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STIMULATED RAMAN SCATTERING

Edited by N. G. Basov

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Volume 99

Stimulated Raman Scattering

**Edited by
N. G. Basov**

*P. N. Lebedev Physics Institute
Academy of Sciences of the USSR
Moscow, USSR*

Translated from Russian by

J. George Adashko



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STIMULATED RAMAN SCATTERING
VYNUZHDENNOE KOMBINATSIONNOE RASSEYANIE SVETA
ВЫНУЖДЕННОЕ КОМБИНАЦИОННОЕ РАССЕЯНИЕ СВЕТА

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PREFACE

Results are presented of an experimental investigation of the angular distribution of the near-axis emission of various components of stimulated Raman scattering which are characterized by a strong forward directivity (repetition effect). "Rings of second class" in off-axis stimulated Raman scattering emission are investigated.

Experiments that have revealed the existence of a new nonlinear-optics phenomenon, namely self-focusing of stimulated Raman scattering, are described.

Results of an investigation of the spectral distribution of the stimulated Raman emission components are reported.

One of the articles is devoted to a theoretical treatment of the angular distribution of stimulated Raman scattering.

All the articles are trail-blazing in their fields. The anthology systematically explains many aspects of the present state of the study of stimulated Raman scattering.

CONTENTS

Investigation of the Angular Distribution of Stimulated Raman Scattering of Light – A. N. Arbatskaya	1
Investigation of the Formation and Self-Focusing of Stimulated Raman Scattering of Light in Condensed Media – A. D. Kudryavtseva	37
Investigation of the Spectral Distribution of the Intensity of the Components of Stimulated Raman Scattering of Light in Condensed Media – E. A. Morozova	77
Stationary SRS Regimes in the Fields of Ultrashort Pulses – T. M. Makhviladze and M. E. Sarychev	113
Angular Distributions of Stimulated Raman Scattering of Light – T. M. Makhviladze and M. E. Sarychev	123

INVESTIGATION OF THE ANGULAR DISTRIBUTION OF STIMULATED RAMAN SCATTERING OF LIGHT

A. N. Arbatskaya

The angular distribution of the paraxial emission of the first, second, third, and fourth Stokes components of stimulated Raman scattering of light (SRS) in organic liquids (benzene, carbon disulfide, nitrobenzene) is investigated. A "duplication effect," consisting in the fact that the angular distribution of the paraxial radiation of all the Stokes components duplicates the angular distribution of the exciting radiation emerging from the scattering medium, is observed. Off-axis class-II SRS emission in the same liquids is investigated. A new interpretation is proposed for the off-axis class-II emission on the basis of the Stokes-anti-Stokes four-photon processes. An estimate is presented of the relative intensity of the off-axis SRS radiation and of the total intensity of the second and higher Stokes components.

INTRODUCTION

Little more than a decade has elapsed since the discovery of stimulated Raman scattering (SRS) of light, but hundreds of papers have already been devoted to this phenomenon. The interest in SRS is fully justified by the variety of the laws that govern it. It should be noted although SRS has been intensively studied, there are still many unclear aspects, both as a result of the complexity of the phenomenon itself and because of its connection with other nonlinear processes that occur when intense optical radiation interacts with matter.

The investigations of the angular distribution of SRS were initiated shortly after its discovery, especially after experiment has revealed radiation at anti-Stokes and higher Stokes frequencies, propagating along the generators of cones with axes along the direction of the exciting radiation. The apex angles of these cones were measured for a number of substances under various SRS excitation conditions. As to the other characteristics of off-axis SRS radiation, including the intensity, they remained practically uninvestigated to this day.

Photography of SRS radiation at anti-Stokes and higher Stokes frequencies reveals usually several rings and a central spot corresponding to the SRS in the direction of the axis of the exciting light. At the first Stokes frequency there is only a central spot (and an absorption ring). Since principal attention was paid to the study of the rings, the angular distribution of the SRS radiation in the central spot remained uninvestigated. Yet for a number of reasons one should expect this distribution to be unusually narrow, only slightly exceeding in width the angular distribution of the exciting radiation. Interest in this question has increased further because the angular distribution at the first Stokes frequency can be used to assess the role of coherent processes and of SRS phenomenon. Therefore the first task of the present investigation was a detailed study of the angular distribution of the first Stokes SRS component in a number of objects under various excitation conditions.

The second task was the study of the angular distribution of the off-axis radiation and a comparison of the obtained data with the available theoretical concepts concerning the processes that occur in the SRS phenomenon. The appearance of the off-axis radiation cones was explained soon after Townes's discovery of this radiation. It became clear subsequently that this explanation is suitable only for part of the observed cones, which were called cones of class I. It was also made clear that SRS is subject to definite perturbing action by other nonlinear optical phenomena, such as self-focusing of the light in the medium. The appearance of off-axis radiation cones, which do not agree with the theory mentioned above (they were called cones of class II), was attributed to self-focusing of the light. It was assumed that thin self-focusing filaments are produced in the medium, and it is in these filaments that the SRS radiation propagating along the class-II cones is excited.

The foregoing treatment of class-II radiation cannot be regarded at present as incontrovertible. According to present-day concepts, the onset of thin self-focusing filaments in a medium in which high-intensity laser radiation propagates does not correspond to the real processes that occur in the medium. We note also that off-axis class-II radiation was observed in some experiments in the absence of self-focusing. It is therefore of great interest to ascertain the causes of the class-II radiation.

