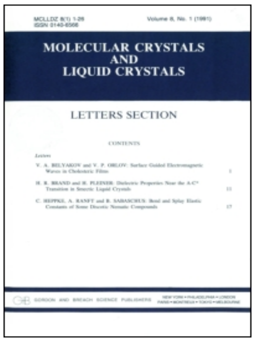

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Regularities of stimulated Raman scattering of dyes in a multiple scattering media

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ABSTRACT

The main regularities influencing stimulated Raman scattering (SRS) occurrence of laser dyes in effective multiple scattering media (vesicular polymeric films) were studied on rhodamine series (R6G, R575, RB and R110) and summarized. It is shown that SRS interact closely with random lasing (RL) of dye what determines its behavior and causes appearance of all Stokes lines within RL spectrum. These effects forms coupled SRS-RL phenomenon. For its occurrence two resonances must be provided: pumping and RL radiation (as two component pump) with dye molecule vibration and pumping radiation with the electronic transition of dye molecule. Both resonances are realized if RL spectrum matches with spectral range of Stokes lines.

This matching may be control with “pseudo-Stokes” spectrum constructed with vibration frequencies revealing in IR absorption spectrum of dye. The matching may be achieved by change of dye concentration and frequency of pumping radiation. The best SRS-RL occurrence realizes when the optimal matching achieves at highest dye concentration. The obtained data may by useful for development of Raman spectroscopy for laser dyes.

KEYWORDS

random lasing; stimulated Raman scattering; vesicles polymeric films; dye

Introduction

In our previous papers we discovered that stimulated Raman scattering (SRS) in dyed multiple scattering media (MSM) is occurred in many case together with random lasing (RL) [1–4]. These effects actually form in MSM coupled process SRS-RL because they influence each other. RL and SRS interaction happens according to CARS-like mechanism in which two pumping components are formed by incident monochromatic pumping (usually second harmonic of YAG-Nd^{3+} laser) and continuous radiation of RL appearing in MSM [4, 5]. Because of continuous spectrum of RL component this mechanism stipulates SRS of those dye Stokes components which appear within RL spectrum. SRS-RL process is supposed to be resonant for dye molecules because only Stokes components of molecule dye, but not polymeric matrix, become apparent in the SRS-RL radiation spectrum [2]. The resonance is caused by coincidence of pumping radiation wavelength with dye absorption band what is necessary for RL initiation, while the matrix at this wavelength is transparent. This feature gives priority to SRS of dye molecule over other molecules. This important peculiarity gives possibility

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applying of SRS-RL effect to obtaining Raman spectra of laser dyes what is very difficult to make by means of routine Raman method because of obstructive luminescent illumination. One more possible technique – CARS (coherent anti-Stokes Raman scattering) [6] is not applicable because of the same reason. These troubles enforce to apply more complicated techniques - SERRS (surface enhanced resonant Raman scattering) [7, 8] or IRS (inverse Raman scattering) [9]. That is why Raman spectra were obtained only of some dyes up to now [7–9].

Thus SRS-RL phenomena may be consider as the first real applying of RL effect from the moment of its discovering [10] because other potential applications [11] did not realize up to now. But wide applying of SRS-RL effect in Raman spectroscopy needs detailed information about conditions influencing SRS lines occurrence. These data would allow choosing optimum conditions of their registration. Firstly SRS regularities in MSM were studied for rhodamine 6G as most investigated dye. In the presented work our researches were expanded on other dyes of rhodamine series that allows to generalize results and to draw more general conclusions.

Samples and instrumentation

We investigated SRS-RL regularities using laser dyes of rhodamine series 6G (R6G), 575 (R575), B (RB) and 110 (R110) in vesicular polymeric films which are effective MSM owing to closely packed micro vesicles [1]. These dyes are expected to be having similar Raman frequencies because of similar structural formulas but different luminescence spectra which are shifted relatively Stokes spectrum on different value [12]. It allows varying interaction of SRS and RL what is important for studying of the SRS-RL regularities.

