Investigation of four-photon processes in stimulated Raman scattering (SRS)

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Off-axis SRS of class II is investigated in benzene, carbon disulfide, and nitrobenzene. The angles and the intensities of the SRS components are measured up to the fourth Stokes component, inclusive. It is shown that rings of the second Stokes component are formed for a given intensity of the exciting radiation and a small intensity of the first Stokes component, I_{-1}. A central spot appears with increase in I_{-1} and begins to grow rapidly. Rings of the second Stokes and first anti-Stokes components arise simultaneously and their intensities vary in proportion to variation of the SRS excitation conditions. The magnitudes of the angles and the regularities of variation of the off-axis radiation intensities of the various components are explained on the basis of the concept of four-photon coherent Stokes–anti-Stokes transitions in SRS, without recourse to self-focusing data.

One of the interesting features of the phenomenon of stimulated Raman scattering (SRS) is the complicated angular distribution of the scattered radiation. Along with the scattered radiation, which has a sharp maximum in the direction of the axis of the beam of exciting radiation, the anti-Stokes and higher Stokes components of SRS have intensity maxima at definite angles to the axis; these maxima are characteristics of the specific material and of the multiplicity of the components.

The phase synchronism condition established by Townes[1] was originally the basis for the interpretation of the angular distribution of the SRS. However, subsequent study of SRS has shown that only a small fraction of the off-axis radiation satisfies this condition; this fraction is known as radiation of class I.[2] The more intense and most frequently observed off-axis radiation (radiation of class II) does not obey the condition of phase synchronism.

A detailed experimental study of the radiation of class II has not yet been carried out and there is much that is unclear in its theoretical interpretation. The starting point of the initial theory was the fact that the radiation of class II emerges from thin filaments produced when light is self-focused inside the sample.[3] This explanation became doubtful after the publication of the researches of Prokhorov, Lugovoĭ, and coworkers.[4]

We have studied radiation of class II in three organic liquids (benzene, carbon disulfide, and nitrobenzene) and have made an attempt at a theoretical explanation of the basic features of this radiation.

In the study, we have used the apparatus illustrated in Fig. 1. The SRS was excited by a ruby laser Q-switched by a solution of cryptocyanine in ethyl alcohol. The mode composition was monitored by a Fabry-Perot interferometer with a plate spacing from 3 to 15 cm. Usually there was a single axial and several angular modes in the laser radiation. The laser operated in a single-pulse regime with a pulse duration of about 30 nsec and a maximum energy 0.34 J.

The laser radiation passing through the diaphragm 4 was focused by the lens 8 into cell 9 containing the liquid under study. The first Stokes component of the SRS was excited in this liquid. The second Stokes component was also usually excited. This was not needed for further study and was therefore attenuated by the selective light filter 12. The spectral composition of the radiation leaving the cell 9 was measured by a photographic method with the help of spectrograph 18. The off-axis laser radiation was excited in the cell 15, the length of which was varied from 10 to 30 cm. The exciting radiation and the first Stokes component of the SRS, which emerged from the cell 9, was focused into cell 15 with the help of the lens 14. The conditions for the excitation of the SRS in the cell 15 were so chosen that only off-axis radiation of class II could be formed. A characteristic attribute of this class of radiation is that the angles it makes with the axis are independent of the focal length of the lens 14. In our experiments, when the focal length of this lens was changed from 15 to 110 cm the diameters of the observed rings remained unchanged. The radiation emerging from the cell 15 was gathered by lens 16 in the plane of the slit of the spectrograph 17 (the slit was removed in the experiments). The plane of the slit coincided with the focal plane of the lens 16.

We studied the angular distribution and the intensity of the various components of the SRS excited in the cell 15 by radiation of two different frequencies: by the laser radiation and by the first Stokes component of the SRS produced in the cell 9. We note that both forms of radiation play the role of the exciting radiation in four-photon processes. The results obtained for the angles and for the intensities of the various SRS components are discussed separately.

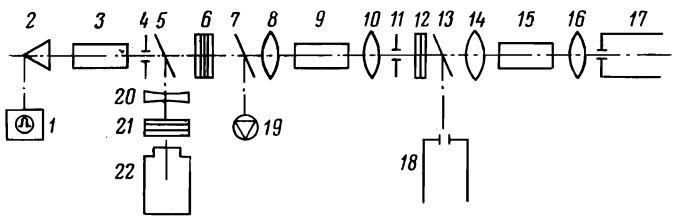

FIG. 1. Diagram of setup for the study of four-photon SRS processes: 1–I2-7 oscillograph; 2–FÉK-09 photocell; 3–ruby laser, 4, 11–diaphragms; 5, 7, 13–hinged plates; 6–set of filters for attenuation of the exciting radiation; 8–lens with f = 500 mm; 9–cell with material; 10–lens with f = 800 mm; 12–set of filters for selection of SRS; 14–lens with f = 140 mm; 15–cell with material; 16–lens with f = 80 mm; 17–spectrograph; 18–spectrograph; 19–calorimeter; 20–scattering lens; 21–Fabry-Perot interferometer; 22–camera with f = 800 mm.