Another independent problem is the study of the relative intensity of the radiation propagating along the axis and of the off-axis radiation for different SRS components, as functions of the character of the scattering objects and of the excitation conditions. We note that no research was carried out in this direction.

The study of the relative intensities of the rings and of the central spot is important from the point of view of explaining the mechanism of formation of various SRS components. Up to now, the measured distributions of the intensities among the various SRS components were the summary intensities of the radiation contained in one component or another. Yet the mechanisms that lead to the appearance of cones of different type and of the central spot can in principle be entirely different. Therefore separate measurements of the intensity of each of these formations can serve as a basis for the understanding of the most important SRS mechanisms.

CHAPTER I

SURVEY OF THE LITERATURE

1. Experimental Investigations of the Angular Distribution of SRS

Much research was done by now on SRS. Soviet and foreign physicists developed the classical and quantum theory of the phenomenon. Numerous experimental studies were made of the SRS spectra of liquids, solids, and gases excited by various methods, to the distribution of the intensities in the SRS spectra, to the energy characteristics and thresholds of the SRS, the waveforms and durations of the SRS component pulses, the coefficients of conversion of the laser energy into SRS-component energy, and to the angular characteristics of the SRS components. The results of these investigations are reflected in a large number of original papers, as well as in reviews and monographs [1-9].

SRS finds practical applications in Raman lasers and amplifiers. The first liquid-nitrogen Raman laser, in which it became possible to exceed the brightness of the pump source, was developed by Grasyuk and co-workers [10].

Principal attention is paid in the present review to the experimental and theoretical investigations of the angular characteristics of SRS.

The SRS phenomenon was first observed in 1962 by Woodbury and Ng [11] in an investigation of the emission of a ruby laser Q-switched by a Kerr cell with nitrobenzene. It was observed that the emission of this laser contained, besides the ruby emission at the fundamental frequency, intense radiation in the infrared region. Hellwarth [12] correctly interpreted this effect as SRS. The communication [11] was soon followed by investigations of the SRS of various liquids placed in the optical cavity of a Q-switched ruby laser, where a "giant pulse" was produced. Eckhardt et al. [13], followed by Geller et al. [14], investigated the SRS of several liquids (benzene, toluene, pyridine, cyclohexane, nitrobenzene, and others). One or two Stokes frequencies were observed in the spectrum of each of the substances.

It was subsequently observed that SRS is produced when the radiation of a giant laser pulse is focused into a medium placed outside the laser cavity. Using an installation of this type, Terhune [15] registered not only Stokes but also anti-Stokes Raman frequencies. It turned out that the anti-Stokes radiation leaves the cell not in the direction of the excited radiation (as does the Stokes component), but at a certain angle – on the surface of the cone whose axis coincides with the direction of the excited radiation. Each harmonic has its own angle of inclination of the cone generator, so that concentric rings of different colors are produced on a color film placed behind the cell with the investigated liquid and perpendicular to its axis. Intense anti-Stokes scattering of liquefied hydrogen, oxygen, and nitrogen was observed by Stoicheff [16]. Later on, SRS spectra were obtained for gases [17, 18] and solids, diamond single crystals, calcite, and sulfur [19].

The unusual character of the angular distribution of the SRS, observed in [15, 16], has attracted the attention of many workers. Following the first experimental studies, a theoretical investigation was made of the questions connected with the appearance and spatial distribution of the SRS components. Townes and co-workers [20, 21] have developed the relations that must be satisfied by the wave vectors of the exciting radiation and of the various components of the scattered radiation (phase-synchronism relations). In the general case these relations take the form

$$\mathbf{k}_0 + \mathbf{k}_{n-1} = \mathbf{k}_{-1} + \mathbf{k}_n, \quad (1.1)$$

$$\mathbf{k}_0 + \mathbf{k}_{-1} = \mathbf{k}_{n-1} + \mathbf{k}_{-n}. \quad (1.2)$$

Here \mathbf{k}_n are the wave vectors of the light waves with frequencies

$$\omega_n = \omega_0 \pm n\omega_v, \quad (1.3)$$

where $n = 1, 2, 3, \dots$; the minus sign corresponds to the Stokes frequencies, and the plus sign to the anti-Stokes frequencies; ω_v is the vibrational frequency of the molecule.

In the simplest case at $n = 1$ we have

$$2\mathbf{k}_0 = \mathbf{k}_{-1} + \mathbf{k}_1. \quad (1.4)$$

It follows from (1.4) that anti-Stokes radiation is emitted only in a direction that forms a cone with an angle θ_1 to the direction of the exciting radiation. For small angles, calculations yield

$$\theta_1^2 = \frac{1}{n} \frac{\omega_1 - \omega_2}{\omega_1 + \omega_2} \left[\Delta n_1 - \Delta n_{-1} + \frac{\omega_2}{\omega_0} (\Delta n_1 + \Delta n_{-1}) \right]. \quad (1.5)$$

Here n is the refractive index of the medium for the frequency ω_0 ; Δn_1 and Δn_{-1} are the differences of the refractive indices for the frequencies $\omega_0 \pm \omega_2$ and ω_0 , respectively. For normal dispersion of the medium, all these quantities are positive. Since $\omega_2/\omega_0 \ll 1$, we get

$$\theta_1^2 \cong \frac{1}{n} \frac{\omega_1 - \omega_2}{\omega_0 + \omega_2} (\Delta n_1 - \Delta n_{-1}). \quad (1.6)$$

It follows therefore that the angle θ_1 is determined by the slope of the dispersion curve of the medium.

