Interpretation of Vibrational Spectra of Liquid Water[*]

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Based on Raman spectral studies of H_2O, D_2O, HOD and aqueous solutions of various salts we suggest a new interpretation of vibrational spectra of liquid water. The striking result is obtained that a quite definite set of weak H-bonds corresponds to a quite definite set of the rotational reorientations of the water molecules. The contribution of each orientation depends on the temperature and on the nature of the solved salts.

Key words: liquid water, Raman spectra, rotational reorientation, molecule mobility

Spectral study of liquid water itself is an important starting point for understanding the structure of hydrogen-bonded systems. Especially it is true with respect to Raman spectral studies. From spectral data we can subdivide previous models of the structure of liquid water into two kinds, when one presents a continuum of geometric and energetic states [1–4] and the other a mixture of discrete species [5–7].

The complex shape of the water stretching band is well-known. In Raman spectra five components of this band were evidenced. Two of them were reported recently by us (3441 and 3473 cm^{-1}) [8–10] and the third weak component (near 3600 cm^{-1}) was observed many years ago by a number of authors [1–7,11,12]. Such a complex shape of the liquid water stretching band is connected closely with the structure of water and requires an appropriate explanation. This is true for the deuterated samples, too.

EXPERIMENTAL

Raman spectra of H_2O, D_2O, HOD and the aqueous solution of various salts were investigated using a DFS-24 (LOMO, Russia) spectrometer with the linear scale of wavelengths. The exciting wavelength was 514.5 nm green line of the argon laser ILA-120 (Carl Zeiss). Water samples were sealed in capillary cells. Raman spectra were obtained with $I_{\parallel}$ and $I_{\perp}$ polarizations. Other experimental details are described previously [8–10].

RESULTS AND DISCUSSION

The bands of O–H and O–D stretching vibrations of H_2O and D_2O consist of five components (Figure 1 a,b); four components are detected for HOD (Figure 2). In the case of H_2O and HOD (35% H_2O in D_2O) we observe two new components at 3441 cm^{-1} and 3473 cm^{-1}. In the case of D_2O and HOD (45% D_2O in H_2O) we also observe two new components at ~2526 cm^{-1} and 2553 cm^{-1}. It is interesting that the new components for HOD are located at the distance from the main band, similar to those for H_2O and D_2O. There is a very good pair correlation between all band components of light and heavy water with the coefficient ~1.36 (Figure 1, 2).
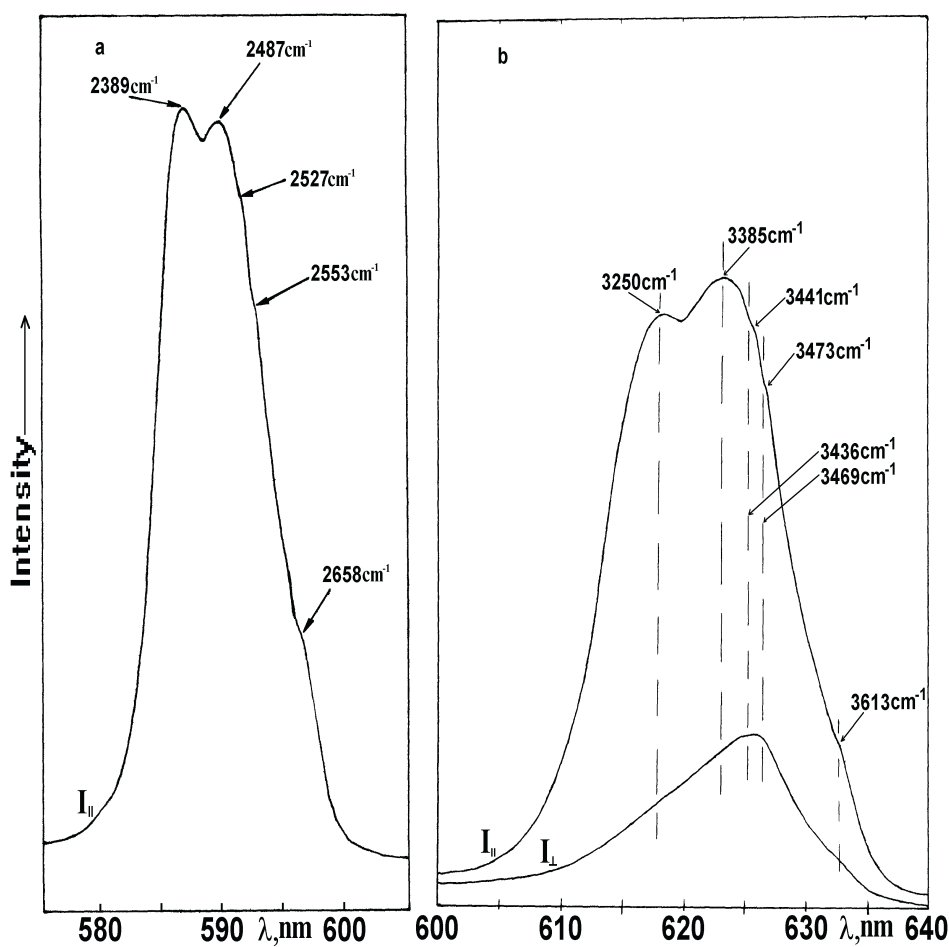

