

The patterns of the SRS-RL phenomenon and their usage in Raman spectroscopy application

Vasil P. Yashchuk, A.P. Smaliuk

Phys. Dep., Kyiv T. Shevchenko National University, Kyiv, Ukraine



Introduction

In a random matrix multiple elastic scattering of light promotes random lasing (RL) of embedded dye under high laser pumping. When RL spectrum (usually continuous) overlaps with Stokes spectrum of the embedded dye, the RL radiation at the Stokes frequencies $\nu_{s(RL)}$ together with laser pumping ν_p forms a set of bichromatic pumps which frequency differences resonate with the corresponding molecular vibrations ν_0 and inducing them (fig.1). The pumping radiation is scattered on this stimulated (and coherence) vibrations and produces resonant stimulated Raman scattering (SRS) at the same Stokes frequencies. This situation is similar to active Raman spectroscopy in Stokes region but with internal arising one component (RL) of the bichromatic pumping.

Raman amplification operating at these frequencies, enhances the corresponding spectral lines, and all of them become visible in the RL spectrum. It resulting in quasi-line SRS-RL spectrum with **continuous RL** and **linear SRS** components [1,2].

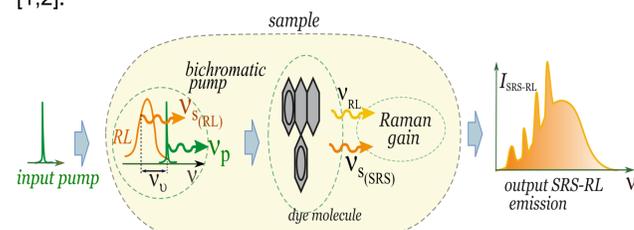


Fig1. Scheme of SRS-RL arising in a random medium.

Usually, the observation of scattered radiation by this method in the Stokes region is impossible due to the interfering luminescence, what forces such measurements to be carried out in the anti-Stokes region (CARS-technique). In the SRS-RL phenomenon, on the contrary, luminescence (through RL) contributes to the appearance and enhancement of Stokes lines. This feature is very important for Raman spectroscopy application for dyes and it encourages to study the patterns and conditions of the best occurrence of this phenomenon.

Samples & Methods

Investigations of SRS-RL phenomena was held with vesicular polymeric films of about 15 mkm thickness deposited on lavsan film. Effective light scattering, needed for RL arising, is provided by internal reflection at surface of close packed micron gaseous vesicles of about 1 micron diameter. Very small transport mean free path (about 3 mkm) may be served as verification of the high efficiency of multiple scattering of light in these films. Scattering efficiency was managed by UV exposition under films fabrication [3]. The investigated samples were colored with effective laser dyes rhodamines 6G, 575, 101, B and pyrromethene 597.

The radiation spectra of the samples were single-shot registered with diffraction spectrograph of 0.2 nm resolution in backward geometry at low and room temperatures. The samples were optically pumped by the second harmonic of Q-switched YAG:Nd³⁺ laser ($\lambda=532\text{nm}$, $\tau=15\text{ ns}$) with pump intensity 0.05 - 0.5 MW/mm².

Results

One of the most necessary condition for SRS-RL is availability of effective random lasing what demands usage random media with effective scattering and sufficient intensity of pumping radiation. Experimental data on fig.2. for rhodamine 575 demonstrate that increase number of vesicles by 1.5 times multifold enhances Raman lines. In addition "red" spreading of the RL spectrum covers a wider spectral range what contributes to the appearance of more Raman lines. Twofold increase of the pumping radiation intensity above 0.29 MW/mm² produces the same result. This is mainly due to the improvement of RL operating and its parameters because SRS intensity is proportional not only to the pumping but also RL intensity [2].

The fundamental necessity of RL is confirmed by the absence of SRS in the vesicular film with the dyes, which have all other necessary parameters, but does not exhibit RL at the same (532 nm) pumping (rhodamine 101).

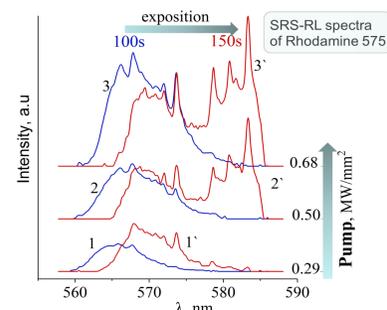


Fig2. Dependence of rhodamine 575 SRS-RL spectrum on vesicles number (proportional to UV exposition under film fabrication) and pumping intensity.

The second important condition is the usage of high dye concentration more than an order of magnitude higher than in conventional dye lasers. The manifestation of SRS starts from the 1 mmol/l. Increase of dye concentration five times above this value leads to RL spectrum expansion and an increase in number of observed Raman lines (fig.3, top). It occurs due to two factors: an increase of luminescence reabsorption which leads to spectral expansion and gain increase conditioned both Raman scattering and stimulated emission which leads to growth intensity of RL intensity and SRS lines.

