Multifrequency parametric processes in dielectric media

A V Skrabatun¹,², V S Gorelik¹,²,⁵, A Yu Pyatyshev³,⁴, A I Vodchits⁴, V A Orlovich⁴ and P A Apanasevich⁴

¹ P.N. Lebedev Physical Institute of Russian Academy of Sciences, Leninskii Pr. 53, Moscow, 119991, Russia
² Bauman Moscow State Technical University, 2-nd Baumanskaya str. 5, Moscow, 105005, Russia
³ JSC Shokin Istok Research and Production Corporation, Vokzalnaya str. 2a, Fryazino, Moscow region, 141190, Russia
⁴ B.I. Stepanov Institute of Physics of the National Academy of Sciences of Belarus, Nezavisimosti Ave. 68, Minsk, 220072, Belarus
⁵ E-mail: gorelik@sci.lebedev.ru

Abstract. Multiple Stokes and anti-Stokes satellites were observed in the spectra of stimulated parametric Raman scattering of light in liquids and crystals when excited by picosecond laser pulses of a YAG: Nd³⁺ solid-state laser with generation wavelengths of 1064 and 532 nm. The Stokes combination satellites of the infrared range were detected as a result of their conversion into the visible spectral region. The results obtained are of interest for the development of the theory of parametric processes of stimulated Raman scattering of light in crystals and liquids, which is also important for creating efficient laser sources from the ultraviolet to the far infrared.

1. Introduction

After the appearance of intense laser light sources, the phenomenon of stimulated Raman scattering (SRS) of light in various dielectric media was discovered [1,2]. In this case, in contrast to spontaneous Raman scattering (RS), a sharp increase in the intensity of one of the strongest spontaneous Stokes RS lines is observed in the spectrum of scattered radiation. With a further increase in the spectral intensity of the exciting radiation in molecular dielectric media and crystals, several Stokes and anti-Stokes components appear, whose intensity is close to the intensity of the exciting radiation [2–4]. In this case, forced parametric combinational processes take place, during which the simultaneous destruction of two quanta of exciting radiation and the simultaneous birth of pairs of Stokes and anti-Stokes components [5–7], i.e. the regime of stimulated parametric Raman scattering (SPRS) is realized. At the first stage of research in liquids and crystals, giant pulses of ruby or yttrium aluminum garnet lasers with a duration of about 10 ns and with sufficiently high energy in each pulse (0.1–1 J) were used to excite SRS. When such radiation was focused on a dielectric medium, destruction processes took place in the sample, which limited the possibilities of observing SRS in many media. Multi-frequency scattering processes were observed in many liquids [8,9] and crystals [10–12] under conditions of resonant or stimulated Raman processes of light.

2. Experimental technique
In this paper, we present the results of investigations of the SPRS in various condensed dielectric media excited by ultrashort (60–80 ps) YAG: Nd³⁺ laser pulses. The second optical harmonic of a YAG: Nd³⁺ laser with an emission wavelength \( \lambda = 532 \text{ nm} \) (see figure 1) and the main generation line of this laser with a wavelength \( \lambda = 1064 \text{ nm} \) (see figure 2) turned out to be very effective for the excitation of the Raman spectra. In figure 2(b) shows a diagram for the observation of the SPRS, in which the conversion of Stokes infrared modes into the visible spectral region is performed. The laser used provided the generation in a pulse-periodic mode of ultrashort pulses with a repetition frequency of 10 Hz with an average power of 10–100 mW and an energy in each pulse of 1–20 mJ. Rapid registration of the spectra of the SPRS was carried out with a compact fiber-optic spectrometer of the FSD-8 type with a multi-element receiver providing digital processing of the spectra in the range of 200–1100 nm with a resolution of 1 nm.