Figure 1. Raman spectra of D_2O (a) and H_2O (b) with $I_\parallel$ and $I_\perp$ polarizations; regions of the stretching O–H and O–D vibrations.
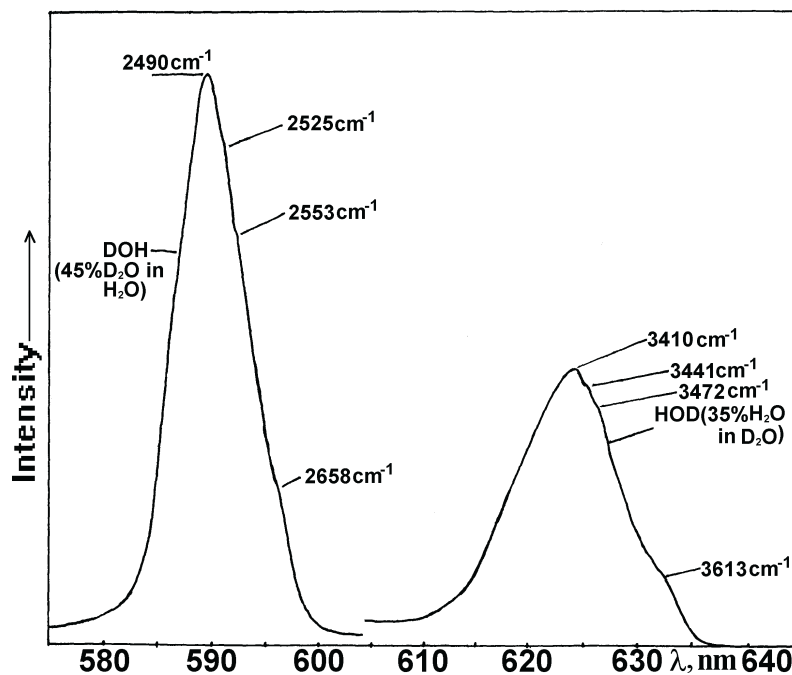
Figure 2. Raman spectra of HOD.

Thus, in each spectrum of Fig. 1, 2 just three very weak components (shoulders) of the water stretching band [3441 cm^{-1} (2527 cm^{-1}), 3473 cm^{-1} (2553 cm^{-1}), 3613 cm^{-1} (2658 cm^{-1})] are visible. All weak components (shoulders) of the water stretching band have the same nature and the same sensitivity to different salts. In the course of our study the separation of those bands was performed. Such a separation can be carried out by the study of solutions of different salts at various concentrations [8–10]. We observe an intensity increase of these components with increasing the salt concentration. The intensity and wavenumber increase of the ~3400 cm^{-1} O–H stretching vibration band with increasing temperature of the liquid water is well-known [2]. In our case the nature of the salt anions plays a great role. Each component of the water stretching band can be separated in the Raman spectra of the aqueous solutions, when using different salts with appropriate anions. A great importance is the size of the anion.