Relations (1.1) and (1.2) for the wave vectors were experimentally confirmed for the SRS components in calcite crystals. Chiao and Stoicheff [22] were the first to observe four anti-Stokes and the second Stokes components in the SRS spectrum of calcite, and measured the apex angles of the emission cones. An absorption ring at the first Stokes frequency was also observed.

In the cited reference, the scattered radiation was photographed directly on a photographic plate placed in the path of the beam emerging from the crystal. If the beam of the exciting radiation is perpendicular to the entrance and exit faces of the crystal, the anti-Stokes components produce on the photographic plate dark concentric rings. By measuring the distance from the photographic plate to the crystal and the diameters of the rings produced on the plate, the angles at which the radiation diverges and the positions of the vertices of the cones were calculated. It turned out that the position of the vertex of the emission cone depends on the position of the focus of the focusing lens relative to the crystal, and a strong dependence of the angles on the focal length of this lens was observed. The authors have therefore extrapolated the data for angles obtained by focusing the exciting radiation with lenses of different focal lengths (8, 20, 30, 50, 127 cm) to the ideal case ($f = \infty$). In this case the pump wave can be regarded as plane.

The SRS-component emission angles calculated from the phase-synchronism relations (1.1) and (1.2) are in much worse agreement with experiment when the angular distribution of SRS in liquids is observed. Thus, for example, Hellwarth and co-workers [23] obtained, in an investigation of the SRS spectra in nitrobenzene, a considerable discrepancy between the experimental results and the calculations.

The calculation of the angles yielded the values $\theta_1 = 2.5 \pm 0.2^\circ$; $\theta_{-2} = 12.4 \pm 1^\circ$; $\theta_{-3} = 16$ or $12 \pm 1^\circ$. Experiment yielded substantially different results: $\theta_1 = 3.1 \pm 0.1^\circ$; $\theta_{-2} = 3.9 \pm 0.1^\circ$; $\theta_{-3} = 3.8 \pm 0.1^\circ$.

Further investigations of the angular distribution of SRS in liquids have shown this phenomenon to be more complicated than it appeared to be at first. Garmire [24] has established that two classes of SRS of higher order exist in liquids. Class-I radiation produces an angular distribution that satisfies the synchronism conditions (1.1) and (1.2). Class-II radiation is emitted along generators of cones whose angles differ from those calculated from the synchronism conditions. In the case of class-II radiation the rings can be diffuse and can sometimes split into several components.

The onset of class-II radiation is attributed in [24] to the breakup of the laser beam in the liquid into very thin filaments (see Section 2).

A prominent place is occupied in Garmire's research [24, 25] by the question of the role of the first Stokes component upon excitation of anti-Stokes components. According to Garmire, anti-Stokes components of class I can be emitted in the presence of a sufficiently intense first Stokes component at the synchronism angle. If there is no emission in this direction, then only class-II radiation can be excited.

In liquids there is usually not enough intense radiation at the Stokes frequency in the direction of the angles corresponding to the phase-synchronism conditions, owing to the strong forward directivity of the radiation at the first Stokes frequency. According to estimates [25], the intensity of the first Stokes component in

benzene, in a cell 10 cm long and at the angle of phase synchronism, is 10^{-6} of the intensity of this radiation in the direction of the exciting beam. Therefore the radiation of the rings of class I will be very weak and the radiation of class II will mask that of class I. Accordingly, the SRS radiation of higher order in liquids at angles that do not coincide with those obtained from phase synchronism, which was observed in the cited paper [23] and in a number of others [26-29], is in fact class-II radiation.

To observe class-I radiation in liquids, Garmire [25] performed a number of experiments. In these investigations, the SRS was excited by a parallel light beam from a Q-switched ruby laser of ~ 10 MW power. To increase the intensity of the Stokes radiation near the direction corresponding to the synchronism conditions the axis of the cell with the investigated liquid was mounted at an angle $\approx \theta$ (the synchronism angle) relative to the direction of the laser beam. The cell was 10 cm long and its windows were strictly parallel. Part of the Stokes radiation at the angle θ was reflected back from the glass-air interface, so that the intensity of the radiation in this direction was increased by 10^4 times. This increase of the intensity of the Stokes radiation was sufficient to excite class-I anti-Stokes components. The first and second class-I anti-Stokes components were observed in the form of intense short arcs. These arcs and the first Stokes component were located on two opposite sides of the laser beam, as expected from the phase-synchronism relations. The radiation of the class-II anti-Stokes components of the first and second orders was observed in these experiments in the form of solid rings. The diameters of the rings and their intensities were independent of the amplification of the first Stokes component.

Anti-Stokes radiation of class I was sometimes observed in organic liquids (benzene, nitrobenzene) in cells of great length (25-50 cm) without special measures to amplify the first Stokes component [25] in multi-mode excitation. The intensity of this radiation was much less than the intensity of the corresponding class-II rings.

