

# Influence of reabsorption and reemission on stimulated Raman scattering of polymethine dyes in multiple scattering media

V.P. Yashchuk, A.O. Komyshan, A.P. Smaliuk, O.A. Prygodiuk, A.A. Ishchenko, L.A. Olkhovyk

**Abstract.** It is shown that reabsorption of the luminescence radiation in the range of its overlapping with the absorption spectrum and the following reemission to a long-wavelength range may noticeably affect the process of stimulated Raman scattering (SRS) in polymethine dyes in multiple scattering media (MSM). This is related to the fact that SRS in such media occurs jointly with the random lasing (RL), which favors SRS and makes up with it a united nonlinear process. Reemission into the long-wavelength spectrum range amplified in MSM causes the RL spectrum to shift to longer wavelengths and initiates the long-wavelength band of RL, in which a main part of the lasing energy is concentrated. This weakens or completely stops the SRS if the band is beyond the range of possible spectral localisation of Stokes lines. This process depends on the efficiency of light scattering, dye concentration, temperature and pump intensity; hence, there exist optimal values of these parameters for obtaining SRS in MSM.

**Keywords:** stimulated Raman scattering, random lasing, dyes, multiple scattering medium, vesicular film.

## 1. Introduction

New properties of multiple scattering media (MSM) revealing under stimulated emission were first considered theoretically in [1]. Experimental studies have been started by Lawandy et al. [2], where in a concentrated suspension of titanium dioxide nanoparticles, the so-called random lasing (RL) has been obtained in a rhodamin 640 perchlorate dye, which attracted attention due to its unusual properties. The radiation of RL has a continuous spectrum without a conventional mode structure, which is explained by a nonresonant character of the feedback originated from multiple elastic scattering of light. This is a rather attractive feature for the spectroscopic applications related to the combined effects of stimulated Raman scattering (SRS) and RL of dyes in MSM [3–6]. Both effects in such media are strongly interrelated and actually form the united nonlinear SRS–RL process. This process can be interpreted as the specific case of active Raman scattering

spectroscopy, in which one of the components of double-frequency pumping (the radiation of RL) is generated in the sample itself and is not monochromatic. Due to a continuous spectrum of this component, SRS is revealed in all the Stokes frequencies matching with the range of the RL spectrum. This gives a chance to identify a vibrational spectrum of dye molecules in the corresponding spectral range by the spectra of secondary radiation in MSM [7].

From the nature of this phenomenon [5, 6] one may conclude that the origin of SRS lines in secondary radiation directly depends on the intensity of RL radiation at the corresponding Stokes frequencies. This intensity, in turn, depends on the parameters of the medium and pumping, which affect the RL spectrum: the dye concentration, scattering efficiency, temperature, and intensity of pumping [6, 7]. Hence, these parameters may substantially affect the conditions of SRS origin in MSM. It is obvious from general considerations that the origin of SRS requires the combination of parameters that would ensure the RL spectrum residing in the range of localisation of the Stokes lines. An incorrect parameter combination with the RL spectrum residing beyond this range may result in impossible or substantially complicated observation of SRS. Thus, while using SRS of dyes in MSM for investigating a vibrational spectrum of the dye molecules it is important to study the mechanisms of influence of these parameters on SRS, which would facilitate goal seeking of the optimal parameter values.

One of the mechanisms of influence of these parameters on the spectrum and intensity of RL is reabsorption of the luminescence radiation of the dye in the range of its overlapping with the absorption spectrum and the following reemission to a longer-wavelength range. This effect depends on the degree of spectrum overlapping mentioned above (Stokes shift) and is inherent in all dyes to a certain degree. In polymethine dyes, the effect is substantial and noticeably increases in MSM due to the longer effective path passed by the luminescence radiation in the sample in the process of RL formation. One may expect that this is a main effect among possible mechanisms of influence.

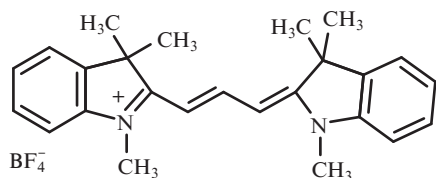
Note that if the first three parameters among those mentioned above are chosen optimal for the sample and fixed during the experiment, the pump intensity usually varies and may substantially change the spectrum of RL due to the discussed effect. Hence, the SRS occurrence may nontrivially depend on the pump power: a maximal SRS intensity may be inconsistent with the maximal pump intensity. The present work is aimed at studying the influence of reabsorption and reemission on the possibility of determination of the vibrational spectrum of dye molecules by their SRS in MSM.

