INTENSITY DISTRIBUTION IN STIMULATED RAMAN SCATTERING SPECTRA

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The line intensity of stimulated Raman scattering spectra (SRS) is investigated as a function of the exciting light intensity. The measurements are carried out in intensity regions above and below the experimental threshold for a single flash. The intensity distribution in SRS spectra is investigated for several Stokes and anti-Stokes components. The existence of a considerable wing accompanying each component is detected. A structure of the first Stokes component of SRS is found and is investigated in the "threshold" region and below the "threshold."

STIMULATED Raman scattering of light (SRS) is a typically nonlinear optical phenomenon occurring when high-power radiation acts on a substance. While it is undoubtedly related to ordinary Raman scattering of light, SRS has many distinguishing features, which are usually considered characteristic of radiation from lasers (small line width, sharply pronounced directivity along the beam of the exciting light, etc.). In view of its distinguishing properties, great interest attaches to the study of the characteristics of SRS and to an elucidation of factors that lead to the transition from ordinary Raman scattering to SRS.

We present in this paper the results of an investigation of the distribution of the intensity in SRS spectra (the main results pertain to the first Stokes component). These results were obtained for different exciting radiation intensities. We also consider in this connection the question of the nature of the SRS threshold.

LINE INTENSITY IN THE SPECTRUM OF STIMULATED RAMAN SCATTERING

According to the general theory of Raman scattering of light,[1] the probability W of Raman scattering is given by the expression

$$W = (k_1 J + k_2) I, \tag{1}$$

where J is the intensity of the Raman scattering lines, I the intensity of the exciting radiation, k_1 characterizes the stimulated Raman scattering, and k_2 the spontaneous scattering. It must be borne in mind that k_1 and k_2 are functions of the frequency and are determined by the convolution of the line contour of the exciting radiation and the contour of the Raman line proper. This convolution characterizes the observed contour of the Raman line.[2]

We consider a simplified model of the phenomenon.[3] Let the exciting radiation and the Raman line be for the time being monochromatic (with frequencies ν and ν' respectively). The exciting radiation, which has an intensity I_0 at the entrance window of the cell, propagates along the cell axis in the form of a plane wave. We assume that only a small fraction of the incident radiation is scattered in this case. The medium is characterized by an absorption coefficient α, which is the same for the exciting radiation and for the Raman scattering. We confine ourselves to consideration of only the first Stokes component, and assume that the intensity of the remaining components is negligibly small. Then the intensity of the scattered radiation J at the exit window of a cell of length l is determined by the expression (see [3])

$$J = \frac{(k_2/k_1)\{\exp[lk_1(k_2/k_1 + I_0)] - 1\}}{1 + (k_2/k_1 I_0)\exp[lk_1(k_2/k_1 + I_0)]} e^{-\alpha l}. \tag{2}$$

We denote by π the exciting light intensity corresponding to the threshold of experimental observation of SRS during one flash, and by J_0 the intensity of the SRS line under these conditions. Expression (2) can be represented in the form

$$\ln\left[1 + \frac{k_1}{k_2}(J - J_0)\right] = k_1 l (I_0 - \pi). \tag{3}$$

This expression is convenient for comparison with experiment, since it contains quantities that can be readily obtained experimentally, namely $J - J_0$, which is the registered SRS intensity, and $I_0 - \pi$, which is the excess of the intensity of the exciting radiation over the threshold value. The solid lines in Fig. 1 indicate the approximate dependence of the intensity of spontaneous and stimulated Raman scattering on the intensity of the exciting light. The spontaneous radiation varies linearly and the stimulated one exponentially.

In the case of negligibly small absorption we can speak only of an experimental observation threshold corresponding to the intensity of the exciting light π, i.e., the threshold due to the sensitivity of the recording apparatus. In the presence of absorption, the picture does not change in principle. The intensity of Raman scattering, whether stimulated or spontaneous, decreases in a cell of fixed length by a factor $e^{-\alpha l}$. Figure 1 shows (dashed) approximate plots of the spontaneous and stimulated scattering intensities in the presence of absorption.

