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Raman Resonance Effect in Liquid Water

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Raman spectroscopy is a technique preferably used for studies of water structure because the proportions of intensities of main OH stretching modes are thought to reflect well a network of “intermonomer” hydrogen bonds as well as its disturbance by the presence of some solutes. The work presented herein demonstrates how the intensity ratio of two main components (around 3200 and 3400 cm^{-1}) depends on the excitation wavelength in the visible range. Polarized Raman spectra indicate that the component at ca. 3200 cm^{-1} is in resonance with light from the red range, which is in agreement with the presence of vibrational overtones in UV–vis absorption spectrum of water. These results are the first report on the occurrence of the Raman resonance effect in liquid water.

Introduction

The dynamic structure of liquid water and its relation to properties of solutions and biological tissues still create considerable discussion. The shape of the Raman OH stretching band in the range 2900–3700 cm^{-1} is thought to reflect well the dynamic microstructure of water^{1–3} as well as its interactions with solutes,⁴ polymers⁵ or biological molecules.⁶ Usually, the mode at 3200 cm^{-1} is thought to be related to strongly hydrogen-bonded water molecules and the mode at 3400 cm^{-1} with loosely bonded ones. Moreover, the intensity of this band is widely employed as a standard in spectrofluorometry of water solutions and plays an important role in estimating pigment biomass from ocean color⁷ as well as in other underwater optical measurements. Thus, how the Raman intensity of the OH stretching band depends on the excitation frequency constitutes a crucial problem. Due to the complexity of this band—it consists of a number of overlapping modes—a question of the occurrence of the Raman resonance effect in water is still unclear. Up to now, in all published research on this effect the OH stretching band was analyzed as one broad peak and the resonance effect has been expected to correlate with the electronic transition of water (excitation in UV region).^{7–9} Here we analyze how the intensity ratio of two main components polarized around 3200 cm^{-1} and depolarized around 3400 cm^{-1} depends on the excitation wavelength in the range 458–647 nm (which corresponds to vibrational overtones of water).

Experimental Section

Raman spectra were obtained using a JobinYvon T64000 triple grating Raman spectrometer (Ar laser lines: 457.9, 476, 488, 514.5 nm, and a He–Ne line 632.8 nm) with a spectral resolution below 1 cm^{-1} . To exclude the apparatus artifacts, additional measurements were performed using the Dilor Z-40 five grating spectrometer (Kr line, 647.1 nm; Ar line, 514.5 nm) with a photomultiplier as a detector. The power at the sample

was in the range 0.4–40 mW. Additional power-dependent measurements for line 514.5 nm in the range 0.1–100 mW (at the sample) allowed us to exclude local sample heating phenomena (Supporting Information, Figure 1). To prove that the observed effects were not connected with the nonlinear sensitivity of the CCD detector in the JobinYvon T64000 spectrometer, a series of excitation wavelength-dependent spectra for cyclohexane (as an external standard) was measured (Supporting Information, Figure 2). These spectra differed in their intensities less than 5% and the influence of the nonlinearity of the detector could thus be neglected. Twice distilled water subsequently purified with a Milli-Q system (Millipore) was measured in a QS quartz cuvette.

Results and Discussion

The Raman spectra were acquired at room temperature in the frequency range 2700–3900 cm^{-1} and normalized to the intensity at 3410 cm^{-1} (i.e., the position of the intensity maximum of the spectrum for $\lambda_{\text{exc}} = 514.5$ nm, which was used as a reference). It can be clearly seen from Figure 1a that the intensity ratio of the low and high frequency components strongly increases with λ_{exc} . Because apparatus artifacts were excluded, two possible physical explanations existed for this phenomenon. The first one was the selective absorption of the Raman scattered light by water which has some weak absorption bands in the visible region. Thus, when the position of the Raman band coincided with the steep slope of the water absorption band, one part of the broad band of the scattered light could be stronger absorbed than the other. Figure 1b presents the UV–vis absorption spectrum of water (Cary 5000 spectrometer) with superimposed Raman spectra obtained for varying λ_{exc} . It is evident that in some cases (3, 4 and 6 in Figure 1b) one component is absorbed stronger than the second; in another case (5 in Figure 1b) the situation is reverse, and in some cases the absorption of both components is similar (1 and 2 in Figure 1b). This effect did not comply with the observed (see Figure 1a) monotonic increase in the 3200 cm^{-1} and 3400 cm^{-1} bands intensity ratio vs λ_{exc} .