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## 2. Samples and experimental method

SRS was studied in the cationic polymethine dye 1,3,3,1',3',3'-hexamethylindocarbocyanine- $\text{BF}_4^-$  (HIC) (see the structure formula in Fig. 1), which is specific in a high sensitivity of the luminescence spectrum to the reabsorption of the latter in the range of overlapping with the absorption spectrum. Hereupon, all the parameters mentioned above that affect the reabsorption efficiency also strongly influence the RL spectrum in this dye.



**Figure 1.** Structural formula of the molecule of polymethine dye HIC.

The dye was incorporated in the two MSM with different degrees of light scattering: a concentrated suspension of corundum microparticles in polyurethaneacrylate and a vesicular polymer film. The suspension was produced by the fast polymerisation of the dye solution in alcohol and polyurethaneacrylate; this eliminated substantial gradients of microparticle concentration caused by sedimentation. The polymer film was deposited to a lavsan substrate by the coating method; vesicles were created in the film by photochemical decomposition of the copolymer component comprising azide. The concentrations of the scattering centres in both the MSM (microparticles and vesicles of gaseous nitrogen, respectively) were approaching the limiting values determined by the close-packed arrangement of the centres, and their average diameters were close ( $\bar{d} = 2$  and  $1.2 \mu\text{m}$ , respectively). The efficiency of light scattering in the vesicular film was substantially higher due to the greater coefficient of Fresnel scattering  $r = (n - 1)/(n + 1)$  at the polymer-vesicle interface (the relative refractive index is  $n = 1.5$ ) as compared to the similar coefficient at the polymer-corundum interface ( $n = 1.13$ ) and due to the total internal reflection. The latter arises because the RL radiation in the vesicular film propagates in the optically less dense, against the scattering centres, active medium, which, in view of this fact, is similar to a ramified waveguide [8]. These two effects provide efficient multiple scattering of RL radiation in the vesicular film despite of its noticeably less thickness ( $15 \mu\text{m}$ ) as compared to that of suspension layer ( $0.6 \text{ mm}$ ). In both the media, the well-defined peak of coherent backscattered radiation is detected with the width of  $\sim 1^\circ$ , which indicates the multiple scattering [9].

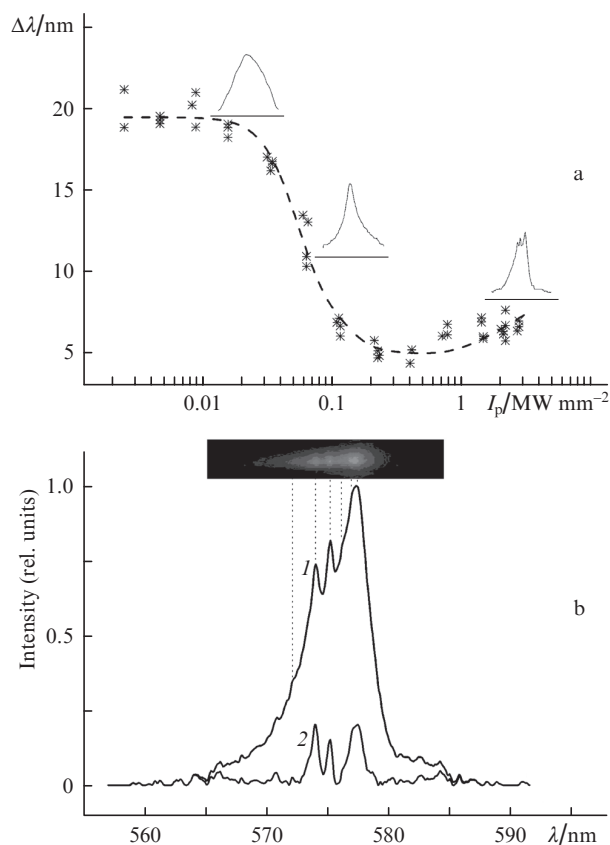
Because the distance between scattering centres ( $\sim \bar{d}$ ) is well above the wavelength  $\lambda$  of RL, the diffuse regime of radiation propagation is realised in both the media so that the interference of scattered waves makes no influence on the spectrum of RL and does not hinder observation of SRS lines.