The third, most important condition is overlapping RL spectrum with the spectrum of Stokes lines (fig.3, top & bottom). One can see that only those Stokes lines reveals itself in SRS which are covered by expanding RL spectrum. It is confirmed by the absence of SRS lines in those dyes which RL spectrum does not overlap with Stokes Raman region (rhodamine B) [3].

To find the location of Stokes lines region one can use the IR absorption spectrum of dye if one use IR frequencies to computation the possible Stokes ones. The spectrum constructed in this way may be conditionally named "pseudo-Stokes" [3]. Because of different selection rules the frequencies and intensity of the lines of "pseudo-Stokes" and real Stokes spectra should not coincide so this spectrum only indicates possible spectral region of Stokes lines.

This possibility very important because Raman spectra of dyes is not available with conventional Raman technique due to intense luminescence. Therefore this requires the use of more technically sophisticated SERRS or IRS methods [4, 5].

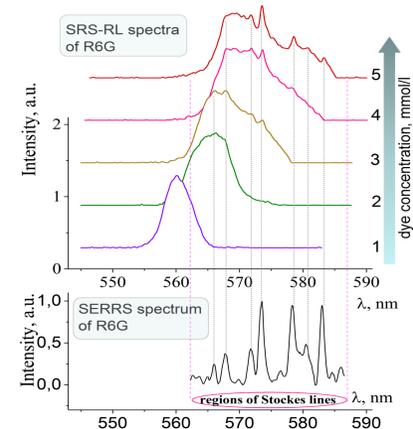


Fig3. Dependence of SRS-RL spectrum of rhodamine 6G on dye concentration under maximal vesicles number (top) and Stokes spectrum of Raman scattering obtained by SERRS [4] (bottom).

An important (but not fundamental) factor is the use of a low temperature (nitrogen or helium), since at these temperatures the contrast of the quasi-line spectrum (the intensity of the SRS lines relative to the continuous RL background) significantly increases (fig4). Beside of that RL spectrum of dye under low temperature expands and cover wider spectral region revealing more Stokes lines.

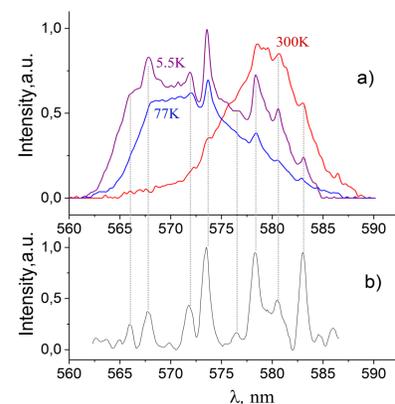


Fig4. a) Dependence of SRS-RL spectrum of rhodamine 6G on temperature. b) Stokes spectrum of Raman scattering obtained by SERRS [4].

RL spectra of all dyes are located nearly the maximum of the dye luminescence spectrum (LS) in the used medium (fig. 5a). Therefore the optimal condition for SRS and RL coupling can be achieved by matching LS spectrum with location of Stokes Raman spectrum (represented by IRS spectrum at fig. 5b).

The matching may be realized not only by tuning of the pumping radiation frequency but also by the shifting of the dye LS, due to reabsorption of luminescence emission. The last depends on optical path which growth with increasing dye concentration and scattering efficiency. Combination both factors affect especially effective: the increase of dye concentration to 5 mmol/l and lengthening of the path caused by effective scattering in the vesicular film, shifts LS by about 20 nm relative to the film without reabsorption (homogeneous and low-concentrated) (fig5a).

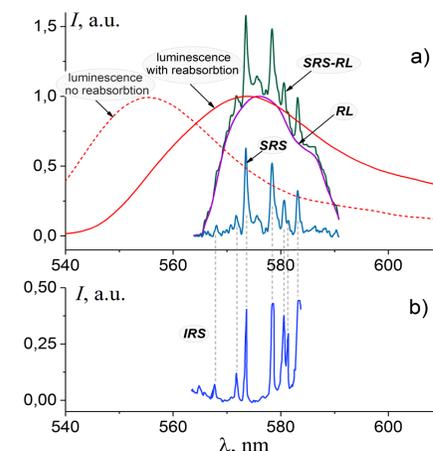


Fig5. a) Disposition RL (violet) and SRS-RL (green) spectra relative to luminescence ones (red) with reabsorption (red solid) and without reabsorption (red dotted) of rhodamine 6G in polymer film; blue line - SRS spectrum evaluated from SRS-RL one. b) Invers Raman scattering (IRS) of rhodamine 6G [5].

Under this shift the matching of the R6G luminescence spectrum with the Stokes region is the best and SRS lines reveal themselves very good (fig.5a). One can see that in this case all Raman lines detected in IRS spectrum (fig5b) are also clearly manifested in the SRS-RL spectrum..

Conclusions

Coupling of stimulated Raman scattering and random lasing in a random media promote to revealing its Raman spectrum. Important conditions for SRS and RL effective coupling are:

- Intensive pumping radiation above 0.05 MW/mm²;
- Effective multiple scattering;
- High dye concentration above 1 mmol/l;
- Coincidence or overlapping of the location of the RL and Stokes spectra of dye Raman scattering;
- Use of low temperature.

Bibliography

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