The anti-Stokes components of class I were observed sufficiently easily in acetone and in cyclohexane [25, 30]. It was suggested in [25] that in acetone and cyclohexane the class-II rings are weaker than in benzene and nitrobenzene, and therefore they do not mask the class-I rings.

The class-I radiation observed in calcite is explained in [25] in the following manner: scattering of the light by the inhomogeneities in the calcite is so strong that the intensity of the first Stokes component is appreciable in a large angle interval (including at the phase-synchronism angle), so that intense class-I radiation at anti-Stokes frequencies is produced and masks the weak class-II radiation. Thus, according to Garmire [25], the ratio of the intensities of the class-I and class-II radiation depends on the properties of the scattering medium and on the experimental conditions. In principle, these two classes of radiation are produced independently of each other.

The angular distribution of the SRS in gases was investigated in [3, 17]. In hydrogen gas, the observed angle of the anti-Stokes radiation agrees well with the value calculated from the phase-synchronism conditions. Since the dispersion in hydrogen is small and is proportional to the density, the anti-Stokes radiation of first order should make an angle proportional to $p^{1/2}$ with the direction of the axis (p is the pressure of the gas). This conclusion is confirmed by experiment. At low pressures the apex angles of the cones of the anti-Stokes and higher Stokes components are small. Therefore the emission of these SRS components in gases takes place in practice within the limits of the aperture of the exciting-light beam.

Among the liquids in which the angular distribution of the SRS satisfies the phase-synchronism conditions (1.1) and (1.2), notice should be taken of liquid nitrogen. As shown in [31], in liquid nitrogen the calculated angles of the cones of the anti-Stokes and second Stokes components of the SRS are in satisfactory agreement with the values of the angles measured in that study. It should be noted that in [32] it was observed that the apex angles of these SRS-component cones depend not only on the focal length of the lens that focuses the exciting radiation beam in the cell, but also on the length of the cell with the liquid nitrogen.

Mention was already made of the good agreement between the theoretical and experimental data for the apex angles of the cones of the SRS components in calcites. It was shown in a group of studies [33-38] that the angular distribution of SRS in crystals is much more complicated than in isotropic media. In addition to the previously observed cones of SRS emission in crystals, identical with the SRS cones in isotropic media (principal radiation), an additional radiation was observed. The existence of this supplementary radiation was theoretically predicted by Lugovoi [35].

In a uniaxial calcite crystal, in accordance with the theory, supplementary-radiation cones were observed in the form of surfaces of revolution [33, 34, 38]. In these experiments, a linearly polarized ruby-laser pump beam passed through the calcite crystal as the ordinary wave. The rings of the principal and supplementary radiation were observed for a number of anti-Stokes and second Stokes components of the SRS. The

principal radiation rings do not depend on the orientation of the crystal relative to the laser beam, and the centers of these rings always remain on the laser-beam axis. The supplementary-radiation rings depend on the angle ν between the direction of the optical axis of the crystal and the wave vector of the pump beam. The centers of the supplementary rings are shifted relative to the center of the principal rings in the direction of the rotation of the optical axis of the crystal.

The dependence of the supplementary-radiation rings on the angle is the following. At small ν , the principal and supplementary rings of a given SRS component are first split apart. On further increase of ν , the shift of the center of the supplementary rings increases, as does the ring diameter. The supplementary radiation is observed only in a limited interval of angles ν .

In [37, 38] they investigated the angular distribution of SRS in the biaxial crystal aragonite. In contrast to the uniaxial crystals, the principal and supplementary radiation of the SRS components in biaxial crystals propagates along cones of revolution only at a definite orientation of the crystal and only at small values of the angle ψ between the direction of one of the optical axis of the crystal and the wave vector of the pump beam. When these conditions are not satisfied, the cones of the SRS are generally speaking not surfaces of revolution. Therefore the photographed radiation rings are not circles.

In [39, 40] they investigated the angular distribution of SRS in diamond (frequency 1332 cm^{-1}). The diamond crystal was a plate 2.2 mm thick. Radiation cones of the first, second, and third anti-Stokes components and of the second Stokes components of the SRS were observed, as well as minima of the intensity in the diffuse scattering of the first Stokes component.

The observed cone angles are in good agreement with the theory based on the phase-synchronism condition obtained by Townes [20, 21]. It turned out that the angles of the cones do not depend on the power of the exciting radiation, but do depend on the convergence angle of the exciting radiation. Rivoire [41, 42] investigated the spatial distribution of SRS radiation in benzene, nitrobenzene, and carbon disulfide. In these investigations, besides the photographic method, a photoelectric method of recording the SRS components was used. The radiation emerging from the cell with the investigated liquid was directed with a total-internal-reflection prism onto the slit of a spectrograph. The total-internal-reflection prism was mounted on the stage of a goniometer. By rotating the stage it was possible to project on the slit of the spectrograph various sections of the scattered-beam cross sections and to study its structure by a photoelectric method. The use of this method, naturally, calls for high stability of the SRS excitation, otherwise a large scatter is obtained in the intensities of the spatial distribution of the SRS. Rivoire obtained a complicated structure of the spatial distribution of the radiation at the first Stokes component and the other SRS component, exceeding the limits of the measurement errors.