The measurements were performed at helium temperatures ( $\sim 7\text{--}8 \text{ K}$ ), which favoured better appearance of SRS lines in the RL spectrum due to a lower threshold of RL, a reduced spectral broadening of Raman scattering (RS) lines and better matching of the RL spectrum with the range in which the RS lines reside. The samples were optically pumped

by second harmonic of a  $Q$ -switched  $\text{Nd}^{3+}$ :YAG-laser. The intensity of pump radiation changed in the limits  $1\text{--}100 \text{ MW cm}^{-2}$  with the help of neutral-grey filters and focusing. The radiation spectra were registered in a single shot by the diffraction spectrograph with a CCD-array and the spectral resolution of  $0.3 \text{ nm}$  (the instrumental function). The correctness of correspondence of the RL spectrum line component to RS was verified by a  $\text{Nd}^{3+}$ -laser on phosphate glass with a varied radiation wavelength.

## 3. Experimental results and discussion

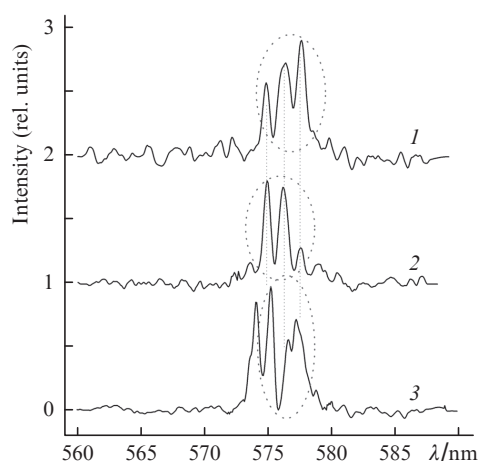
Figure 2a presents the dependence of the spectral width  $\Delta\lambda$  of HIC secondary radiation on the pump intensity  $I_p$  for the case of the concentrated suspension of corundum microparticles. The spectra of secondary radiation shown in insets illustrate the width variation under an increasing pump intensity. The dependence  $\Delta\lambda(I_p)$  has the feature specific for the emission of dyes in MSM [2, 10]: under the pump intensity exceeding a certain value, the emission spectrum sharply narrows to the minimal value, which is close to the lasing spectral width of this dye in a nonselective cavity. The onset of radiation with the minimal spectral width [10] (in this particular case of  $\sim 4 \text{ nm}$ ) is an indication to the RL onset, the pump intensity at which this effect is observed corresponding to the threshold of RL ( $I_{th} \approx 0.1 \text{ MW mm}^{-2}$ ).



**Figure 2.** (a) Dependence of the spectral width  $\Delta\lambda$  of secondary radiation of HIC dye in the concentrated suspension of corundum microparticles in polyurethane vs. the pump intensity  $I_p$ ; (b) the spectrum of secondary radiation in HIC in suspension at a maximal pump intensity ( $I$ ) and the line component separated from it ( $2$ ). Spectra of secondary radiation at the corresponding pump intensities are given in the insets.

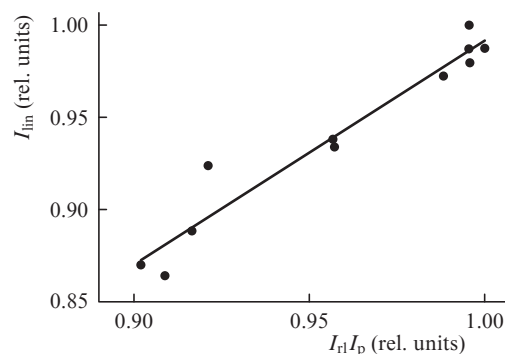
At a further increase in  $I_p$  the emission spectrum noticeably broadens and at the intensities exceeding  $I_{th}$  by approximately an order of magnitude, the narrow lines of width  $\sim 0.5$  nm are observed, whose intensities raise relative to the continuous spectrum of RL as the pumping raises. Under the utmost realised intensity of the pump radiation ( $\sim 2$  MW mm $^{-2}$ ), five lines are observed (Fig. 2b), among which two lines (with the shorter wavelengths  $\lambda = 574$  and 575.2 nm) are well resolved, and three long-wavelength lines form a weakly resolved triplet (576.3, 576.8, and 577.4 nm). In the line spectrum component [curve (2)], this triplet looks like an asymmetrical band, but at greater magnification of the spectrum image (inset in Fig. 2b) its components are definitely revealed.