ANGULAR DISTRIBUTION OF THE SRS RADIATION

In our research the principal attention was paid to measurement of the angles between the axis and the higher Stokes components, about which there are almost no data in the literature. The apparatus described above allowed us to excite the Stokes components of the SRS up to the fourth order, inclusive. The data obtained for angles of the radiation of class II are shown in Tables I—III and compared there with the published values.[2-5] As can be seen, the data obtained by us for the first anti-Stokes and the second Stokes components are in satisfactory agreement with the published data (in all cases, the angles are given for air).

The results obtained on the angular distribution of SRS radiation of class II can be explained on the basis of the theory of coherent four-photon processes, developed in[6]. In this theory, conditions are determined for which two processes of Raman scattering of light, A and B, with amplitudes ψ_a and ψ_b, respectively, are coherent, i.e., the probability

$$W=\psi_a\psi_a^*+\psi_b\psi_b^*+\psi_a\psi_b^*+\psi_b\psi_a^* \quad (1)$$

has a nonzero part $\Delta W = \psi_a\psi_b^* + \psi_b\psi_a^*$.

For the amplitudes of the given processes, we use the well-known expressions (see[6,7])

$$\psi_a=a_0\exp\{i(\mathbf{k}_a-\mathbf{k}_a')\mathbf{r}\},\quad \psi_b=b_0\exp\{i(\mathbf{k}_b-\mathbf{k}_b')\mathbf{r}\}, \quad (2)$$

where $\mathbf{k}_a$ and $\mathbf{k}_b$ are the wave vectors of the incident photons, while $\mathbf{k}_a'$ and $\mathbf{k}_b'$ are those of the scattered photons in processes A and B, respectively. If the process A and B are both Stokesian, then the amplitude of the four-photon process is $\psi_{ss} = \psi_a + \psi_b$. In this case, the quantity ΔW does not vanish under the condition (see[6])

$$\mathbf{k}_a-\mathbf{k}_a'-\mathbf{k}_b+\mathbf{k}_b'=0, \quad (3)$$

This relation represents the usual condition of phase synchronism. It is satisfied for the wave-vector diagram shown in Fig. 2a (the vectors of the incident photons are represented by the solid lines and those of the scattered photons by the dashed lines).

TABLE I. Angles of off-axis radiation of SRS in benzene (in rad)

Angle	Calculation	Experiment			
		[2]	[5]	Our data	
				Series I	Series II
θ_3	0.0810	0.085	0.0853	—	—
θ_2	0.0568	0.060	0.0553	—	—
θ_1	0.0348	0.0325	0.0313	—	0.035
θ_{-2}	0.0433	0.038	—	0.040	0.037
θ_{-3}	0.0435	—	—	0.037	0.036
θ_{-4}	0.0436	—	—	0.035	0.037

TABLE II. Angles of off-axis radiation of SRS in carbon disulfide (in rad)

Angle	Calculation	Experiment		
		[2]	[5]	Our data
θ_3	0.0812	0.080	0.078	—
θ_2	0.0580	0.051	0.050	—
θ_1	0.0358	0.033	—	—
θ_{-2}	0.0412	—	—	0.030
θ_{-3}	0.0409	—	—	0.034
θ_{-4}	0.0406	—	—	0.033

TABLE III. Angles of off-axis radiation of SRS in nitrobenzene (in rad)

Angle	Calculation	Experiment		
		[2]	[5]	Our data
θ_2	0.100	0.101	—	—
θ_1	0.0566	0.058	0.0569	—
θ_{-2}	0.0760	0.065	—	0.073
θ_{-3}	0.0756	—	—	0.072

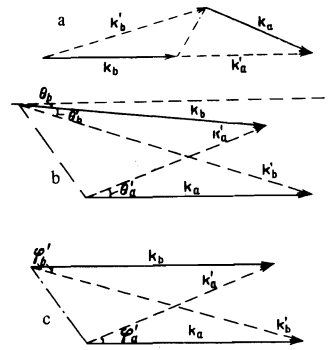

FIG. 2. Diagram of the wave vectors corresponding to the various conditions of phase synchronism.

