Shape of stimulated secondary-radiation spectra of dye solutions

B. S. Neporent, A. G. Spirō, V. B. Shilov, and B. D. Faĭnberg
S. I. Vavilov State Optical Institute

(Submitted 2 October 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **33**, No. 3, 133–136 (5 February 1981)

It is shown that the resonant stimulated Raman scattering (RSRS) spectra of dyes ("dip-line"), which are observed against the background of their broad superluminescence bands, are not related to molecular processes: they are, however, attributed to the propagation anomalies in an amplifying medium of a narrow-band signal, which is located in the overlap region of its superluminescence and weak-absorption bands.

PACS numbers: 42.65.Cq, 42.50. + q, 78.30.Cp

The peculiar shape of the secondary-luminescence spectra was established in studies[1–3] of the resonant Raman scattering for laser excitation of frozen and liquid solutions of polymethine and xanthene dyes. The lines of the Stokes resonant stimulated Raman scattering (RSRS), which are accompanied by dips on the high-frequency side (i.e., on the low-frequency side of the molecular vibrations that participate in the Raman scattering), are observed in these spectra against the background of the continuous superluminescence (SL) band. A typical spectrum of this kind for a solution of rhodamine 6G in ethyl alcohol, according to our data, is shown in Fig. 1 (curve 1a) at the top. About two dozen papers, in many of which the characteristic shape of the "dip-line" spectra was attributed to the interference of the states responsible for the transitions, or to the influence of relaxation processes which restrict the rate of emptying or filling of these states, or to inverse Raman scattering, or, finally, to four-photon parametric processes, have been devoted to possible causes of the appearance of such spectra. We have shown[4] that the discussed explanations are in consistent.

We show in this communication that the unique shape of the examined secondary-luminescence spectra is a consequence of the propagation and amplification in an inverted superluminescing medium of any independent narrowband signal that is located in the region of the broad SL spectrum $S^* \rightarrow S_0$, provided that a small absorption $S_0 \rightarrow S^*$ exists in this region. This condition is satisfied in the systems discussed in Refs. 1–4 because of severe overlapping of the equilibrium absorption and the luminescence spectra.

We shall consider the experimental evidence of the formulated hypothesis.

Figure 1 (curve 1a) shows the secondary-luminescence spectrum of a rhodamine 6G solution in ethyl alcohol, which was excited by a high-power ($\Phi_e \approx 10^{25}$–10^{26} quanta/cm^2·sec) pulse of the doubled frequency of neodymium-laser radiation ($\nu_e \approx 18{,}800$ cm^{-1}). At this excitation frequency the RSRS lines, which correspond to the frequencies of the molecular vibrations $\nu^v = 1067$–1652 cm^{-1}, are superimposed on the SL spectrum of the solution. All measures were taken in the experiment (see Ref. 5) to

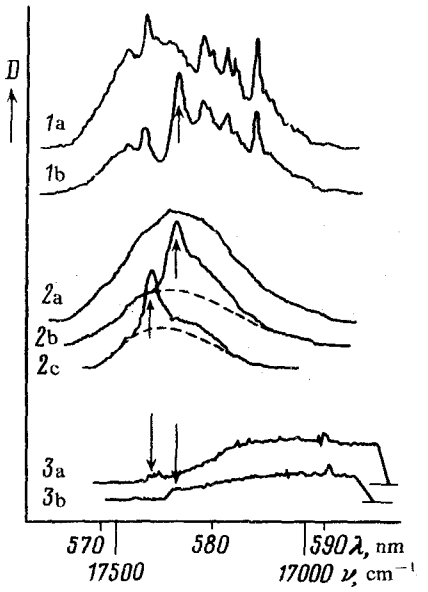

FIG. 1. Photomicrograms of spectra. The frequencies ν_c of the narrow-band radiation "lines" are indicated by arrows.

exclude the intrinsic interference structure of the superluminescence spectrum. As a result of excitation by the tripled frequency of the Nd laser ($\nu_e \approx 28{,}200$ cm^{-1}), the Raman scattering spectrum (RSRS) is located far outside the SL region, whose smooth spectrum is shown in Fig. 1 (curve 2a).