The spectral positions of the lines observed depend on the wavelength of pump radiation: the shifts of lines of secondary radiation and of pumping are equal within the accuracy of better than the instrumental function of spectrograph. This is well illustrated in Fig. 3, where the line components obtained at various wavelengths of pumping ( $\lambda_p = 530.2$ , 531, and 532 nm) are shown. For clearness, the upper spectra (1) and (2) are shifted relative to bottom spectrum (3) to longer wavelength side by 1.8 and 1 nm, respectively. A good coincidence of the lines in the shifted spectra proves that they are related with RS.



**Figure 3.** Line components of the spectra of HIC secondary radiation in the concentrated suspension of corundum microparticles at the wavelengths of exciting radiation  $\lambda_p =$  (1) 530.2, (2) 531 and (3) 532 nm. Spectra (1) and (2) are shifted relative to spectrum (3) to the longer-wavelength side by 1.8 and 1 nm, respectively.

In addition, these lines exhibit all the features specific for the SRS of dyes in MSM occurring in these media jointly with the RL as a united process [5, 7]: the lines only arise after establishing the RL and at pump intensities substantially exceeding  $I_{th}$  (although the process of their origin has no threshold) and are only observed within the range of the RL spectrum. Because of the sufficiently high threshold of RL of the dye in suspension these lines arise in a sufficiently narrow range of the pump intensities closely to the light breakdown limit of the sample. However, despite this fact, one can see from the approximation in Fig. 4 that the intensity of lines  $I_{lin}$  is proportional to the product of the pump and RL radiation intensities (to the continuous component of secondary radiation):  $I_{lin} \propto I_p I_{rl}$ . These data make one to conclude that the



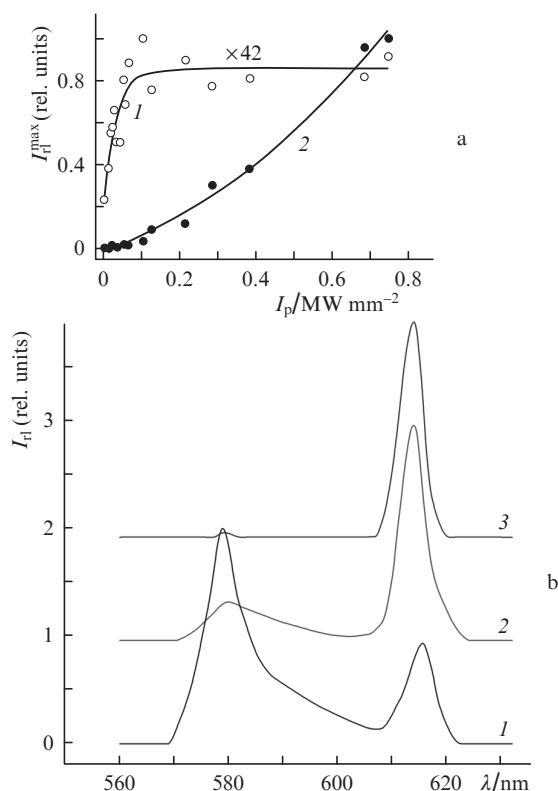
**Figure 4.** Dependence of the intensity  $I_{lin}$  of spectral lines of secondary radiation of HIC in the concentrated suspension of corundum microparticles on the product of the intensities of RL radiation ( $I_{rl}$ ) and pumping ( $I_p$ ).

observed lines of HIC secondary radiation in the suspension of corundum microparticles are the SRS lines for this dye.

Since  $I_{lin} \propto I_{rl}$  the relative intensity and the number of observed lines depend on the pump wavelength, which is well seen in Fig. 3. This is caused by the fact that the Stokes lines shift along with the pump radiation line relative to the RL spectrum, which position remains almost unchanged. Therefore, different Stokes lines appear (and are revealed in the SRS spectrum) within the range of the RL spectrum by varying the pump wavelength. For example, under a short-wavelength pumping ( $\lambda_p = 530.2$  and 531 nm), the line with the shortest wavelength, which is revealed in the SRS spectrum under long-wavelength pumping ( $\lambda_p = 532$  nm), does not fit the range of the RL spectrum. Thus, comparison of line components in Fig. 3 was performed using only the lines marked by dotted ovals, which are revealed at all the pump wavelengths. The relative intensities of the lines depend on their positions in the spectrum of RL – a most intensive is the line that matches with the maximum of the RL spectrum, which is seen by the example of curves (1) and (2).

