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INDICATRIX AND SPECTRA OF STIMULATED RAMAN SCATTERING EXCITED BY PICOSECOND OPTICAL PULSES IN LIQUIDS

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Results of a study of stimulated Raman scattering (SRS) in liquids excited by the second harmonic of a mode-locked (picosecond) neodymium laser are reported. The SRS phenomenon becomes significantly nonstationary with pumping pulses 10^{-11}–10^{-12} sec long. The nonstationary state may be due to group retardation (wave nonstationarity) and to the finite relaxation time of the molecules (local nonstationarity). The SRS indicatrix is fairly sensitive to group retardation, particularly in the case of a forward–backward scattering asymmetry. Measurements of this asymmetry in benzene and carbon bisulfide yielded values $> 5 \times 10^4$ which exceed the values obtained with nanosecond pulses by at least three orders. The investigation of SRS spectra and conversion coefficients revealed a number of effects that are not observed in the nanosecond pulse field. An asymmetric broadening of the pumping line and Stokes components in carbon bisulfide, and the fine structure of SRS Stokes lines in benzene were recorded. The high-power radiation of the nanosecond generator excited SRS in water, a phenomenon not observed before in the field of the usual giant pulses.

1. INTRODUCTION

THE availability of picosecond pulse generators affords the opportunity to study a number of new SRS effects. This opportunity arises in (a) the study of nonstationary phenomena accompanying SRS, and (b) the s study of SRS in strong optical fields that significantly exceed those obtained from conventional Q-switched lasers. The nonstationary SRS phenomena are due to two factors. When the pumping pulse $\tau \sim \tau_r$, where τ_r is the relaxation time of molecular oscillations, gain is reduced and the spectral characteristics of SRS are altered. The other important factor is the effect of group retardation of pumping pulses and scattered radiation that sharply changes the scattering indicatrix and the shape of the spectral lines of SRS.

Strong optical fields achieved in picosecond pulses allow us to study higher order SRS effects and to attempt an experimental investigation of SRS in media characterized by broad lines and small cross sections of spontaneous scattering.

Important is also the fact that SRS excitation by picosecond pulses significantly changes the role of other nonlinear processes: the stimulated Mandel'shtam–Brillouin scattering (SMBS) is practically eliminated and the role of self-focusing is considerably altered. The last effect was studied in [1] where the effectiveness of SRS was investigated in typical self-focusing liquids subject to picosecond pumping.

The aim of the present work is the study of the indicatrix and spectra of SRS with picosecond pumping. Along with liquids typical of SRS (benzene and carbon bisulfide) we observed SRS in water having a fairly broad line of spontaneous Raman scattering. Some results of the experiments described below were published earlier.[2]

2. THE EXPERIMENTAL SETUP

SRS was investigated in benzene, carbon bisulfide, and in water, excited by the second harmonic ($\lambda = 0.53\ \mu$) of a mode-locked neodymium laser. Figure 1 shows the diagram of the experimental setup. The generator energy measured with a thermocouple calorimeter was $W_1 \approx 0.1$ J. The number of generation pulses N was recorded with a coaxial FÉK-15 photocell matched to an I2-7 oscilloscope. In our experiments N = 23–25. Pulse length τ was measured by the method of "colliding" light pulses in a medium that luminesced in two-photon absorption.[3-5] For this purpose the laser beam was split into two beams of the same intensity by a transparent glass plate. Both beams reflected from mirrors were sent into the opposite ends of a cell with a solution of rhodamine 6G in ethyl alcohol. The contrast of the luminous region at the intersection of the pulses was ~2 relative to the luminescent trail. The intensity of luminescence from both beams passing through the cell was twice as high as in the case of a single beam. The value of $\tau \approx 3 \times 10^{-12}$ sec was computed from the measured length of the luminous region. Thus the generator peak power $P \approx 1.3$ GW. The emission of the generator was converted to the second harmonic in a KDP crystal. The KDP crystal cut at a phase matching angle was 3 cm long. The measured second harmonic energy was $W_p \approx 0.01$ J. It is estimated that the peak power at the frequency 2ω is $P_p \approx 100$ MW. To increase pumping radiation density either a focusing lens with a focal length of 40 mm or a 5× telescope were placed in front of the cell with the investigated liq-

