Lowering of stimulated Raman scattering threshold as a result of light capture

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Abstract. Stimulated Raman Scattering in globular photonic crystals and globular photonic glasses at different diameters of globules (250 - 400 nm) with embedded molecular liquids is studied under excitation by nanosecond or picoseconds laser pulses. Substantial decrease of Stimulated Raman Scattering threshold was observed. Such phenomenon was explained as the result of laser radiation field increase in globular photonic structures due to photonic density of states enhancement near the edges of photonic stop bands of photonic crystals and due to Mie resonance or whispering gallery modes effect revealing in photonic glasses. Stimulated Raman Scattering threshold lowering as a result of light capture in globular photonic crystals and photonic glasses opens the way to new efficient laser sources created on the base of composite globular photonic structures. Experimental data on spectra of Stimulated Raman Scattering in light and heavy waters are presented. As sources of exciting light the powerful ultra short solid state laser pulses with 532.0 nm wavelength and giant pulses of Ruby laser (694.3 nm) have been used. Several Stokes and anti-Stokes satellites were observed. Libration modes have been excited and resulted in some additional Raman bands at low frequency region and also as combining tones.

1. Introduction and background

Spontaneous Raman Scattering (RS) effect is widely used for obtaining of information on vibration spectra of solids and liquids [1-3]. However RS spectra are difficult for registration because of very small cross-section (10^{-28} cm^2) and accordingly very small value of intensity in comparison with exciting emission one (10^{-6} -10^{-8}) . Stimulated Raman Scattering (SRS) effect has been observed for a number of liquids and solids. In this case the scattering intensity is comparable with exciting emission one. However, as a rule, SRS threshold is high enough (10-100 GW/cm^2) and is close to destruction threshold of condensed media. So there is a problem of searching the ways of SRS threshold lowering. Before [4-6] there were made predictions of lasing- threshold lowering in strongly scattering condensed disordered systems (powders or composites).

New possibilities in SRS investigations have been opened in connection with composite technologies development [7-9]. Very promising materials for SRS threshold lowering are highly scattering composite media. The examples of such type media are artificial opals, consisting from SiO_2 – globules, packed into cubic face centered lattice. Crystalline lattice constant of artificial opal is close to visible radiation wavelength (300-600 nm). If the globules with the same diameter are disordered in the space, so called photonic glass is formed. Between the globules in initial globular photonic

structures there is free space; so this space may be filled by some Raman active substances. Modern technology permits also to construct spherical photonic structures from amorphous SiO_2 – units with diameters of micro- or millimeter scales. Thus globular photonic structures with Raman active embedding substances between globules are perspective objects for SRS threshold lowering. Other examples of globular photonic structures are spherical particles of micrometer scale, consisting from thin amorphous quartz spherical walls with air inside. It is interesting also to use the ordered in space amorphous quartz balls of millimeter size for realizing strongly light scattering structures. In this work we report the results of experimental investigations of SRS in some homogeneous liquids, including light (H_2O) and heavy (D_2O) waters, and embedded into pores of photonic structures liquid media.

2. Experimental technique

SRS was excited whether by giant (10 ns) pulses of Ruby laser or by ultra short (60 ps) pulses of the second harmonic radiation of Nd:YAG laser. Experimental scheme for SRS spectra recording under ultra short laser pulses excitation is presented at figure 1a. In this case exciting emission corresponded to the second harmonic (532.0 nm) radiation of Nd:YAG laser (1064.0 nm).