The films were fabricated of nitrogen-containing ternary copolymer [1, 4] containing dissolved dye. The films were deposited on the lavsan (dacron) substrate by coating; thickness of the film was about 10 mkm. Vesicles were created by heating of the films preliminary irradiated with an ultraviolet radiation owing to association of photo generated gaseous embryos. Number and concentration of the vesicles increase under growth of UV exposure duration. In such way efficiency of light scattering may be changed. Under sufficient long-duration exposition the vesicles are closely-packed in some layers and their mean diameter is less 0.5 mkm. Effective light scattering of the vesicular film is caused not only by close packing but internal reflection of propagating light in polymeric media having more refractive index than gas vesicles [13]. Reflection at film surfaces promote to confinement of the light in the film as was demonstrated earlier in work [14]. Owing to these features mean free path, which is fundamental parameters of multiple scattering, equal 3 mkm [5] in these films what is appreciably less than in suspensions of high refractive dielectric microparticles which is applying as usual. This property makes vesicular film better MSM than the suspensions [1, 10, 15–17].

Pumping of the films was executed by the second harmonic of Q-switched YAG:Nd^{3+} ($\lambda = 532$ nm) laser. For checking of the spectral lines belonging to the Raman scattering wavelength tunable phosphate glass: Nd^{3+} laser was used instead of YAG:Nd^{3+} one. The laser pulse durations were $\tau = 15$ns and 25 ns respectively. Pump radiation is slightly focused at sample so the beam diameter at the front surface of the sample was d = 0.5 mm. Pump intensity was varied with absorbing gray filters within the range 0.005 ÷0.5 MW/mm^2.

Radiation of the films was registered in backward direction to the incident pump beam. SRS-RL spectra were single-shot registered by means of 900 mm diffraction spectrograph (grating 1200 gr/mm) and CCD camera with total spectral resolution about 0.2 nm. The experiments were performed at temperatures near to liquid helium ones (8K) to decrease

Raman lines width [18] and to shift RL spectrum to short wave direction for improving overlap of it with spectral region of Stokes lines what is need for interaction SRS and RL.

Spectral calibration of the spectrograph was checked constantly by Ne emission spectrum for accuracy improvement of radiation frequency registration. So registration accuracy of the spectral lines frequency corresponded to spectral resolution.

Results and discussion

Main results were obtained for R575 and R6G which luminescent and laser properties are similar. The date for R6G was depicted and analyzed before in [2–4]. The results for R575 are similar generally to ones for R6G which luminescent and laser properties are similar. But SRS-RL phenomena of R575 dye reveals itself more distinctly. Therefore in the next we will show mainly data for this dye, noting its difference from R6G as needed.

The main feature of SRS of the dyes in vesicular film is demonstrated on the example of R575 on fig. 1, where development of SRS-RL spectra of R575 was showed depending on pump intensity. Initially spectrum of vesicular film with R575 rather dramatically narrows under pump intensity I_p growth: spectrum width decrease about order under five-fold I_p increase (fig 1a). Minimal spectrum width corresponds to RL threshold which define transition from amplifying spontaneous emission (ASE) to stimulated emission of RL [15, 16]. SRS lines appear under following 4-fold pump increase and then their intensity grows nonlinearly under pump increase against continuous background of the RL spectrum (fig. 1b). As a result radiation of the films under this pumping consists of continuous RL and linear SRS component. SRS lines occur only within the RL spectrum; beyond its range they don't emerge as it was observed for other investigated dyes too. Emergence and growth of the lines is followed by the spectrum widening (fig 1a) to longwave direction (fig 1b). Frequencies of the lines are shifted in strong concordance with the frequency change of the pump radiation under pumping with phosphate glass neodymium laser. The shift concordance and nonlinear growth of the lines intensity prove that they are conditioned by SRS phenomenon as other investigated dyes in vesicular films [2–5, 17, 19].

At fig. 2 the relative disposition of absorption (1, 2), luminescence (3–5) and SRS-RL radiation (6) spectra of R575 (fig. 2a) and R6G (fig. 2b) are shown subject to dye concentration C_d and presence of vesicles. As appears from these data multiple scattering caused by vesicles shifts the luminescence spectrum (5) of the both dyes to longwave direction approximately on $\delta\lambda = 9$ nm and 6 nm respectively with respect to the spectrum of net film (4). This shift is stipulated by reabsorption and reemission of luminescent radiation in overlapping region of luminescence (3) and absorption (1) spectra which efficiency increases because of lengthening of a path of a scattered light. The same shift causes also the increase of dye concentration C_d, which increase reabsorption/reemission too. Considerable spectral the shift of the vesicular film (5) relative to net one (4) of the same dye concentration indicates efficient multiple scattering of light in it.