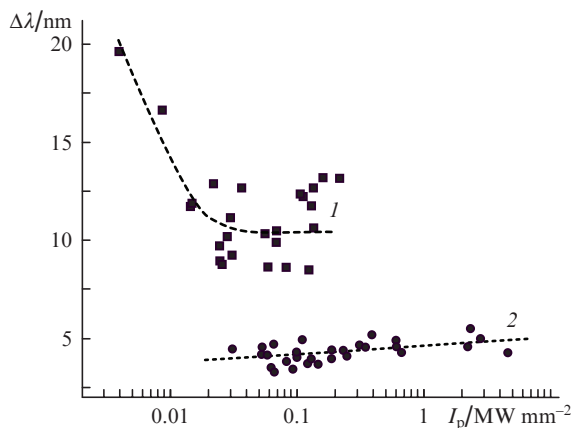
In the vesicular film the evolution of SRS is quite different. At a high concentration of the dye (3 mM L $^{-1}$ ) under an increasing pump intensity, at first the spectrum of secondary radiation dramatically narrows and the RL arises; similar phenomena are observed in the concentrated corundum suspension. However, unlike the case of suspension, just after the origin of RL, in the band having the maximum at approximately the same wavelength  $\lambda = 575$  nm as in suspension, one more longer-wavelength band arises with a maximum at  $\lambda = 612$  nm (Fig. 5). In contrast to the first band, it arises immediately without the preliminary narrowing of the spectrum, which was observed in the band with  $\lambda = 575$  nm (Fig. 6). Hence, the thresholds for RL in both the bands are actually equal. The intensity of the second band sharply raises with an increase in the pump intensity  $I_p$ , whereas the intensity of the first band remains constant and is approximately equal to the one at the threshold value (Fig. 5a). A further increase in  $I_p$  leads to a greater intensity of only the RL band with  $\lambda = 612$  nm, and at maximal  $I_p$  actually all the RL energy is accumulated in this band. Its width under an increasing pump intensity raises by a factor of  $\sim 1.5$ , which was observed earlier in a suspension for the band with  $\lambda = 575$  nm (Fig. 2a) and is typical of the RL spectrum of dyes at their sufficiently high concentration [6].

Taking into account these features of RL in the band with  $\lambda = 612$  nm and the substantial dependence of the probability



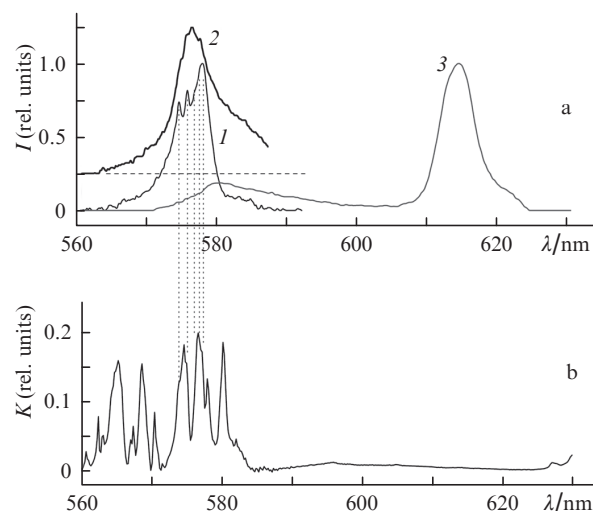
**Figure 5.** (a) Dependences of the RL intensity  $I_{rl}^{\max}$  at maxima of the spectral bands with  $\lambda = (1)$  575 and  $(2)$  612 nm in the vesicular film at the HIC concentration of  $3 \text{ mM L}^{-1}$  and (b) redistribution of the intensity  $I_{rl}$  among these bands under varied pump intensity:  $I_p = (1)$  0.03,  $(2)$  0.2 and  $(3)$   $0.7 \text{ MW mm}^{-2}$ .

for it to arise on the efficiency of light scattering in MSM, one may assume that the onset of this RL is caused by reabsorption of the RL energy in the band with  $\lambda = 575 \text{ nm}$  by unexcited dye molecules followed by reemission of this energy to the longer-wavelength range. This effect becomes stronger when the optical density of the distance passed by radiation increases due to the higher efficiency of light scattering, which makes the distance longer and due to the higher dye concentration, which increases reabsorption. These conclusions



