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EFFECT OF IMPURITY CONTENT ON STRUCTURE OF LIVING WATER

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In order to study the influence of impurities content on the water structure, Raman spectra and degrees of depolarization of different living water are measured by Raman spectroscopy, the relationship between the depolarization ratio and the impurity content in drinking water was obtained by the utilisation of computer deconvolution for the stretching vibration peak. The results showed that the intensity of different bending vibration is almost the same, and the intensity of the stretching vibration reflects different content of impurities in water. Depolarization calculation of water molecules showed that the stretching vibration is stronger than the bending vibration. The interaction of impurity ions and water molecules enhances the vibration rate of water molecules, making the symmetry of stretching vibration reduced, and leading to increased depolarization ratio. Therefore, the impurities content can be determined from the relative intensity of Raman characteristic peaks and the degrees of depolarization.

Keywords: Raman spectroscopy, water structure, impurity content, depolarization ratio.

Introduction

Many unique properties of water have relationships with micro-structure of water. Water molecular association with different size formed by hydrogen bonds between water molecules [1, 2]. The association degree of water molecular is not only influenced by temperature, but also by other substances dissolved in water such as various ions and other factors [3]. Raman spectroscopy is

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an effective mean to study water and aqueous solutions. However, due to the overlap of the Raman vibration modes, there are many difficulties for analyzing the changes of water structure using Raman spectrum, Measurements of depolarization degree and multi-peak-resolution processing can effectively solve this problem.

In this paper, Raman spectroscopy and multi-peak-resolution processing are used to investigate the affection from containing impurities on the microstructure of water, and to provide alternative method to detect the impurity concentration in drinking water using Raman spectroscopy.

Experimental

In this paper, Raman spectra were studied using LRS-III laser Raman spectrometer (made in Tianjin Port East Company, China) with frequency YVO₃: Nd laser as the light source, the exciting wavelength was 532.0 nm, and spectral range is from 200 to 800 nm. An interference light filter was used. Spectra were received in I_{||} and I_⊥ polarisations using a polarisation prism and a $\lambda/2$ plate. Automatic control and automatic signal acquisition were obtained with computer, and data processing was analyzed with the origin software.

Raman spectra of different water (purified water and running water) were measured, by comparing the spectral intensity of the different water and analyzing the relationship between the peak intensity and the impurities in water. The depolarization degree of different Raman spectra of water, are studied using peakfit software with which the stretching vibration spectra are divided into two peaks (low and high frequency spectrum), and the depolarization degree of low-frequency peak caused by the hydrogen bonds and intermolecular OH vibration peak are calculated respectively. The relationship between the impurity content in living water and the depolarization ratio is analyzed.

Results and discussion

Structure, vibration modes and Raman spectroscopy of water molecules.

Water (H₂O) molecule is a non-linear molecule made up of one oxygen atom and two hydrogen atoms. Water molecule has three normal vibration modes, which belong to three different types of vibration: the vibration with changing OH bond length known as stretching vibration, which can be divided into asymmetric stretching vibration (ν_3) and symmetric stretching vibrations (ν_1) according to

the inversion symmetry; the vibration whose bond angle \angle HOH is changing is called bending vibration or deformation vibration (ν_2), Corresponding to these three forms of vibration mode, Raman shift of water molecules are: 3756; 3652 and 1595 cm^{-1} . Fig. 1, *a* shows the measured Raman spectra of water. Because water molecules are poor Raman scatters, the result of 3756 cm^{-1} does not appear. At 1630 cm^{-1} there is a relatively weak peak (corresponding to the bending vibration). From 3200 to 3400 cm^{-1} , there is a relatively strong Raman band, whose peak should be due to OH stretching vibration. Fig. 1, *b* shows that the symmetric stretching vibration of water is not a sharp peak but a broad peak with certain width (3100 ~ 3700 cm^{-1}). Because the OH stretching vibration of water molecules has intermolecular and intramolecular vibrational modes [4], hydrogen bonds are the intermolecular mode, and their bond strength is weaker than the bond strength of intramolecular OH, so the vibration frequency of the OH molecule caused by hydrogen bonds is also lower than the OH vibration frequency. The coupling of the two vibrations results a relatively large width (stack together) in the raman peaks.

