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Investigation of Water Cluster Structure Using Raman Spectra Temperature Dependences

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The Raman spectra temperature dependences of water in the range 2900-3700 cm^{-1} were investigated. This is the region of the valence symmetric and asymmetric bands vibrations of water OH-groups. The cluster model of water which consists of small clusters (from one to six molecules in the formation) was used. The relative cluster contribution in the water spectrum was found. The low frequency region 2800-3300 cm^{-1} is formed mainly by cluster types $(H_2O)_3$, $(H_2O)_4$, $(H_2O)_5$, $(H_2O)_6$ and the high frequency region 3300-3800 cm^{-1} is formed mainly by cluster types $(H_2O)_2$, $(H_2O)_3$, $(H_2O)_4$. Cluster type $(H_2O)_3$ dominates at the temperature 20 °C and this dependence don't change extremely within all measured temperature range 0-95 °C.

Keywords: Raman spectroscopy, Raman spectrum of water, Cluster concentration, Temperature dependence.

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1. INTRODUCTION

Water has a lot of unusual properties, for example, it is the temperature dependence of the shape of valence symmetric and asymmetric bands vibrations of water OH-groups in Raman spectrum. The halfwidth of the valence band vibrations of OH groups in the Raman spectra has a value ~ 300-380cm^{-1}. But common values of any other bands in Raman spectra of liquids are in the range from ~ 5-20 cm^{-1} to ~ 100-150 cm^{-1}. The analyses of the shape of valence band vibrations of OH groups reveals three possible reasons of the broadening:

- the wide band is a result of blending of many narrow bands, which include the different types of clusters [1];

– interaction between valence vibrations of OH groups and low-frequency vibrations of hydroxyl bond is a result of the broadening;

– the overtone of deformation vibration of OH group is located in this region. Its intensity is amplified by the Fermi resonance with the symmetric valence vibrations of OH groups [2].

The explanation of the Fermi resonance broadening was critically discussed in [3]. The comparing spectra analysis of water and ethanol was performed in this paper. The shape of the valence band vibrations of OH groups of water and ethanol has two distinct peaks within the range ~ 3200 cm^{-1} and ~ 3400 cm^{-1}. The existence of the pick in a region ~ 3200 cm^{-1} explained as an overtone contribution of deformation vibrations of OH groups in a region ~ 1640 cm^{-1} according to the hypothesis of Fermi resonance. Ethanol has also a maximum in a region ~ 3200 cm^{-1}. But there are no deformation vibrations of OH groups in a region ~ 1640 cm^{-1}. Consequently the overtone of these vibrations can not exist. Therefore the idea of Fermi resonance is disproved.

Generally speaking, mixture models describe liquid water as an equilibrium mixture of species which are distinguishable in an instantaneous picture. For many years they have been used to explain the properties of water and aqueous solutions. Contrary to the continuum models, the mixture models have been proposed with more variety. Most mixture models assume that water molecules exist in a few (often two) classes of more or less well-defined structural entities. However, as properly stressed in [4], the term "mixture" has often been used in different contexts. Sometimes it implies only that a hydrogen-bond forming and breaking equilibrium is considered, and the existence of distinct molecular species is not explicitly assumed. Therefore, one should differentiate between mixture models of certain species and mixture models which discuss H-bonded and non-H-bonded OH groups.

Modern history of mixture models starts with a paper [5], which describes water as a saturated solution of ice in a liquid composed of common molecules. Later, authors in [6] proposed a three-component model and assigned the names hydrol, dihydrol and trihydrol to H_2O, $(H_2O)_2$ and $(H_2O)_3$, respectively. Over the next 50 years a number of simple mixture models were proposed, based on a coupled equilibrium of small water aggregates [7], amongst which the associate model in [8], involving the formation of $(H_2O)_n$, with $n = 1, 2, 4, 8$, was probably more successful than others to predict some physical properties of water. For the following three decades, the mixture models gradually evolved towards systems composed of large, not necessarily regular, clusters.

The past 10-15 years has brought a real flood of computer simulation studies on fundamental properties of small isolated clusters of water, including their geometry, energetics, thermochemistry, and vibrational (infrared and Raman) spectra. Recent progress in laser spectroscopy experiments (e.g. the jet-cooled direct absorption spectroscopy in the microwave, terahertz, and infrared regions of the spectrum) has also facilitated new highly detailed studies of water clusters. Since the water trimer, tetramer, pentamer and hexamer are some dominant structures identified in room-temperature liquid water [9], it is believed that these studies will provide a means of quantifying the intermolecular forces and hydrogen-bond rearrangements.

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The paper describes the influence of the water cluster concentration in the Raman spectrum in the region 2900-3700 cm $^{-1}$. These information will help to analyze the temperature dependences of Raman spectra and to make conclusions about the change of cluster structure of liquid water.

