

MODERN TRENDS IN THE SPECTROSCOPY OF RAMAN SCATTERING OF LIGHT

V. A. ZUBOV, M. M. SUSHCHINSKIĬ, and I. K. SHUVALOV

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Usp. Fiz. Nauk **89**, 49-88 (May, 1966)

INTRODUCTION

THE spectroscopy of Raman scattering of light has been undergoing intensive development in recent years, and the field of its application has greatly expanded. Progress in this branch of spectroscopy has been made possible primarily by the extensive introduction of photoelectric techniques for spectrum registration. Many new procedures and research methods have been developed on this basis and used for precision measurements of the Raman line intensities and for registration of spectra against strong backgrounds. Another important circumstance is the use of principally new sources of light—lasers—for Raman spectroscopy. At high excitation power, Raman scattering of light acquires utterly new properties, making investigation of this phenomenon more interesting.

In this review we pay principal attention to those new trends in Raman spectroscopy which have appeared in recent times and are only weakly reflected in the previously published reviews (see, for example, [1]). In the section devoted to ordinary Raman scattering, we confine ourselves to a description of those new methods which offer principally new possibilities of obtaining and investigating Raman spectra. New data on the spectra are given only by way of illustration. In the section devoted to the rapidly developing field of induced Raman scattering of light, we present essentially the results of experimental papers published after our earlier review [2].

I. ORDINARY RAMAN SCATTERING OF LIGHT

1. Spectrophotometric Schemes for Recording Raman Spectra

In measurements of Raman line intensities, great importance attaches to the operating stability of the apparatus. Causes of instability may be changes in the sensitivity of the photomultiplier, in its supply voltage, in the gain of the recording circuit, in the intensity of the source of exciting radiation, etc. Several spectrophotometric schemes to eliminate such instabilities have been proposed. Their operating principle is based on the fact that they record not simply the intensity of spectral lines, but the ratio of the Raman line intensity to the intensity of the light of a suitably chosen comparison source (most frequently, to the intensity of the exciting line). Such systems can be subdivided into two classes:

1. Systems with electric division of the signals obtained from the scattering sample (measured signal) and directly from the source of excitation of the spectrum (comparison signal).

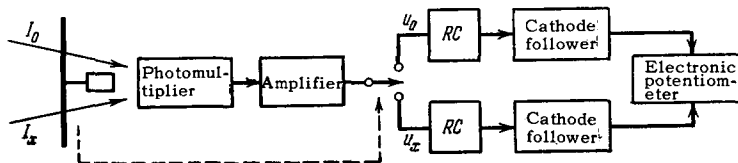
2. Optical division systems.

To explain the advantages and disadvantages of each class, let us consider their operation briefly.

a) Electric division systems. There are two systems based on the principle of electric division. In the first the separation of the signals is by frequency [3] and in the second, by phase [4]. Light from the scattering sample (measured signal) is modulated by a chopper and passes through a monochromator to a photomultiplier. The light from the spectrum-excitation source—the comparison signal—is also modulated, but either at a different frequency (separation by frequency), or in counterphase to the measured signal (separation by phase, Fig. 1). The comparison signal strikes the same photomultiplier, but bypasses the monochromator. The line used for excitation of the scattering spectrum is separated by a filter placed in the light beam of the comparison signal. The signal picked off the photomultiplier load is the sum of the two voltages and is amplified. The frequency characteristic of the amplifier in the first circuit variant should ensure identical amplification of both signals. This is followed by a device which separates the signals. In the case of frequency separation, such a device may be, for example, two synchronized detectors to separate the signals modulated at different frequencies. In the case of phase separation a commutator is used, which feeds the signal to one channel during one half of the cycle and to the other channel during the second half. The operation of the synchronous detectors and of the commutator is controlled by synchronizing electric signals obtained from special pickups. To this end, the light from an incandescent lamp is modulated by the same chopper as the working signals, and strikes a photocell (in the first case two photocells are used, each for its own frequency). The signal from the photocell is amplified and is fed to a synchronous detector or commutator. The synchronization phase is usually set by moving the photocell modulator along a circle. In both systems the comparison signal is fed after separation, rectification, and smoothing further to a helipot and the measured signal is fed to the input of an electronic potentiometer. This separates the signals. The pen of the automatic recorder, which is coupled to the helipot, records the ratio of the working-beam signal to that of the comparison beam. Since the signals are proportional to the light intensities, the chart produced gives the ratio of the intensities of the measured line and the comparison line.

The quality of stabilization afforded by such systems is characterized by the following data: the ratio of the voltages of the measured and comparison signals remains constant when the signal from the photomultiplier changes by a factor more than two.

FIG. 1. Electric separation system in which the signals are separated by phase.



b) Optical division system^[5, 6]. A block diagram of the setup is shown in Fig. 2. Light scattered by the investigated substance, placed in cell C, is aimed by condenser lens L_1 into the input slit Sl_1 of monochromator M. In front of the slit is located the disc of the chopper Ch. The light of the comparison beam is fed directly from the spectrum excitation source S through an optical wedge to slit Sl_3 . Lens L_2 acts as a condenser, that is, it produces an image of the source S on the slit Sl_3 . This beam is modulated in counterphase to the main beam. The measured beam from the monochromator exit slit Sl_2 strikes the photomultiplier PM. The comparison beam, bypassing the monochromator, strikes the same photomultiplier. The exciting line is separated in this beam by filter F. The obtained electric signal is amplified by preamplifier PA and by the main selective amplifier A, tuned to the modulation frequency, and is then fed to the synchronous detector SD. The reference signal for the detector is taken from a photoresistor PR illuminated by a small incandescent lamp, and is amplified by the synchronizing signal amplifier SSA. The system operates in the following manner. If the light intensities in the main beam and in the comparison beam are equal, then the electric signal across the photomultiplier output load contains no ac component and consequently is not passed by the selective amplifier to the synchronous detector. But if one of the signals has changed, then an ac component is produced across the photomultiplier load, and is then amplified and fed to the synchronous detector whose output, with appropriate polarity, is fed to the block controlling the reversible motor (Cont). The reversible motor rotates the optical wedge OW, which is coupled to it, in a direction such as to change the intensity of the comparison beam until it becomes equal to the intensity of the measured beam. The pen of the plotter P, which is coupled to the optical wedge, records in this case the ratio of the intensity of the main beam to the intensity of the comparison beam.

