are split into in- and out-of-phase vibrations $\nu_{s\text{-in}}$, $\nu_{s\text{-out}}$ and $\nu_{a\text{-in}}$, $\nu_{a\text{-out}}$ (υ_s and υ_a are the intermolecular coupling constants). Due to intermolecular interactions, the bending vibration ν_2 is split into $\nu_{2\text{-in}}$ and $\nu_{2\text{-out}}$ (overtones $2\nu_{2\text{-in}}$ and $2\nu_{2\text{-out}}$). As frequencies of overtones of the bending vibration are closed to frequencies of symmetric valence vibrations, it is possible that FR can take place between pairs of vibrations of the same symmetry—($\nu_{s\text{-in}}$ and $2\nu_{2\text{-in}}$) and ($\nu_{s\text{-out}}$ and $2\nu_{2\text{-out}}$) [1]. At the same time, vibrations with $\nu_{s\text{-in}}$ and $2\nu_{2\text{-out}}$ are transformed into vibrations with $\nu'_{s\text{-in}}$ and $2\nu'_{2\text{-in}}$, and vibrations with $\nu_{s\text{-out}}$ and $2\nu_{2\text{-out}}$ are transformed into vibrations with $\nu'_{s\text{-out}}$ and $2\nu'_{2\text{-out}}$ (Figure 1).

In the literature [1, 6] it is assumed that FR is caused by anharmonicity of vibrations and from the point of view of the perturbation theory authors describe the FR by the following system of equations:

$$R = I_1/I_2 = (\Delta + \Delta_0)/(\Delta - \Delta_0), \quad \Delta = \sqrt{\Delta_0^2 + 4W^2}, \qquad (1)$$

where R is the ratio of intensities of FR components, Δ_0 is the initial splitting of levels in absence of FR, Δ is the splitting of levels in presence of FR, and W is the matrix element of interaction of two vibrations, or the coupling constant of FR.

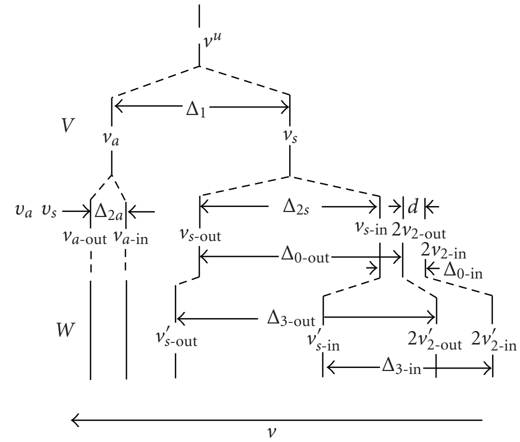

Figure 1: Model diagram of Fermi resonance in water. The vertical lines mark the band positions; the dashed lines show the splitting.

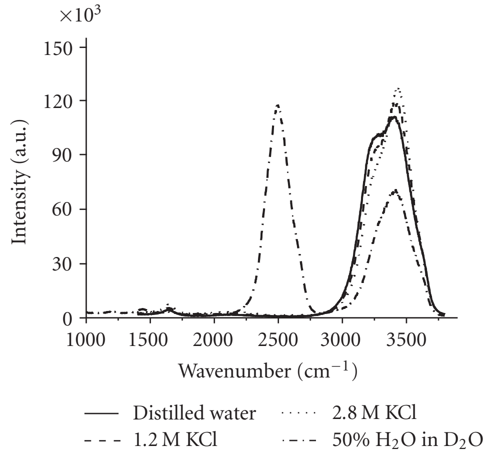

Figure 2: Experimental water Raman valence band of water solutions of KCl and HDO.

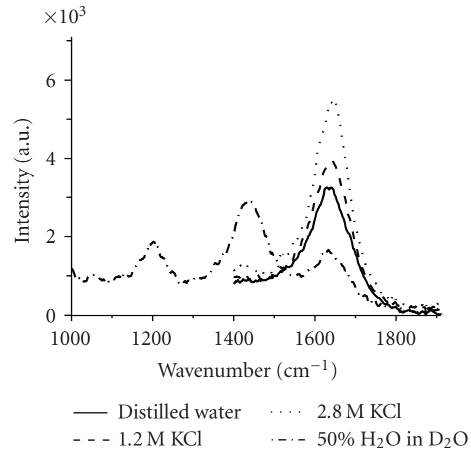

Figure 3: Experimental bending bands of water Raman spectra in solutions of KCl and HDO.

The values Δ and Δ_0 cannot be measured experimentally. Furthermore, now there are no precise methods for calculating frequencies of bending and valence vibrations without FR and in presence of FR. This is why calculation of the coupling constant of FR W is a complicated problem.

