NONLINEAR OPTICAL PHENOMENA

Stimulated Raman scattering of laser dye mixtures dissolved in multiple scattering media

V.P. Yashchuk, A.O. Komyshan, E.A. Tikhonov, L.A. Olkhovyk

Abstract. Stimulated Raman scattering (SRS) of a mixture of rhodamine 6G and pyrromethene 605 laser dyes in vesicular films is studied. It is shown that a peculiar interaction of dyes occurs under conditions of multiple scattering of light from vesicles. This interaction manifests itself as SRS excitation of one of the dyes by random lasing of the other dye, provided that the random lasing spectrum overlaps the Stokes lines of the first dye. In addition, there is energy transfer between molecules of these dyes if their luminescence and absorption spectra overlap. The results obtained confirm that the mechanism of SRS from laser dyes in multiple scattering media is similar to that in coherent-active Raman spectroscopy. These results extend the possibility of determining the vibrational spectrum of dye molecules from their secondary radiation in these media.

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

1. Introduction

The first results of studying the induced radiation in multiple scattering media (MSM) were published in [1, 2]. Lawandy et al. [2] observed the so-called random lasing (RL) of a dye in MSM (rhodamine 640 in a concentrated suspension of submicron rutile particles in ethyl alcohol). The emission spectrum of RL was found to be continuous due to the nonresonant feedback caused by multiple scattering of light. Due to this feature, RL differs significantly from that of conventional lasers, whose spectrum is a set of lines because the phase lasing condition is satisfied for cavity modes. In addition, since RL radiation propagates along random trajectories, it is practically isotropic.

Stimulated Raman scattering (SRS) of light from dyes in MSM (vesicular films) was found for the first time in [3–5]. As was shown in [6, 7], SRS from laser dyes in MSM is stimulated by RL of these dyes according to a mechanism similar to that of coherent-active Raman spectroscopy (CARS), in which one of the components of dual-frequency pumping is

external laser pumping, while the other component (RL radiation) is formed in the sample. Since the pump wavelength lies within the dye absorption band, the SRS from dye molecules is resonant. Hence, one can easily record Raman lines of dyes in any matrices, because the molecules of the latter are nonresonant and their lines have negligible intensity.

Since RL has a continuous spectrum, SRS manifests itself at all Stokes frequencies lying within this spectrum; therefore, one can select the spectrum of Raman-active vibrations of dyes molecules in the corresponding spectral range. Thus, the continuous RL spectrum makes it possible to determine relatively easily the Raman spectrum of laser dyes (this spectrum is difficult to obtain by conventional Raman spectroscopy because of the luminescence; hence, researchers must use complex methods of inverse Raman scattering [8] or surface-enhanced Raman scattering (SERS) [9, 10]).

In this context, we should mention the works on spontaneous resonant Raman scattering [11, 12] and stimulated resonant Raman scattering (SRRS [13–15]) from dyes. These methods also yield information about Raman spectra; however, these results should be treated with caution, because the physical conditions under which the aforementioned methods are implemented differ significantly from those typical of recording Raman spectra of laser dyes. For example, a necessary condition for recording pontaneous resonant Raman scattering spectra is almost complete quenching of dye luminescence; this procedure calls for special additives, which may affect the vibrations of molecules under study. Recording pontaneous resonant Raman scattering spectra of dyes in crystalline state (in which they generally do not luminesce) is not quite correct either, because intermolecular interactions in crystals differ considerably from those in solutions. In both cases the range of application of the spectra obtained is rather restricted, because one cannot be sure that these spectra correspond to the Raman spectra of dyes in luminescent solutions.

As for SRRS, the main limitations of the method based on this process is the uncertainty in its physical conditions used at high ($\sim$10 GW cm^{-2}) excitation intensities [13–15], which exceed significantly the sample damage threshold, as well as the uncertainty in the mechanism of this process. In this case, it is difficult to identify the state of dye molecules and the conditions under which they exist; accordingly, the interpretation of the results yielded by this technique is ambiguous. At such high excitation intensities, SRS may hypothetically occur with participation of excited electron states of molecules. Some researchers [13–15] proposed that SRS occurs in this case as a result of transitions through a lower intermediate state in the presence of resonance between the scattered radiation and luminescent electronic transition. However,

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since there is no convincing experimental confirmation, the proposed SRS scheme is still debated and there is an uncertainty in interpreting SRS data.