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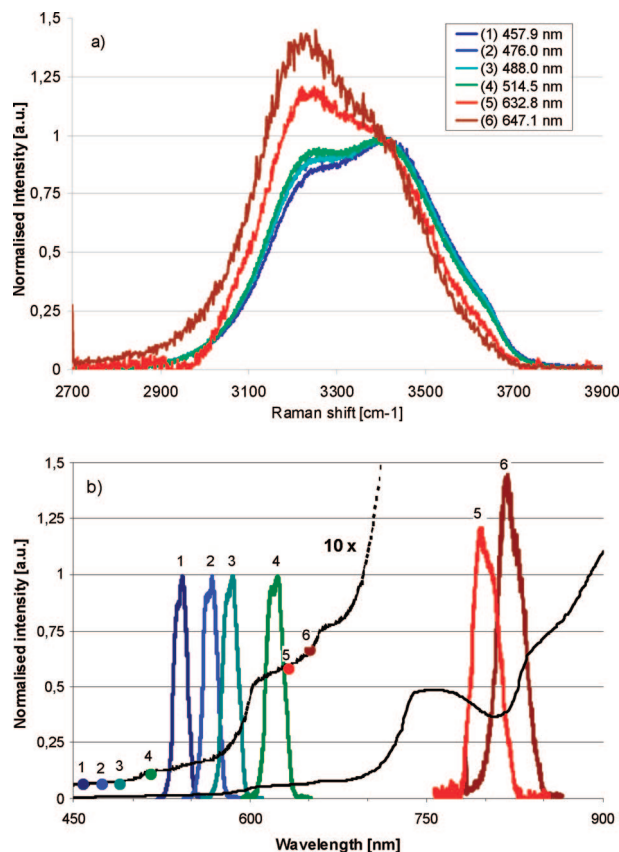


Figure 1. Raman spectra of water obtained at room temperature for different excitation wavelengths λ_{exc} presented as (a) a Raman shift and (b) in absolute scale. The black curves in Figure 1b corresponds to the absorption UV–vis spectrum of water; the particular excitation wavelengths λ_{exc} are marked with colored circles.

Another possible explanation was that a Raman resonance effect was observed. Such an effect in water has been intensively researched⁹ and its occurrence was expected for the excitation wavelengths of energy corresponding to the electronic transition in water at ca. 130 nm.^{7,8} Summarizing the current state of knowledge, the intensity of the OH stretching bands in water was measured for an excitation in the range $\lambda_{\text{exc}} = 200\text{--}550$ nm and deviations from the theoretical wavelength λ^{-4} dependence of the Raman scattering were noticed. The observed dependencies, λ^{-x} with $x = 4.5\text{--}5.5$,^{7–9} were consistent with the Raman resonance theory and indicated the presence of a Raman preresonance effect for excitation in the UV region. However, in all cited publications,^{7–9} the Raman spectra were acquired with the use of spectrofluorometers. The very low intensity of Raman signal (especially for longer excitation wavelengths) demanded the use of a wide bandpass leading to a low spectral resolution, and as a consequence the Raman OH stretching multimode band was considered to be single mode.

According to theory,¹⁰ the presence of Raman resonance in a material can be claimed if

- (1) there is an increase in signal intensity for a specific excitation wavelength λ_{exc} ;
- (2) the resonance excitation wavelength λ_{exc} is close to the wavelength of the electronic or vibronic absorption band of the substance;
- (3) there is a change in the depolarization ratio of the scattered light for the wavelength λ_{exc} .