2. Influence of Self-Focusing of the Light in the Scattering Medium on the Angular Distribution of the SRS Components

When intense light waves propagate through a material medium, an important role is played by effects of self-action of the waves, effects that frequently determine the course of the nonlinear processes in the medium. Within the framework of nonlinear optics, the effects of self-action of intense light waves is described by the real part of the nonlinear susceptibility χ_{ijk} , χ_{ijkl} , etc.

In a strong optical field, the refractive index, just as the susceptibility, depends on the field intensity E . For transparent media this dependence is quadratic,

$$n = n_0 + n_2 |E|^2. \quad (2.1)$$

Because of the nonlinear dependence of the refractive index on the field intensity, a number of phenomena occur, and the most interesting from our point of view is the self-focusing of the light. The causes of the nonlinear part of the refractive index can vary. The most important of them are the change of the polarizability and the change of the density of the medium in the strong optical field. The change of the polarizability is due to the high-frequency Kerr effect [43-45], to deformation of the electron shells [45, 46], or to the increase of the polarizability of the excited molecules [47, 48]. The change of the density of the medium may be due to electrostrictions [49]. Generally speaking, the nonlinear increment of the refractive index can be due to all the foregoing causes. Usually, however, it is possible to separate the most significant mechanism that produces this increment.

In the high-frequency Kerr effect and electrostriction, the regions of maximum light intensity are usually simultaneously also the ones with the highest optical density. Therefore the nonlinearity of the refractive index

leads to a concentration of the energy, i.e., the beams contract from the periphery into a region where the field is maximal. This effect was named self-focusing of the light beam.

An effect counteracting the concentration of the optical energy is diffraction. There should exist consequently a certain critical density, starting with which the focusing effect can exceed the diffraction divergence of the beam. The critical power is equal to [43, 50-53]

$$P_{cr} = (1.22 \lambda)^2 C / 256 n_2, \quad (2.2)$$

where λ is the laser emission wavelengths; n_2 is the change of the refractive index in a constant electric field, and is connected with the Kerr constant B by the relation

$$n_2 = 2\lambda B/3. \quad (2.3)$$

When the power P exceeds the critical value, self-focusing sets in. It was believed for a long time that self-focusing causes the laser beam to split into thin filaments with high light intensity in each, and these filaments form unique optical waveguides.

Lugovoi, Prokhorov, and others have developed a different model of self-focusing of light – the model of moving focal planes [54-58]. It was established that beyond the point where the beam collapses there is produced not a waveguide regime, but a certain number of foci – regions with very high energy concentration and small dimensions, $\sim 5-10$ wavelengths. As a result of the nonstationary character of the laser beams in time, the focal regions move along the axis of the light beam. What were previously assumed to be self-focusing "filaments" are the trails of the "traveling foci."

In the presence of self-focusing in the medium, the conditions for the excitation of SRS are significantly changed. These two phenomena are the subject of a large number of experimental and theoretical studies [2, 25, 59-76].

From the point of view of the angular distribution of SRS in media with self-focusing, great interest attaches to the papers by Garmire [24, 25], who pointed out the existence of rings of class II (see Section 1).

According to Garmire, there are two distinguishing features of class-II radiation.

1. Class-II radiation does not satisfy the phase-synchronism conditions (1.1) and (1.2). To compare the calculated and experimental values of the angles between the axes and the generators of the cones of classes I and II, exact measurements were performed in [24, 25] of the dispersion of a number of investigated liquids. For the cones of class I, satisfactory agreement was obtained between the calculated and experimental data. The angles of the cones of class II in the anti-Stokes region are larger, and in the Stokes region are smaller, than the corresponding phase-synchronism angles, the difference reaching as high as 30%.

2. Class-II rings are much more intense than class-I rings, and are more diffuse. Therefore in those media in which scattering of class II is excited, the class-II rings usually mask the class-I rings. It is important that the intensity of the class-II rings of the first anti-Stokes component is much higher than the intensity of the radiation of the first Stokes component propagating at the synchronism angle. In addition, the anti-Stokes radiation of class II does not depend on the intensity of the Stokes radiation propagating at the phase-synchronism angle to the axis. The rings of the anti-Stokes radiation remain symmetrical and homogeneous when the cell is tilted away from the axis (see Section 1). All this indicates that the class-II anti-Stokes radiation cannot be due to Stokes radiation propagating at the phase-synchronism angle. According to Garmire, this radiation can be excited only by Stokes radiation propagating near the axis of the exciting radiation (at an angle not exceeding 0.01 rad).

3. When the SRS is excited by focused laser radiation, the diameter of the rings of class I varies with the focal length of the focusing length, whereas the diameter of the class-II rings does not depend on this quantity. When laser radiation is focused with a cylindrical lens, the class-I rings turn into ellipses, whereas the class-II rings remain circles. Because of this property of the class-II rings, they can be distinguished experimentally from those of class I.

It is noted in [25] that the angular distribution of SRS has a complicated structure in a number of liquids, namely, the rings of class II of higher order usually split into two or more components; in a number of cases one observes in the anti-Stokes radiation, besides the off-axis radiation, also radiation directed along the axis. It is noted also that the diameters of the rings are not quite stable (the uncontrollable change of the diameter can reach 20%).