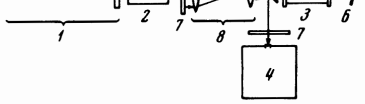

FIG. 1. Experimental setup: 1–neodymium mode-locked laser; 2–KDP crystal; 3–cells with the investigated liquid; 4–ISP-51 spectrograph with UF-89 camera; 5–mirror; 6–glass plate; 7–optical filter; 8–telescope.

uid. The radiation density behind the telescope was $S_p \approx 100$ GW/cm^2. The SRS spectrum propagating both along the pumping beam and in the opposite direction was recorded with the ISP-51 spectrograph with a UF-89 camera. Both beams were separated in space and allowed to fall on different regions of the spectrograph slit to investigate the SRS asymmetry.

3. INDICATRIX AND EFFICIENCY OF SCATTERING IN BENZENE AND CARBON BISULFIDE

In the study of the scattering indicatrix particular attention was paid to the measurement of the energy ratio of the forward–backward SRS Stokes components W_+/W_-. In the case of the investigated liquids $W_+/W_- > 5 \times 10^4$ when the telescope was used. This ratio exceeded by 3–4 orders the corresponding ratio recorded in experiments with the conventional giant pulses. We attempted to observe SMBS with picosecond pumping; measurements of conversion efficiency yielded values lower than 10^{-4}. The absolute values of stimulated scattering efficiency in benzene and carbon bisulfide for experimental runs with the telescope are given in the table. The conversion efficiencies obtained in these runs appear sufficiently high. It should also be noted that scattering in CS_2 is less effective than that in benzene in the case of picosecond pumping. The observed situation is radically different from that of SRS excited by nanosecond optical pulses. In the latter case scattering in CS_2 is more effective because of the larger static gain and more effective self-focusing of pumping. The data given here emphasize the importance of nonstationary phenomena.

According to [6] the principal factor determining the indicatrix in picosecond pumping is the effect of group retardation of pumping pulses and the scattered radiation. If the coherent interaction lengths are l_+ for forward scattering and l_- for backward scattering,

$$l_\pm = \frac{\tau}{v_p^{-1} \mp v_s^{-1}}, \tag{1}$$

where v_p and c_s are group velocities of pumping and Stokes radiation, the forward–backward scattering energy asymmetry is expressed by

$$\frac{W_+}{W_-} = \frac{l_-}{l_+} \exp\left[gS_p(l_+ - l_-)\right], \tag{2}$$

where g is the effective gain and S_p is the peak power density of pumping. We note that (2) pertains to the case when we can neglect nonstationarity due to the finite relaxation time of molecular oscillations. Consequently (2) gives an excessive value of asymmetry when the wave and local nonstationarities appear simultaneously. Although exact theoretical results accounting for both types of nonstationarity are difficult to obtain, as shown in [6], the following relation is valid for the estimate of minimal asymmetry when $\tau_r \gg \tau$, and $l_+ \gg l_-$:

$$\frac{W_+}{W_-} \sim \frac{l_-}{l_+} \exp \sqrt{gS_p l_+}. \tag{2a}$$

Considering that the conversion efficiency for CS_2 where $\tau_r \gg \tau$ reached several percent in our experiments, the forward–backward asymmetry $W_+/W_- \sim 10^6$ (we assume that $g \sim 10^{-3}$ cm/MW, $S_p \approx 10^5$ MW/cm cm^2, $l_+ \approx 3.6$ cm, and $l_-/l_+ \sim 10^{-2}$).