In accordance with the first condition: changes in the intensity ratio of the 3200 and 3400 cm^{-1} bands were observed with changing λ_{exc} . However, because Raman spectroscopy is not a

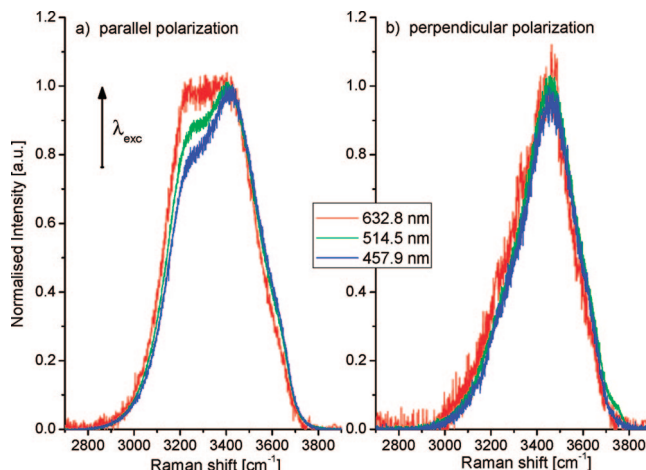


Figure 2. Polarized Raman spectra of water for (a) $x(y,y)z$ (parallel) and (b) $x(y,x)z$ (perpendicular) configurations, for excitation wavelengths $\lambda_{\text{exc}} = 457.9$, 514.5 and 632.8 nm.

quantitative method, it was unclear whether this effect was due to an increase in the intensity of the 3200 cm^{-1} band for excitation with red light or due to an increase in the intensity of the 3400 cm^{-1} band for excitation with blue light. The answer could be deduced by considering the second and third aspects of the Raman resonance. As shown in Figure 1b, both the 632.8 and 647.1 nm excitation lines were close to the absorption bands of water at 606 and 660 nm; contrarily, there were no absorption bands close to the 457.9, 476 or 488 nm excitation wavelengths. This suggests that it is the low frequency 3200 cm^{-1} band that is in resonance with excitation light from the red range (for which the absorption was ca. ten times stronger than for the blue light). To confirm this suggestion, the third condition from the above list was investigated by studying the changes of the depolarization ratio for various excitation wavelengths.

According to Placzek's theory,¹¹ the intensity of the scattered light into a solid angle $d\Omega$ is proportional to $\mathbf{e}_e \alpha_{xyz} \mathbf{e}_s$ where \mathbf{e}_e and \mathbf{e}_s are the unit vectors defining the directions of the electric fields of the exciting and scattered radiation respectively, and α_{xyz} is a polarizability tensor. The intensities for parallel (I_{\parallel}) and perpendicular (I_{\perp}) configurations can be expressed as follows:

$$I_{\parallel} = K(\bar{\alpha}^2 + \frac{4}{45}\gamma^2) \quad I_{\perp} = K(\frac{1}{9}\delta^2 + \frac{2}{30}\gamma^2) \quad (1)$$

where $\bar{\alpha}$ represents the isotropic part of the α_{xyz} tensor, δ and γ describe symmetric and antisymmetric components of its anisotropy, respectively, K is a constant proportional to ν^4 (where ν is the wavenumber of scattered light). In ordinary nonresonant Raman scattering, $\delta^2 = 0$ and the depolarization ratio ρ , defined as

$$\rho = \frac{I_{\perp}}{I_{\parallel}} = \frac{10\delta^2 + 6\gamma^2}{90\bar{\alpha}^2 + 8\gamma^2} \quad (2)$$

varies between 0 and $3/4$. Moreover, $\bar{\alpha}$ is equal to 0 for the asymmetric vibrations and ρ becomes $3/4$. In the case of the resonance Raman effect, $\delta^2 \neq 0$, leading to an anomalous polarization with respect to (2). It is important to notice that the strongly polarized modes are more susceptible to resonance than the depolarized ones.¹⁰

The polarized Raman measurements for water were performed in the $x(y,y)z$ (parallel) and $x(y,x)z$ (perpendicular) configurations for excitation wavelengths of 457.9, 514.5 and 632.8 nm. In Figure 2, one can see that although for the parallel polarization