2. EXPERIMENTS

Water with purity was used in this research. The spectral-computation complex on the base of double monochromator system DFS-52 was used in the measuring process. Argon laser with wavelength 488 nm was used, the laser power was 100 mW.

Raman spectra were measured with a spectral resolution of 2 cm $^{-1}$. The quartz sell with the volume of 3 ml was used. The temperature of liquid samples was within the range 0 ÷ 95 °C. The precision of temperature measurement was 1 °C and the precision of the ditch temperature stabilization was 0.5 °C. As it was noted in [10], the average shift factor of OH-vibration band is $-2{,}1 \pm 0{,}9$ cm $^{-1}$/ °C. Accordingly, the specified difference in temperature was within the error of monochromator measurement.

3. RESULTS AND DISCUSSION

The Raman spectra temperature dependences of water in the region 2800-3800 cm $^{-1}$ are shown in Fig. 1.

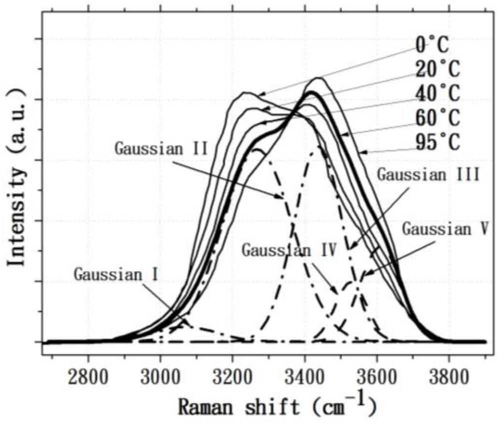

Fig. 1 – Raman spectra for water at different temperatures (0-95 °C)

Thick lines connect with the shape of Raman spectra, and the dotted lines decompose the spectra shape by five Gaussian components. Deconvolution procedure of the spectrum contour was performed separately for each of the spectra, which were measured at different temperatures. The minimum temperature of the measurement was 0 °C and the maximum temperature was 95 °C. The dependence of the intensities of the Gaussian components II and III with central frequencies 3240 cm $^{-1}$ and 3408 cm $^{-1}$ on temperature change are presented in Fig. 2. The central frequencies of Gaussian components I, II,…V at $T = 20$ °C were 3111 cm $^{-1}$, 3240 cm $^{-1}$, 3408 cm $^{-1}$, 3539 cm $^{-1}$ and 3629 cm $^{-1}$, consequently.

The tendency to decrease of intensity of the Gaussian II and the tendency to increase of intensity of the component Gaussian III is clearly represented on the graph. The explanation of this dependence will be described using the analysis of quantum-chemical calculations of small water clusters ($n = 1, 2,…6$).

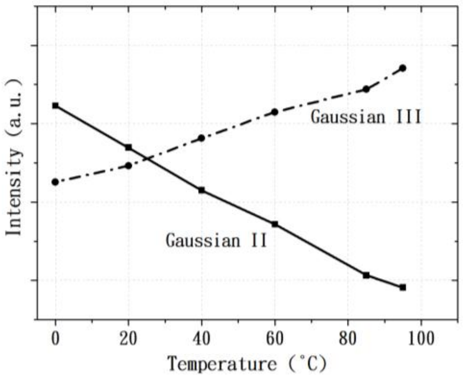

Fig. 2 – The temperature dependence of intensities of the gaussian components II and III with central frequencies 3240 cm $^{-1}$ and 3408 cm $^{-1}$.

Assuming that association-dissociation processes like

$$\left(\mathrm{H_2O}\right)_{i-1} + \mathrm{H_2O} \xleftrightarrow{K} \left(\mathrm{H_2O}\right)_i , i = 2, \ldots n , \qquad (1)$$

continuously occur in liquid water, where K is the constant of chemical equilibrium, n is the quantity of molecules in a cluster and that water is a thermodynamical ideal mixture of this clusters in a state of chemical equilibrium like

$$K_i = K_i^{\circ} \exp\left[\frac{\Delta H_i}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right], i = 1, 2, \ldots n-1 , \qquad (2)$$

where ΔH_i is the enthalpy of cluster reaction, K_i° is the constant of chemical equilibrium at temperature T_0 it is possible to simulate the change of the shape of the valence band vibrations of OH groups in Raman spectrum of water at different temperatures using the analysis of quantum-chemical calculations of small water clusters. Both the frequency and intensity corresponding to the possible valence vibrations of OH groups for different types of clusters were calculated in the work [1]. The obtained values were turned out within the range of experimentally measured valence band vibrations of hydroxyl OH groups in water. If we attach the Lorentz broadening to each of the theoretically derived peaks, we can satisfactorily describe both form of valence vibrations of OH groups and its change at different temperatures of water.