The relation between the absolute values of SRS conversion efficiencies in CS_2 and in benzene is due apparently to the different role of the relaxation processes. Indeed in the case of pumping pulse length ($\tau \approx 3 \times 10^{-12}$ sec) used in our experiments, the nonquasistationarity of gain due to the total line width of spontaneous scattering should be more pronounced in carbon bisulfide; for benzene $\tau_r \sim 10^{-11}$ sec and in carbon bisulfide $\tau_r \sim 5 \times 10^{-11}$ sec. CS_2 is known to have a strong inequality $\tau_r \gg \tau$ which according to [6] renders the Stokes component energy $W_S = W_{Sp} \exp \sqrt{gS_+l_+}$, where W_{Sp} is the spontaneous scattering energy.

Excitation conditions	Observed lines	Line half-width (Å)	Relative intensity (% of pumping)
Benzene, $\Omega_1 = 984$ cm^{-1}, $\Omega_2 = 3060$ cm^{-1}, $\tau_r \approx 10^{-11}$ sec			
In lens focus	ω_p	2.5	100
	$\omega_p + \Omega_1$	—	—
	$\omega_p - \Omega_1$	3.1	1
	$\omega_p - 2\Omega_2$	3.7	0.02
	$\omega_p - \Omega_2$	5.6	0.08
In collimated beam	ω_p	3.4	100
	$\omega_p + \Omega_1$	—	—
	$\omega_p - \Omega_1$	2.5	10
	$\omega_p - 2\Omega_1$	3	0.7
	$\omega_p - \Omega_2$	3.4	0.7
Carbon bisulfide, $\Omega = 656$ cm^{-1}, $\tau_r \approx 5 \times 10^{-11}$ sec			
In lens focus	ω_p	4.4	100
	$\omega_p + \Omega$	—	—
	$\omega_p - \Omega$	12	7
	$\omega_p - 2\Omega$	15	0.04
In collimated beam	ω_p	32	100
	$\omega_p - \Omega$	—	2
Water, $\Omega = 3300 - 3600$ sec^{-1}, $\tau_r \approx 10^{-13}$ sec			
In collimated beam	ω_p	6	100
	$\omega_p - \Omega$	200	1

4. SRS IN WATER

The conversion coefficient of pumping radiation into the Stokes band in water was of the order of 1%. Figure 2 shows an SRS spectrogram that was decoded with the MF-4 microphotometer. We can clearly see maxima at 3240 cm^{-1} and 3440 cm^{-1} corresponding to the symmetric oscillations of water molecules with "normal" and "defective" hydrogen bonds.[7] Furthermore we see a series of maxima in the region of 3350 cm^{-1} which are apparently due to anti-symmetric oscillations of molecules with "normal" bonds.

As it was pointed out in [8] we can assume that the selection rules that prohibit these oscillations in the Raman spectra of vapors are less rigid in liquids especially when the liquid molecules are at the nodes of a quasi-crystalline lattice and are subject to a strong perturbing effect from the neighboring molecules. We did not observe maxima in the region of 3620 cm^{-1} ap-

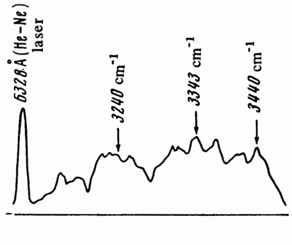

FIG. 2. Microphotographs of SRS in water.

parently because there are much fewer free water molecules than bound molecules in the liquid and the available pumping is insufficient to excite SRS at this frequency.

It was shown in [9] that the spontaneous Raman scattering band in water can be regarded as a superposition of four lines with a half-width of $\approx 200\ \text{cm}^{-1}$ and of Gaussian shape. The width of these lines corresponds to a relaxation time of molecular oscillations of $\sim 2 \times 10^{-13}$ sec which is much shorter than the laser pulse length. Therefore the absolute values of SRS intensities in water can be estimated by using a theory that takes only the group retardation effect into account. In this case the most important property of picosecond pulses is their high peak intensity.