**Figure 6.** Dependences of the widths of  $(1)$  short-wavelength and  $(2)$  long-wavelength bands of RL spectrum in vesicular film on the intensity of pump radiation at the HIC concentration of  $3 \text{ mM L}^{-1}$ .

completely correlate with the observations (Fig. 7a): the long-wavelength band with  $\lambda = 612 \text{ nm}$  arises neither in the medium with lower efficiency of light scattering (suspension) at a higher dye concentration [curve  $(1)$ ], no in the case of the HIC concentration reduced from 3 to  $1 \text{ mM L}^{-1}$  [curve  $(2)$ ] in the medium with a higher light scattering efficiency (vesicular film); whereas at higher values of both parameters this band dominates [curve  $(3)$ ].



**Figure 7.** (a) Spectra of secondary radiation of HIC in MSM with lower  $[(1); \text{concentrated suspension}]$  and higher  $[(2, 3); \text{vesicular film}]$  efficiencies of light scattering at the HIC concentration of  $(2)$  1 and  $(1, 3)$   $3 \text{ mM L}^{-1}$  and the pump intensities of  $\sim 1 \text{ MW mm}^{-2}$  [spectrum  $(2)$  is shifted up by 0.25 of its height] and (b) 'pseudo-spectrum of RS' obtained from the IR absorption spectrum of HIC;  $K = 1 - T$  is the attenuation factor,  $T$  is the measured coefficient of sample transmission.

Reabsorption of the luminescence energy may substantially change the spectrum of luminescence and the gain profile of dye in MSM, which broadens the RL spectrum and causes the second longer-wavelength band to arise. This phenomenon was discovered as early as in the first work on investigation of RL in rhodamin 640 [2], but it was weakly pronounced: the dominating band was still the short-wavelength one, whereas not more than 10% of energy was converted to the long-wavelength band. At a higher HIC concentration ( $3 \text{ mM L}^{-1}$ ) in the vesicular film this phenomenon was most strongly pronounced which revealed in an almost perfect energy transfer to the long-wavelength band.

It is important that in the band with  $\lambda = 612 \text{ nm}$  the SRS lines do not arise even under a 100-fold excess of pumping over the RL threshold value, which differs from the band  $\lambda = 575 \text{ nm}$  where in the concentrated suspension these lines arise already at  $(6-8)$ -fold excess over the RL threshold. The SRS lines are also observed in the band with  $\lambda = 575 \text{ nm}$  in the vesicular film: distinctly at a low dye concentration (in this case the band  $\lambda = 612 \text{ nm}$  does not arise) and at the detection limit at a higher concentration (where the band  $\lambda = 612 \text{ nm}$  is observed).

The reason for SRS appearance in the concentrated suspension and in the vesicular film with a low dye concentration and actually lacking SRS in the vesicular film with a high concentration of the dye becomes clear from consideration of the mutual dispositions of RL spectra and spectral ranges of possible Stokes lines of the dye. For this purpose one may use the

spectrum of IR absorption and juxtapose it to the Raman shift. The possible Stokes frequencies  $\nu_{sl}$  may be defined as  $\nu_{sl} = \nu_p - \nu_{IR}$ , where  $\nu_p$  and  $\nu_{IR}$  are the frequencies of pumping and IR absorption, respectively. In view of this, the spectrum obtained from the absorption IR spectrum by the corresponding transformation (the mirror-image relative to the ordinate axis and the shift by  $\nu_p$  along the spectral axis) points to the frequencies of probable Stokes lines within the accuracy of different selection rules for RS and IR absorption. The 'pseudo-spectrum' of HIC obtained in this way is shown in Fig. 7b in the wavelength scale for comparing with the spectrum of RL.

From Fig. 7 one can see that among two possible RL bands only the first one (575 nm) fits the range of probable Stokes lines whereas the second band (612 nm) is beyond these limits. Hence, SRS lines can only appear in the band with  $\lambda = 575$  nm.

In MSM with a relatively weak reemission (the suspension, the vesicular film with low dye concentration) where the RL emission resides in the band with  $\lambda = 575$  nm, higher  $I_p$  leads to an increase in  $I_{rl}$  and the intensity of SRS lines sharply raises according to the relationship  $I_{lin} \propto I_p I_{rl}$ . In MSM with a noticeable reemission (the vesicular film with a high concentration of the dye) the intensity of the band with  $\lambda = 575$  nm is negligible over the whole range of pump intensities, and the product  $I_p I_{rl}$  remains small even at high  $I_p$ . This is why SRS is not revealed in this band as well.