**Figure 1.** Schematic diagram of an experimental setup for recording the SPRS spectra in condensed media when the second optical harmonic of a YAG: Nd³⁺ laser is excited (\( \lambda = 532 \text{ nm} \)); 1 — laser mirrors; 2 — active element; 3 — nonlinear optical crystal; 4, 11 — lenses; 5 — rotary dielectric mirror; 6 — photonic crystal based on anodic alumina; 7 — mini spectrometer; 8 — computer; 9 — single crystal under study; 10 — laser radiation and SPRS.

**Figure 2.** Schematic diagrams of experiments for the excitation of SPRS in crystals with the main generation line (\( \lambda = 1064 \text{ nm} \)) of a YAG: Nd³⁺ laser (a) and with conversion of Stokes radiation into the visible region of the spectrum (b); 1 — laser radiation source; 2 — rotary dielectric mirror; 3 — lenses, 4 — spectrometer, 5 — computer; 6 — sample; 7 — light guide; 8 — frequency doubler.
3. Experimental results and discussion

As objects, liquids (light and heavy water, ethanol, glycerin) and single crystals (barium nitrate, calcite, sodium bromate, KGW) and crystalline powders (LiOH, LiOD) were investigated. Equidistant frequency combs were detected in the form of a large number (2–8) of Stokes and anti-Stokes components, extending from the far infrared region to the ultraviolet range (see figure 3). In accordance with the synchronization conditions for the elementary processes of the four-particle SPRS, the energy conservation laws of the quasimomentum must be satisfied. In the simplest case of the decay of two quanta of exciting radiation into the corresponding Stokes and anti-Stokes components, such laws have the form:

\[ \begin{align*}
2\omega_L &= \omega_{1S} + \omega_{A1}; 2k_L = k_{1S} + k_{A1}; \\
2\omega_S &= \omega_{2S} + \omega_{A2}; 2k_S = k_{2S} + k_{A2}; \\
2\omega_A &= \omega_{3S} + \omega_{A3}; 2k_A = k_{3S} + k_{A3}; \\
2\omega_L &= \omega_{4S} + \omega_{A4}; 2k_L = k_{4S} + k_{A4}. 
\end{align*} \]

Other SPRS processes are also possible, in which, at the first stage, two photons of Stokes or anti-Stokes satellites break up into corresponding quanta of scattered radiation. In particular, there may occur processes for which the conditions of synchronism take the form:

\[ \begin{align*}
2\omega_{1S} &= \omega_{2S} + \omega_L; 2k_{1S} = k_{2S} + k_L; \\
2\omega_{2S} &= \omega_{3S} + \omega_A; 2k_{2S} = k_{3S} + k_A; \\
2\omega_{3S} &= \omega_{4S} + \omega_{A2}; 2k_{3S} = k_{4S} + k_{A2}; \\
2\omega_{1A} &= \omega_{2A} + \omega_L; 2k_{1A} = k_{2A} + k_L; \\
2\omega_{2A} &= \omega_{3A} + \omega_A; 2k_{2A} = k_{3A} + k_A; \\
2\omega_{3A} &= \omega_{4A} + \omega_{A4}; 2k_{3A} = k_{4A} + k_{A4}. 
\end{align*} \]
Figure 3. Normalized spectra of SPRS in ethanol (a,b), calcite (c,d), excited by the second optical harmonic of a YAG:Nd<sup>3+</sup> laser with an emission wavelength of \( \lambda = 532 \) nm, and a barium nitrate crystal (e,f) during the excitation of secondary radiation YAG:Nd<sup>3+</sup> laser line with a wavelength \( \lambda = 1064 \) nm. The SPRS in ethanol was recorded with the geometry of the experiment «on the light» (a) and «on reflection» (b).

The SPRS was generated in ethanol by pumping radiation from a second-harmonic cell of a YAG:Nd<sup>3+</sup> laser (see figure 3(a,b)). With the geometry of the experiment «on the light», one anti-Stokes and two Stokes lines were recorded with an average frequency shift \( \Delta \nu = 2923 \) cm\(^{-1}\). From figure 3(a), it can be seen that the half width of the blue anti-Stokes mode is much larger than that of the first and second Stokes lines. The registration of the SPRS spectrum with the reflection geometry (see figure 3(b)) leads to a change in the number and shape of the observed lines. The first Stokes line in figure 3(b) has more half width than in figure 3(a) as a result of the formation of a two-component band with frequencies of 2836 and 2921 cm\(^{-1}\) instead of one narrow line at a frequency of 2947 cm\(^{-1}\) (see figure 3(a)). On both sides of the high-intensity first and second Stokes components, wings of low intensity were detected (see figure 3 (b)).