In view of the aforesaid, we proposed a method for determining the Raman spectrum of laser dye molecules from their secondary radiation in MSM [6, 7]; currently, this method is being developed. The secondary radiation is excited by radiation of relatively low intensity (few MW mm^{-2}), which does not cause any sample damage. The spectrum of this radiation consists of two components: an RL-induced continuous component and a line component, which is due to SRS. This secondary radiation can be referred to as SRS–RL; this term reflects not only its nature but also the close relationship of SRS and RL, because SRS does not occur in MSM in the absence of RL. Note that the first attempts of studying SRS in MSM were made by Zubov et al. [16], who experimented with stilbene powders. However, since RL did not occur in these powders, the SRS observed did not differ radically from its analogue in homogeneous media.

The Raman spectrum recorded according to the technique proposed in [6, 7] is totally determined by the position of the RL spectrum with respect to possible Stokes Raman lines for dye, because only those of these lines that fall within this spectrum can be observed. The position of this spectral region can be varied in some range by changing the dye concentration [3, 6], pump power and scattering efficiency in MSM [17]. These possibilities can be significantly extended using the RL radiation of an additional (intentionally introduced into MSM) dye, the spectrum of which is beyond the RL spectrum of the dye under study. Upon excitation of this additional dye, its RL may stimulate SRS on Stokes lines within its spectrum, i.e., in the wavelength range that was previously inaccessible. To implement this version, it is necessary to study the specific features of SRS from a mixture of laser dyes in MSM. Such studies may be of even greater value, because they make it possible to find out important details of interaction between RL and SRS, which must be known to gain a deeper insight into this phenomenon.

2. Characteristics of samples and experimental conditions

Based on the problem stated and the mechanism of SRS excitation in MSM, the pair of dyes should satisfy the following requirements: when a dye mixture is pumped by one source, both dyes must be excited, but RL should occur in only the additional (lasing) dye (A), whereas the RL of the main (scattering) dye (B) must be suppressed.

Excitation of dyes is a fundamental condition for RL of dye A and switching on the resonant SRS mechanism on B molecules [5], which multiply increases the scattering efficiency. The latter circumstance is very important, because SRS may develop only in the region where RL occurs; this region is fairly small (∼0.2 mm in diameter) due to the RL spatial confinement [18, 19]. Since the concentration of dye molecules is relatively low (lower than that of matrix molecules by three orders of magnitude), it is rather difficult to observe nonresonant SRS. Excitation of RL in only dye A is not fundamental for expanding the spectral range in which the Stokes lines of dye B can be observed; however, it is important for unambiguous interpretation of the RL origin.

In view of the aforesaid, we chose a pair of dyes satisfying the following conditions:

(i) the pump wavelength should lie in the absorption bands of both dyes;

(ii) RL should occur in additional dye A;

(iii) the RL spectrum of additional dye A should be in the range of possible Stokes lines of basic dye B;

(iv) to exclude RL of dye B, its gain (luminescence) spectrum must overlap the absorption spectrum of dye A; and

(v) the gain (luminescence) spectra of dyes A and B should be significantly separated to exclude overlap of their RL bands. This requirement is important for determining the origin of the RL of the mixture (i.e., to assign RL to a certain dye) and for expanding the spectral range of the observed Stokes lines of scattering dye B.

Optimal matching (with allowance for the above requirements) can be obtained by choosing appropriate dye concentrations, light scattering efficiency and pump intensity, which affect the mutual position of the luminescence spectra of the dyes and their position with respect to the Raman spectrum of dye B.

In addition, the Raman spectra of the dyes in the pair should significantly differ to facilitate identification of the observed Stokes lines, because Stokes lines of both dyes may arise within the RL spectrum of dye A. Taking into account the fact that the molecules of the dyes have generally similar bonds between atoms and atomic groups (C–C, C–H, C–CH$_3$, etc.) and, therefore, similar vibration frequencies, one should choose dyes belonging to different classes (having a larger number of differing bonds) to facilitate interpretation of the data obtained.