The threshold is usually defined in the literature[4, 5] as the exciting light intensity at which the loss or decrease in Raman-scattering intensity is compensated by the increase in intensity due to the stimulated emission. In other words, the threshold is assumed to be the exciting light intensity at which the total intensity of the stimulated and spontaneous Raman scattering is equal to the intensity that would be possessed by the spontaneous Raman scattering in the absence of absorption. This point is designated in Fig. 1 by an asterisk. We emphasize that in experimental studies of the dependence of the Raman-scattering intensity on the exciting light intensity this point is not distinguished in any way.[1)]

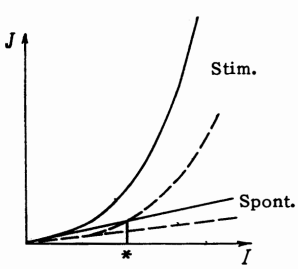

FIG. 1. Character of the dependence of the intensity of spontaneous and stimulated Raman scattering on the intensity of exciting radiation.

To obtain the SRS spectra we used an ordinary setup with a ruby laser Q-switched by a rotating prism. The method of measuring the SRS line intensity was described in detail in earlier papers.[6, 7] For control purposes, the total energy of the exciting radiation was registered in several series of experiments by means of a vacuum photocell, the measurements being based on the discharge of a capacitor with the aid of the photocurrent.[8]

In the registration of the spectrum, we confined ourselves in most cases, as is customary, to a single flash. The terms "threshold" and "threshold value" will pertain from now on to a single flash. In the case when several flashes were used for registration, we succeeded in recording SRS at exciting light intensity below the "threshold value." For example, after 30 flashes the intensity of the exciting light could be five times lower than the "threshold" (the main results obtained by us pertain to an intensity smaller than "threshold" by a factor 2–3).

We note that "ordinary" Raman scattering could not be registered even after 40 flashes of the laser.

We proceed to quantitative results. For a dependence of the intensity of the first Stokes SRS line on the intensity of the exciting radiation, in accord with formula (3), a direct proportionality should exist between the logarithm of the registered SRS intensity and the excess of exciting-light intensity over the "threshold value." An experimental study of this dependence was reported in [3]. The agreement between the calculation and the experiment turned out to be perfectly satisfactory. The results obtained for the relation in question in the region below "threshold" are given for nitrobenzene in Fig. 2 (the intensities are given in arbitrary units). The "threshold value" corresponds in the figure to the null point. The experimental results are represented by the circles, and the calculation results by the straight line. It is seen that agreement between the calculation and the experiment is perfectly satisfactory.

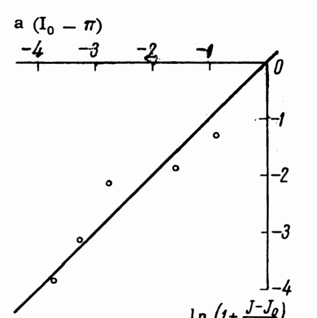

FIG. 2. Intensity of stimulated Raman scattering vs. intensity of the exciting light for nitrobenzene ($\Delta\nu$ = 1365 cm^{-1}) below the "threshold" (a, b—constants, c[3]).

The data clearly demonstrate the arbitrary nature of the SRS "threshold." The "threshold" intensity of the exciting radiation is a purely experimental quantity, due only to the sensitivity of the recording part of the apparatus. It can also be concluded that the simplified model of the phenom-

1)The authors are grateful to V. N. Lugovoi for a useful discussion of this question.

enon presented above describes sufficiently well the observed dependence of the SRS line intensity in the region below the "threshold."

LINE STRUCTURE IN SRS SPECTRA

It is of great interest to determine the distribution of the intensity in the SRS spectra. The ratio of the intensities of the different Stokes and anti-Stokes components and the distribution of the intensity within these components have a complicated character and depend on the intensity of the exciting light.