The presence of five components in the water stretching band and the similarity of temperature and solution effects on changes related to the intensities and wavenumbers is an analogy to the rotational isomerism and provides the possibility to consider that liquid water molecules have four conformations (with respect to the central molecule) as the result of rotational reorientation in the five-molecule unit (Fig. 3) as "structural unit" of the spatial hydrogen bond network (Fig. 4) [8].
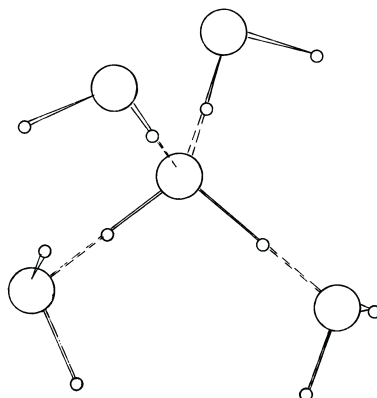
Figure 3. The fully hydrogen-bonded five-molecule structural unit found in liquid water and in some ices.
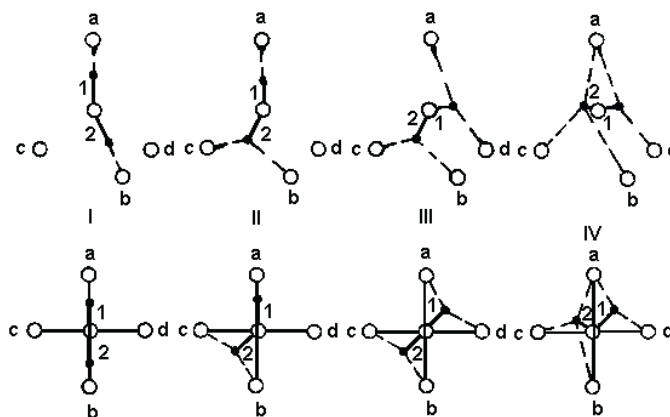

Figure 4. Possible conformations of the H$_2$O molecule in the five-molecule structure unit after rotational reorientations around its bonds.

Now, it is desirable to consider the question related to the interpretation of all the components of the water stretching band. This is important, because we find only five components of the water stretching band in the Raman spectra. In reality we observe five components, but say about four "conformers". Each "conformer" must be reflected by two frequencies of a central molecule of the five-molecular unit. We must explain such a contradiction. We noted already a great similarity of the subpeaks of H$_2$O and D$_2$O on the one hand with the HOD on the other hand. Such similarity is possible only if the O–H(D) liquid water bonds 1, 2 are not the same. This means that the bonds of the liquid water molecules are independent vibrators. Such situation is favourable for the successive turning of the water molecules around their bonds, as presented in the "Model of the rotational reorientations of molecules in the liquid water" [8] (Fig. 4) by the action of the temperature or solved salts. Depending on the salt anions (their nature as well as their size), we see a different picture in the Raman spectra of aqueous solutions.