The quality of stabilization afforded by this system is illustrated by Fig. 3. The upper series of curves was obtained with a single-beam system, using an ac amplifier. The lower series of pictures was obtained with a two-beam system, using the described system. We see that a change in the intensity of the spectrum-exciting source by a factor of 2, which leads to a

change in the recorded signal in the single-beam scheme by a factor of 2, has hardly any effect on the registered intensity in the two-beam system. In both systems, the signals are received by the same photomultiplier, and the same amplifier channel is used for both signals. Inasmuch as the ratio of two signals is recorded, the instabilities in either the receiver and the amplifier circuit, and the instability in the incandescence of the spectrum-excitation source are automatically eliminated.

Let us examine the noise characteristics of these systems. As is well known, the photomultiplier noise consists of dark-current noise and photocurrent noise, the rms noise being proportional to the total current. Under ordinary conditions, the photocurrent from intense Raman lines is several times larger (by up to ~ 100 times) than the dark current or the photocurrent of the light background (in the case of a well purified sample). If a good specially-selected photomultiplier is used, the photocurrent due to the light background also exceeds the dark current. Thus, the principal role is played by the photocurrent noise, which we shall henceforth call the light noise. The rms light noise of the photomultiplier is proportional at the same time to the photocurrent. The latter, on the other hand, is proportional to the light flux incident on the photocathode. Comparison, on the basis of this parameter, of the optical-division scheme with the usual single-beam system with signal modulation and with ac amplification shows that the rms light noise of the photomultiplier is twice as large in the optical-division system, since two light fluxes of equal magnitude (measured and comparison) are incident on the photocathode. In the electric-division system with frequency separation, the influence of the light flux in the comparison channel should be equal in magnitude to the largest recorded light flux, that is, to the light flux

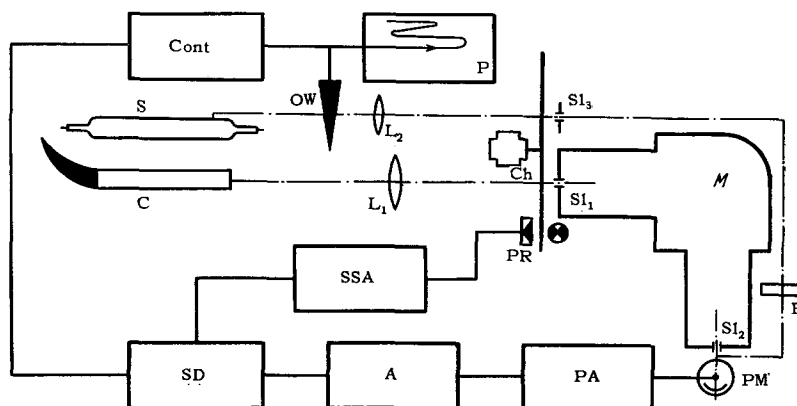


FIG. 2. Diagram of optical separation system.

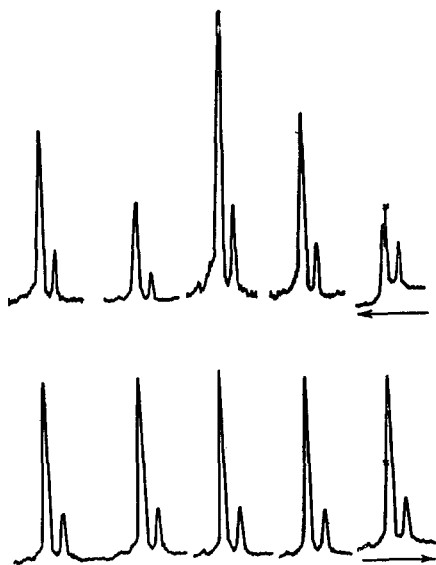


FIG. 3. Illustration of the quality of stabilization ensured by the optical separation system.

which produces a full-scale signal. Only in this case is it possible to equalize by means of the helipot the electric signals of the measured beam and of the comparison beam. When small signals are recorded, this circumstance is quite unfavorable, since the comparison signal may exceed by several times (n times) the measured signal. The rms light noise will in this case be $n+1$ times larger than in the case of the single-beam system with modulation and with ac amplification, and consequently larger by a factor $(n+1)/2$ than in the case of a system with optical division.

In the system using electric division with phase separation of the signals, the light flux in the comparison channel should also be equal in magnitude to the largest recorded light flux. In this case, however, the commutator that separates the measured and comparison signals makes the noise connected with these signals entirely independent. Thus, the rms light noise of the photomultiplier for the measured signal is the same as in the case of the single-beam system with modulation and ac amplification. The noise connected with the comparison signal can be made arbitrarily small by suitable choice of the comparison signal. Consequently, from the point of view of noise characteristics, preference must be given first to the system using electric division with phase separation of the signals, and then to the optical-division system. At the present time, a commercial spectrophotometer based on the electric-division system with phase separation of the signal is being developed jointly by the Leningrad Joint Organization of Optical-mechanical Enterprises and by the Academy of Sciences Commission on Spectroscopy^[7].

Notice should be taken of the advantages of optical division from the point of view of construction of the amplifier for the recording unit. In the electric-division system, the electric signal passing through

the amplifier is proportional to the registered light flux. Therefore the amplifier must have a sufficiently large range of linearity, covering the largest obtained signals. In the optical-division system this is not required, since the amplifier carries only the difference signal which is merely required to actuate the reversible motor.

In conclusion, let us consider the system for automatic regulation of the voltage on the dynodes of the photomultiplier, used to increase the operating stability of the photomultiplier and the amplifier circuit^[3]. Just as in the system described above, the measured and comparison signals are fed to a photomultiplier, amplified, and then separated. In this case the comparison signal is used to regulate the operation of the system that controls the supply to the photomultiplier.

