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On Raman spectra of water, its structure and dependence on temperature

S.M. Baschenko, L.S. Marchenko

Institute of Physics, NAS of Ukraine

46, prospect Nauky, 03028 Kyiv, Ukraine

E-mail: baschenk@iop.kiev.ua

Abstract. Raman spectra of water within the temperature range 20 to 3 °C were investigated. Best of all, the complex shape of the obtained spectra was approximated by four (or five) Gaussian-shaped peaks with their positions 3070, 3230, 3440, 3600 (and 3650) cm^{-1} . The most intensive constituents were 3230 and 3440 cm^{-1} lines, their total contribution to the Raman spectrum of water is higher than 90%. These lines are the most sensitive to the temperature, too. When the temperature decreases from 20 down to 3 °C, the positions of these peaks were shifted from 3232 to 3224 cm^{-1} and from 3441 to 3434 cm^{-1} , respectively; and the intensity of 3230 cm^{-1} line was increased approximately by 14% in its magnitude.

Keywords: Raman spectra, water structure, temperature, pressure.

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1. Introduction

Investigations of water, its structure and properties are actual and important due to the role that water plays at the Earth and in human life. Such investigations have been carried out for many years. But up to date, there is no total clearance in understanding and explanation of the water structure, its dependence on environment, the main parameters of which are temperature and pressure [1, 2].

“Water clusters” – groups of water molecules held together by hydrogen bonds – have been the subject of a number of intensive experimental and theoretical investigations [3] because of their importance for understanding the water properties.

The most informative and non-disturbing method to investigate various media is the Raman scattering of light in them [4, 5]. Since its discovery in the 1920s, the Raman spectroscopy has become an important tool for understanding the nature of hydrogen bonds. Raman spectroscopy is called a “fingerprint” technique – every chemical element gives a unique Raman signal, or spectrum. Hundreds of books have been published concerning the fingerprints of various chemical compounds. Raman spectroscopy provides the

possibility to conclude that the water molecules retain their molecular character in every phase of H_2O and that the four-coordinated tetrahedral configuration of water molecules is preserved in each phase.

2. Experimental setup

For these investigations, the authors have created a typical multi-pass optical cuvette, in which provided were the changes within the ranges: from +30 °C down to –10 °C for temperature and from 1 to 100 atm for pressure. The scheme of this cuvette is presented in Fig. 1. As seen from this figure, the exciting laser beam is directed into the cuvette through the window 1 (or 2 in dependency on experimental geometry) under an angle α (slightly less than 90°) to the cuvette axis in such a manner that maximum possible reflections of the beam from the mirrors 3 and 4 occurred. These mirrors 3 and 4 form the so-called optical wedge with the angle β near the top. These angles α and β may be preliminary adjusted in some intervals and were chosen in the way that the exciting beam passes a maximum possible length in a medium under study up to its full absorption. The beam scattered under the angle of 90° to the cuvette axis (when dealing with Raman, Rayleigh, Mie

scattering, etc.) exits from the cuvette through the window 5 and is collected by a lens to the receiving system. To increase the useful signal, the additional mirror 6 was used. Our receiving system consists of a double monochromator MSA-130 and the connected to it photomultiplier FEU-106 that operates in “photon counting” mode.

For the best heat conduction, the cuvette was fabricated of aluminum. But its inner surface was coated with stainless foil thus providing the contacts of liquid under study only with stainless steel, teflon and glass (or silica). Such cuvette construction makes it possible to investigate not only water or neutral liquids, but also the aggressive ones.

Outer sides of the cuvette were equipped with several thermoelectric coolers that provides changes in temperature inside the cuvette within the range +30 to – 10 °C. Due to negligible water compressibility, the pressure change inside the cuvette from 0 to 100 atm is available by using the stainless diaphragm.

3. Results

Raman spectra of distilled water were excited by laser irradiation with wavelengths 488 and 532 nm. The scattered Raman signal was collected at the angle close to 90° relatively to the exciting laser beam, then directed to a double monochromator and detected by the photomultiplier $\Phi\Omega\Upsilon$ -106 operating in the “photon counting” mode. It should be mentioned that shorter wavelengths provides a higher Raman signal but simultaneously higher background. Therefore, there exists optimum in the signal-to-noise ratio for wavelengths of exciting light. We did not find this optimum, but for the wavelengths 488 and 532 nm we did not observe any difference.

It is well known that Raman spectra of water have a complex structure [4]. Typical obtained Raman spectra of water are presented in Figs 2 and 3. It is clearly seen that with great precision the complex spectrum shape may be approximated by four or five Gaussian-shaped constituents: two main and two or three minor ones. Positions of maxima for these five constituents are close to 3070, 3230, 3440, 3600 and 3650 cm^{-1} . The most intense constituents are 3230 and 3440 cm^{-1} lines that contribute more than 90% to the Raman spectrum of water. The obtained experimental results for 20 and 3 °C are presented in Figs 4 and 5, respectively. The lines peaking at 3230 and 3440 cm^{-1} proved to be the most sensitive to change with temperature. So, when decreasing the temperature from 20 down to 3 °C, the following changes in these two lines were detected:

- positions of their maxima move from 3232 to 3224 cm^{-1} and from 3441 to 3434 cm^{-1} , respectively;
- relative magnitude of the line 3230 cm^{-1} was increased by 14%.

All the rest constituents give less than 10% contribution to the total Raman spectrum intensity, and determination of their number, magnitudes and maximum positions in the conditions of our experiments were very unreliable.