If one of the considered processes is a Stokes process, and the other an anti-Stokes process, then, as a consequence of the Hermitian-conjugate character of the matrix elements for the Stokes and anti-Stokes transitions (see[7]) the amplitude of the four-photon process is $\psi_{sA} = \psi_a + \psi_b^*$. Accordingly, we obtain the coherence condition for the wave vectors in Stokes-anti-Stokes transitions in the form ($\mathbf{k}_a \neq \mathbf{k}_b$)

$$\mathbf{k}_a-\mathbf{k}_a'-\mathbf{k}_b'+\mathbf{k}_b=0. \quad (4)$$

The wave-vector diagram shown in Fig. 2b corresponds to this condition. For the angle θ_b' between the vector $\mathbf{k}_b'$ and the direction of the vector $\mathbf{k}_a$, we obtain after straightforward but rather cumbersome calculations

$$\sin(\theta_b'-\theta_b)=-\frac{k_a\sin\theta_b(Q^2+k_b'^2-k_a'^2)}{2k_b'Q^2}+\frac{(k_b+k_a\cos\theta_b)}{2k_b'Q^2}[(k_b'+k_a'+Q)\times(Q+k_a'-k_b')(Q+k_b'-k_a')(Q+k_a'+k_b')]^{1/2}. \quad (5)$$

Here $Q^2 = k_a^2 + 2k_ak_b\cos\theta_b + k_b^2$; θ_b is the angle between the vectors $\mathbf{k}_a$ and $\mathbf{k}_b$. In the important special case when the vectors $\mathbf{k}_a$ and $\mathbf{k}_b$ are parallel (Fig. 2c), Eq. (5) is materially simplified. Denoting the angles between the vectors $\mathbf{k}_a'$ and $\mathbf{k}_b'$ and the axis by φ_a' and φ_b', respectively, we have

$$\sin\varphi_b' = \frac{[(k_b'+k_a'-k_b-k_a)(k_a+k_b+k_a'-k_b')(k_a+k_b+k_b'-k_a')(k_a+k_b+k_a'+k_b')]^{1/2}}{2k_b'(k_a+k_b)} \quad (6)$$

$$\sin\varphi_a'=(k_b'/k_a')\sin\varphi_b'. \quad (7)$$

We note that the anti-Stokes radiation in Stokes-anti-Stokes transitions arises in four-photon scattering by unexcited molecules. Therefore, the intensity of such radiation can be quite appreciable.

The evolution of the SRS process with participation of Stokes-anti-Stokes transitions can be visualized in the following fashion. First, there is SRS radiation in the investigated material (cell 15 in Fig. 1) only at the first Stokes frequency, with a wave vector $\mathbf{k}_a = \mathbf{k}_{-1}$, parallel to the vector of the exciting radiation $\mathbf{k}_b = \mathbf{k}_0$. These two vectors are the starting ones in the Stokes-anti-Stokes transition (Fig. 2c) with formation of the

second Stokes component ($k'_a = k_{-2}$) and the first anti-Stokes component ($k'_b = k_1$). At sufficient intensity of the first anti-Stokes component propagating at an angle $\varphi'_b = \theta_b$ to the axis, this component and the exciting radiation k_0 give rise in the new Stokes-anti-Stokes transition to a second anti-Stokes component $k'_b = k_2$ and a first Stokes component $k'_a = k_{-1}$, the two propagating at the angles θ'_a and θ'_b to the axis (Fig. 2b). In the same way, the components k_2 and k_0 produce the third anti-Stokes component, and so on.

The source of formation of rings of class II of Stokes components of higher order is the axial radiation produced by the successive excitation of the Stokes components of the SRS. This radiation is more intense than the radiation generated in four-photon processes taking place at angles to the axis. Therefore, formation of rings of higher Stokes components takes place each time according to the scheme shown in Fig. 2c. For example, the third Stokes component $k'_a = k_{-3}$, which propagates at the angle φ'_a to the axis, stems from the first and third axial Stokes components ($k_a = k_{-2}$; $k_b = k_{-1}$), and so forth.

The results of calculations according to the formulas (6) and (7) given above (the angles θ_1, θ_{-2}, θ_{-3}, θ_{-4}) and according to Eq. (5) (the angles θ_2, θ_3) are given in Tables I–III together with the experimental data. Owing to the lack of sufficient experimental data on the dispersion the refractive indices for the higher Stokes components were found by extrapolation. If we take into account the experimental errors in the measurement of the angles and some uncertainty in the dispersion due to the extrapolation, then the agreement of the calculated and experimental data can be regarded as satisfactory.