A great sensitivity of the liquid water molecules to the nature of the salt anion has to be emphasized. It is interesting that each component of the water stretching band of liquid H_2O, D_2O and HOD can be separated in the Raman spectra of aqueous solutions by selection of suitable salts. Gaussian deconvoluted Raman spectra of H_2O, of the 5.17 m (m – molality) CsC1 solution in H_2O and of the saturated aqueous solution of CsI are shown in Fig. 5. In Fig. 5a one can see all components of four "conformers" of the fully hydrogen-bonded five-molecule structural unit found in liquid water. The "conformer" numbers in Fig. 4 and Fig. 5 correspond to each other. In the case
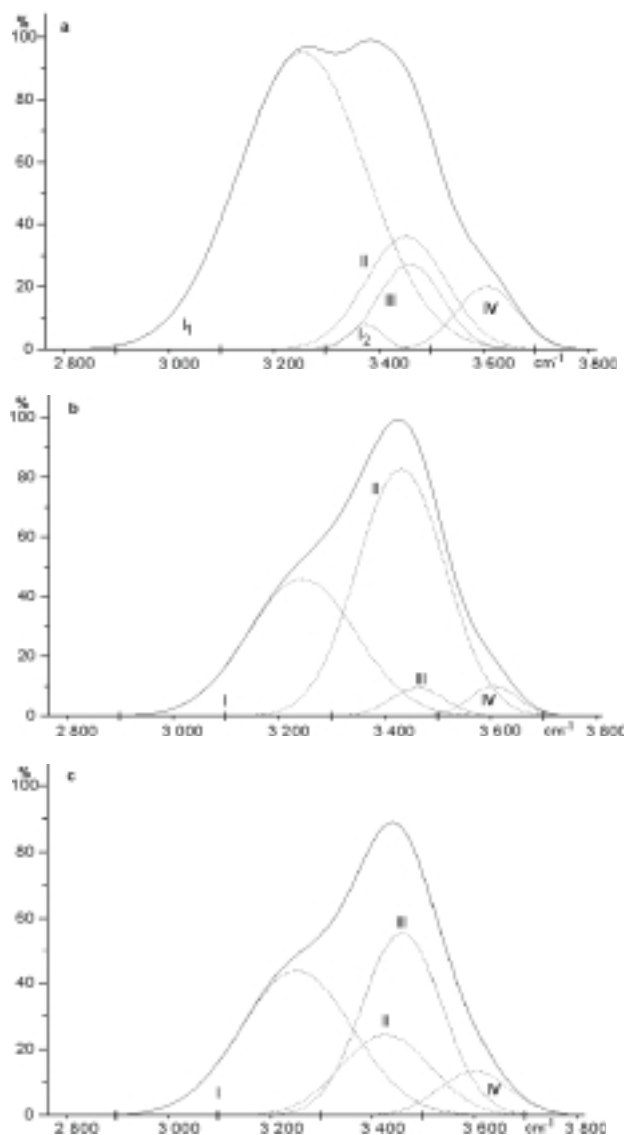

Figure 5. Gaussian computer deconvoluted Raman spectra of H_2O (a), of the 5.17 m solution CsC1 in H_2O (b) and saturated solution CsI in H_2O (c).

of CsC1 solution we see (Fig. 5b) the predominance of the 3436 cm^{-1} component (II) and in the case of the saturated CsI solution (Fig. 5c) the predominance of the 3467 cm^{-1} component (III) is visible. We must bear in mind that we cannot observe all the components of the water stretching band because of bands overlapping. We offer an interpretation of the vibrational spectra of liquid water based on all data from the light, heavy and half-heavy liquid water including solutions of electrolytes (Table 1). From this Table it follows that the bond 1 (band I_1 in Fig. 5a) of the first "conformer" (I in Fig. 4) is the same as for the second conformation ("conformer" II in Fig. 4) after the molecule turning around its bond 1. For that we must compare the spectra a and b from Fig. 5. We see the bond 1 (band I_1) and the bond 2 (band I_2) (Fig. 5a) for the first "conformer". We also see the same bond 1 (band I), but the other bond 2 (band II) too (Fig. 5b) for the second "conformer". Such consideration is valid for the III and IV "conformers". In the case of the "conformer" III we must see the wavenumber of the "conformer" II too (Table 1).

Table 1.

	bond 1	(cm^{-1})	bond 2	(cm^{-1})
	H$_2$O (23°C)			
conformation I		3250		3385
conformation II		3250		3441
conformation III		3473		3441
conformation IV		3473		3613
	D$_2$O			
conformation I		2389		2487
conformation II		2389		2527
conformation III		2553		2527
conformation IV		2553		2658
	HOD			
conformation I		2490		3410
conformation II		2525		3410
		2490		3441
conformation III		2525		3472
		2553		3441
conformation IV		2658		3472
		2553		3613

It is clear that the spatial H-bonds network of the liquid water is a set of different conformations of the five-molecule unit. This "mixture" of conformations is always present in the liquid water, but their proportion depend on temperature and the solved salts. From spectra in Fig. 5 we can estimate roughly the number of the I type "conformer". Its contribution is in the range 4–10%.