RL spectrum of the both dyes is coordinated with maximum of their luminescence spectra in the vesicular film what is conditioned by the maximal light amplification in this spectral range. In accordance with CARS-like mechanism of SRS in MSM [2, 5], in which RL radiation is the component of bichromatic pump, matching of RL spectra and spectral localization of the Stokes lines is important on principle. This matching is the best for these dyes in the vesicular film under $C_d = 5$ mmol/l. Under this concentration most intensive Stokes lines of the dyes are located near the RL spectrum maxima. The SRS spectra of these dyes lines are very close what is caused by proximity of their structural formulas which differ only by one

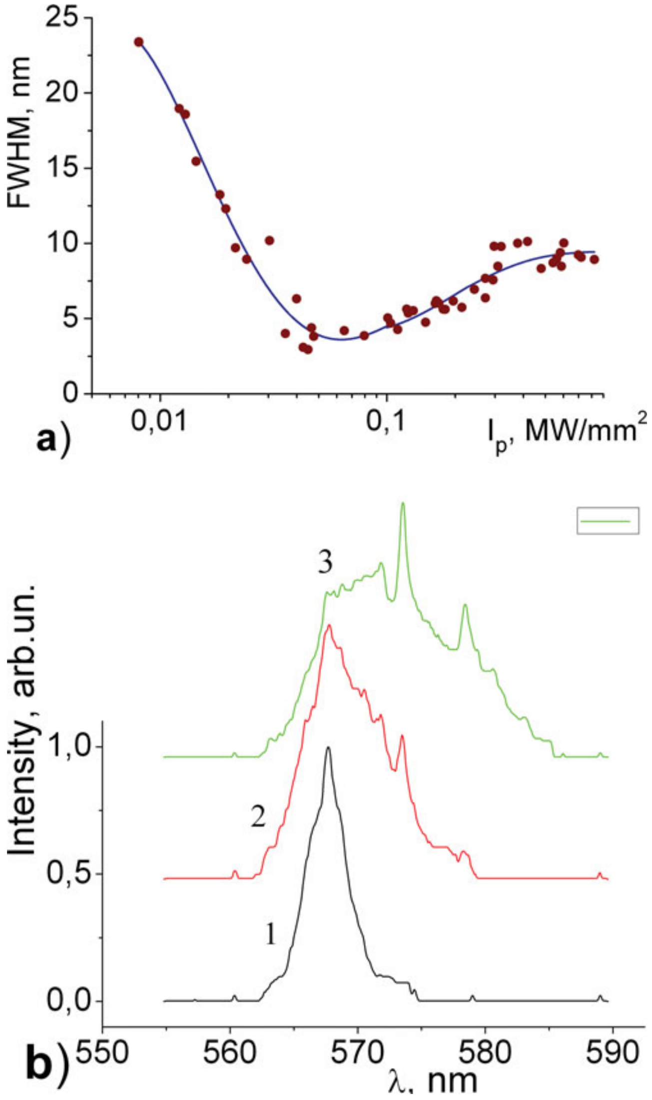

Figure 1. Pump dependence of spectrum FWHM (a) and its contour (b) of Rh575 in polymeric vesicular film. $I_p = 0.15$ (1), 0,27 (2) and 0.67 (3) MW/mm^2; T = 7 K.

auxochrome group while skeletons of the molecules are identical [12]. It is important the optimal matching is achieved at high dye concentration what provides high Raman amplification at Stokes frequencies. These features provide the best occurrence of SRS-RL phenomenon of these dyes in these films among other dyes. For this reason SRS-RL phenomenon in this film is most significant.