The results presented demonstrate the importance of choosing optimal values for the efficiency of light scattering in MSM and dye concentration. On the one hand, as was shown in [3, 11], an increased efficiency of light scattering substantially reduces the threshold of RL and increases its intensity, which favours revealing of SRS lines. On the other hand, an increased efficiency of light scattering results in reemission and formation of the long-wavelength band of RL, which may occur beyond the range of probable appearance of Stokes lines. Similarly, an increase in the dye concentration reduces the threshold of RL [6] and, however, intensifies reemission. For example, for a particular dye it was found that in studying SRS it is reasonable to reduce the efficiency of light scattering or the concentration of the dye.

Note that the long-wavelength reemission may play a positive role if it does not result in the origin of the far residing second band but only broadens the spectrum of RL to longer wavelengths. In this case the RL spectrum extends and makes it possible to observe a greater number of SRS Stokes lines. This is the case of rhodamin 6G in vesicular films [3, 5]. The spectrum broadens at a higher pump intensity; hence, a most intensive pumping is needed for observing a maximal number of Stokes lines. If the reemission forms the second (long-wavelength) band of RL (similarly to HIC) then intensive pumping is not reasonable for observing SRS lines because the background of the dominating long-wavelength band with  $\lambda = 612$  nm may substantially hinder their detection in the band with  $\lambda = 575$  nm.

#### 4. Conclusions

Results of the experiments performed show that reabsorption of luminescence radiation of dyes with the following reemission to a longer-wavelength range may substantially influence the process of SRS in MSM. The influence is realised through RL, which occurs jointly with SRS as a united nonlinear process. The condition for SRS to arise in MSM is a coincidence

of the RL spectrum with the range of possible appearance of Stokes lines. This range can be found from the IR absorption spectrum of the dye. The joint reabsorption and reemission may result in a substantial long-wavelength shift of the RL spectrum beyond the limits of the spectral range of possible appearance of Stokes lines, which would make impossible their observation in the process SRS-RL.

In view of the fact that the efficiency of scattering and concentration of the dye oppositely affect the process of reemission and the RL intensity at Stokes frequencies, there exist optimal values of these parameters at which the RL spectrum is not shifted and the RL intensity remains sufficiently high for SRS to arise.

The results obtained in the present work should be taken into account in studying RL and nonlinear properties of MSM with dyes and in employing the method for determining vibrational spectra of dye molecules by their SRS spectra in MSM [7].

#### References

1. Letokhov V.S. *Zh. Eksp. Teor. Fiz.*, **53**(4(10)), 1443 (1967).
2. Lawandy N.M., Balachandran R.M., et al. *Nature*, **368**, 6470 (1994).
3. Yashchuk Vasil P., Tikhonov E., Prygodjuk O., Koreniuk V., Paskal L. *Proc. SPIE Int. Soc. Opt. Eng.*, **6728**, 67280N1 (2007).
4. Yashchuk Vasil P., Tikhonov E., Prygodjuk O. *Proc. 4-th Int. Conf. on Advanced Optoelectronics and Lasers* (Alusta, 2008) pp 220–222.
5. Yashchuk V.P., Tikhonov E.A., Prygodjuk O.A. *Pis'ma Zh. Eksp. Teor. Fiz.*, **91**, 174 (2010).
6. Yashchuk V.P., Tikhonov E.A., Prygodjuk O.A. *Mol. Cryst. Liq. Cryst.*, **535**, 156 (2011).
7. Yashchuk V.P., Tikhonov E.A., Bukatar A.O., Prygodjuk O.A. *Kvantovaya Elektron.*, **41**, 875 (2011) [*Quantum Electron.*, **41**, 875 (2011)].
8. Yashchuk Vasil P., Prygodjuk O., Koreniuk V., Tikhonov E., Bezrodny V. *Appl. Phys. B*, **92**, 593 (2008).
9. Wolf P.-E., Maret G. *Phys. Rev. Lett.*, **55** (24), 2697 (1985).
10. Tikhonov E., Yashchuk Vasil P., Prigodiuk O., Bezrodny V. *Solid State Phenomena*, **94**, 295 (2003).
11. Tikhonov E., Yashchuk Vasil P., Prigodiuk O., Koreniuk V. *Ukr. J. Phys.*, **52**, 346 (2007).