In statistical approximation for lengths shorter than l_+ the efficiency of the Stokes component in water is given by

$$\frac{W_s}{W_p} = \frac{W_{sp} \exp [g_0 S_p l_+]}{W_p}, \tag{3}$$

where g_0 is the static gain. If according to [9] the width of the spontaneous Raman scattering line in water is taken as $200\ \text{cm}^{-1}$, then even with a maximum estimate of pump peak power the SRS gain would not exceed e^5 ($g_0 \sim 10^{-5}$ cm/MW, $S_p \approx 10^5$ MW/cm^2, and $l_+ \sim 5$ cm), which is in disagreement with the obtained conversion coefficient. The cause of this disagreement can be an additional increase of the light field intensity due to self-action effects of cubic nonlinearity (this cause seems to have a low probability although these effects should not be completely discounted in a strong field of picosecond pulses (see [10])). Another source of possible explanation is based on the fact that the Raman scattering band for water consists of a series of sufficiently narrow ($\sim 30\ \text{cm}^{-1}$) lines that are independently excited; in this case however $\tau_r \sim 10^{-12}$ sec and the condition $\tau_r < \tau$ remains valid.

5. SRS SPECTRAL LINE SHAPE IN BENZENE AND CARBON BISULFIDE

As it was noted above SRS in benzene and carbon bisulfide was studied with focused and parallel (passed through a telescope) beams using an ISP-51 spectrograph with a UF-89 camera. Normal density of photographic emulsion was obtained by a selection of neutral and color filters. The resulting spectrograms were measured with an MF-4 microphotometer and were analyzed according to the standard method. Typical microphotographs of the exciting radiation and SRS component lines in carbon bisulfide and benzene are given in Fig. 3. We note the difference in the structure of carbon bisulfide lines in focused and collimated pumping beams (Figs. 3a and 3b). In both cases we observe asymmetric broadening of the pumping and SRS Stokes component lines. The prevalent line distortion is in the direction of the Stokes region.[1] In the case of focused pumping the line broadening of the exciting radiation is considerably weaker. In the telescope-collimated beam the pumping line broadens into the low-frequency region to such an extent that its wing covers the frequency interval down to the first Stokes line and beyond. The wing intensity was so high in the Stokes component region that we could not determine the shape of the latter.

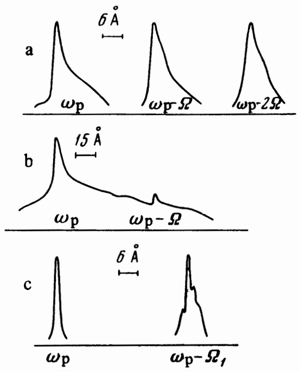

FIG. 3. Microphotographs of SRS in carbon bisulfide and in benzene; a—in carbon bisulfide, focusing radiation into the cell; b and c—in carbon bisulfide and benzene respectively, using a parallel pumping beam.

This difference in the nature of spectral lines excited under different conditions shows that the distance-dependent cumulative effect is significant in line broadening mechanisms. We note that the mechanisms discussed below develop under comparable electric field intensities of the light wave and that therefore the broadening and deformation of spectral lines observed in the experiments are the result of their joint action. We now consider a few of these mechanisms.

A strong deformation of the amplitude profile up to the formation of shock waves is possible in media whose index of refraction depends on the incident wave intensity ($n = n_0 + n_2 |E|^2$).[12] The characteristic length necessary to effect a significant deformation of the amplitude profile is $z \approx 0.2 \tau v_0 n_0 / \delta n$, where v_0 is the group velocity of the pulse, and $\delta n = n_2 |E|^2$ is the nonlinear portion of the index of refraction. We note that this mechanism seems to be possible only for picosecond pulses since for the usual giant pulses of light ($\tau \sim 10^{-8}$ sec) and for values of $\delta n \sim 0.1$ close to saturation (in thin self-focusing filaments) the value of z amounts to several meters. In our case the process of a shock wave formation can proceed over the entire cross section of the beam, since for $\tau \approx 3 \times 10^{-12}$ sec and $\delta n / n_0 \sim 4 \times 10^{-3}$ (for CS_2 the value $n_2 = 9 \times 10^{-12}$ CGSE; $S_p \approx 10^5$ MW/cm^2) the length $z \sim 3$ cm.