Based on these considerations, we chose the following two dyes: rhodamine 575 (Rh575) and pyrromethene 605 (Pm605). The dyes were introduced (either one at a time or jointly) into a ternary copolymer (vinylidene chloride with acrylonitrile and methyl methacrylate), a layer of which (∼15 μm thick) was coated onto a lavsan substrate. The dye concentrations were, respectively, 3.3 and 1.65 mmol L^{-1}. At these concentrations dye molecules did not form associates in the polymer, as was evidenced by the absence of changes in the absorption and luminescence spectra (at liquid-helium temperatures) in comparison with the spectra of similar films with low dye concentrations (less than 10^{-5} mol L^{-1}).

Closely packed vesicles of gaseous nitrogen with an average diameter of 1.2 μm were formed in the film by photochemical decomposition of azido-containing additive. The radiation of dyes propagated and was amplified in the dye-containing polymer between vesicles, being efficiently reflected from their boundaries due to the total internal reflection, which increases the effective reflectance of diffuse light to 57 % [20]. Due to the close packing of vesicles and effective reflection from their boundaries, the thus obtained film is an efficient MSM, as is evidenced by the presence of a pronounced coherent backscattering peak [21, 22] (Fig. 1), observed in the scattering diagram of the film irradiated with a semiconductor laser (λ = 650 nm). The peak amplitude exceeds the diffuse background amplitude by a factor of 2, which corresponds to the theoretical value. The peak width was $\Delta\theta \sim 2°$; thus, the so-called transport mean free path of radiation $\bar{l} = \lambda/(2\pi\Delta\theta)$ should be 3 μm, a value smaller than the active region diameter (∼0.5 mm) and the film sizes (5×10 mm) by more than two orders of magnitude. This fact indicates that multiple scattering is implemented in the film plane. With allowance for the effective reflection of diffuse light from the film surface, the same regime is implemented in the transverse direction. The efficiency of the film as an MSM is also confirmed by the low RL threshold intensity (∼0.01 MW mm^{-2}, see Fig. 7).
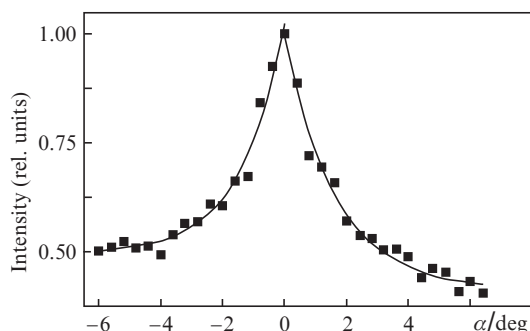
Figure 1. Coherent backscattering peak for a vesicular film: dependence of the scattered laser radiation intensity on the observation angle (counted from the direction inverse to the incident beam direction).

Figure 2. (1, 2) Absorption and ($1'$, $2'$) luminescence spectra of the (1, $1'$) Rh575 and (2, $2'$) Pm605 dyes in a uniform (vesicle-free) polymer film. The horizontal segments indicate the position of the SRS–RL spectra of the (3) Rh575 and (4) Pm605 dyes and (5) their mixture in a vesicular polymer film and (6) the range of likely location of SRS spectra for Rh575.

The SRS–RL spectra of dyes in vesicular films were recorded at liquid-helium temperatures ($\sim 7-8$ K). Under these conditions, the SRS was more pronounced in the RL spectrum because of the reduced RL threshold, less spectral broadening of Raman lines and better matching of the RL spectral profile with the spectral range of Stokes Raman lines. For correct comparison of the mutual position of SRS–RL spectral ranges and the luminescence and absorption spectra, the latter were recorded at the same temperatures.

The effective scattering of radiation from vesicles led to the red shift of the luminescence spectrum due to the increase in the re-absorption efficiency of this radiation in the overlap region of its spectrum with the absorption spectrum and subsequent re-emission into the red wing [17]. We did not observe any additional bands in the luminescence spectrum, which would indicate the influence of surface vesicles on the emission of dye molecules.

The samples were optically pumped by the second harmonic of a Q-switched Nd^{3+}:YAG laser. The pump intensity was varied within $0.01-2$ MW mm^{-2} using neutral filters. The laser beam diameter was ~ 0.5 mm. The emission spectra per pulse were recorded by a diffraction spectrograph equipped with a CCD array (spectral resolution 0.3 nm). The assignment of the line component of the RL spectra to the SRS spectrum was verified using a tuned Nd^{3+}:phosphate glass laser.