Should note this matching is achieved owing to significant ($\delta\lambda = 18$ nm) shift of luminescence spectrum conditioned reabsorption/reemission effect owing to both causes: multiple scattering and high dye concentration. It demands such concentration increase (up to 5 mmol/l) which hypothetically could lead to association of dye molecules and formation of dimers what might misrepresent the SRS spectrum of the dye molecules. Dimers (or higher associates) presence is usually detected by change absorption spectrum under dye concentration increase [20]. But in real absorption spectrum of R575 in the films don't depend on

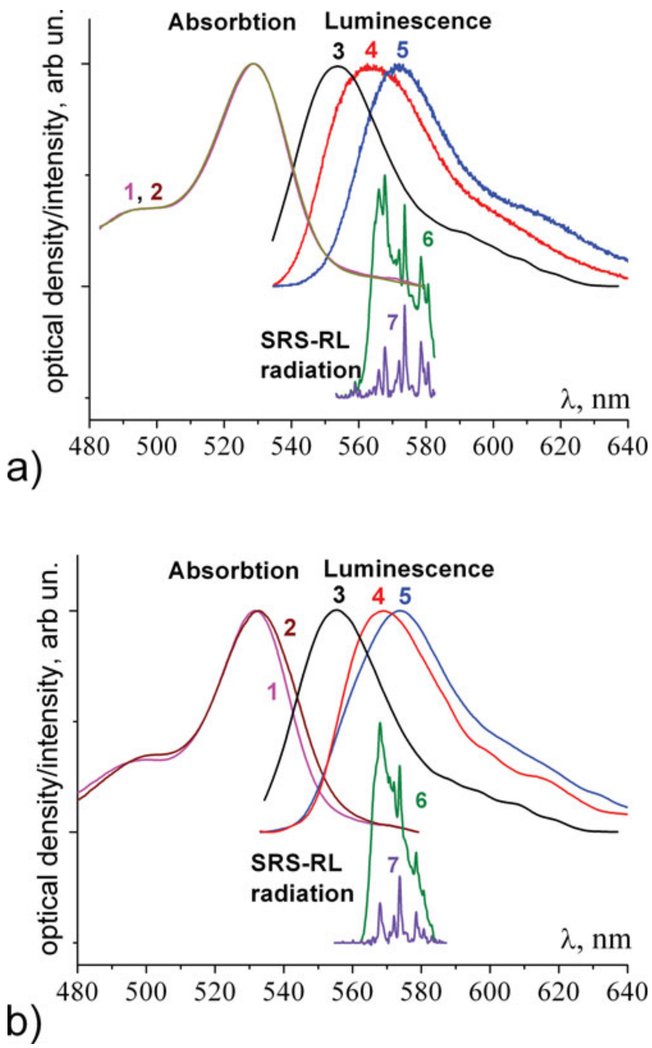

Figure 2. Relative disposition of absorption (1, 2), luminescence (3–5) and SRS-RL radiation (6) spectra with its linear component (7) of rhodamines 575 (a) and 6G (b). The dye concentration is 0,05 (1, 3) and 5 (2, 4–7) mmol/l, temperature T = 8 K. The spectra of the films with small concentration (1, 3) are shown as reference for demonstration of influence of the dye concentration increase up to the working value 5 mmol/l (2, 4) and multiple light scattering by vesicles under before RL threshold (5) and over RL threshold (6, 7) pumping.

concentration in operational range: they are identical under $C_d = 0.05$ and 5 mmol/l (curves 1 and 2, fig 2a). It confirms that the molecules of this dye doesn't associate up to this concentration.

Absorption spectrum of R6G in the films are identical at $C_d = 0.05$ and 1 mmol/l but slightly differ at 5 mmol/l. It may indicate the beginning of a molecular association at this concentration. This conclusion is coordinated with decrease of quantum yield of the luminescence at this concentration which is also usually observed under molecules association. This association may worsen condition for SRS-RL phenomenon due to decrease of RL radiation intensity. This circumstance may be probable reason why this phenomenon occurs better in R575.

One should note that emergence of associates might bring additional frequencies in SRS-RL spectrum which corresponds to new bonds between the molecules. But the energy and