To estimate the value W, the authors of [3, 5] decomposed the valence band of isotropic water Raman spectrum into components (the curves of Gaussian shape or the components of Fourier deconvolution). If the difference of maximum frequencies Δ of two from these components and the ratio of their intensities $R = I_1/I_2$ are determined, the values of Δ_0 and W will be found from system (1). According to the data of different authors, the calculated values of W are changed in wide ambits: for H_2O-97 cm^{-1} [3], 99.5 cm^{-1} [5], 36 cm^{-1} [6], 151 cm^{-1} [8], 83.5 cm^{-1} [9]; for solutions of LiCl (12 m)-70 cm^{-1} [3]. The most of obtained values W confirm the assumption about significant role of FR in formation of water Raman valence band in comparison with intramolecular ($V = 23$ cm^{-1} [3], 32 cm^{-1} [5]) and intermolecular interactions ($\upsilon = 96$ cm^{-1} [3], 42 cm^{-1} [5]).

It is obvious that next steps in the discussion about the role of FR in formation of water valence band should be connected with new experimental approaches and new methods of spectra processing. In this paper, parallel measurements of characteristics of valence and bending bands of water were carried out for solutions of HDO and of KBr and KCl salts. For precision analysis of bands, the genetic algorithms [10] were used together with variation methods. This allowed increasing the accuracy of estimation of FR coupling constant and of its contribution into the formation of water Raman valence band.

2. Experiment

Excitation of Raman signal was performed using argon laser radiation (wavelength 488 nm, power 450 mW). The spectra were measured in 90° geometry using monochromator (Acton 2500i, resolution 2 cm^{-1}) and photomultiplier (Hamamatsu H 8259-01) with photon counting system.

To study the FR in water, the polarized and depolarized Raman bending and valence bands of distilled water and of water in solutions of KBr, KCl salts (the concentration range was from 0 up to 4 M with the step 0.4 M) and in solutions of HDO (the concentration range of H_2O in D_2O was from 0 up to 100 mole % with the step 5–10 mole %) were obtained simultaneously.

3. Results and Discussion

Raman bending and valence bands of water in solutions of salts and HDO in the region 1000–3800 cm^{-1} are presented in Figures 2 and 3. With increasing concentration of salts, the intensity of the high-frequency region of Raman valence band increases; and that of the low-frequency region decreases, the band shifts towards higher frequencies. Under this, the position of the bending band remains practically unchanged, and the intensity increases significantly (1.5–2 fold under high concentrations).

In this study, the method of calculation of Fermi coupling constants using formula (1) is suggested. This method differs from the one used previously by the following. First, we obtained the experimental bending and valence bands of isotropic Raman spectra of water in solutions of HDO. Therefore, at our service we had the frequencies of overtones of bending vibrations OH groups under low concentration of H_2O in D_2O, that is in absence of FR. Second, formulas in (1), which were used by many authors [3, 5] to calculate the Fermi coupling constants, suppose measuring of the value R—the ratio of intensities of FR components (in [3, 5] this is the ratio of intensities of the curves of Gaussian shape or the components of Fourier deconvolution). Such determination of R is correct on the hypothesis that the intensity of the low-frequency region of water Raman valence band (3250–3350 cm^{-1}) is caused only by FR. But the role of FR in the formation of water Raman valence band is now only being ascertained. Therefore, calculation of the R values by the components intensities is a procedure that is not fully correct.

The experimental bending Raman bands of water in HDO solutions obtained in this study allowed us to calculate the value of W without using R. It is calculated by

$$\Delta^2 = \Delta_0^2 + 4W^2. \qquad (2)$$

To calculate the FR coupling constant W by (2), it is necessary to know the frequency of the bending vibration overtone and the frequency of the symmetrical valence vibration without FR (*unperturbed* frequencies) and in presence of FR (*split* frequencies).

The *unperturbed* frequencies were determined from experimental water Raman spectra in solutions HDO. It is supposed [2, 3] that in HDO solutions with low concentration of H_2O groups, OH in molecules HDO, and in surrounding of D_2O molecules are isolated from interactions with the other OH groups, that is, there are no intermolecular interactions between OH groups; and the FR is absent too. Therefore, as the *unperturbed* frequency of bending vibrations, the frequency of maximum of the Raman bending band of OH groups in HDO solution with very low concentration of H_2O in D_2O was choused. According to our experimental data $\nu_2^u = 1640\,cm^{-1}$.