The IR absorption spectra of the dyes, which must be known to determine the vibrational frequencies of their molecules, were recorded with a Nicolet 470 Fourier spectrometer by the standard technique (using KBr pellets).

3. Experimental results and analysis

Figure 2 shows the absorption and luminescence spectra of the Rh575 and Pm605 dyes in a homogeneous (vesicle-free) polymer film. It can be seen that the absorption spectrum of the Pm605 dye is red-shifted by 25 nm with respect to the similar spectrum of the Rh575 dye and significantly overlaps the luminescence spectrum of the latter. Hence, the RL of the Rh575 dye in the mixture must be suppressed, and, therefore, this dye plays the role of scattering dye B, while Pm605 acts as the additional (lasing) dye A. It can also be seen in Fig. 2 that both dyes are excited equally well by the second harmonic of Nd^{3+}:YAG laser ($\lambda_p = 532$ nm).

Figure 2 shows the position of the SRS–RL spectra of the Rh575 and Pm605 dyes and their mixture in the corresponding vesicular films, as well as the range of likely existence of
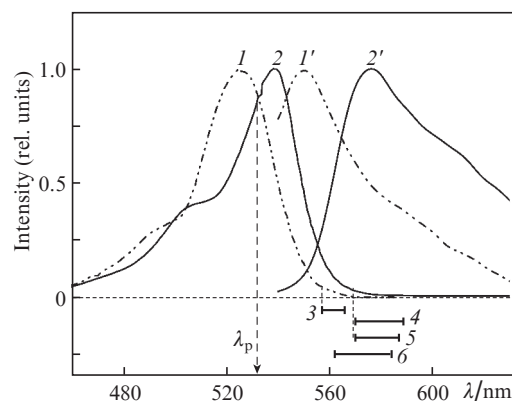
Rh575 Stokes lines, which was found from the vibrational frequencies of the Rh575 IR absorption spectrum. It can be seen that, due to the mutual shift of the luminescence spectra of the dyes, their SRS–RL spectra are separated. Since the position of RL spectra depends strongly on the dye concentrations in the mixture [3, 6], the latter were chosen to exclude overlap of these spectra (3.3 and 1.65 mmol L^{-1}).

The range of location of Rh575 Stokes lines cannot be found directly by recording the Rh575 Raman spectrum because of the strong luminescence (typical of laser dyes). To date, these spectra have been recorded for only few dyes using inverse Raman scattering [8] and SERS [9, 10]. However, this hindrance can be overcome using the so-called Raman pseudo-spectrum, plotted on the basis of the IR-absorption vibrational frequencies, which are comparable with the Raman-shift frequency. Within this approach, the frequencies of the pseudo-spectrum are determined as $\nu_S = \nu_p - \nu$, where ν_p and ν are, respectively, the pump and IR absorption frequencies [17]. The Raman pseudo-spectrum does not reflect the real intensity distribution for possible Stokes lines; however, it allows one to find their frequencies. It can be seen in Fig. 2 that the thus determined range of location of likely SRS lines of Rh575 overlaps the SRS–RL ranges of the Pm605 laser dye and the Rh575–Pm605 mixture.

The Raman pseudo-spectra also make it possible to draw conclusions about the differences in the likely SRS spectra of the pair of dyes in use. It can be seen in Fig. 3 that most of the frequencies within an isolated window (corresponding to the spectral range of the SRS–RL mixture) in the pseudo-spectra of the Rh575 and Pm605 dyes do not coincide. Hence, one can unambiguously assign these lines to a particular dye.

Thus, proceeding from the spectroscopic data for Rh575 and Pm605, this pair of dyes satisfies the above-stated conditions for experimental study.