The dependence of separate cluster type concentration on the molecular quantity in a cluster (cluster size) is built using the analysis of quantum-chemical calculations with the simulation of the spectrum shape at different temperatures (Fig. 3).

It is possible to see that monomers and dimers are practically absent at low temperatures. But there is a significant number of trimers, tetramers, pentamers and gexamers. The situation somewhat changes at high temperatures. The quantity of tetramers, pentamers and gexamers decreases while the quantity of monomers

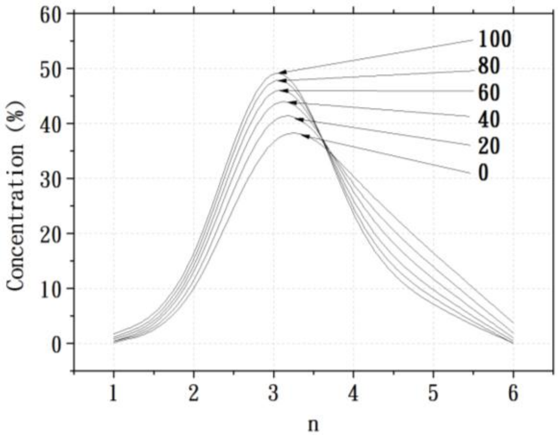

Fig. 3 – Dependence of the separate cluster type concentration on the molecular quantity in a cluster

monomers and dimers increases. Liquid water consists mostly of trimers at room temperature.

The data of quantum-chemical simulation of small water clusters ($n = 1, 2, \ldots 6$) in [1] were used to assess the contribution of vibrational modes in the valence band of hydroxyl OH groups for each of the five Gaussian components. The intensities of vibrational modes of a certain cluster types were normalized to their concentration in liquid water at $T = 20$ °C for this purpose. The coefficients $k_n, n = 1,2,\ldots 6$ were calculated from Fig. 3. The intensity of cluster modes can be found using these coefficients. The intensities will be proportional to the concentrations of cluster modes of separate type:

$$I_n = \sum_j k_n I_n^j, , \tag{3}$$

where I_n^j is the intensity of vibrational mode j of cluster n.

Considering liquid water to consist only of mixture of clusters including from 1 to 6 molecules, we can write down the total concentration of all clusters in the mixture in the following way:

$$N_{tot} = \sum_n N_n \ , \tag{4}$$

N_n is the concentration of cluster n.

Then coefficients k_n can be found like as follows:

$$k_1 + k_2 + \ldots + k_n = 1 \, , \tag{5}$$

The coefficients k_n for each type of the cluster have the following values: $k_1 = 0.002$, $k_2 = 0.04$, $k_3 = 0.53$, $k_4 = 0.27$, $k_5 = 0.14$, $k_6 = 0.018$.

The next step was to determine the proportional contribution $k_n I_n^j$ of each normalized intensity of vibrational mode j of cluster n in separate Gaussian component. It is clear that the value of intensity $k_n I_n^j$ can simultaneously consist of the intensities of several Gaussian components. Therefore its contribution was determined by the formula:

$$k_n I_n^j = I_I^{\nu_j} + I_{II}^{\nu_j} + I_{III}^{\nu_j} + I_{IV}^{\nu_j} + I_V^{\nu_j} \, , \tag{6}$$

where $I_{I,II,,\ldots V}^{\nu_j}$ is the value of separate Gaussian curve intensity at the fixed frequency ν_j. Moreover the frequency ν_j corresponds to the frequency of vibrational mode j of cluster n.

As the characteristic line intensity of Raman scattering for harmonic approximation is proportional to the quantity of scattered molecules of separate substance type and our measured object consists of cluster mixture, it is possible to find the contribution of separate cluster concentration in a separate Gaussian component by the following relation:

$$N_n \propto I_n = \sum_j (I_I^{\nu_j} + I_{II}^{\nu_j} + I_{III}^{\nu_j} + I_{IV}^{\nu_j} + I_V^{\nu_j}) \, , \tag{7}$$

Then

$$\begin{cases} N_n^I = \sum_j I_I^{\nu_j}; \\ N_n^{II} = \sum_j I_{II}^{\nu_j}; \\ N_n^{III} = \sum_j I_{III}^{\nu_j}; , \\ N_n^{IV} = \sum_j I_{IV}^{\nu_j}; \\ N_n^V = \sum_j I_V^{\nu_j}. \end{cases} \tag{8}$$