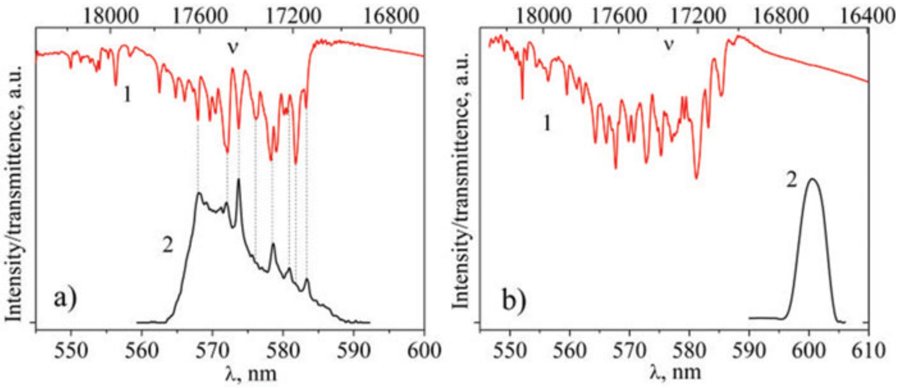

Figure 3. Radiation spectra (2) of rhodamines Rh575 (a) and RhB (b) in vesicular films under 0.6 MW/mm^2 excitation intensity and their "pseudo-Stokes" spectra (1) derived from IR absorption. Dye concentration $C_d = 5$ mmol/l, temperature $T = 10$ K.

therefore vibration frequencies of these bonds is expected much lower than intramolecular ones. Therefore corresponding Stokes lines can't get to RL spectra and exhibit themselves in SRS-RL.

Importance of the matching of RL spectra and spectral localization of the Stokes lines is illustrate on fig. 3 for R575 and RB. As the frequencies of dye Stokes lines are usually not available the possible spectral region of their location may be found out by juxtapose of IR absorption and RL spectra. Using of vibration frequencies ν_{IR} in IR absorption spectra one may calculate possible Stokes frequencies ν_s by the formula $\nu_s = \nu_p - \nu_{IR}$, where ν_p - frequency of the pump radiation. IR absorption spectrum, represented in ν_s coordinate, named conditionally as "pseudo-Stokes" spectrum indicates possible location of the Stokes lines. One can see that SRS of R575 occurs very well because its "pseudo-Stokes" spectrum (1) matches optimally with RL spectrum (2) of the dye (fig 3a). The radiation spectrum (2) is quasi linear and it contains spectral lines whose frequencies coincide with the frequencies of "pseudo-Stokes" spectrum (1). And SRS of RB doesn't arise because its "pseudo-Stokes" spectrum (1) mismatches with RL spectrum (2) of this dye (fig 3b). Its radiation spectrum contains only continuous component of RL radiation and does not contains spectral lines of SRS. The matching may be achieved for any dye by selection of frequency of pump radiation. But for given monocromatic pump radiation (second harmonic of YAG-Nd^{3+} laser for example) the matching restricts quantity of dyes able to reveal SRS-RL phenomenon.

Same correlation was observed and for R6G and HIC [14] and therefore it may be assumed as common rule for all dyes. It allows using "pseudo-Stokes" spectrum as instrument for establishment of SRS-RL observation. Should note that "pseudo-Stokes" spectrum may indicate only region of possible location of Stokes lines but not their intensity and frequencies because of different selection rules for Raman scattering and IR absorption.

Important regularity of dye SRS in MSM is its resonant behavior. Really, in SRS-RL phenomenon Raman lines of dye occur while the lines of matrix does not arise despite of much more (about three order) concentration of their constituent molecule (fig. 4). The cause is that molecules of dye and matrix are in different condition under SRS-RL phenomenon: dye molecules are excited by pumping but molecules of matrix are not excited because the matrix is usually selected to be transparent. Thus pump radiation is in resonance with electronic level of dye molecule and its SRS is resonant what multiply increase probability of this effect for dye

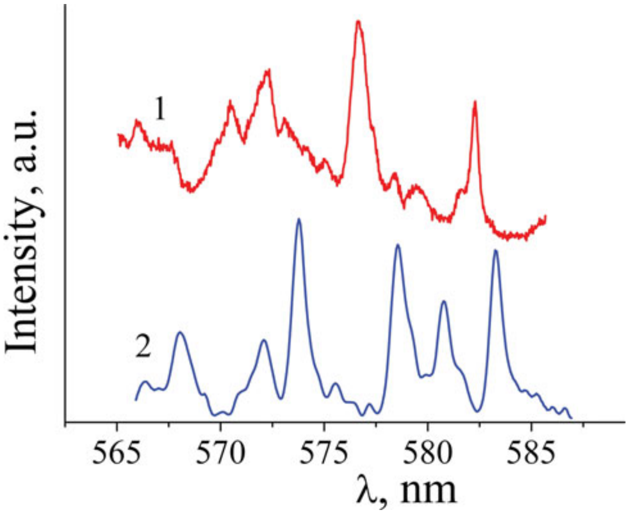

Figure 4. Spontaneous Raman spectrum (1) of PUA samples with Rh575 and spectrum of Stokes lines (2) observed in SRS-RL spectrum of Rh575 in vesicular polymeric film under same dye concentrations ($C_d = 5$ mmol/l).