Figure 4a presents the SRS–RL spectra of a vesicular film with a Rh575–Pm605 mixture (a two-component film) with dye concentrations of 3.75 and 1.65 mmol L^{-1}, respectively, with a change in the pump intensity by an order of magnitude. For comparison, Figs 4b and 4c show similar spectra for the films containing separately dyes A and B (one-component films). In the one-component films the Rh575 concentration is approximately the same (3 mmol L^{-1}) as in the mixture,
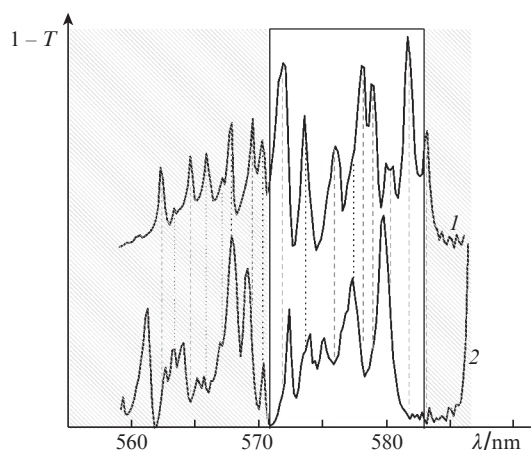
Figure 3. Raman pseudo-spectra of the (*1*) Rh575 and (*2*) Pm605 dyes, plotted on the basis of their IR absorption spectra; it is assumed that the line intensities in the pseudo-spectra are proportional to the attenuation $1 - T$, where T is the IR transmittance of the dyes. For clarity, the spectra in Figs 3, 4 and 6 are shifted along the ordinate axis.

while the Pm605 concentration is taken to be higher by a factor of almost 2 (3 mmol L^{-1}) to make the SRS lines of this dye more pronounced (these lines can hardly be observed at lower concentrations).

As follows from Fig. 4, an increase in the pump intensity leads to a shift and expansion of the SRS–RL spectra to the longer wavelength region for all three films, which is caused by the red shift of the gain spectrum [17]. It can also be seen that the RL spectra of the two-component film, which correspond to the continuous components of the secondary-emission spectra, lie in the same spectral range and change practically in the same way as the similar spectra of Pm605 in the one-component film. On the contrary, the RL spectra of Rh575 in the one-component film are beyond this range (at the same dye concentration as in the mixture) at any pump intensity and change differently with an increase in this parameter. This finding proves that specifically the Pm605 dye emits in the mixture-containing film, whereas RL of the Rh575 dye is absent.

A general feature of the one- and two-component films is the occurrence of spectral lines within the RL spectrum at pump intensities exceeding the RL threshold by almost an order of magnitude. The intensities I_S of these lines are proportional to both the pump intensity I_p and the RL intensity at the corresponding-line wavelength (I_{RL}) (Fig. 5); this correlation is in agreement with the above-considered mechanism of SRS excitation by dual-frequency pumping, which is similar to CARS. Therefore, the observed linear dependence $I_S = f(I_{RL}I_p)$ (shown in Fig. 5 for one of the strongest Rh575 lines in the spectrum of the two-component Rh575–Pm605 film) confirms that these lines are due to SRS. The observed SRS from the film is resonant, because the excitation wavelength falls in the absorption bands of both dyes. This is evidenced by the absence of Raman lines of the polymer matrix in the secondary-emission spectrum of the films, the molecular vibrations in which are not resonant, although these lines are fairly strong in the aforementioned range and are well-pronounced under conditions of nonresonant spontaneous Raman scattering.

Figure 6a shows the SRS–RL spectrum for the two-component Rh575–Pm605 film [curve (*1*)] and a similar spec-
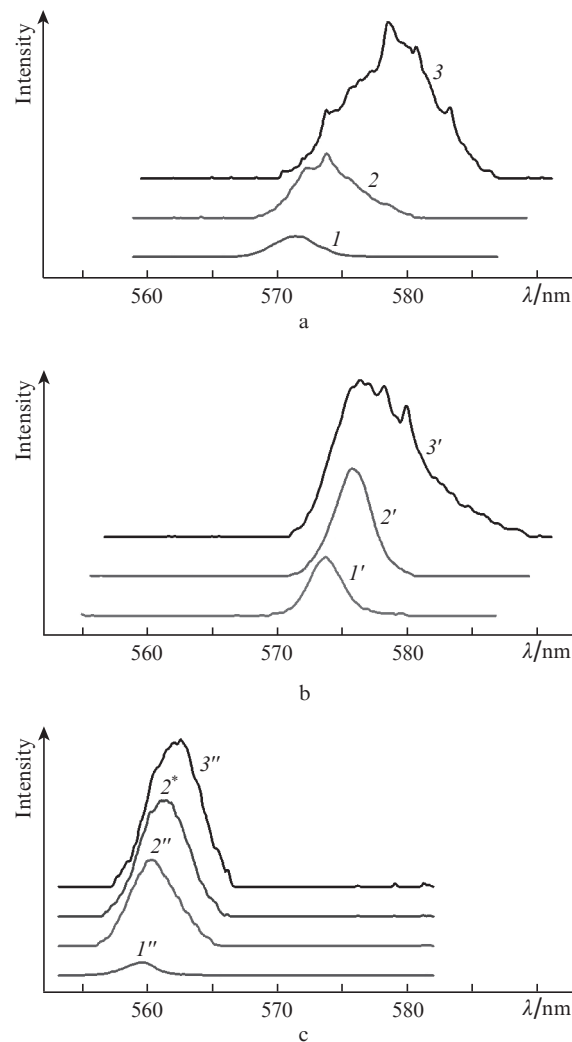