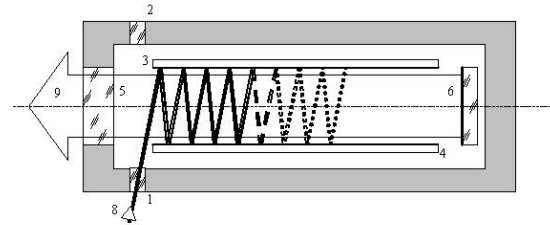


Fig. 1. Scheme of the cuvette for liquid in our Raman scattering investigations: 1, 2 – entrance windows, 3, 4 – mirrors of the “optical wedge”, 5 – exit window, 6 – additional mirror, 8 – exciting light, 9 – scattered light.

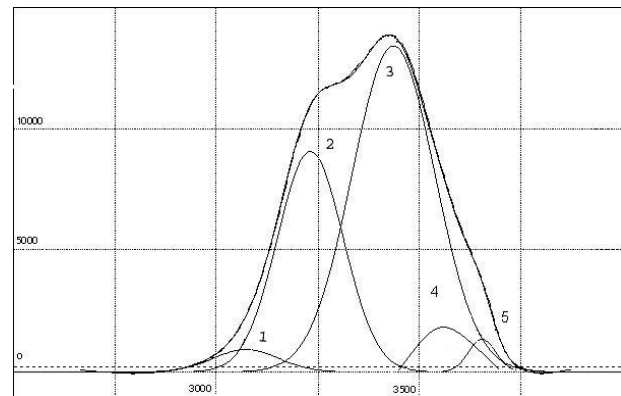


Fig. 2. Typical complex Raman spectrum of water, approximated by five constituents with positions of peaks near: 1 - 3074, 2 - 3233, 3 - 3437, 4 - 3596 and 5 - 3666 cm^{-1} . Main constituents 3230 and 3440 cm^{-1} form more than 90% of the total spectrum area, always present and were detected reliably.

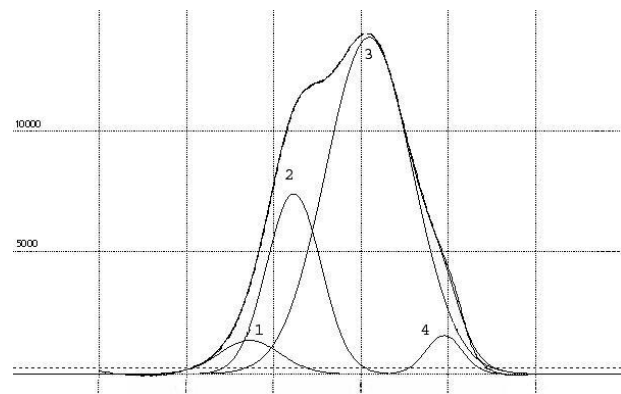


Fig. 3. Typical complex-shaped Raman spectrum of water decomposed by four constituents: 1 – 631,3 nm; 2 – 642,3 nm; 3 – 651 nm; 4 – 659,5 nm under pumping by 533 nm. It is obvious that two or three minor ones do not play significant role in spectrum approximation.

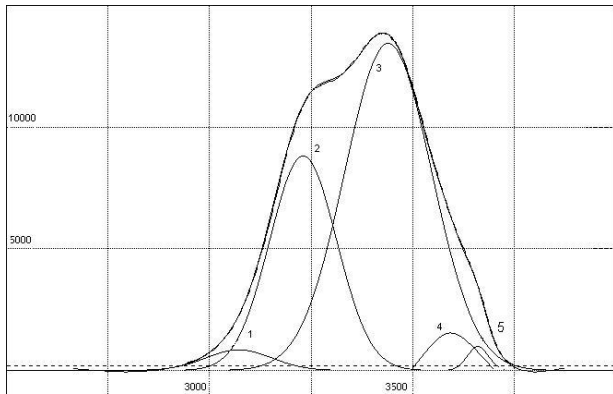


Fig. 4. Obtained Raman spectrum of water at the temperature 20 °C. Positions of constituents: 1 – 3073,5; 2 – 3231,9; 3 – 3441; 4 – 3611,6 and 5 – 3661,5 cm^{-1} .

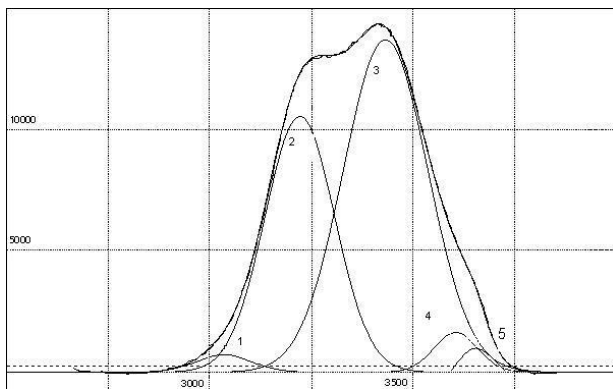


Fig. 5. Obtained Raman spectrum of water at the temperature 3 °C. Positions of constituents: 1 – 3036,7; 2 – 3223,1; 3 – 3434; 4 – 3606,7 and 5 – 3657,2 cm^{-1} . It is clearly seen that the magnitude of 3230 cm^{-1} line has been increased and positions of 3230 and 3440 cm^{-1} lines have been shifted by 7-8 cm^{-1} into the shortwave range.

4. Conclusion

The structure of Raman spectra of distilled water as well as their dependency on temperature within the range 20 to 3 °C and pressure up to 100 atm were investigated. The revealed shift up to 7–8 cm^{-1} for positions of two main constituents in short-wave direction can be explained as “freezing” the vibrations. And the changes in their amplitude relation can be explained as water structure redistribution. The pressure increase up to 100 atm causes no changes in the Raman spectra structure.

References

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