Excitation of a single crystal of calcite by laser radiation with a wavelength of \( \lambda = 532 \) nm leads to the generation of SPRS with the formation of four Stokes and three anti-Stokes Raman satellites in the visible and near-infrared ranges (see figure 3 (c,d)). Taking into account the measurement error, all the observed lines belong to the full-dimensional oscillation \( A_{1g} \) with a frequency shift \( \Delta \nu = 1086 \) cm\(^{-1}\).

When a SPRS was excited in a Ba(NO<sub>3</sub>)<sub>2</sub> crystal by a picosecond repetitively pulsed YAG:Nd<sup>3+</sup> laser with a pump wavelength of \( \lambda = 1064 \) nm, a large number of combinational satellites were recorded (see figure 3(e,f)) located in a wide spectral range, in the near IR and visible regions of the spectrum. According to figure 3(e,f) with a pulse-periodic picosecond pumping of YAG:Nd<sup>3+</sup> by a barium nitrate
crystal laser, in the spectrum of multifrequency parametric SRS, eight anti-Stokes components are shifted relative to each other by Δν = 1047 cm⁻¹ (taking into account the measurement error of ± 50 cm⁻¹). Such a frequency shift corresponds to fully symmetric internal vibrations of nitrate ions [NO₃]. In multifrequency parametric SRS processes, it is expected that each anti-Stokes component (see figure 3(e,f)) corresponds to a Stokes satellite in the infrared region of the spectrum.

**Figure 4.** The spectra of the SPRS in barium nitrate (a) and glycerol (b), excited by the main YAG:Nd³⁺ laser line with an emission wavelength of λ = 1064 nm with conversion of infrared Stokes modes to the visible region of the spectrum.

Figure 4 shows the SPRS spectra of barium nitrate and glycerol obtained during the experiment on a device with a frequency doubler of scattered radiation (see figure 2(b)). The spectrum of SPRS of barium nitrate in figure 4(a) consists of four anti-Stokes lines, obtained as a result of the sample being excited by a laser source, and combination components, which appeared as a result of the passage of secondary radiation through a crystal—a frequency doubler. As a result, modes were detected corresponding to twice the frequencies of the first (ν = -7250 cm⁻¹) and the second (ν = -5170 cm⁻¹) Stokes, which are in the infrared region. As a result of the scattered radiation passing through the frequency doubler, additional combination satellites are formed, corresponding to the combination of exciting radiation with the first Stokes line (ν = -8282 cm⁻¹) and the sum of the frequencies of the first and second Stokes (ν = -6208 cm⁻¹) components of the spectrum. In figure 4(b) shows the spectrum of the SPRS of glycerol
with the conversion of the first Stokes ($\nu = -6448 \text{ cm}^{-1}$) component to the red region of the visible range. Thus, the registered SPRS satellites from the IR range, which are not registered by our spectrometer.

4. Conclusion

The excitation of a large number of Stokes and anti-Stokes components (see figure 3) when pumping single crystals and liquids with laser radiation in the visible and near infrared ranges provides the possibility of obtaining lasing frequency bands in a wide spectrum: from far infrared to ultraviolet. Biphoton radiation can be used as a source of exciting radiation to generate a second optical harmonic, hyper-combination scattering. The results obtained are of interest for the development of the theory of parametric SRS processes in crystals under conditions of strong photon-phonon interaction, and are also of practical importance for creating efficient laser sources in different spectral ranges.

Acknowledgments

This work was supported by the RFBR (grants №18–02–00181, 18–32–00259).

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