Figure 4. SRS–RL spectra of vesicular films: (a) two-component Rh575–Pm605 film and (b, c) one-component (b) Pm605 and (c) Rh575 films at pump intensities $I_p = ($ *1, 1′, 1″*$)$ 0.1, (*2, 2′, 2″*) 0.6, (*2**) 1.3 and (*3, 3′, 3″*) 2 MW mm^{-2} and dye concentrations (a) 3.3 and 1.65 mmol L^{-1} and (b, c) 3 mmol L^{-1}.
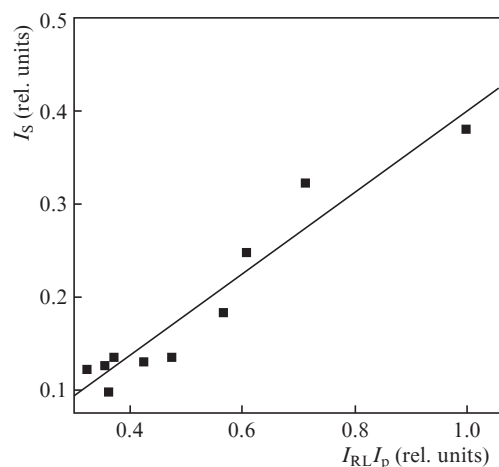

Figure 5. Dependence of the line intensity at $\lambda = 573.6$ nm in the secondary-radiation spectrum of the two-component vesicular Rh575–Pm605 film on the product of pump intensity I_p and the RL intensity I_{RL} at this wavelength.

trum for the one-component Pm605 film [curve (2)]. It can be seen that the spectrum of the two-component Rh575–Pm605 film contains spectral lines that are absent in the SRS–RL spectrum of the one-component film containing only the Pm605 dye. Figure 6b presents difference spectrum (3) obtained by subtracting spectrum (2) from spectrum (1), with a factor chosen so as to make the line component dominate in spectrum (3). It can be seen that the wavelengths of the spectral lines in the difference spectrum coincide well with the line wavelengths for the line component [Fig. 6c, curve (4)] of the SRS–RL spectrum of the film containing only the Rh575 dye. This component was obtained using a high (5 mmol L^{-1}) Rh575 concentration, at which the RL spectrum significantly expands and stimulates SRS in a wider range. With a change in the pump wavelength by 3.5 nm, this component is shifted by the same value [Fig. 6c, curve (5)], which proves its Raman scattering nature.
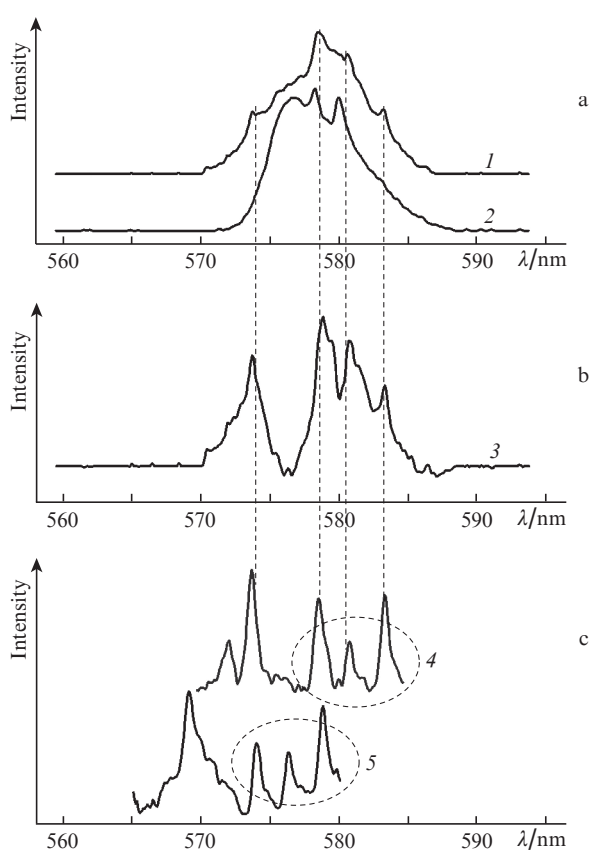