It should be pointed out that the system operates over a wide range of sensitivity variation. The ratio of the measured signal to the comparison signal is maintained accurate to 3–7% as the sensitivity changes by a factor of 100. Another advantage of this system is that it can readily be used simultaneously with any other system in which a comparison signal is separated, for additional stabilization of the operating conditions.

A remark should be made concerning the operating range of all the systems considered above. Stabilization is assured only if the variation of the operating conditions occurs at frequencies lower than the modulation frequency.

The use of two different receivers and of two amplifier channels for the comparison and measured signals can hardly be advantageous, although this variant is frequently used both in laboratory apparatus^[8–10] and in the factory instruments (for example, in the "Cary" instrument, and the instrument of the "Hilger" firm^[11]). In this variant, variations of the photomultiplier sensitivity may not be eliminated at all when the supply voltage changes, especially since the variation of the sensitivity to different signals is frequently different for different photomultipliers.

2. Photoelectric Registration of Raman Spectra in the Pulsed Mode

The method of pulsed excitation of Raman spectra, proposed in^[12–14], has in principle definite advantages over other methods. Its realization, however, entails certain difficulties, principal among which is the rapid degeneration of the mercury-vapor spectrum (line broadening, relative increase in the continuous background) in the lamp used for the excitation.

Comparison of the operation of the recording system in the continuous and pulsed modes shows clearly the advantages of pulsed recording. Let us assume that the same light source is used, that the power supply has identical average power, the same receiver with the same dark-noise spectrum is used, and the

spectra are recorded by the same method at the same time constant. Let T be the discharge repetition period, τ the duration of the discharge, Φ_0 the light flux incident on the photomultiplier in the continuous operating mode, and Φ the flux incident during the continuation of the discharge, averaged over the time τ ; we then have $\Phi = \Phi_0 T/\tau$. Consequently, in the pulsed mode the signal at the photomultiplier output, meaning also at the amplifier input, is T/τ times larger than in the case of the continuous mode.

The increase of the signal at the amplifier input alone affords certain advantages. First, an amplifier with smaller gain is required, and second, the role of inductive interference is greatly reduced. This makes it possible to operate at 50 cps, which in turn greatly facilitates the construction of the generator feeding the exciting-light source.

The noise at the output of the photomultiplier is due to two main causes: the dark current of the photomultiplier (dark-current noise) and the photocurrent (light noise). Since it is precisely the comparison of the noise in the two cases under consideration which is essential, it can be assumed that the average power density of the dark current at the output of the photomultiplier, σ^2 , is the quantity characterizing the employed photomultiplier under the given conditions (temperature, supply voltage, etc.), and which we assume to be the same in both cases. Since the signal at the photomultiplier output is increased in the pulsed mode by a factor T/τ , the relative magnitude of the dark noise increases by the same factor, that is, the ratio of the signal to the dark noise at the photomultiplier output improves by a factor T/τ . This is the main advantage of the described method.

When the exciting-radiation source is fed by different methods but at constant average power, no change takes place in the total number of photons. Pulsed excitation of the spectrum is tantamount to emitting the photons of the exciting radiation only during the time intervals τ . The noise due to the photocurrent depends only on the total number of photons and cannot be changed by any means.

In order to conserve the gain in the ratio of the signal to the dark noise, it is necessary to make rational use of the constructed amplifier circuit. The circuit must contain an element which turns the amplifier on in the presence of a signal for a time τ , and shuts it off during the remainder of the time. A circuit with such an element makes it possible to retain the gain in the ratio of the signal to the dark noise at the input of the amplifier when using the broadband needed for pulse registration. A block diagram of a recording unit of this type is shown in Fig. 4.

The exciting-radiation source is a low-pressure mercury lamp fed with direct current. The mercury itself serves as the electrodes. This is essential, since metallic electrodes are rapidly evaporated by pulsed discharges. The lamp was not filled with an inert gas, since the presence of gas in the discharge gives

rise to the large number of interfering lines. The lamp was ignited, after preliminary heating, by continuously feeding it at low power, on which the pulses were superimposed. The measured ratio of the peak intensity in the pulsed mode to the intensity of the light in the normal continuous mode was 10^4 at a supply voltage up to 10 kV and a flash duration of approximately 40 μ sec; this ratio increased more slowly when the voltage was increased to 100 kV, probably because of faults in the technique used to produce discharges at 100 kV (energy lost in the discharge gaps etc.).

The spectrum of the described source, obtained at 7–10 kV, contains all the arc-discharge lines of mercury; in addition, spark-discharge lines which are missing from photographs of spectra taken in the continuous mode, are observed. In the region where Raman scattering of light is usually investigated (4358–4916 Å), three lines of rather low intensity are observed at 4401, 4556, and 4812 Å. In the pulsed mode, a continuous background is observed in the spectrum, extending from 2800 Å to the visible region. However, the intensity of the background, relative to the intensity of the lines, is much smaller than in the case of high-pressure lamps, and it does not interfere with the study of Raman lines. The self-inversion of the 2537 Å resonance line is much larger than in the continuous mode. Some lines are broadened, but a study of the 4358 and 4047 Å lines has shown that their broadening is negligible.

The discharge spectrum at 100 kV differs appreciably not only from the arc spectrum but also from the discharge spectrum at 10 kV. The relative intensities of the lines change, and the widths of some of them increase appreciably. These changes occur essentially in the ultraviolet region. A noticeable attenuation at wavelengths shorter than 2700 Å also takes place.

The most favorable conditions for the investigation of Raman scattering in the pulsed mode occur at 7–10 kV. Nonetheless, discharges at 100 kV can also be used for excitation, since no noticeable continuous background is observed in the entire operating region of the spectrum, and the blue line at 4358 Å is perfectly acceptable for excitation. Discharge at 100 kV is of interest in that respect that at the same average power it is possible to use shorter pulses and by the same token increase still further the ratio of the signal to the dark noise.

The described method, as estimated by the author, affords a gain of approximately 500 times at a voltage 10 kV and a duration $\tau = 40 \mu$ sec, that is, it is equivalent to a decrease of the dark noise by a factor of 500. By way of illustration, Fig. 5 shows a sample spectrum of toluene.

The most promising is the use of this method in high-speed Raman spectroscopy^[15–17].

