Multi-frequency stimulated raman scattering in protium and deuterium water

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Abstract. Multi-frequency stimulated Raman scattering spectra were recorded with excitation of infrared (λ0=1064 nm) emission of picosecond solid state laser. The registration of spectra was with the fiber-optic technique by minispectrometer at wide frequency region.

1. Introduction

Water molecule consists of two hydrogen atoms and one oxygen atom, which are connected by a covalent bond [1–3]. The study of the properties and testing of light (protium) water quality is a prerequisite for a normal healthy existence. Of particular interest to the biosphere is heavy (deuterium) water (D2O), the presence of which in organisms leads to significant changes in metabolic processes, suppression of enzymatic reactions and cell growth [4]. The presence of deuterium water is established by analyzing the corresponding spontaneous Raman scattering spectra [5]. Earlier, the spectra of spontaneous Raman scattering (RS) in water were studied in [6–9]. In this case, the frequency range in the region of 2800–3500 cm−1 was mainly studied. In [10–13], combination bands were also found that correspond to cluster modes: translations and librations of protium water molecules. The stimulated Raman scattering (SRS) in light water was studied in [14]. In this case, the spectra in the region of the high-frequency fully symmetric mode with a frequency of ≈3300 cm−1 were analyzed. The absorption spectra in heavy water were studied in [15] in the frequency range 4000–8000 cm−1. In this case, the bands corresponding to the overtone transitions of the D2O molecule were detected. In [16], SRS in D2O was excited by nanosecond laser pulses of the second optical harmonic of a YAG: Nd3+ laser. The excitation of SRS in deuterium water by picosecond laser pulses was considered in [17]. In this case, the duration of the pulses of exciting radiation was 5–6 ps. Due to the short duration of such pulses and the self-focusing of radiation, the observed spectrum of the stimulated Raman scattering had the form of a continuum with a weakly pronounced peak of intensity at the frequency of the fully symmetric stretching vibration.

In this work, we present the results of multi-frequency SRS investigations in light and heavy water at wide spectral region. SRS in light and heavy water was observed when excited by infrared (λ0=1064 nm) YAG: Nd3+ laser pulses with a duration of 60 ps, i.e. an order of magnitude longer than the duration of the pulses used in [18]. This ensured the absence of the continualization of the observed spectra.
2. Experimental procedure
For the excitation of SRS in water we have used the powerful YAG: Nd$^{3+}$ laser, generating ultrashort (60 ps) pulses with a wavelength $\lambda_0=1064$ nm with a repetition rate of 100 Hz at an average power of 10–100 mW in every pulse-periodic mode. The schematic diagram for the study of SRS in protium and deuterium water is shown in figure 1.

![Schematic diagram for the study of SRS in protium and deuterium water](image)

**Figure 1.** Experimental scheme of setup for registration of SRS spectra in water: 1—laser radiation source, 2—rotating dielectric mirror, 3—lenses, 4—mini-spectrometers, 5—computers, 6—cell with water, 7—nonlinear optical plate, 8—light guide.

The registration of the SRS was carried out for scattering geometries “forward” and “backward” by fiber-optic mini-spectrometers (4) providing the ability to analyze the spectra in a wide spectral range: 200–1000 nm.

3. Results and discussion
Figure 2 shows the recorded spectra of multi-frequency stimulated Raman scattering in light water obtained by laser excitation of the infrared range ($\lambda_0=1064$ nm). It is known [13] that the water Raman spectrum contains bands corresponding to three fundamental types of vibrations of the H$_2$O molecule: $A_1$ type, $\nu_1=3345$ cm$^{-1}$ (stretching full symmetric vibration), $A_1$ type, $\nu_2=1645$ cm$^{-1}$ (deformation fully symmetric vibration) and $B_1$ type, $\nu_3=3600$ cm$^{-1}$ (stretching non-symmetry vibration). As can be seen from figure 2, several anti-Stokes satellites are found in the spectrum of multi-frequency SRS, corresponding to the fully symmetric valence vibration $\nu_1(A_1)$. Its frequency (3024 cm$^{-1}$) is somewhat lower than the frequency of the corresponding RS mode ($\nu_1=3345$ cm$^{-1}$). The highest intensity in the spectrum of the SRS corresponds to the second anti-Stokes satellite. The third and fourth anti-Stokes satellites are characterized by a large width and consist of several components. We also note that the frequency shift of the fourth anti-Stokes satellite (11530–11939 cm$^{-1}$) is higher than the frequency of the exciting radiation (9398.5 cm$^{-1}$). This can be explained as a consequence of the cascade processes of SRS, in which the role of exciting radiation is assumed by one of the SRS anti-Stokes satellites.
Figure 2. Multi-frequency SRS spectrum in light water.