According to estimates given in [12], taking the anisotropy relaxation time into account, the formation of a shock wave results in an asymmetric broadening of the spectrum with $\Delta\nu \sim 1000\ \text{cm}^{-1}$.

Another possible broadening mechanism can be the stimulated scattering of the Raleigh line wing.[13] This type of scattering also results in a significant asymmetry of the spectrum. In strong optical fields of picosecond generators there is a possibility of an appreciable strengthening of the far regions of the wing that are related to the fast oscillations of anisotropic molecules with a quasistatic amplification process (fast relaxation time in CS_2: $\tau_r \sim 0.2 \times 10^{-12}$ sec, and condition $\tau_r \ll \tau_p$ holds).

Media whose refraction index depends on the light intensity may have self-action effects leading to phase modulation of the waves.[14, 15] Such effects can cause a significant broadening of the spectrum which increases with the strength of the time modulation of the

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[1] The asymmetric broadening of pumping and SRS spectra in CS_2 excited by a single-mode generator was reported in [11].

original wave (the richness of its spectrum). In this sense the phase modulation mechanism is not a unique feature of picosecond pulses since a similar situation also occurs when nanosecond laser pulses in multimode operation are used to excite the medium.[16, 17] In this case the instantaneous frequency shift $\Delta\omega \sim (\delta n/n)kz\partial F/\partial z$, where F is the initial amplitude modulation of the wave.[15] Specific of picosecond pulses is the appearance of nonlinearity relaxation that causes phase modulation of the wave. According to rough calculations, without taking the relaxation of the nonlinear susceptibility of the medium into account, the spectral broadening due to phase modulation can amount in our case to $\Delta\nu \sim 10^3$ cm^{-1}. This is undoubtedly an exaggerated value and an exact calculation is difficult because of the absence of an analytic solution of the problem in the region $\tau \sim \tau_r$. Consideration of relaxation also leads to an asymmetric picture of the spectrum. In conclusion we note that in the experiments with CS_2 the most interesting are the extremely large absolute values of $\Delta\nu \sim 1000$ cm^{-1} in work with telescope-collimated beams, and a sharp decrease of the gain of the SRS Stokes component. The latter effect can be due to the phase mismatch of the molecular oscillations by the components of the broadened pumping spectrum. The possibility of such a mechanism was first noted by Brewer and others.[18]

In the experiments with benzene we note the appearance of a fine structure of SRS Stokes components (Fig. 3c). At the same time the pumping line spectrum emerging from the cell remains symmetric and unbroadened. Such a structure was observed earlier in CS_2 excited with a ruby laser that was Q-switched with a rotating prism.[17] The observed structure of SRS lines is apparently determined by the characteristics of the Raman scattering process itself rather than by the mechanisms described above. It can be due either to the saturation of the lower vibrational levels or to the excitation of isotronic molecules, or else to a number of other effects. In our experiments the observed shifts of the fine components of SRS lines amount to ≈ 3.5 Å towards the Stokes and ≈ 1.8 Å towards the anti-Stokes region. These shifts are in agreement with the fine structure of the spontaneous Raman scattering lines due to the presence of $C_5^{12}C^{13}H_6$ isotopes.[19]

In conclusion we note that the use of a powerful picosecond generator of light as an SRS excitation source permits us to widen the range of investigated liquids and to study a number of new effects due to nonstationary phenomena in SRS. Moreover the nature of SRS phenomena itself (such as a strong asymmetry of forward-backward scattering) can serve as an indicator of the picosecond regime of laser operation.

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