To simulate the Raman scattering line, we introduced into the exciting radiation with ($\nu_e \approx 18{,}800$ cm^{-1}) an additional narrow-band radiation from a tunable dye laser ($\nu_c \approx 17{,}340$ cm^{-1}, $\Delta\nu_c \approx 30$ cm^{-1}, and $\Phi_c \approx 10^{24}$ quanta/cm^2·sec). In this case the scattered "line" $\nu_c \approx 17{,}340$ cm^{-1}, which is accompanied by the same characteristic "dip" as the RSRS lines surrounding it (Fig. 1, curve 1b), is also superimposed on the superluminescence spectrum. If the narrow-band radiation ν_c is added to the exciting radiation $\nu_e \approx 28{,}200$ cm^{-1}, then the smooth SL spectrum will be weakened significantly (see the dashed curves 2b and 2c in Fig. 1) and the radiation consisting of a scattered narrow-band "line", which is sharply limited on the short-wavelength side and has a peculiar wing on the long-wave side (see Fig. 1, curve 2b for $\nu_c \approx 17{,}340$ cm^{-1} and curve 2c for $\nu_c \approx 17{,}410$ cm^{-1}) will be superimposed on it. Finally, the figure shows (curves 3a and 3b) the spectra of the "wings" excited by the "lines" $\nu_c \approx 17{,}340$ cm^{-1} or $\nu_c \approx 17{,}410$ cm^{-1}, which are obtained with no pump radiations ν_e. The power $\Phi_c \approx 10^{24}$ quanta/cm^2·sec of the narrow-band radiation is sufficient to obtain inversion, although it is relatively low.

The mechanism of the examined effects can be summarized as follows.

Secondary-radiation signals (RSRS and SL) are formed as a result of amplification in an inverted medium of the components of fluorescence and Raman scattering, which are produced independently of each other in the entire active volume when it is

excited (at right angles to the cell length) and which propagate along the length of the cell. The signals, which are produced at the edge of the cell opposite the exit window and which traverse the longest path in the active medium in which they are converted into stimulated radiation (RSRS and SL), experience the largest amplification. It is important that, according to Ref. 6, the inversion distribution along the length of superluminescing solution has a sharp maximum in the middle of the cell and decreased to low values at its edges. The small inversion in the vicinity of the edges, where the secondary radiation is mainly formed, corresponds to relatively high values of the absorption coefficient of the solution. The RSRS and SL signals undergo different conversions after absorption: the SL signal is re-emitted, while each absorbed RSRS line is converted into an SL band which is shifted toward the red side in accordance with the amplification curve for small inversion. This is illustrated by curves 3a and 3b in Fig. 1 for the two "lines."

As the signals propagate toward the center of the cell in presence of high-intensity pumping, all three signals (the primary "lines" and SL, as well as the re-emitted SL) are amplified, and the band maxima are shifted toward the blue side in accordance with the shape of the amplification spectrum for high inversion. In this case the secondary SL bands approach the lines that excite them. This situation is illustrated in Fig. 1 by curves 2a (SL spectrum in the absence of "lines"), 2b and 2c (intrinsic SL spectrum is attenuated because of the loss of some inversion due to amplification of the "lines"; the lines with red wings caused by the secondary SL are superimposed on it).

It is easy to see from the foregoing discussion that the observed RSRS + SL spectrum (curve 1a in Fig. 1) consists of an attenuated continuous SL band on which a series of RSRS lines with their wings are superimposed. A mental extrapolation of the edges of the SL spectrum to its center in the earlier papers created the illusion of a continuous SL spectrum with dips.

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Translated by Eugene R. Heath.
Edited by S. J. Amoretty