3. Difference Method of Registration of Raman Spectra

The use of photoelectric registration with an ac amplifier having a sufficiently narrow bandwidth uncovers additional possibilities of investigating Raman spectra. It becomes possible to use a difference method, that is, a method in which only a certain fraction of the radiation is recorded, after subtraction of a second definite fraction^[18].

The optical system and a block diagram of the recording part of such an installation are shown in Fig. 6. Here S_1 and S_2 are two exciting-light sources, C_1 and C_2 are two cells with scattering substances, which produce two light fluxes—the investigated one and the “subtracted” one. These two fluxes are directed to the input

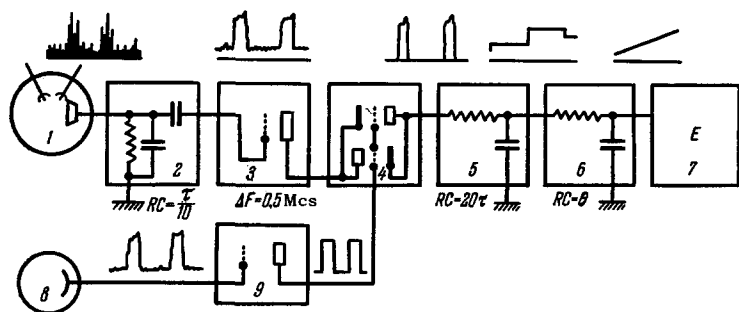


FIG. 4. Block diagram of recording unit. 1—Photomultiplier, 2—integrator, 3—amplifier, 4—chopper to switch the element, 5—second integrator, 6—recorder integrator, 7—recorder with pen, 8—photocell producing synchronization signal, 9—shaping unit for synchronization signals.

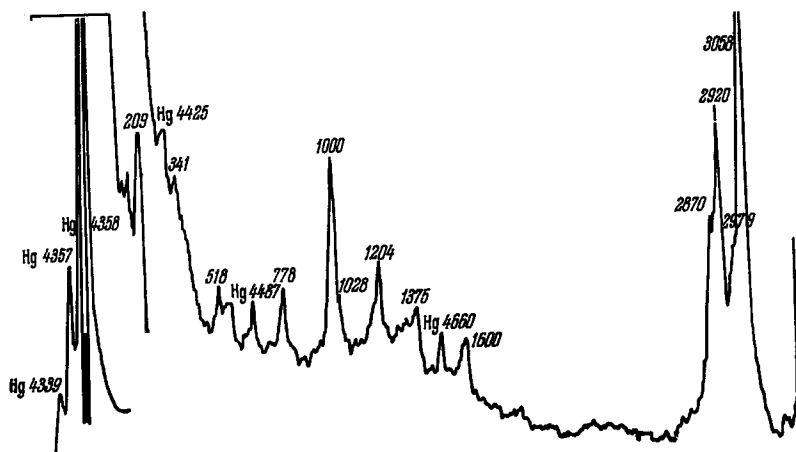


FIG. 5. Raman spectrum of toluene.

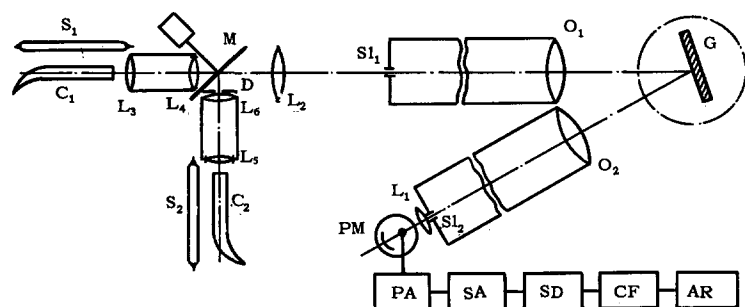


FIG. 6. Optical system and block diagram of recording section of the difference method. G—Diffraction grating; O_1 and O_2 —objectives of spectrometer, S_1 and S_2 —slits, L_1 —lens; S_1 and S_2 —spectrum excitation sources; C_1 and C_2 —cells with scattering substances; L_3 , L_4 , and L_5 , L_6 —telescopic systems, which produce intermediate images of the cells; L_2 —condenser lens; D—diaphragm to regulate the intensity of the “subtracted” light flux; M—modulator, near which are installed a photoresistor and an incandescent lamp, used to obtain the synchronization signal; PM—photomultiplier; PA—pre-amplifier; SA—selective amplifier; SD—synchronous detector; CF—cathode follower, AR—automatic recorder.

slit S_1 of the spectrometer with the aid of a modulator M (a rotating mirror with slots). The investigated light passes through the slot to the slit, while the “subtracted” light is reflected from the mirror. When the mirror is rotated, the investigated light flux and the “subtracted” flux are alternately incident on the input slit. After passing through spectral instrument, the light is fed to a photomultiplier with the aid of lens L_1 . The recording system operates in standard fashion. In the case when the light fluxes of the investigated and “subtracted” signals are equal, the resultant photocurrent of the photomultiplier is unmodulated and is not passed by the selective amplifier SA, which is tuned to the modulation frequency. On the other hand, if one of the light fluxes prevails, then the resultant photocurrent contains an ac component, which is amplified and recorded in the automatic recorder AR. The dc component which is present does not pass in this case through the filter of the selective amplifier. Thus, the recorded spectrogram is the difference of the two signals. To regulate the magnitude of the “subtracted” light flux, diaphragm D is used, which can be an optical attenuator that does not change the quality of the

optical image. This may be a set of wedges, a wedge made of neutral dark glass, etc. To obtain a good difference spectrum, it is very important to adjust the illuminating system very carefully. Even a small angle difference during the illumination of slit by the different sources will prevent production of a high grade difference spectrogram. Therefore, strictly identical telescopic systems (L_3 , L_4 and L_5 , L_6) are installed in the two channels. These produce intermediate images of the cells, which are carefully made to coincide during the adjustment of the system.

It must be noted that difference methods are widely used in infrared spectroscopy. However, they have not yet found extensive application in Raman scattering.