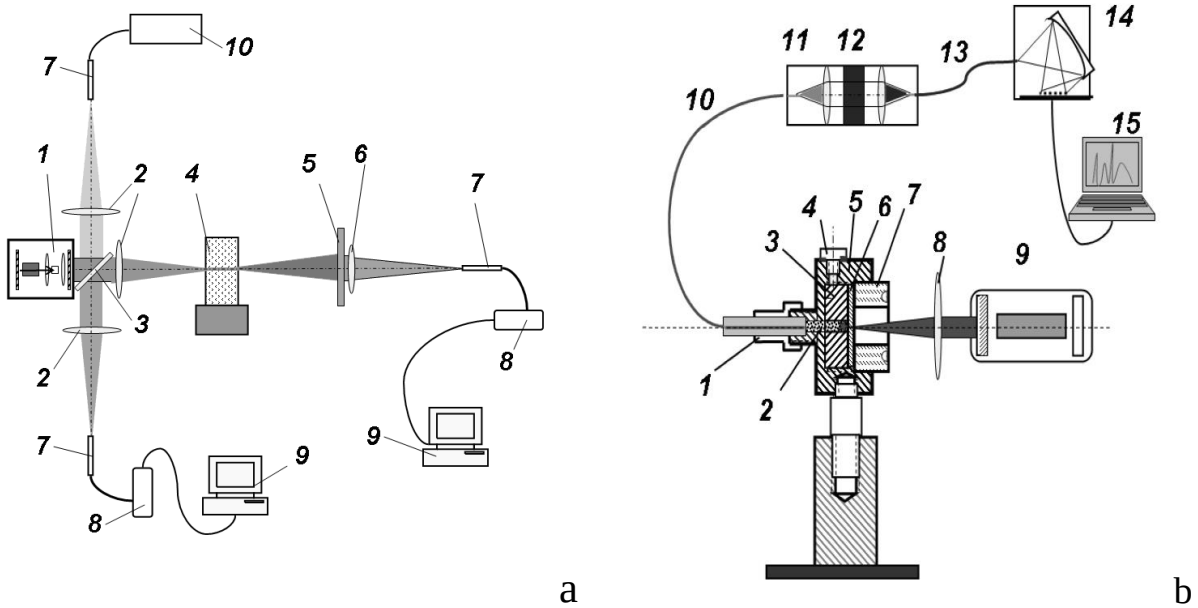

Figure 1. Experimental setup for SRS spectra , excited by powerful laser pulses (a) with the help of ultra short pulses: 1-laser, 2,6-lens, 3-qurtz plate, 4-sample, 5-filter, 7-fiber, 8- minispectrograph, 9-computer, 10 - detector; b- with the help of giant laser pulses: 1-fiber holder, 2-photonic crystal (glass), 3,6-plates, 4,7-covering cylinders, 5-cuvette, 8-lens, 9-Ruby laser, 10,13-fibers,11- -filter, 14-minispectrograph, 15-computer.

The exciting laser (1) emission was focused into cuvette with investigated liquid or to photonic structure (crystals or glasses), pores of which were filled with investigated liquid. Experimental setup permitted us to register the Raman scattered light spectrum in the forward and backward directions with the help of minispectrograph 8 and computer 9. Detector 10 allows to measure the laser intensity. The similar scheme has been used for the case of giant pulses of Ruby laser (694.3 nm) SRS excitation (see figure 1b). We have used picoseconds YAG:Nd^{3+} laser with the following parameters: energy was in the range 0.1 - 35 mJ at 532 nm wavelength, pulse duration - 60 ps, pulse repetition rate - 20 Hz. Laser beam was focused into the quartz cell with water with the help of large focus lens (200 mm). After suppression of exciting emission by prism, diffraction lattice or absorbing filter, the secondary emission from water sample was directed to the fiber tip. SRS spectra were registered by FSD-8 minispectrograph, having CCD-detector with 200 – 1000 nm spectral range.

3. Experimental results and discussion

Figure 2 illustrates SRS-spectra for nitrobenzene filled photonic crystal, excited by giant single pulses of red (694.3 nm) emission of Ruby laser. We have seen two Stokes components at 766 and 854 nm correspondingly. The diameters of quartz globules of artificial opal in this case were 310 nm. So the spectral positions of exciting line (694.3 nm) and the first Raman satellites (766 nm) were close to the edges of the first photonic stop-band positions. At shorter wavelengths (see figure 2) there was a number of satellites, which we attribute to Two-Photon Excited Photoluminescence. We have established that the threshold of SRS-processes in nitrobenzene filled photonic crystal was essentially lower than in pure nitrobenzene as a result of light capture.

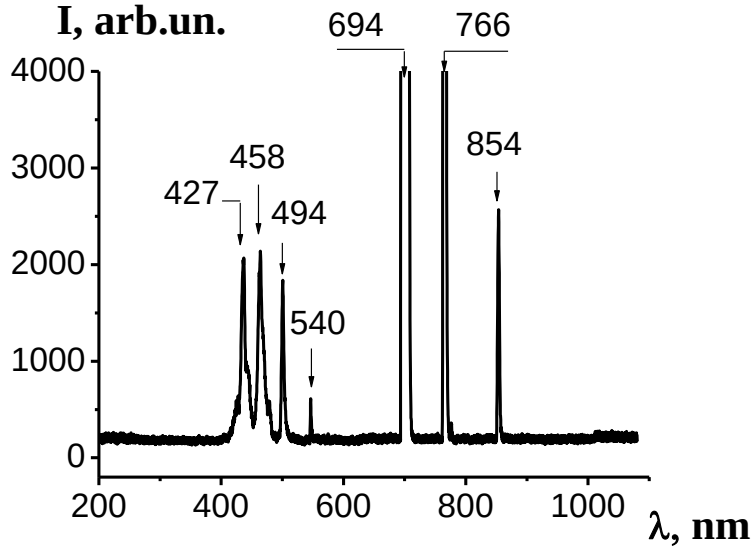

Figure 2. SRS spectra of nitrobenzene-filled photonic crystal, excited by giant pulses of Ruby laser.