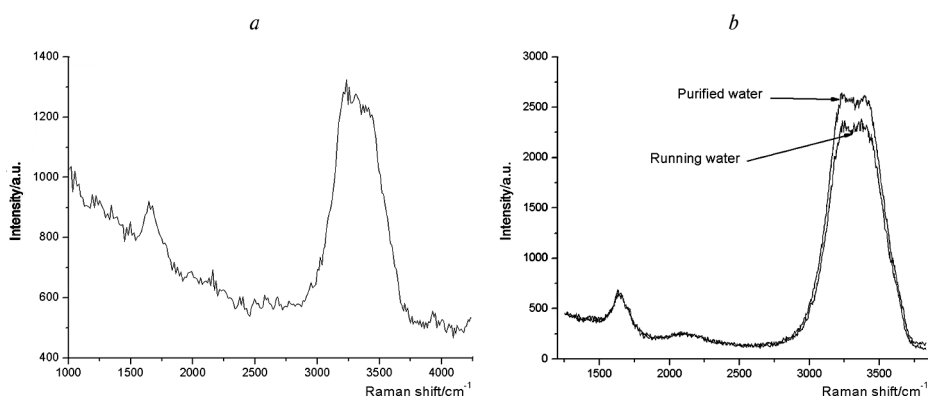


Fig. 1. Raman spectra of water (a) and different water (b).

Comparative analysis of Raman spectra intensity of different living water.

Raman spectra of purified water (five lever filtered water purified by the Qinyuan RO-185 water purification machine) and running water are shown in Fig. 1, *b*, in which the strong peak is the purified water and the small intensity peak is the running water. Because different water samples containing varying concentrations of impurities. When the water contains impurities, the impurity ions interact with water molecules, the hydrogen side of water molecules take effect on anions impurity and oxygen-side interact with cation impurities, and

hydrogen atoms interacting with the anion of water molecules can no longer maintain the hydrogen bonds action with other water molecules, making the hydrogen bonds between water molecules weaken [5]. The more the concentration of impurities in water, the stronger the reduction of hydrogen bonds effect between water molecules, the intensity of OH vibration peak decrease. The above results will affect the ratio of bending vibration and stretching vibration peak intensity of water molecules, since the intensity of bending vibration spectrum of all the water are the same, the intensity of stretching vibration (intensity can be averaged) may reflect the content of impurities in the water. The greater the stretching vibration intensity is, the less impurities the water contains.

Depolarization analysis of different living water. The value of the depolarization ratio of a Raman band depends on the symmetry of the molecule and the normal vibrational mode. Under Placzek's polarizability approximation, it is known that the depolarization ratio of a totally symmetric vibrational mode is less than 0.75, and that of the other modes equals 0.75. A Raman band whose depolarization ratio is less than 0.75 is called a polarized band, and a band with a 0.75 depolarization ratio is called a depolarized band [6].

When incident light is linearly polarized, depolarized Raman spectra are measured for the purified water and running water, respectively. Raman depolarization spectra of purified water and running water are shown in Fig. 2, *a*, *b*. The depolarization ratio of bending vibration ($\sim 1630\text{ cm}^{-1}$) and stretching vibration ($3200 \sim 3400\text{ cm}^{-1}$) were calculated for purified water and running water, as shown in Table 1.

Table 1. Depolarization ratio of different water and different vibration mode

Water	Bending vibration (1630 cm^{-1})	Stretching vibration (3425 cm^{-1})
Purified	$31/80.5 = 0.39$	$57.5/260.0 = 0.22$
Running	$36/86.5 = 0.42$	$57.4/248.7 = 0.23$

The calculated data from Table 1 shows that for the same kind of water the depolarization ratio of stretching vibration is less than that of the bending vibration, indicating the symmetry stretching vibration of water molecules is stronger than the bending vibration. Because more impurities containing in the running water do brownian motion, the interaction of impurity ions and water molecules enhances the vibration rate of water molecules, making the symmetry of water molecules decrease and their depolarization ratio increases.

The whole results are that depolarization ratio of purified water is slightly less than that of running water.

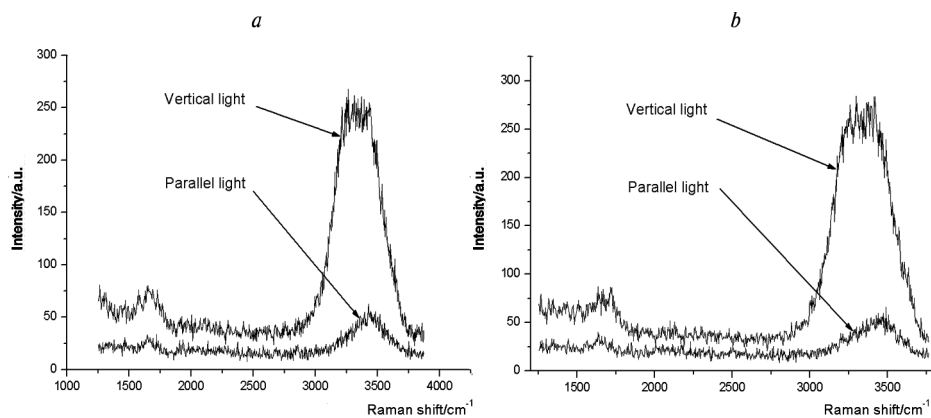


Fig. 2. Raman depolarization spectra of purified water (a) and running water (b).