The change of the character of the angular distribution of the SRS, according to the data of [77], can serve as a criterion for the onset of self-focusing in a medium. In the cited reference they investigated

radiation at anti-Stokes frequencies in acetone and cyclohexane and in a mixture of these substances with carbon disulfide. The content of the carbon disulfide in the mixtures was $\sim 5-10\%$. In pure acetone, only radiation of class I was observed. In the mixture of acetone with carbon disulfide the character of the angular distribution of the first anti-Stokes component changed. Near the threshold, a sharp "surface radiation" ring was observed with a diameter given by the equation

$$k_1 \cos \theta = 2k_0 - k_{-1}. \quad (2.4)$$

(The theory of surface radiation is considered in [78].) With increasing pump a broad ring of smaller diameter, belonging to class-II radiation, appeared simultaneously with the sharp surface-radiation ring.

Similar observations were made when SRS was excited in cyclohexane and, respectively, in a mixture of cyclohexane with carbon disulfide.

The conclusions drawn in [25, 77] that self-focusing influences the structure of the class-II rings seem too categorical to us. The point is that in the cited studies the SRS was excited in a number of cases by a laser in the multimode regime, and this leads (according to our data) to a complication of the angular distribution of the SRS. We note that in nitrobenzene, in which the self-focusing is very clearly pronounced, the rings of class II remain sharp, a fact that likewise does not agree with the conclusions of the cited papers.

The assumption that the class-II rings are due to emission from self-focusing filaments, advanced in [25, 77], is also ambiguous. For example, in [25] results are presented of experiments in which in pure acetone and cyclohexane they observed sharp rings of class II and class I simultaneously. No special investigations of self-focusing in these liquids were made in [25].

There is no doubt that in many substances self-focusing sets in ahead of SRS. For example, in such substances typically used in SRS experiments as benzene, nitrobenzene, and carbon disulfide, the self-focusing threshold estimate from Eq. (2.2) is, in agreement with experiments [72], 10-20 times lower than the SRS threshold. This means that the SRS phenomenon in these substances takes place in a medium in which the exciting radiation has already been subjected to self-focusing. Thus, the change of views on the nature of the self-focusing makes the assumption that the rings of class II are connected with self-focusing filaments unfounded. Subsequent studies lead to an even more complicated character of the connection between SRS phenomena and self-focusing.

The connection between the distribution of the SRS radiation over the beam cross section (in the "near field") and the phenomenon of self-focusing was investigated in [66, 73-76]. The substances investigated had both large Kerr constants (carbon disulfide) and small Kerr constants (liquid nitrogen, calcite). Self-focusing at the first Stokes component of SRS was observed in liquid nitrogen in the absence of self-focusing at the exciting radiation (SRS self-focusing). The discovery of the SRS self-focusing phenomenon shows that even in substances with small Kerr constants the SRS phenomenon is subject to such complicating nonlinear effects as self-focusing.

There is no doubt that self-focusing and SRS very frequently accompany each other. Self-focusing leads to a redistribution of radiation density and to an increase of the density at individual points of the exciting beam, and this contributes to the appearance of SRS.

A detailed analysis of the entire aggregate of questions connected with self-focusing and excitation of SRS is beyond the scope of the present article. Our task is to trace the relation between these phenomena only for those cases when they have a direct bearing on our experiments.

3. Intensity Distribution in the SRS Spectrum

Usually only a small number of the frequencies from the total Raman scattering spectrum of a given substance appears in the SRS spectra. Most frequently the SRS spectrum contains one of the vibrational frequencies. In some substances, for example in styrene [79, 80], two frequencies are simultaneously excited. In mixtures, likewise at high exciting-radiation powers, frequencies of two components appear [81, 82].

The most essential feature of the SRS spectra is the considerable intensity of the anti-Stokes and Stokes harmonics compared with the harmonics of the spontaneous Raman scattering.

The ratio of the intensities of the various SRS components depends on the experimental conditions. It must be borne in mind that a significant role is played in SRS, besides the radiation processes, also by processes of absorption at various frequencies (inverse Raman scattering). If we recognize that at each Stokes and anti-Stokes frequency the radiation can be produced by different mechanisms and also have different angular

characteristics (rings of classes I and II, radiation along the axis of the exciting light), then the overall picture of the distribution of the SRS intensity turns out to be most complicated. An investigation of the distribution of the intensity in the SRS spectra under various excitation conditions casts light on the roles of the different excitation mechanisms. Such investigations, however, are still quite few and insufficiently detailed.

Sokolovskaya et al. [66] investigated the relative intensity of the first and second Stokes lines and the first anti-Stokes line in the CS_2 spectrum at temperatures from $+20$ to -100°C . The intensities of the lines of the ordinary Raman spectra of CS_2 increase with decreasing temperature [83]. Accordingly the line intensity in the SRS spectrum also increases with decreasing temperature, and becomes radically redistributed among the various components. In particular, they observed in [66] a considerable increase of the relative intensity of the second Stokes component.

The intensities of various SRS components were investigated [84, 85] as functions of the energy of the exciting radiation, using a photographic method for CS_2 (656 cm^{-1} line) and a calorimetric method for liquid nitrogen (2330 cm^{-1} line). At low values of the exciting-radiation energy, the intensities of the SRS components increase approximately exponentially, with the argument of the exponential decreasing with increasing number of the harmonic. With increasing E , the rate of growth of the energy of the SRS components decreases. At large values of E , the curves corresponding to the SRS components of lower order reveal a pronounced "saturation" (horizontal section of the curves). Attention is called also to the fact that the energy of the exciting radiation passing through the sample remains practically constant when the energy E of the exciting radiation entering the sample is changed significantly.