An investigation of the structure of the spectra of several Stokes and anti-Stokes components, using an instrument with relatively small dispersion, has shown that the spectral line is accompanied by a relatively strong background. This intensity distribution, which can be called the "coarse structure of the line," was investigated in greater detail by us in carbon disulfide. Examples of microphotograms of the intensity distribution of the background, with a sharp line superimposed on it, are shown in Fig. 3 for different components. In the Stokes region of the spectrum, the background has the form of a wing on one side of the corresponding component. This wing is shifted aside from the exciting line. The intensity of the wing relative to the intensity of the line increases with increasing number of the harmonic. The width of the wing, measured from the center of the line, is approximately 30 cm^{-1}.

In the anti-Stokes region, the lines are also accompanied by wings, but the picture is in this case much more complicated. For the first anti-Stokes component, the background is located on the side remote from the exciting line. For the second, third, and fourth components the background is located on the side close to the exciting line, is much more clearly pronounced, and has a higher intensity relative to the line than in the Stokes region. Under certain conditions one observes a clearly pronounced maximum of the background, shifted relative to the maximum of the line. The shift increases on going from the second component to the third and fourth, reaching 30–35 cm^{-1} for the third component and 50–60 cm^{-1} for the fourth. The band width of the background increases in the same direction.

The intensity of both the Stokes and the anti-Stokes components of the background changes little with change of the exciting light intensity, whereas the intensity of the lines themselves changes very strongly. Therefore the best conditions for disclosing the indicated background occur at a slight excess over threshold. There are indications in the literature that certain SRS lines have a tendency to smear and that the background near them has a complicated structure.[9] This, however, does not pertain to the first Stokes component, whose sharpness is usually emphasized. It must be noted, to be sure, that the observation of the background in the case of the first Stokes component is greatly hindered by the fact that the intensity of this background is much lower than the intensity of the line. The origin of this background still seems unclear to us.

Let us proceed to the intensity distribution within the limits of the SRS line proper.

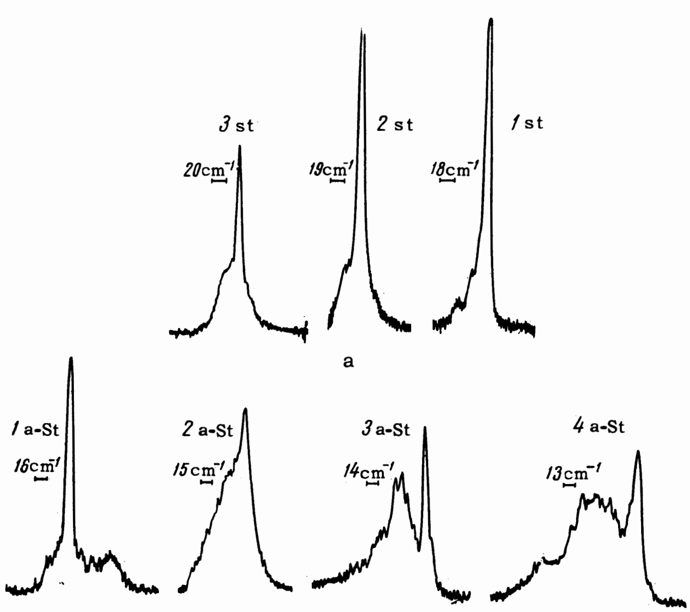

FIG. 3. Distribution of the intensity of the background near the stimulated Raman scattering lines: a—for Stokes components, b—for anti-Stokes components.