We can point to several possible applications of the difference method. Initially such a method was used in simpler form^[19]. Light flux from one vessel was modulated with a polaroid disc. This modulated only the polarized light. Therefore only the difference between the ordinary spectrum and the depolarized component

was recorded, i.e., the polarization component. No other method of registration of Raman spectra yields this component. This method makes it easy to register and separate the polarized lines of the spectrum. An example of such a recording is shown in Fig. 7, which contains spectra of the CH group of n-hexane. It can also be used to measure the degree of depolarization^[20].

Another application of the difference method is based on its ability to eliminate the interfering background in the region close to the exciting line^[18]. In this case one "subtracts" from the Raman spectrum of one substance the Rayleigh-scattering line of a substance which is close in structure to the first substance, but which has no line in the investigated region. This is essential because it makes it possible to attain better compensation of the wing of the Rayleigh-scattering line. This method permits the study of lines of small frequencies, which are difficult to investigate by other methods. To be sure, one stipulation must be made. In this case, both the investigated and the "subtracted" spectrum represent light of high intensity. A large light flux is incident on the photomultiplier at all times. This causes a noticeable increase in the photomultiplier noise, since noise connected with the light flux incident on the cathode increases in proportion to the square root of the light flux. Nonetheless, this method may turn out to be very useful. Figure 8 shows a sample of the recorded spectra.

We can point to two other possible applications of the difference method: 1) Investigation of mixtures, where the lines of interest in the analysis are suppressed by the lines of the other component. In this case one can "subtract" from the mixture spectrum the spectrum of the interfering component with suitably chosen intensity. 2) Study of small changes in the width and intensity of the lines, and also of the line shifts under the influence of a solvent, temperature, and other effects. In this case, if total cancellation of the spectra is attained under identical conditions (the "difference" is equal to zero), then only the change in the spectrum will be recorded when the conditions change. Examples of such an application of the difference method in infrared spectroscopy can be found in^[21].

4. Registration of Spectra Differentiated with Respect to Frequency

A rather unique method was used in several investigations^[22-24] of the infrared region of the spectrum, but the procedure used in them may turn out to be useful also in the investigation of Raman lines. The advantage of the method is demonstrated in Figs. 9 and 10. The former shows a dispersion line contour and its first, second, and fourth derivatives. What is striking is that the even derivatives are similar to the investigated line, but are much narrower (only the width of the positive part is considered). The second figure is a real spectrogram of the 4.25 and 4.28 μ bands of car-

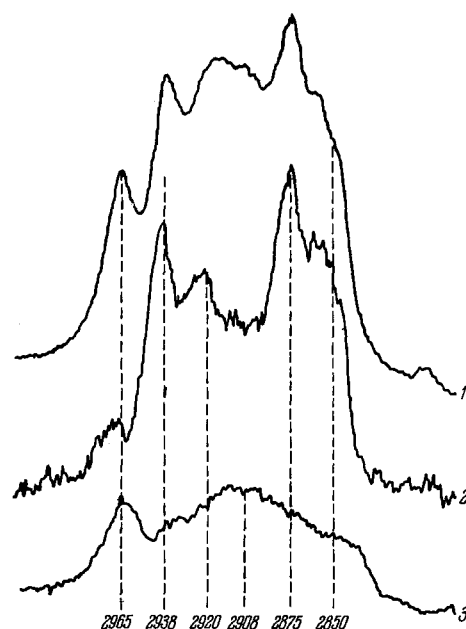


FIG. 7. Line spectrum of the CH group of n-hexane. 1—Spectrum recorded with an ordinary sample; 2—difference spectrum—polarized component; 3—depolarized ("subtracted") component.

bon dioxide. This example is taken from infrared spectroscopy. The appreciable narrowing of the observed lines facilitates further reduction of the spectrum. Estimates show that the resolution is also improved.^[25]

The spectra obtained in this manner are used for qualitative and quantitative analysis. The possibility of carrying out an analysis by means of spectra differentiated an even number of times is obvious. The

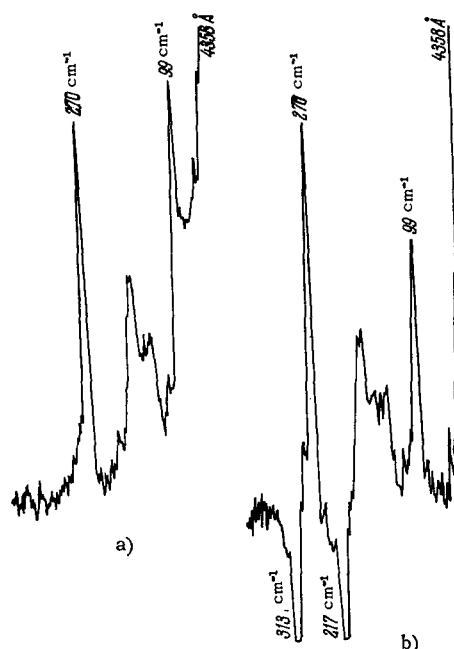


FIG. 8. Spectrum of germanium dimethyldibromate $(\text{CH}_3)_2\text{GBr}_2$. a) Ordinary spectrum; b) difference spectrum (the spectrum of carbon tetrachloride is "subtracted").

frequency maximum of the even derivative coincides in position with the maximum of the line. The magnitude of the derivative is proportional to the concentration if the magnitude of the intensity is proportional to the concentration, inasmuch as the concentration is independent of the frequency. Moreover, for a qualitative analysis one can use also other derivatives, if the position of the maximum of the investigated line is determined from the vanishing of the first or third derivative [26].

The technique of registration of the differentiated spectra, as shown by further analysis, is quite simple. To obtain the second derivative it is sufficient to use two differentiating RC networks of the usual type. It must be borne in mind here that the use of differentiating elements greatly attenuates the signal. Consequently, additional amplification stages are necessary. The use of complicated circuits, which give the exact value of the derivative [25] in instruments intended for measurements of this type, is hardly justified, as will be shown in the subsequent analysis.

Let us now consider several complicating circumstances which accompany the registration of derivatives of spectra, thereby limiting their extensive use.