The stretching vibration broadening of water molecules located in the 3100~3700 cm^{-1} is due to the existence of hydrogen bonds [7]. The stretching vibration was divided into two parts (low and high-frequencies) using peakfit software, as shown in Fig. 3, 4 Table 2 shows the corresponding calculation results of depolarization.

Table 2. Depolarization ratio of stretching vibration

Water	Low-frequency (3200 cm^{-1})	High-frequency (3400 cm^{-1})
Purified	$5.6/165.2 = 0.034$	$33.8/166.5 = 0.203$
Running	$12.5/169.2 = 0.074$	$33.2/187.28 = 0.177$

Table 2 data shows that low-frequency part of stretching vibration of the purified water is far less than the running water. Low-frequency part is caused by the hydrogen bonding of OH vibration. For example, mineral impurities dissolved in water are common factor affecting hydrogen [8]. There are more impurities in running water than purified water, resulting in an increase in non-symmetric vibration components, and causing decreased depolarization ratio. The high-frequency part is the intermolecular OH vibration peak, which is less affected by impurities in the water, so depolarization ratio change little. Accordingly, the depolarization ratio can determine the relative content of impurities in different water.

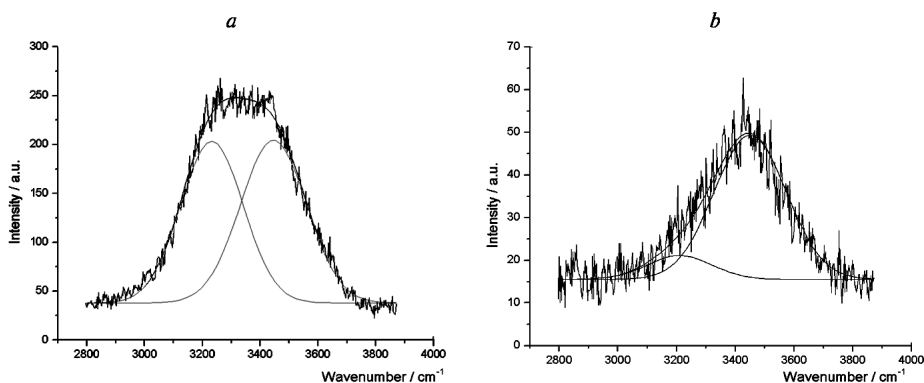


Fig. 3. Gaussian deconvolution Raman spectra of purified water high-frequency (a) and low frequency (b).

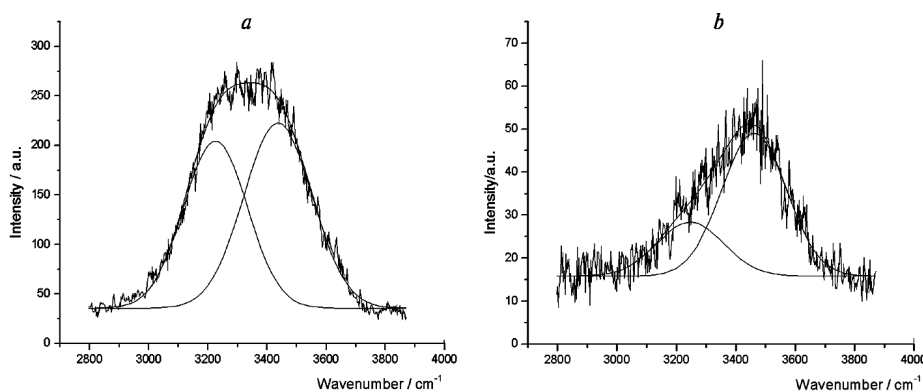


Fig. 4. Gaussian deconvolution Raman spectra of running water high-frequency (a) and low frequency (b).

Conclusion

Water molecule has a relatively weak Raman peaks (corresponding to the bending vibration) with wavenumbers 1630 cm^{-1} , and has a relatively strong Raman spectrum bands (corresponding to the OH stretching vibration) with wavenumbers $3200 \sim 3400\text{ cm}^{-1}$. The depolarization ratio of stretching vibration is less than that of bending vibration, indicating that the symmetry of stretching vibration of water molecules is stronger than that of bending vibration.

The intensity of bending vibration of different living water is almost the same, the stronger the intensity of stretching vibration, the fewer the impurities in water.

The depolarization ratio is different for different water. Mineral impurities dissolved in water are common factor affecting hydrogen bonding, and the

interaction of ionic impurities in water with water molecules enhances the vibration rate of water molecules, making the symmetry of the stretching vibration of water molecules reduces, thereby leading to the increase of their depolarization degree.

Therefore, based on the relative intensity of Raman characteristic peaks and the depolarization ratio under the terms of the same characteristic peaks, the relative impurities content in living water can be determined.

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