The foregoing analysis has pertained to the case of monochromatic exciting radiation and a monochromatic Raman line. Allowance for the finite line width of the exciting radiation and the finite width of the proper Raman line makes it possible to obtain the contour of the radiation line. In this case we must use in place of the frequency-independent k_1 and k_2 (see [2])

$$k_1 = k_1{}^0 \int_{-\infty}^{+\infty} \rho(\nu' - \nu)\rho_0(\nu)\,d\nu,$$

$$k_2 = k_2{}^0 \int_{-\infty}^{+\infty} \rho(\nu' - \nu)\rho_0(\nu)\,d\nu. \tag{4}$$

Here k_1^0 and k_2^0 are constants, $\rho_0(\nu)$ is the contour of the exciting line, and $\rho(\nu')$ the proper contour of the Raman line. Taking these expressions into account, we can evaluate the expected narrowing of the Raman line with increase in intensity of the exciting radiation. We assume dispersion equations for $\rho(\nu')$ and $\rho_0(\nu)$, and then for an intensity J_{sp} of the spontaneous Raman scattering the contour will have a dispersion shape

$$J_{sp} = I_0 l k_2{}^0 \frac{1}{1 + (\nu - \nu_0')^2} \tag{5}$$

with half width $\nu - \nu_0' = \delta = 1$.

In the case of SRS, the contour is described by the complicated function (2). For large excess above "threshold," taking into consideration the smallness of the ratio k_2/k_1 compared with I_0 and the smallness of the absorption, expression (2) can be written in the form

$$J = (k_2 / k_1) \exp(l k_1 I_0). \tag{6}$$

where k_1 and k_2 are given in (4). The half-width of this distribution can be represented in the form

$$\delta = \nu - \nu_0' = \left(\frac{\ln 2}{I_0 l k_1{}^0 - \ln 2}\right)^{1/2} \approx \left(\frac{\ln 2}{I_0 l k_1{}^0}\right)^{1/2}. \tag{7}$$

This expression determines the dependence of the SRS line width on the exciting light intensity within the framework of the model under consideration.

Experiment yields the following results. At an exciting-radiation power exceeding the "threshold" by a factor 2–4, a single narrow line is observed with approximate half-width 1.5 cm^{-1}, due to the width of the apparatus function of the employed spectral instrument. These results confirm the narrowing of the SRS line compared with the ordinary line. In investigating the line structure near the "threshold value" and for a small excess of "threshold," one observes a unique splitting of the lines into several components.[10] The splitting has an irregular character: the number of the components changes from one or two to five or six, and the distance between the extreme components changes from 2–3 to 10–12 cm^{-1}. Sample microphotograms for this case are shown in Fig. 4.

The results of the investigation of the line structure at an exciting light intensity 2–3 times smaller than "threshold" turns out to be quite unexpected. Measurements were carried out with the nitrobenzene line $\Delta\nu$ = 1365 cm^{-1}, the width of which in ordinary Raman scattering is quite large—approximately 8 cm^{-1}. Since the registration was carried out in this case by superimposing on one place scattered lines due to many flashes, we can expect a single sufficiently broad line to be observed. The nature of the width of this line could be connected with the line width in ordinary Raman scattering, or else with averaging, over many photographs, of the structure observed at exciting-line intensities close to "threshold." Experiment has shown, however, that the line structure is conserved, and the spectrum displays several components. A sample microphotogram is shown in Fig. 4. The reason for the occurrence of this structure is unclear to us. To explain many questions connected with the distribution of intensity in SRS spectra it is apparently necessary to develop a more complete and rigorous SRS theory.

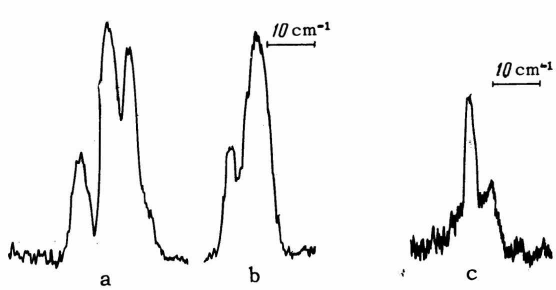

FIG. 4. Samples of microphotograms of lines in spectra of stimulated Raman scattering for nitrobenzene: a, b—near the excitation "threshold," c—below threshold by a factor of 3.

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