Figure 3 illustrates SRS-spectra of light water filled artificial opal, excited by second harmonic (532.0 nm) of picoseconds YAG: Nd^{3+} - laser. At figure 3a we can see exciting line (532.0 nm) and the first Stokes component of water at 650 nm (3339 cm^{-1}). In this case the diameter of quartz globules of artificial opal was 260 nm. Accordingly we have a proximity of laser line spectral position (532.0 nm) and the first Stokes position(650.0 nm) to the edges of corresponding stop- band of photonic crystal. The SRS emission of light water or ethanol, excited by powerful picoseconds pulses, was well seen as red emission with naked eye. In this case SRS beams propagated in forward and backward directions. SRS spectrum of light water consists of Stokes (see figure 3) and anti-Stokes satellites.

Some shoulder appeared near anti-Stokes fundamental $\nu_1(A_1)$=3424 cm^{-1} mode spectral position. At small exciting energy (~1mJ), before threshold achieving, the observed Stokes SRS spectrum had the shape of wide band with several peaks, corresponding to fundamental $\nu_1(A_1)$ mode (figure 3c). After increasing of the exciting energy (to 10mJ) Raman intensity of this band increased and its width essentially decreased (figure 3d). With increasing of exciting emission power, spectral position of SRS peak intensity shifted from 3186 up to 3424 cm^{-1}. At backward scattering geometry, at low frequency region there were two wide additional satellites (Stokes and anti Stokes) at 780 cm^{-1}, attributed to librational mode $\nu_{Lib.}$. Weak maximum at 1650 cm^{-1} corresponds to $\nu_2(A_1)$ fundamental mode.