relative to matrix. In consideration of this feature is appropriately to use acronym SRRS-RL (stimulated resonant Raman scattering – random lasing) instead of previous SRS-RL.

At fig. 4 Stokes spectrum of vesicular film with R575 obtained from SRS-RL phenomena (2) with the method [3, 4] compares with Stokes spectrum of bulk polymeric (polyurethane acrylate - PUA) sample with the same dye obtained by routine spontaneous Raman technique (1). The bulk sample was used instead of the film to increase number of scattering molecules and to enhance signal of spontaneous Raman scattering dye which is too weak for film because of small number of dye molecules in the thin film. Excitation of spontaneous Raman scattering was carried out beyond the absorption band of dye (i.e. nonresonant Raman scattering) to avoid of obstructive luminescent illumination. Stokes spectrum from SRS-RL was obtained for bulk sample with R575 too but it was available experimentally within smaller spectral region because RL spectrum of the dye in this sample is narrower. In this range the spectra of both samples are identical that gives the grounds to assume that these spectra are identical in wider range too. Therefore one may consider that spectrum 2 of the film represents Stokes spectrum of R575 in bulk polymeric also.

One can see that these spectra are quite different. It demonstrates that Strokes lines of the dye presented by spectrum 2 are not detected under spontaneous Raman scattering even in thick sample. So the lines occurring in nonresonant spontaneous Raman scattering of dyed polymeric sample don't belong to the dye but to the molecules of matrix. It occurs as the condition for the Raman scattering of both molecules (dye and matrix) is identical under nonresonance spontaneous Raman scattering and therefore matrix molecules get great advantage because of large concentration.

Resonant spontaneous Raman scattering is not applicable for laser dyes because luminescence radiation arising under this condition is much intensive and so detection of scattered light is impossible. Resonant SRS arising in MSM under RL of dye and pumping gives advantage to the dyes molecules because only electronic transition of dye molecules resonates with pumping radiation what causes large Raman amplification just at their Stokes frequencies. In this case the initial luminescence radiation of dye (initial spontaneous Raman scattering is negligible) is undergone mainly to Raman amplification at Stokes frequencies of dye. As a result intensity at these frequencies much increase and the Stokes lines become apparent through the SRS.

This advantage disappears if the frequency of pumping radiation is beyond the absorption band of a dye and so the radiation was not in resonance with its electronic transition. In addition RL is not excited and RL radiation disappears in this case. Thus necessary operation condition of CARS–like mechanism is not implemented. So SRS does not occur owing to two both these reasons. Such condition is implemented for rhodamine 110 (R110) under second harmonic of Nd3+ laser (532 nm) excitation and therefore SRS-RL phenomenon for it does not observed under any high pumping.

As it was noted above one should expect that all investigated must have similar Stokes spectra. It is proved by similarity of linear component of R6G and R575 SRS-RL spectra presented at fig 2 which differ only by intensity of the lines what is explained by some difference of mutual disposition of RL and luminescence spectra of the dyes. Therefore different manifestation of SRS-RL phenomenon under the same excitation and other experimental conditions has to be referred to distinction of the phenomenon behavior in these dyes.

Data presented above allows making conclusion that SRS-RL requires double resonance. The first one is resonance of two component pump of CARS-like mechanism (external pumping and RL radiation) with dye molecule vibration. It requires equality of the difference of radiation frequencies of two component pump to the frequency of molecule vibration and may be provided with matching of RL spectra and spectral range of Stokes lines. The second one is resonance of the scattering radiation (external pumping) with the electronic transition of molecule dye which requires hit of frequency of pumping radiation in absorption band of dye. Both resonances are realized in dyed MSM if to excite RL and to match its radiation spectrum with spectral range of Stokes lines.