As seen from Figs. 9 and 10, certain "satellites," located on the other side of the null line relative to the central maximum, appear in the spectra of the second or fourth derivative of a single band. The picture becomes even more complicated if we consider a band consisting of several lines. The presence of such "satellites" may lead to the appearance of an apparent structure of the investigated band, to the appearance of spurious lines, or, to the contrary, to the vanishing of certain real lines. Therefore in the analysis of the derivatives of the spectra, it is necessary to use additional information in their preliminary interpretation, viz., to use a direct recording of the spectrum, to use comparison of the spectrum with known spectra of similar compounds, and to use, finally, numerical calculations of the frequency. In quantitative analysis, when the frequency of the line used for the analysis is known, these difficulties are eliminated to a considerable degree.

Another circumstance which is of fundamental character, in the sense of a limitation on the possibilities of the considered method, is the influence of random errors, since it is obvious that differentiation leads to

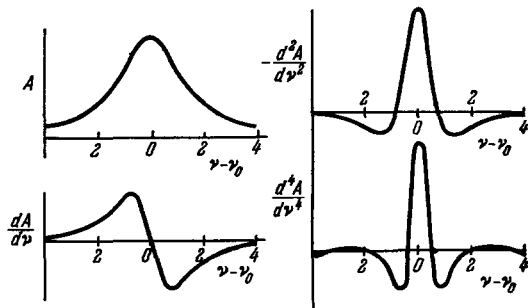


FIG. 9. Dispersion line and first, second, and fourth derivatives with respect to frequency.

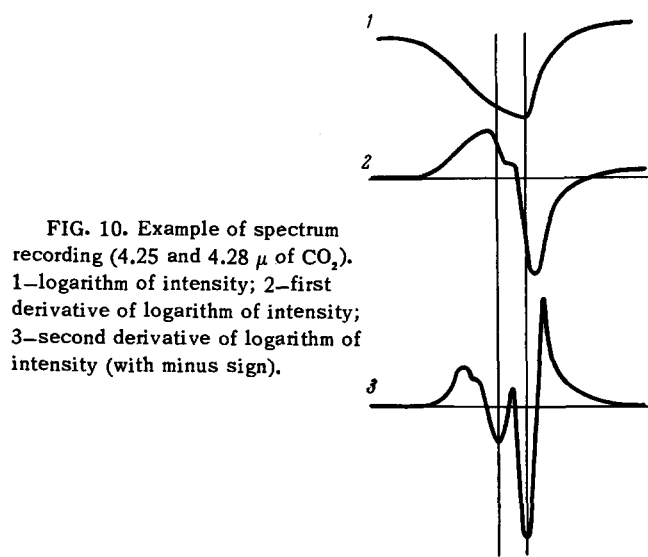


FIG. 10. Example of spectrum recording (4.25 and 4.28 μ of CO_2). 1—logarithm of intensity; 2—first derivative of logarithm of intensity; 3—second derivative of logarithm of intensity (with minus sign).

a sharp increase of these errors. This circumstance can be clearly understood and considered by the spectral approach. [27,28]. An illustration of the influence of random errors is shown in Fig. 11.

Figure 11 shows that double differentiation leads, on the one hand, to a broadening of the spectrum of the investigated line, that is, to a narrowing of the observed line, and on the other to a considerable increase in the rms random error. If the differentiation is carried out exactly in the entire spectral interval, and the spectrum of the investigated line and of the random errors is not bounded in any way, then $\Psi(\omega)\omega^4$ increases to infinity. To avoid this, it is necessary to introduce a certain limitation of the Fourier spectrum. In real instruments this limitation is brought about by the inertia of the recording system. In addition, it is clear that it is meaningless to attempt to carry the differentiation exactly in a wide interval of the Fourier

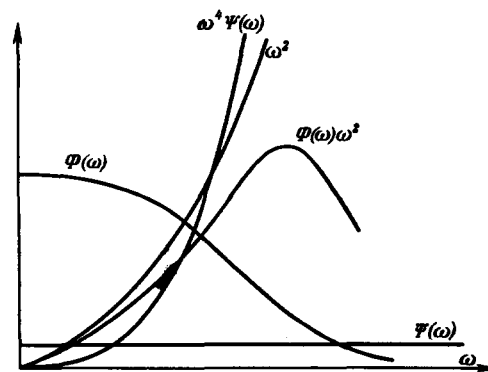


FIG. 11. Effect of random error on the spectrum of a signal and on the spectrum of a twice-differentiated signal. $\Phi(\omega)$ —Fourier transform of the investigated line; $\Psi(\omega)$ —Fourier transform of the rms random error; ω^2 —Fourier transform of the operation of double differentiation (with minus sign); $\Phi(\omega)\omega^2$ —Fourier transform of the twice-differentiated investigated line; $\Psi(\omega)\omega^4$ —Fourier transform of the rms random error after double differentiation.

spectrum. This circumstance allows us, as mentioned earlier, to confine ourselves to the use of simple differentiating networks in the registration circuits.

It is clear from the foregoing that to estimate the gain resulting from differentiation it is necessary to compare the line widths obtained when working without and with differentiation, and also to compare the random errors in the measurements of the line intensity and of the derivative (we have in mind the intensities at the maximum and the extremal value of the even derivative). A similar analysis for the case of double differentiation is given in [29] under the following simplifying assumptions: 1) the investigated line has a dispersion form; 2) the apparatus function has a Gaussian form; 3) the random errors do not depend on the magnitude of the signal and have a uniform spectrum; 4) approximate differentiation is used, with sharp limitation on the side of the high Fourier frequencies at the frequency ω_0 . The observed line widths were calculated without and with differentiation at identical value of the random error. When differentiation was used, the random error was decreased by widening the slits; it was assumed here that the rms random error decreases in proportion to the square of the slit width. The widening of the slits leads, of course, to a broadening of the observed line. The results of the calculations are plotted in Fig. 12, showing the widths of the observed lines δ against the limiting frequency ω_0 for values of S/γ equal to 0.5, 1.0, 3.0, 4.0, and 5.0, where S is the width of the slit without differentiation and γ is the width of the observed line. The results of the calculation show that the smallest width is obtained at $\omega_0 = 4/\gamma$ in the case of double differentiation and at $\omega_0 \approx 10/\gamma$ without differentiation. In this case, differentiation and use of $\omega_0 = 4/\gamma$ yielded a gain of 1.25–1.5 times in the observed width, together with a gain of ≈ 1.6 times is obtained for the level of the random error, due to the narrowing of the bandwidth of the recording equipment. When operating with $\omega_0 = 4/\gamma$, the gain in the width of the observed line may reach a factor of 2.