Figure 3 shows the SRS in heavy water. In this case, there are five anti-Stokes satellites, with the first satellites having a small width. The first anti-Stokes satellite is the narrowest, the following anti-Stokes satellites gradually broaden and pass into a continuous background (continuum). In this case, as in the case of light water, the frequency of stimulated Raman scattering is less than the frequency of the corresponding spontaneous Raman scattering. In addition, from figure 3 it is seen that the fifth satellite has a frequency shift exceeding twice the value of the exciting line. Thus, in this case too, cascade processes play a certain role.

Multi-frequency SRS occurs as a result of the decay of two quanta of exciting radiation into the corresponding Stokes and anti-Stokes components. So, the laws of conservation of energy and quasimomentum at the case light water are:

\[ 2 \omega_L = \omega_{ls} + \omega_{lA} ; 2k_L = k_{ls} + k_{lA} ; \]
\[ 2 \omega_L = \omega_{2S} + \omega_{2A} ; 2k_L = k_{2S} + k_{2A} ; \]
\[ 2 \omega_L = \omega_{3S} + \omega_{3A} ; 2k_L = k_{3S} + k_{3A} . \]  \hspace{1cm} (1)

Accordingly, for heavy water instead of (1) we have:

\[ 2 \omega_L = \omega_{ls} + \omega_{lA} ; 2k_L = k_{ls} + k_{lA} ; \]
\[ 2 \omega_L = \omega_{2S} + \omega_{2A} ; 2k_L = k_{2S} + k_{2A} ; \]
\[ 2 \omega_L = \omega_{3S} + \omega_{3A} ; 2k_L = k_{3S} + k_{3A} ; \]
\[ 2 \omega_L = \omega_{4S} + \omega_{4A} ; 2k_L = k_{4S} + k_{4A} . \]  \hspace{1cm} (2)
4. Conclusion
Thus, the spectrum of multi-frequency SRS of water with a sufficiently high intensity of exciting laser radiation contains several satellites corresponding to various types of oscillations, as well as four-photon parametric processes. Excitation of SRS by infrared radiation ($\lambda_0=1064$ nm) leads to the emergence of a frequency comb, extending from the far infrared range to the blue spectral region.

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References
[1] Voloshin V P, Zheligovskaya E A, Malenkov G G, Naberukhin Yu I and Tytik D L 2001 Russian Chemical Journal 45 31
[2] Mosin O V, Ignatov I 2013 Internet journal "Naukovedenie" 3 1
[3] Frenkel Ya I 1975 Kinetic Theory of Liquids (Leningrad: The science) p 592
[4] Mosin O V and Ignatov I 2013 Water and water treatment technologies 2 12
[5] Deulin B I 2008 News of Volgograd State Technical University 9 3
[6] Brysev A, Bunkin A, Klopotov R, Krutyanski L, Nurmatov A and Perchin S 2002 Optics and Spectroscopy 93 282
[7] Perchin S 2004 Optics and Spectroscopy 96 811
[8] Burikov S, Dolenko T and Fadeev V 2008 Research Letters in Optics 2008 4
[9] Hafizi B, Palastro J P, Penano J R, Gordon D F, Jones T G, Helle M H and Kaganovich D 2015 Optics Letters 40 1556
[10] Rahn O, Mauer M and Kaiser W 1969 Opt. Commun 1 109
[11] Gorelik V S 1999 Journ. of Russian Laser Research 20 152
[12] Gorelik V S, Kudryavtseva A D, Orlovich V A, Tcherniega N V, Vodchits A I and Voinov Yu P 2012 Nonlinear Phenomena in Complex Systems 15 360
[13] Gorelik V S and Sverbil P P 2004 Optical Spectroscopy and frequency standards, ed E A Vinogradov and L N Sinitza (Tomsk: Publishing House of the Institute of Atmospheric Optics SB RAS) pp 85-100
[14] Vodchits A I, Voinov Yu P, Gorelik V S, Kudryavtseva A D, Orlovich V A and Tcherniega N V 2013 Bulletin of the Lebedev Physics Institute 40 329
[15] Workman Jr J and Weyer L 2013 *Practical Guide And Spectral Atlas For Interpretive Near-Infrared Spectroscopy* (London: Taylor and Francis Group) p 320
[16] Li Z, Li Z, Zhou M, Wang Y, Men Z and Sun C 2012 *Optics Letters* **37** 1319
[17] Penzkofer A, Beidoun A and Lehmeir H J 1993 *Optical and Quantum Electronics* **25** 317
[18] Zatsepina G N 1974 *Properties And Structure Of Water* (Moscow: Moscow State University Press) p 168