Summary

The main regularities influencing on stimulated Raman scattering (SRS) occurrence of laser dyes in effective multiple scattering media (vesicular polymeric films) were studied and summarized. SRS interact closely with random lasing (RL) what determines its behavior. The interaction causes appearance of all Stokes lines of dye coinciding with RL spectrum.

SRS of dyes in multiple scattering media is resonant. For SRS-RL phenomenon occurrence two resonances must be provided: frequency difference of two component pumping consisting of external laser radiation and random lasing with frequency of dye molecule vibration; frequency of the external laser radiation with the electronic transition of dye molecule. Both resonances are realized in dyed MSM if to excite RL and to match its radiation spectrum with spectral range of Stokes lines.

This matching may be control with “pseudo-Stokes” spectrum constructed with vibration frequencies revealing in IR absorption spectrum of dye. The matching may be achieved by change of dye concentration and frequency of pumping radiation. The best SRS-RL occurrence realizes when the optimal matching achieves at highest dye concentration which doesn’t cause substantial associates formation.

References

[1] Yashchuk Vasil, P., Tikhonov, E., Prygodjuk, O. et al. (2007). *Proc.of SPIE*, *6728*, 67280N1.
[2] Yashchuk, V. P., Tikhonov, E. A., & Prigodiuk, O. A. (2010). *JETP Letters*, *91*, 174.

[3] Yashchuk Vasil, P., Tikhonov, E., Bukatar, A. O., Prygodiuk, O., & Smaliuk, A. P. (2011). *Quantum Electronics*, *41* (10), 875.
[4] Yashchuk Vasil, P., Tikhonov, E. A., & Prygodiuk, O. A. (2011). *Mol. Cryst. Liq. Cryst.*, *535*, 156.
[5] Yashchuk Vasil, P., Komyshan, A. O., Tikhonov, E. A., & Olkhovic, L. A. (2014). *Quantum Electronics*, *44*(10), 921.
[6] Akhmanov, S. A., & Koroteev, N. A. (1977). *Usp.Fiz.Nauk*, *123*, 405, [(1977), *Sov. Phys. Usp*., V.20, 899.]
[7] Meixner, A. J., Vosgrone, T., & Sackrow, M. (2001). *J.Luminescence*, *94*, 147.
[8] Zhon, Zeng-Hui et al. (2006). *Chinese Physics*, *15*, 126.
[9] Werncke, W., Lau, A., Pfeiffer, M. et. al. (1976). *Opt.Comm.*, *16*(1), 128.
[10] Lawandy, N. M., Balachandran, R. M., & Gomes, A. S., & Sauvain, E. (1994). *Nature Lett.*, *368*, 436.
[11] Wiersma Diederik, S. (2008). *Nature physics.*, *4*, 359.
[12] Brackmann,. U. (2000). *Lambdachrome Laser Dyes*, 3-rd edit. Lambda Physik: Goettingen.
[13] Tikhonov, E. A., Vasil P. Yashchuk,, Prygodiuk, O. A. et. al. (2008). *Appl.Phys.B: Lasers and Optics.*, *92* (N4), 593.
[14] Tikhonov, E. A., Vasil, P., Yashchuk Prygodiuk, O. A., & Bezrodny, V. I. (2004). *Solid State Phenomena.*, *77*, 99–100.
[15] Tikhonov, E. A., Vasil, P., Yashchuk, Prygodiuk, O. A., & Bezrodny, V. I. (2003). *Solid State Phenomena.*, *94*, 295.
[16] Vasil P., Yashchuk, E. A., & Tikhonov, O. A. (2012). *Prygodiuk. J. of Optical Technology.*, *79* (9), 550.
[17] Yashchuk Vasil, P., Komyshan, A. O., Smaliuk, A. P. et al. (2013). *Quantum Electronics.*, *43*(12), 1127.
[18] Yashchuk Vasil, P., & Smaliuk, A. P. (2013). *Bulletin of Taras Shevchenko National Univ. of Kyiv, Ser. Physics & Mathematics.* №*4*, 289.
[19] Yashchuk Vasil, P. (2015). *Laser physics.*, *25*(7), 075702.
[20] Grachev, A. V., & Ponomarev, A. N. (1991). *Juzhakov. Sov. J of Appl. Spectr.*, *54*(3), 418.