Figure 6. (a) SRS–RL spectra of (1) vesicular two-component Rh575–Pm605 film and (2) one-component Pm605 film, (b) the difference spectrum (3) and (c) the line components of the SRS–RL spectrum of the Rh575 dye at pump wavelengths λ_p = (4) 532 and (5) 528.5 nm. The dye concentrations are (1) 3.3 and 1.65 mmol L^{-1} and (2) 3 mmol L^{-1}; the pump intensity I_p = 2 MW mm^{-2}.

The above data indicate that the RL of the Pm605 dye in the two-component film stimulates SRS of the Rh575 dye and thus makes its Stokes lines pronounced beyond the RL spectral range (Fig. 4). Based on this fact, one can draw two important conclusions. First, this stimulation corresponds to the classical CARS version, in which scattering molecules (Rh575) are excited by external radiation (from Pm605 molecules); therefore, it is a direct experimental confirmation of

the SRS–RL mechanism (similar to CARS) in MSM. Second, the formation of Stokes SRS lines beyond the RL spectrum of intrinsic molecules makes it possible to extend the observation range of these lines and thus increase the potential of the method used to obtain the Raman spectrum of dye molecules from the spectrum of dye secondary emission in MSM [7].

The data in Fig. 4 suggest an important conclusion on the interaction between dyes in a dye mixture film when RL is formed (the continuous spectral component in Fig. 4). Since only some part of absorbed pump energy is spent to excite each (kth) dye in the mixture, it is expedient to compare the RL spectra of two- and one-component films at identical effective pump intensities I_{eff}, which correspond to identical energies absorbed by dyes in these films. In the one-component film the effective value is equal to the incident pump beam intensity I_p. In the two-component film, it can be estimated from the ratio of the absorption coefficient of this dye to the total absorption coefficient of both dyes:

$$I_{\text{eff}\,k} = I_p(1 - T)\frac{\sigma_k C_k}{\sigma_k C_k + \sigma_{k'} C_{k'}},$$

where $\sigma_k, \sigma_{k'}$ and $C_k, C_{k'}$ are, respectively, the absorption cross sections at the pump wavelength and the concentrations of the kth and k'th dyes; T is the component of the vesicular film transmittance that is due to the absorption of both dyes.

For the dye concentrations and film thicknesses used by us, $T \ll 1$. In a vesicular film the T value decreases additionally because of the increase in absorption [23], which is due to the elongation of the pump radiation path under multiple scattering. Neglecting the relatively low ($\sim$30%) difference in the absorption cross sections of the Pm605 and Rh575 dyes [24], one can assume that the effective intensities for the two-component film are mainly determined by the ratio of their component concentrations (2:1); at the pump intensity I_p = 2 MW mm^{-2}, they are, respectively, 0.6 and 1.3 MW mm^{-2}. These values correspond to the RL spectra of dyes 2' and 2* (Figs 4b, 4c). If the dye emission intensities in a two-component film corresponded to the effective intensities, the RL spectrum of this film [Fig. 4a, curve (3)] would be (at the aforementioned I_p value) a superposition of spectra (2') and (2*). However, since the RL of the Rh575 dye in the two-component film is suppressed, its spectrum should be close to spectrum (2') of the one-component Pm605 film. However, in reality the RL spectrum of the two-component Rh575–Pm605 film is close not to spectrum (2') (corresponding to the pump intensity acting on Pm605) but to spectrum (3'), corresponding to the total beam intensity incident on the film. The same holds true for other pump intensities: the RL spectra of the two-component Rh575–Pm605 film (1, 2) and the one-component Pm605 film (1', 2') are similar under identical pumping conditions.