With regards to the foregoing estimates, we must make the following remarks. First, in the case of registration of Raman spectra with the aid of a photomultiplier, the average spectral density of the fluctuation intensity, or the random error, depends on the magnitude of the light signal. This circumstance reduces somewhat the obtained advantage. Second, a decrease in the random error, inversely proportional to the square of the slit width, takes place only when working with slits whose spectral width is smaller than the width of the investigated line, that is, when working with broad lines.

In conclusion it must be stated that the use of the foregoing procedure is apparently of greatest interest when investigating bands consisting of several broad strongly overlapping lines. Such objects, for example, are the vibrational bands of CH groups in the region

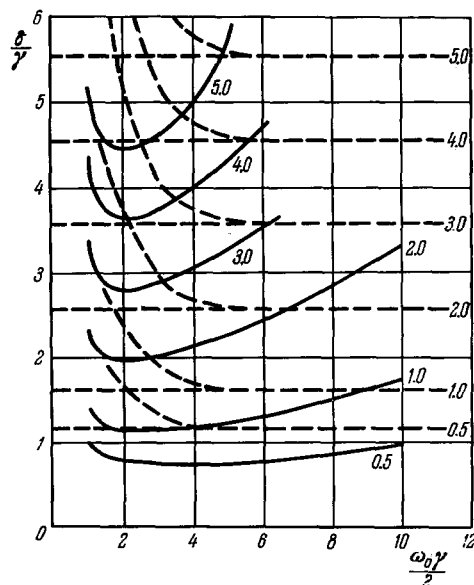


FIG. 12. Widths of observed lines, δ , as functions of the limiting frequency ω_0 for different values of S/γ . S —width of slit when working without differentiation; γ —width of investigated line. Solid curves—double differentiation, dashed—without differentiation.

near 2800–3000 cm^{-1} . In this case, to reduce the random error one can greatly widen the slit without fear of broadening the individual lines. At the same time, narrowing of the lines as a result of differentiation may help disclose certain additional details of the spectrum.

5. Use of Lasers in Raman Spectroscopy

The recently developed new sources of monochromatic light—lasers—are of great interest from the point of view of their use in Raman spectroscopy. The question of the advantages of lasers for the excitation of Raman spectra began to be discussed in the literature immediately after their appearance. The presence of a narrow single line and the large radiation power make sources of this type nearly ideal for the excitation of Raman spectra. The first experiments with lasers used for the excitation of Raman scattering have shown, however, that they possess their own specific difficulties.

In the first applications to the excitation of Raman spectra, ruby lasers were used [30–32].

Figure 13 shows the diagram of a setup intended for the production of Raman spectra of liquid samples. A helical flash lamp illuminates ruby R, which is cooled with nitrogen. The liquid sample is in a cylindrical vessel coated with a layer of BaSO_4 . The radiation excited in the ruby passes through filter F and is focused inside the cell by lens L_1 . The scattered light is focused with lens L_2 on the slit of a spectrograph. The spectra were recorded photographically, the number of flashes required for this purpose ranging from 16 to 100. A somewhat modified cell was described by Stoicheff [32], who used total internal reflection of light by the cell walls. The laser beam enters the cell (Fig. 14) through a small window on the side, and is multiply reflected from the mirror-finish walls until it reaches a light trap at the end

of the cell. The scattered light experiences total internal reflection from the cell walls and, after leaving through the front window of the cell, is focused on the spectrograph slit.

The described apparatus yielded only rather weak spectra of substances such as CS_2 , benzene, and CCl_4 . Some shortcomings of the ruby laser as a source of exciting light were also disclosed. It turned out that the exciting line shifts noticeably with changing temperature, and therefore, when several flashes are produced during the photography of the spectrum, it is necessary to see to it that the temperature of the ruby laser remains constant. It turned out further that the spectrum of the ruby laser is contaminated by extraneous lines of different origin, the intensity of which is comparable with the intensity of the Raman lines. To attenuate these lines it is necessary to move the cell away from the laser. Then the intensity of the laser beam, which is highly parallel, remains practically unchanged, whereas the intensity of the extraneous lines is attenuated in proportion to the square of the distance.

The scanty material available on the use of ruby lasers for the excitation of Raman scattering demonstrates that such lasers are not suitable for liquids that are transparent in the blue-green region of the spectrum. Much better results can be obtained with such substances with the aid of a mercury lamp, using the standard well-developed procedure. The situation changes if it necessary to investigate colored objects. Thus, for example, in our earlier investigation^[33] we obtained Raman spectra of green or red powders which could not be investigated with other sources (such as a cadmium lamp). We note that in the investigation of powders (and other strongly scattering objects) the problem of rational utilization of the laser-beam energy becomes much simpler. In the cited investigation^[33] the cell with the powder was mounted directly ahead of the slit of a high-transmission spectrograph. The spectrograph aperture was uniformly filled even when the thickness of the cell with the powder was only

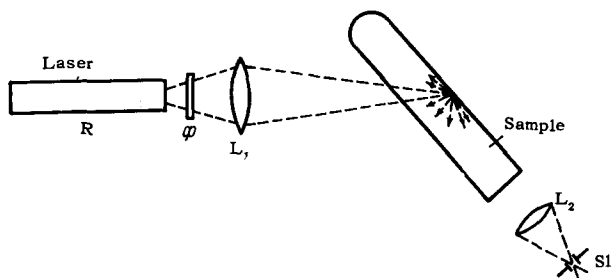


FIG. 13. Diagram of apparatus for obtaining Raman spectra with the aid of a ruby laser.

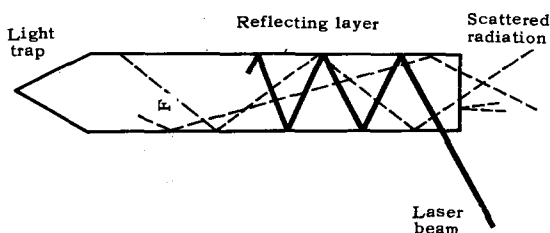


FIG. 14. Cell for liquid samples.