An interesting situation takes place for the HOD molecule, when one band is related to the O–H frequency 3467 cm^{-1} and the other to the O–D frequency 2553 cm^{-1}. This is well reflected in Fig. 6. In the case of the HOD one can see all four components as for the O–H or O–D vibrations (Fig. 2, Table 1).
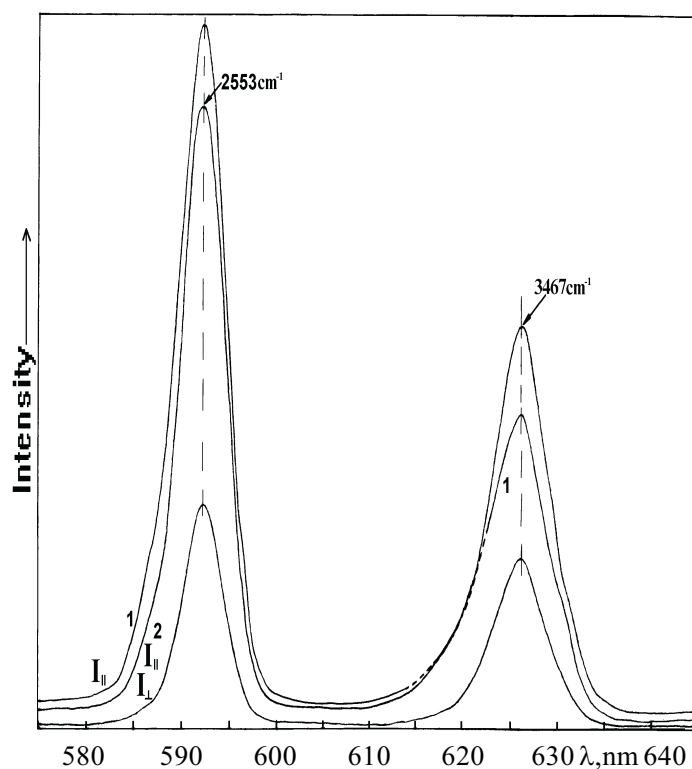

Figure 6. Raman spectra of saturated solution KI in 1 – HOD (45% H_2O in D_2O) and 2 – DOH (45% D_2O in H_2O) with $I_{\parallel}$ and $I_{\perp}$ polarizations; stretching O–D and O–H vibrations.

CONCLUSIONS

One of principal questions of the liquid water state is connected with the mobility of water molecules forming a hydrogen-bonded three-dimensional network.

The computer simulation methods yield contradictory results, but confirm the conclusion that mobility of liquid water molecules is due to defects of the hydrogen bonds network without necessity to accept the vacancy mechanism.

Our experimental data on O–H and O–D stretching vibrations were obtained from Raman studies of light and heavy water and some aqueous salt solutions. We analyse the previous results in this field under new aspects. The mechanism of the defect formation was suggested as rotational reorientation of the liquid water molecules

by analogy to the rotational isomerism when hindered rotation around single bonds takes place. Based on Raman spectral studies of light, heavy liquid water, HOD and aqueous solutions of various salts we consider nonhomogeneity of the spatial H-bond network of liquid water. We think that it is connected closely with the H-bond furcation, leading to the change in wavenumbers and intensities of the water stretching band components. The consequence of that is the presence of defects of the H-bond network from the different conformations of fully hydrogen-bonded five-molecule structural units found in liquid water. The presence of each of them depends on temperature, pressure and solute concentration. Each component of the water stretching band is assigned to the corresponding conformation and can be separated in the Raman spectrum of aqueous solution by selection of different alkali metal halides or other salts. The frequencies and intensities of these components practically do not depend on the nature of the cation, but on the nature and size of the anion. Our result suggests an important water molecule mobility across the defects of the H-bond network and not vacancies in liquid water structure, often reported in literature.

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