In some cases the task is to obtain maximum conversion of the energy of the exciting radiation in a single (first Stokes) SRS component. To solve the problem, a system consisting of a driver laser and amplifier was used in [86]. In such a system, when the propagation directions of the exciting radiation and of the first Stokes components in the amplifier coincided, three regimes were observed: a) linear amplification, wherein the signal pulse retained its waveform; b) the start of saturation, when the amplified pulse deviated from the input pulse but still did not duplicate the pump; c) strong saturation, wherein the output signal duplicated the waveform of the pump pulse. The signal quantum yield at the first Stokes frequency then approached 100%.

From the point of view of identifying the principal SRS mechanism, a great interest attaches to data on the correlation between the intensity of the first anti-Stokes component and the first Stokes component [84].

The scattered radiation was registered at angles 20 – 25° , i.e., the intensity integrated over the angles was registered. The intensity of the first anti-Stokes component increased rapidly with increasing intensity of the first Stokes component. This function agrees well with the mechanism of the Stokes – anti-Stokes four-photon coherent process, which will be considered in Chapter IV.

The mechanism of successive excitation of various SRS components was treated in [87] as a parametric process. The SRS at the Stokes component is in this case a parametric process due to interaction of the light waves with the phonon waves, while at the anti-Stokes component it constitutes parametric interaction of four waves: laser, Stokes, anti-Stokes, and phonon. It is assumed that the laser wave is plane and that the power of the laser radiation does not vary over the length of the cell. Under these assumptions they solved in [87] a system of equations that connect the intensities of Stokes components of different orders for different beam path lengths in the medium. Numerical computer calculations were performed for nitrobenzene. It was shown that as the radiation propagates along the cell the energy is being transferred to higher and higher Stokes components. Regions in which the waves of only one component exist alternate along the cell with overlap regions containing two components, with the intensity of one of the waves decreasing rapidly, and that of the other increasing.

The theory developed in [88] agrees qualitatively with experiment. However, such a distinguishing feature of SRS as the almost constant ratio of the intensities of the exciting radiation, of the first Stokes component, and of the second Stokes component contradicts the conclusions of this theory.

The initial premises of this theory were refined in [89] to conform with the real conditions of the experiment. In particular, account was taken of the fact that some of the intensity of the exciting radiation becomes distributed over the cross section of the cell (radial distribution). Computer calculations were performed for carbon disulfide under the assumption that the radial distribution is Gaussian. The calculations have shown that all the Stokes components are simultaneously present at the exit from the cell (if the exciting radiation is strong enough).

Experiment [88] showed good agreement with the calculations by the theory of [87]. The object of investigation in [88] was carbon disulfide, which is a self-focusing liquid. To exclude the influence of self-focusing

and of stimulated Mandelstam–Brillouin scattering (SMBS) on the SRS process, the SRS was excited by short pulses of duration τ from 0.6 to 1.5 nsec, not long enough for the indicated accompanying processes to develop.

The efficiency of conversion of the radiation into the various SRS components reached 60%. With increasing τ , this efficiency decreased and the intensity of the SMBS increased.

In the papers cited above, no account was taken of four-photon processes of SRS excitation. Without going into details, we mention that the theory of these processes was developed in [7, 90–92].

As indicated above, to ascertain the real mechanisms that lead to the onset of different SRS components, great interest attaches to the ratio of the intensity of the radiation propagating in the direction of the exciting radiation into the cones.

An attempt to explain the singularities of the anti-Stokes radiation propagating along the axis (i.e., in the direction of the exciting light) and into the cones was made in [31, 32, 93].

In [93] they investigated carbon disulfide, benzene, cyclohexane, acetone, as well as a mixture of acetone with carbon disulfide. In carbon disulfide, the picture of the angular distribution always had a smeared out and diffuse character. A uniformly distributed background was observed inside a blurred ring. The central spot was only lightly discerned against this background. Clear-cut photographs were obtained for benzene. For the first anti-Stokes component, the intensity of the radiation propagating along the axis was approximately equal to the intensity of the radiation propagating in the cones. Axial radiation was observed also in the distribution of the second anti-Stokes component, but its intensity was lower than for the radiation going into the cones.

In cyclohexane, at low values of the pump energy, the radiation produced was that of the first anti-Stokes component and propagated along the axis. With increasing pump energy, anti-Stokes radiation was produced and propagated in a cone whose intensity increased rapidly with increasing pump energy. Similar results were obtained for acetone.

Morozova [32] investigated in detail the anti-Stokes radiation propagating along the axis and in the cones, in substances with small Kerr constants, namely liquid nitrogen and calcite. It was observed that at low pump energies the first anti-Stokes component is produced and is directed only along the axis. With increasing pump energy, an anti-Stokes ring also appears. Further increase of the pump leads to an increase of the intensity of the ring and to a decrease of the intensity of the central spot, which vanishes at still pump energies.

A similar change in the ratio of the intensities of the central spot and of the ring results from a decrease in the focal length of the lens that gathers the laser radiation into the scattering medium. At a large focal length of the lens, only a central spot is observed. Decreasing the focal length leads first to the appearance of a ring simultaneously with the central spot. At short focal lengths, only the ring is observed.