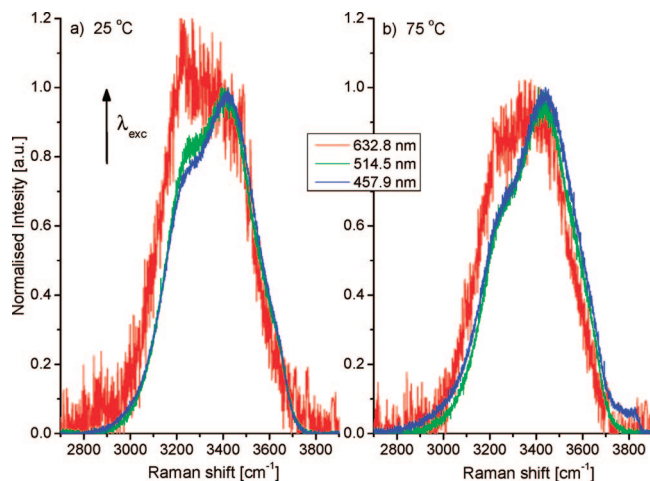


Figure 3. Raman spectra of water at (a) room temperature (25 °C) and (b) 75 °C, for excitation wavelengths $\lambda_{\text{exc}} = 457.9, 514.5$ and 632.8 nm.

(Figure 2a), the relative intensity of the band at 3200 cm^{-1} increases with increasing λ_{exc} , in the case of the perpendicular polarization (Figure 2b), the spectra reveal practically no dependence on λ_{exc} . These results confirmed that we observed indeed the resonance Raman effect in water, and that the low frequency, polarized OH stretching mode was enhanced by resonance with red light. This band is usually assigned to highly structured water where the water molecules are engaged in strong hydrogen bonds. The high frequency, depolarized band at 3400 cm^{-1} is related to water molecules interacting only weakly with neighboring molecules.^{1,12–14} These results are consistent with the conclusions of Woutersen and Bakker concerning the decay of rotational anisotropy for pure H_2O and for solutions of HDO in D_2O .¹⁵ Their studies showed that the rate of observed decay strongly increased with OH concentration (and consequently the average number of hydrogen bonds) in the solution and ran in a resonant way. This thesis is in compliance with our observations of the weakening of the resonance Raman effect with temperature (Figure 3) resulting from the breaking of hydrogen bonds. We suppose that OH oscillators of water molecules can reach the resonant state providing that they were strongly linked to each other via hydrogen bonds.

Moreover, it is apparent from the theoretical considerations¹⁶ that the frequencies of OH stretching vibrations are anharmonically modulated by intermonomer stretching vibrations Q_s and librations (predominantly). It means that OH stretching vibrations of strongly H-bonded water molecules are much more anharmonic than the OH vibrations of loosely bonded water. Consequently, the overtones of the OH stretching vibrations may exhibit much larger Raman cross-sections for strongly hydrogen bonded water than for loosely bonded ones. As the overtones and combination tones of the OH stretching vibrations absorb in the near-infrared and red part of the visible spectrum^{17,18} (for which we observed the resonance enhancement), it gives rise to the observed Raman resonance of strongly hydrogen bonded

water when the excitation wavelength is tuned to red. Hence, the reported herein presence of the resonance enhancement should be taken into account during Raman investigations of water structure, especially these based on the ratio of intensities of OH stretching modes. Possibly, this effect could also explain the discrepancy between the absolute Raman cross-section of water molecule determined by several authors.^{7,8}

Conclusions

The results presented herein constitute, to the best of our knowledge, the first report of the Raman resonance enhancement of water by visible light. It should therefore be taken into account in analyses of water structure and water interactions with other substances based on intensities of Raman OH stretching modes. We hope that further detailed investigations of resonance Raman effect in water and water solutions will bring a better comprehension of the composition of the OH stretching multimode band as well as the water structure itself.

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Supporting Information Available: Supporting Figure 1, Raman spectra of water performed for various laser power on a sample, for excitation wavelength $\lambda_{\text{exc}} = 514.5$ nm. Supporting Figure 2, Raman spectra of cyclohexane obtained for different excitation wavelengths λ_{exc} ; spectra were normalized to the intensity of band at 2940 cm^{-1} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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