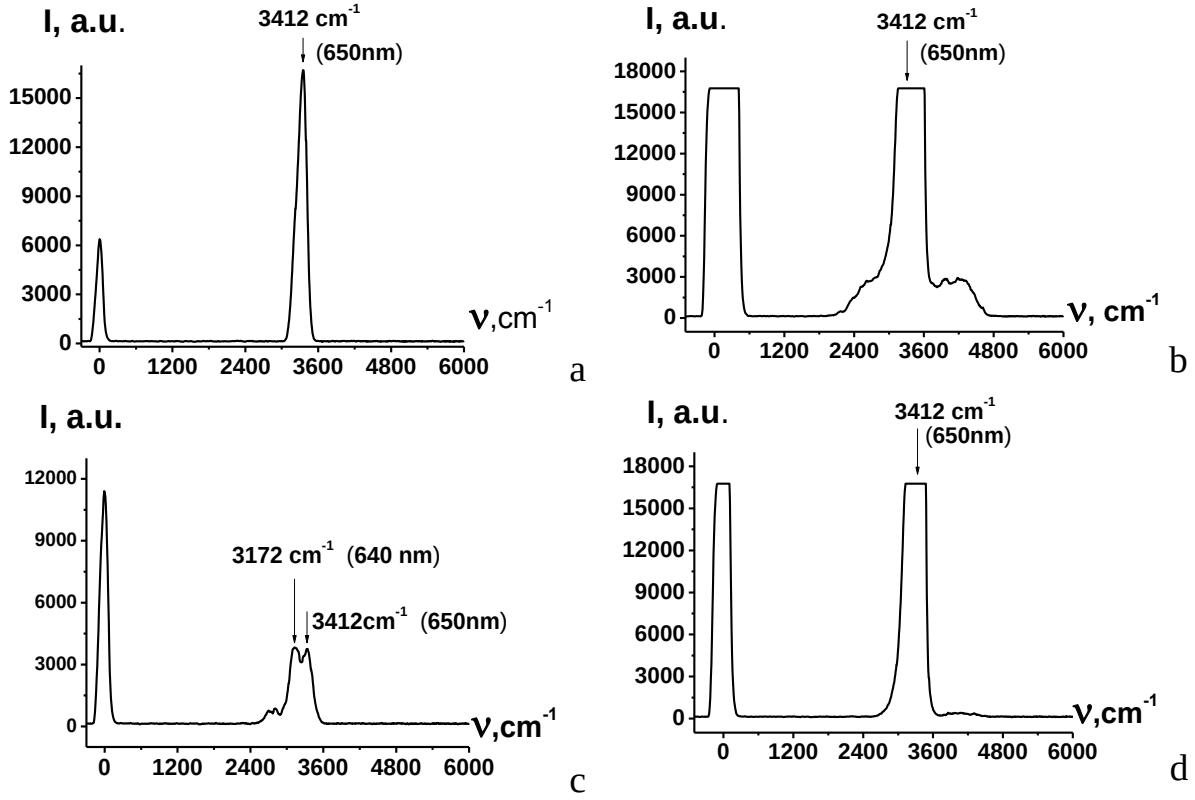

Figure 3. The shape of forward SRS spectra recorded near the surface of artificial opal filled by water at lower (a) and higher (b) values of exciting laser power and in pure water (c, d), correspondingly.

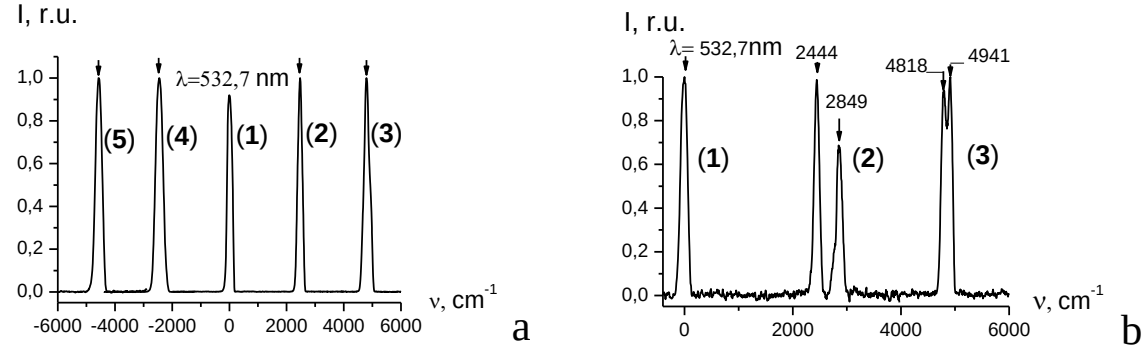

Figure 4. The shape of the normalized heavy water SRS-spectrum under picosecond excitation; a- Stokes(2,3) and antiStokes(4,5) satellites;(1)-exciting line; b- the shape of the first and second Stokes bands at higher power of exciting radiation.

Figure 4 illustrates registered SRS spectra of heavy water under picoseconds excitation for backward scattering geometry. In SRS spectrum of heavy water the most intensive line with frequency $\nu_1(A_1)$=2448 cm^{-1} has been observed. We can see in figure 4a two Stokes and two anti-Stokes satellites. The shape of the first and second Stokes bands under higher intensity of exciting emission is illustrated in figure 4b. We can conclude, there at the first Stokes region there are two distinct lines, one of which corresponds to $\nu_1(A_1)$ fundamental mode and another – to combinational states: $\nu_1(A_1)$ $+\nu_{Lib}$ of heavy water. Accordingly some additional structure was at the second Stokes band (see figure 4b).

4. Conclusions

As it was predicted by theory [10-12], the spontaneous Raman scattering cross sections in liquids filled photonic crystals should depend on the photonic stop-band spectral position due to the sharp increase of photonic density of states near the edge of photonic stop-band. Therefore, SRS threshold in liquids filled artificial opals should decrease as a result of light capture when the wavelengths of the exciting light and the Stokes component value were near the photonic stop- band edges. Accordingly, for a diameter of globules D=260 nm, the spectral position of water infiltrated photonic crystal stop-band corresponds to the value of λ_{max} = 607.0 nm. The spectral width of the corresponding stop-band is about 70 nm. Taking into account that in this case the spectral position of the first Stokes component corresponds to 650 nm and exciting line – to 532 nm, we have the conditions of the first Stokes threshold lowering. Such theoretical prediction is in agreement with obtained experimental results. Similar effect was observed for nitrobenzene and ethanol filled opal matrices with corresponding globules diameters.

We have also shown SRS threshold lowering as a result of light capture in liquid filled photonic glasses, constructed from spherical globules with diameters of micro- or millimeter scales size. In this case SRS threshold lowering may result from resonance Mie [13] or whispering gallery modes.

Thus we have concluded that SRS threshold of liquids embedded into photonic structures may be essentially lowered with comparison to pure liquids.

Acknowledgments

This work was supported by RFBR (grants 12-02-00491, 13-02-00449, 13-02-90420, 14-02-00190, 14-02-90406, 14-02-90007).

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