The *unperturbed* frequency of valence vibrations was calculated as the point of intersection of the dependences of the maximum frequencies for isotropic ν_{max}^{isotr} (C_{H2O}) valence and anisotropic valence $\nu_{max}^{anisotrop}$ (C_{H2O}) Raman bands on concentration of H_2O in D_2O (Figure 4). According to data of [3], these dependences intersect at point 3434 cm^{-1} at concentration 12 molar % H_2O in D_2O. According to our data (Figure 4) the straight lines of the dependences ν_{max}^{isotr} (C_{H2O}) and $\nu_{max}^{anisotr}$ (C_{H2O}) intersect at 10% concentration of H_2O in D_2O in the point $\nu_{max}^u = 3432\,cm^{-1}$.

According to the diagram of vibrations splitting (Figure 1), one can suggest that the isotropic valence band consists of four components: the overtone of bending vibrations, symmetric valence vibrations of molecules with C_{2v} symmetry participating in FR, symmetric vibrations of water molecules with another symmetry (e.g., C_s) not participating

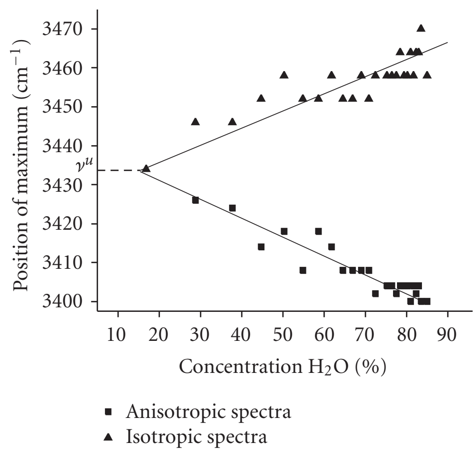

Figure 4: Determination of ν^u—crossing ν^{iso} (C_{H2O}) and ν^{aniso} (C_{H2O}).

in FR, the component corresponded to nonboned (or weekly bonded) molecules, the vibrations of which provided the peculiarity of high-frequency shoulder of valence band (Figure 2). Therefore, to find the *split* frequencies of symmetric valence vibrations of H_2O molecules, the decomposition of the isotropic valence band into four Gaussian curves was performed.

The decomposition of the isotropic valence band into the components was performed with the help of genetic algorithm (GA) [10] (GeneHunter add-on from Ward Systems Group, Inc. for Microsoft Excel) in combination with the generalized reduced gradient (GRG2) algorithm of nonlinear optimization (standard Solver add-on to Microsoft Excel).

As the *split* frequencies of the overtone of bending and symmetric valence vibrations of water molecules, the frequencies of maximums of the first two Gaussian components were accepted. The values of FR coupling constants W were calculated by (2).

The results of decomposition of valence bands of isotropic water Raman spectra into Gaussian curves and the calculated FR coupling constants for distilled water and for solutions of maximal concentrations are presented in Table 1.

Calculations showed that at concentration of KBr and KCl increasing from 0 up to 4 M, the FR coupling constant decreases approximately 1.4 fold. Because of increasing frequencies of symmetric valence vibrations of water molecules in hydrated shells of anions, the FR is relaxing. Anions Br^- ℵ Cl^- are negatively hydrated, so mobility of H_2O molecules in hydrated shells of these anions increases [11] (in comparison with pure water), the hydrogen bonds between water molecules become weaker, and the frequencies of valence vibrations increase. As the result, the detuning of frequencies of overtone bending and symmetric valence vibrations becomes large, and FR weakens.

The obtained values of FR coupling constants show that FR apparently makes a contribution into the forming of water Raman valence band. However, at present the quantitative estimations are possible only with accuracy up to tens of cm^{-1}.

Table 1: The frequencies of the Gaussian components maxima and the calculated FR coupling constants for distilled water and for solutions of maximal concentrations.

	$\nu^{1Gaus} = 2\nu_2$, cm^{-1}	ν^{2Gaus}, cm^{-1}	ν^{3Gaus}, cm^{-1}	ν^{4Gaus}, cm^{-1}	W, cm^{-1}
Distillate	3211	3318	3436	3611	54
KBr, 4 M	3241	3371	3488	3541	39
KCl, 4 M	3233	3365	3479	3548	38

4. Conclusion

In this study, the values of FR coupling constants W in water and in water solutions were improved. This was possible due to the additional experimental spectral information about frequencies of bending and valence bands of OH groups isolated in solutions of HDO, which allowed calculating the value of W using only the values of frequencies of water molecules vibrations in absence and in presence of FR. The decomposition of isotropic Raman valence bands was performed using the modern mathematical methods (GA and GRG2), thus increasing stability of solution of the incorrect inverse problem—decomposition of valence band into components.

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