INTENSITY OF THE SRS COMPONENTS

The probability of a four-photon Stokes-anti-Stokes coherent process with formation of second Stokes and first anti-Stokes components propagating at the corresponding angles to the axis is determined by the expression (see[6,7])

$$W_{ang} = C^2(\omega_0\omega_1\omega_{-1}\omega_{-2})^{1/2} \times [n_0 n_{-1}(n_1+g_a)(n_{-2}+g_b)]^{1/2}, \quad (8)$$

where $g_a = \omega_1^2/(2\pi c)^3$ and $g_b = \omega_{-2}^2/(2\pi c)^3$; C is a constant, which ω_i and n_i are the frequency and number of photons of the given type of radiation (ω_0 and n_0 refer to the radiation of the ruby, ω_{-1} and n_{-1} to radiation at the first Stokes frequency, and so forth). For radiation at the second Stokes frequency, which is generated in the process of successive excitation and is propagated along the axis, we have, correspondingly (see[6-8]):

$$W_{ax} = 2C^2\omega_{-1}\omega_{-2}n_{-1}(n_{-2}+g_b). \quad (9)$$

It follows from a comparison of these formulas that at low intensity of the first Stokes component, when $n_0 \gg n_{-1}$, formation of off-axial radiation is the principal consequence, and gives rise to rings of class II in the pictures. The condition $W_{ang} = W_{ax}$ is satisfied for

$$n_{-1}/n_0 = 1/4\ \omega_0\omega_1/\omega_{-1}\omega_{-2}. \quad (10)$$

Here the intensities of the central spot and the ring at the second Stokes frequency are about equal. Further increase of n_{-1} leads to a more rapid growth of the intensity of the central spot of the second Stokes component. All these conclusions have only a qualitative character, inasmuch as in the propagation of the radiation

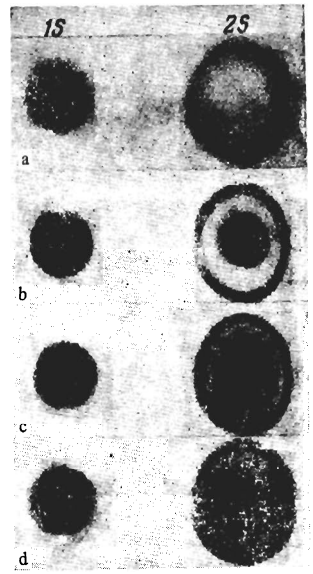

FIG. 3. Axial and off-axis radiation of the second Stokes component of SRS in benzene as a function of the energy of the first Stokes component I_{-1}: a) I_{-1} = 0.02; b) I_{-1} = 0.05; c) I_{-1} = 0.08; d) I_{-1} = 0.12 J.

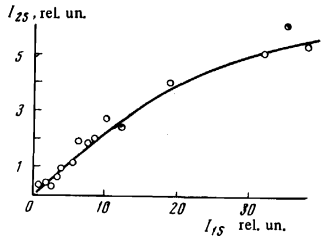

FIG. 4

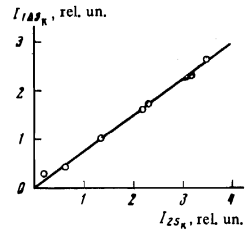

FIG. 5

FIG. 4. Dependence of the intensity of off-axis radiation of the second Stokes component of SRS in benzene on the intensity of the first Stokes component.

FIG. 5. Ratio of the intensities of the off-axis radiation of the first anti-Stokes and second Stokes components.

along the cell the numbers of photons n_1, n_0, n_{-1}, n_{-1} change, photons of higher Stokes and anti-Stokes components arise, etc.

In our experiments we also realized SRS-excitation conditions under which the intensity of the radiation with frequency ω_0 (i.e., the number of photons n_0) entering the cell 15 was kept constant, and only the intensity of radiation with frequency ω_{-1} (i.e., the number of photons n_{-1}) changed. The results are shown in Fig. 3.[1)] As can be seen, only a ring of the second Stokes component is formed at low intensity of the first Stokes component I_{-1}. As I_{-1} increases, the central spot becomes steadily more intense. The intensity of the ring I_{-2k} also increases, but more slowly. The dependence of the intensity of the off-axis radiation of the second Stokes component I_{-2k} on the intensity of the first Stokes component I_{-1} is shown in Fig. 4. Qualitatively, it is in agreement with Eq. (8). At large values of I_{-1}, the growth of I_{-2} slows down, evidently because of the transfer of energy to the other SRS components.

We also studied the ratio of the intensity I_{1k} of the off-axis radiation of the first anti-Stokes component to the intensity I_{-2k} of the off-axis radiation of the second Stokes component. The results are shown in Fig. 5. The rings of the first anti-Stokes and second Stokes components are formed simultaneously, and their intensities vary proportionally when the experimental conditions are varied. These conclusions are in good agree-

ment with Eq. (8), according to which both forms of radiation are generated in the same four-photon SRS process.

Thus, the motion of four-photon coherent processes in SRS permits us to explain the basic laws which the off-axis radiation of class II obey. It has been shown by us previously[8] that the "effects of repetition" in SRS are explained by similar processes. It should be noted that we are not dealing with the problem of the reasons for the appearance of the indicated coherence. The researches of[9-11] are devoted to this problem.

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[1)]In the pictures, the first Stokes component (which passed through both cells) was strongly overexposed.

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