These facts indicate that, despite the absorption of the pump radiation by both dyes, the total energy absorbed in the mixture is accumulated in the Pm605 dye. This means that there is an efficient energy transfer from Rh575 molecules to Pm605 molecules in the two-component film. Taking into account the significant overlap of the luminescence spectra of Rh575 and absorption spectra of Pm605 (Fig. 2), this transfer can be caused by both re-absorption of the energy (emitted by Rh575) by the other dye and the nonradiative energy exchange between molecules of these dyes. The former mechanism is favoured by multiple scattering, which significantly elongates the radiation path in the film and thus increases the re-absorp-

tion probability. The latter mechanism is facilitated by the commensurability of the average distance between dye molecules (~ 5 nm at a concentration of 5 mmol L^{-1}) and the molecular sizes, which makes resonant dipole mechanism likely.

Another evidence of active energy transfer is the coincidence of the RL thresholds (defined as the pump intensity at which emission with a minimum spectral width is settled [25]) of the two-component Rh575–Pm605 film and one-component Pm605 film [Fig. 7, curves (*1, 2*)]. If the emission of the Pm605 dye in the mixture was determined by the molecules excited by only intrinsic absorption (i.e., the effective pump intensity), this threshold would be higher by a factor of 3, because only one third of the pump energy would be spent on their excitation. The coincidence of the thresholds can be explained on the assumption that the pump energy absorbed by both dyes is accumulated in the lasing Pm605 dye. This conclusion is also consistent with the shape of the curve $\Delta\lambda(I_p)$, which is identical for the two-component Rh575–Pm605 film and the one-component Pm605 film but differs significantly from the shape of the curve for the similar Rh575 film. The RL energies of the two-component (Rh575–Pm605) and one-component (Pm605) films are also close: they differ by no more than 15% rather than by a factor of 3, as one would expect if the RL energy of the mixture was determined by the pump energy absorbed by only Pm605 molecules.
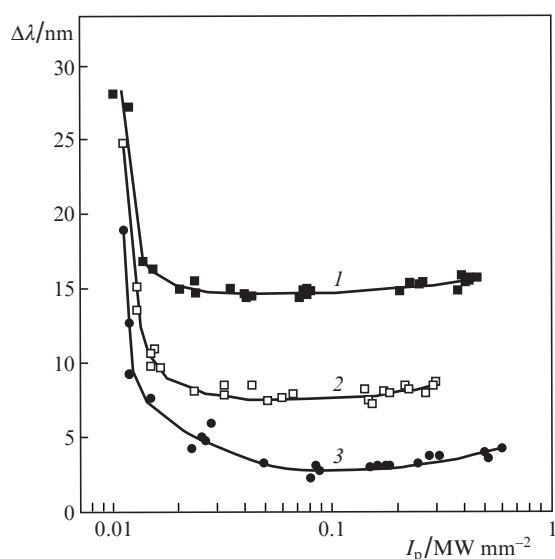

Figure 7. Dependences of the width $\Delta\lambda$ of the secondary-emission spectrum of the (*1*) vesicular two-component Rh575–Pm605 film and (*2, 3*) one-component (*2*) Pm605 and (*3*) Rh575 films on the pump intensity. Curves (*1*) and (*2*) are shifted for clearness along the vertical axis by 12 and 6 nm, respectively.

The data obtained demonstrate that different dyes in MSM can efficiently interact. This interaction occurs through stimulation of SRS for one dye by the RL radiation of the other dye according to a mechanism similar to CARS and via excitation-energy exchange between their molecules. The energy transfer yields additional possibilities for optimising the conditions for observing SRS lines by choosing a proper ratio of the dye concentrations in the mixture.

4. Conclusions

Our studies revealed that the RL of a dye additionally introduced into an MSM with a mixture of laser dyes may efficiently stimulate SRS on the Stokes lines of the main dye within the RL spectrum. This is a direct confirmation of the fact that the mechanism of SRS excitation for laser dyes in MSM is similar to CARS.

The stimulation by additional-dye RL allows one to observe Stokes SRS lines for the main dye in a new spectral region. This circumstance makes it possible to extend the observation range of the Raman spectrum for this dye and thus facilitate determining the vibrational spectrum of dye molecules from the SRS–RL emission spectrum [7].

There is interaction between dyes in an MSM, which manifests itself both in stimulation of SRS from one dye by the RL of the other dye and in the energy exchange between molecules of these dyes, provided that their luminescence and absorption spectra overlap. This effect allows using more rationally the pump energy absorbed in an MSM with a dye mixture for RL excitation.

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