Calculation of separate cluster concentration contribution in each of fifth Gaussian components was carried out by the above-mentioned scheme. The intensity values of vibrational modes of Raman spectra were represented in the relative units. Therefore it is better to interpret the results if the lasts are recalculated in percentages of concentration contributions in order that the concentration sum of all six types of clusters makes the 100 % contribution in each Gaussian component. The following percentages of $N_{1,2,\ldots 6}^{I,II,\ldots V}$ were obtained:

$$\begin{cases} N_{1,2,\ldots 6}^I = (0;0;0;34,7;44,2;21,1); \\ N_{1,2,\ldots 6}^{II} = (0;0;13,83;52;27,62;7,05); \\ N_{1,2,\ldots 6}^{III} = (0;0,97;91,45;1,7;0,08;5,8); \\ N_{1,2,\ldots 6}^{IV} = (0,28;19,44;38,9;11,57;8,2;21,61); \\ N_{1,2,\ldots 6}^V = (0,61;2,1;36;30,04;23,08;7,83). \end{cases} \quad , \tag{9}$$

From the expression (9), we can see that the concentration contribution of monomers in the fifth Gaussian component is very small. Therefore we can neglect it. Concentration contribution of water dimers was manifested largely only in the high-frequency region in the Gaussian component IV with the central frequency 3539 cm^{-1}. This contribution was about19 %. This result is in good correlation with the work [11], where the absorption spectrum investigation of vapor and liquid water as well as calculations of heat and entropy were carried out. The absorption spectrum of liquid water within the range from 600 nm to 1800 nm at $T = 25$ °C was investigated in [12], where the concentration of non-bonded water molecules also appeared very small.

From the expression (9), it is possible to conclude that trimer is the most common water cluster at the room temperature. This dependence don't change extremely within temperature range of water 0-95 °C. It can be seen from the Fig. 3. The results of diffusion coefficient measuring of water molecules with oxygen isotopes ^{18}O [13] also confirm the fact that water trimer is the most abundant cluster at ambient temperature.

4. CONCLUSIONS

The measurements of Raman spectra of liquid water within the range 2900-3700 cm^{-1} at different temperatures (from 0 °C to 95 °C) were performed by the authors. It was determined that the main contribution in the valence symmetric and asymmetric bands vibrations of water OH-groups connected with water trimmers at the room temperatures. The concentration of cluster types $(H_2O)_4$, $(H_2O)_5$, $(H_2O)_6$ increase at the low temperatures (0-10 °C) and the concentration of cluster types $(H_2O)_2$ increase at the high temperatures (30-95 °C). But trimer became the most common cluster type within all measured temperature range (0-95 °C).

Исследование кластерной структуры воды посредством анализа температурных зависимостей спектров комбинационного рассеяния света

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Исследован характер температурных зависимостей спектров КРС в области частот 2900-3700 см$^{-1}$ воды. Данный диапазон отвечает за валентные симметричные и антисимметричные ОН колебания воды. В работе использована кластерная модель, в которой вода рассматривается в виде набора кластеров от одной до шести молекул в комплексе. В результате исследований был найден относительный концентрационный вклад кластеров в спектр КР воды. Низкочастотная часть спектра 2800-3300 см$^{-1}$ образована преимущественно кластерами типа $(H2O)_3$, $(H2O)_4$, $(H2O)_5$, $(H2O)_6$, а высокочастотная часть спектра 3300 см$^{-1}$ до 3800 см$^{-1}$ образована преимущественно кластерами типа $(H2O)_2$, $(H2O)_3$, $(H2O)_4$. При этом тример остается наиболее распространенным кластером в жидкой воде в температурном диапазоне 0-95 °C.

Ключевые слова: Спектроскопия КР, Спектр КР воды, Концентрация кластеров, Температурная зависимость.

Дослідження кластерної структури води з аналізу температурних залежностей спектрів комбінаційного розсіювання світла

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Вивчено характер температурних залежностей спектрів КРС в області частот 2900-3700 см$^{-1}$ води. Даний діапазон відповідає за валентні симетричні та антисиметричні ОН коливання води. В роботі використана кластерна модель, в якій вода розглядається у вигляді набору кластерів від однієї до шести молекул у комплексі. В результаті досліджень був знайдений відносний концентраційний внесок кластерів в спектр КР води. Низькочастотна ділянка спектру 2800-3300 см$^{-1}$ утворена переважно кластерами типу $(H2O)_3$, $(H2O)_4$, $(H2O)_5$, $(H2O)_6$, а високочастотна ділянка 3300-3800 см$^{-1}$ утворена переважно кластерами типу $(H2O)_2$, $(H2O)_3$, $(H2O)_4$. При цьому тример залишається найбільш розповсюдженим кластером в рідкій воді в температурному діапазоні 0-95 °C.

Ключові слова: Спектроскопія КР, Спектр КР води, Концентрація кластерів, Температурна залежність.

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