Morozova [32] investigated also the influence of the length of the cell with the liquid nitrogen on the angular distribution of the SRS. It turns out that an increase of the length of the cell causes the same change in the picture of the angular distribution as an increase in the energy of the exciting radiation, but the changes of this picture manifest themselves less strongly than when the energy is changed.

The results of [32] are attributed to the presence of a unique SRS self-focusing in media with small Kerr constants, with the self-focusing assuming an increasing role when the energy density of the exciting radiation is decreased.

The angular distribution of the intensity of the Stokes components of SRS in benzene and in carbon disulfide was investigated in [94–96]. The SRS was excited by a harmonic of a YAG-Nd³ laser at a wavelength 0.53 μm . Owing to partial mode locking, the exciting radiation comprised a sequence of short pulses of 0.5 nsec duration. At such a short exciting-pulse duration, the SRS in the benzene was not encumbered by accompanying SMBS and self-focusing (it was impossible to get rid of the self-focusing in CS₂).

In benzene, at a cell length 20 cm, the second Stokes component was produced in the form of a beam having the same directivity and the same divergence as the first Stokes component (4 mrad). The threshold value of the pump at the wavelength 5300 Å was 150 MW/cm² for this process. At a cell length 10 cm, the SRS threshold increased to 300 MW/cm² and the second Stokes component was radiated into a cone whose generator made an angle $2.4 \pm 0.2^\circ$, or 0.040 ± 0.003 rad, with the axis. This angle corresponds to off-axis radiation of class II. Thus, class-II radiation was observed in the cited studies in the absence of self-focusing, a fact which we consider to be worthy of much attention. The vertex of the cone was located at the end of the cell. When the

pump power was increased by 1.3 times, radiation was produced both in a cone and along the axis. The authors attribute the difference they observed in the angular distribution of SRS to the different geometrical conditions of the excitation of the SRS in the long and short cells.

Judging from the published data cited in the present section, we can conclude that the laws governing the formation of axial SRS radiation and radiation into cones are different.

4. Theory of the Angular Distribution of the SRS Components

As follows from the review of the experimental material, the laws governing the angular distribution of SRS are quite complicated and varied. The emission of each SRS component follows some selected direction, and a strong concentration of the energy of the scattered radiation along this direction is observed. The ratio of the intensities of the radiation propagating along the axis of the exciting radiation (central spot) and at different angles to the axis (rings of various classes) depends on the singularities of the nonlinear medium and on the excitation conditions.

The task of the theory of the angular distribution of SRS is to explain the predominant concentration of the scattered radiation along certain selected directions and the laws governing the partition of the intensities among the axial radiation and the radiations in the cones of various classes. It should be noted that only the first of these problems has been dealt with in detail up to now.

1. Semiclassical Theory of SRS. Some features of the angular distribution of SRS can be understood even on the basis of a very simple semiclassical treatment of the process of SRS production [20, 21, 97].

We consider a molecule with polarizability α , situated in an electric field \mathbf{E} . Under the influence of this field, the molecule acquires an electric moment $\mu = \alpha \mathbf{E}$ and a potential energy $u = 1/2 \alpha E^2$.

Let x be the vibrational coordinate describing a certain vibrational process in the molecule. Assuming that the molecule is acted upon by a driving force of

$$F = -\frac{\partial u}{\partial x} = \frac{1}{2} \frac{\partial \alpha}{\partial x} E^2, \quad (4.1)$$

we obtain the equation of the intramolecular vibrations

$$m\ddot{x} + R_0\dot{x} + fx = F = \frac{1}{2} \frac{\partial \alpha}{\partial x} E^2 \quad (4.2)$$

or

$$m\ddot{x} + R_0\dot{x} + fx = F_0 \cos \omega t \quad (4.3)$$

(the driving force is assumed harmonic). The solution of this equation for the frequency ω close to the resonant frequency $\omega_r = \sqrt{f/m}$ is

$$x = \frac{F_0}{R_0 \omega} \sin \omega t. \quad (4.4)$$

Here R_0 is a phenomenological damping constant; f is the quasielastic constant of the considered molecule, and corresponds to a normal vibration with frequency ω_r .

We assume now that the electric field \mathbf{E} is an aggregate of a certain number of plane waves that differ in frequency by an amount ω or (in the more general case) by a multiple of ω . In the simplest case of two such waves

$$\mathbf{E} = \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_0 \mathbf{r})} + \mathbf{E}' e^{i(\omega' t - \mathbf{k}' \mathbf{r} + \varphi')}, \quad (4.5)$$

where $\omega_0 - \omega' = \omega$. In this case

$$E^2 = E_0^2 + E'^2 + 2E_0 E' \cos [(\omega_0 - \omega')t - (\mathbf{k}_0 - \mathbf{k}') \mathbf{r} - \varphi'], \quad (4.6)$$

the constant terms can be left out here, and we obtain

$$F_0 = \frac{d\alpha}{dx} \mathbf{E}_0 \mathbf{E}'. \quad (4.7)$$

Accordingly

$$x = \frac{\mathbf{E}_0 \mathbf{E}' \frac{d\alpha}{dx}}{R_0 (\omega_0 - \omega')} \sin [(\omega_0 - \omega')t - (\mathbf{k}_0 - \mathbf{k}') \mathbf{r} - \varphi']. \quad (4.8)$$