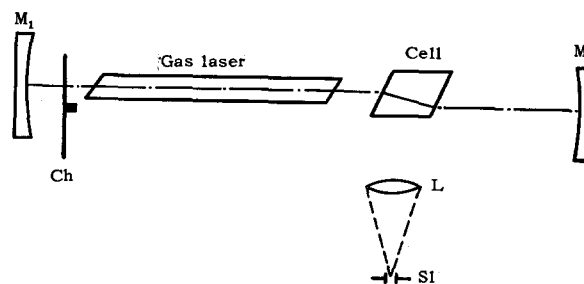


FIG. 15. Diagram of setup for obtaining Raman spectra with the aid of a ruby laser.

1 mm. The laser radiation was focused on the cell with a simple lens.

The use of lasers for Raman spectroscopy progressed after continuous-operation gas lasers were perfected. In 1964 several papers^[34,35] reported successful registration of the Raman spectra of CS_2 , C_6H_6 , and CCl_4 by a photoelectric method using an He-Ne gas laser (6328 Å line) for the excitation of the spectra.

In^[34], the cell with the investigated substance was placed inside the laser cavity (Fig. 15). The gas laser operated with a 5:1 mixture of He and Ne. The windows of the laser and of the cell were inclined at the Brewster angle in order to improve the conditions for reflection in multiple passage of the beam through the system. The external mirrors, M_1 and M_2 , were dielectric with high reflection coefficients. A mechanical chopper Ch was placed in the path of the beam to obtain a modulated signal. The scattered light was focused by lens L on the spectrometer slit. The laser power (without the cell) was 18 MW. The diameter laser beam inside the cell was 0.5 mm.

Figure 16 shows the CCl_4 spectrum obtained with this apparatus. During the photography, the monochromator slit was 12 cm^{-1} . The scanning rate was 2 $\text{cm}^{-1}/\text{sec}$, and the time constant 3 sec. We note that in the experiments the dark current of the photomultiplier, which was cooled with dry ice, was 2×10^{-11} A, whereas the signal for the 459 cm^{-1} line of CCl_4 was 1.5×10^{-4} A.

In^[35] the cell was mounted outside the cavity. Such an arrangement is more convenient in practice, although it leads to an approximately 50-fold loss in intensity. At a laser power of 40 MW, it was possible to obtain satisfactory spectra of CS_2 , CCl_4 , and benzene, and by recording at a sufficiently slow rate it was possible to resolve the isotopic structure of the 459 cm^{-1} line of CCl_4 . Figure 17 shows the CCl_4 spectra obtained in this investigation. The spectra were registered with a spectrometer with diffraction grating of 600 lines per mm, having a relative aper-

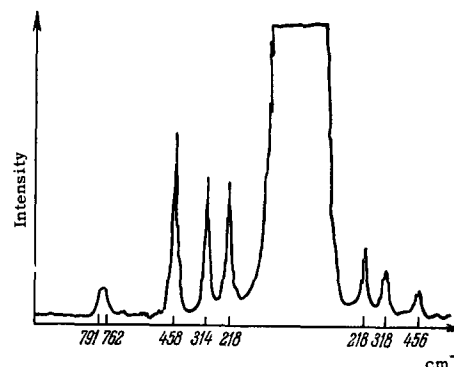


FIG. 16. CCl_4 spectrum obtained by excitation with gas-laser radiation (cell inside resonator).

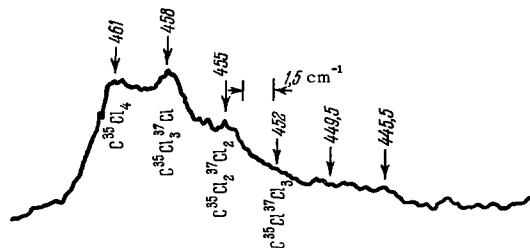


FIG. 17. CCl_4 spectrum obtained with the aid of a gas laser (cell outside resonator).

ture 1:8.6 at a focal distance of 1 meter. The photomultiplier was cooled with nitrogen gas that had passed first through liquid nitrogen.

Thus, even the first experiments on the excitation of Raman spectra with gas lasers have yielded spectra close in quality to those obtained with a mercury lamp. If it is recognized that the laser radiation has, in comparison with the mercury lamp, the advantages of 1) very low width of the exciting line, 2) being completely polarized, and 3) being located in a spectral region with specific advantages for many substances, then it becomes obvious that the use of gas lasers is most promising in Raman spectroscopy. There are indications^[35] that the gas laser power can be raised to 1 W; then this source will also be superior to the mercury lamp even with respect to power.

Of special interest is the use of gas lasers for the investigation of the angular dependence of Raman line intensity (scattering indicatrix). In such research, in view of the smallness of the divergence angle of the light beam from the laser, it becomes unnecessary to install special diaphragms to reduce the aperture of the exciting radiation.

A successful attempt at investigating the scattering indicatrix with a gas laser as an exciting source is reported in^[36].

The experimental setup is shown in Fig. 18. The monochromator was mounted on a rotating frame whose center of rotation coincided with the center of the spherical vessel with the scat-

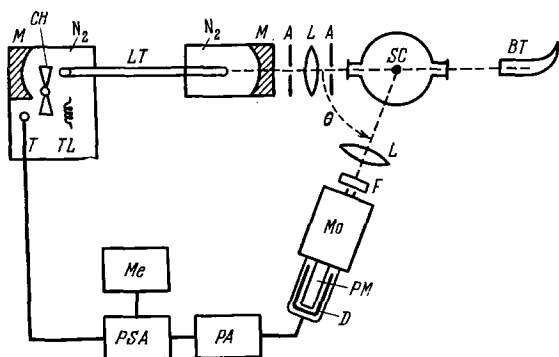


FIG. 18. Diagram of setup for the investigation of the scattering indicatrix. LT—gas laser, M—mirror, A—diaphragms, L—lenses, SC—vessel for scattering substance, BT—light trap, CH—chopper, TL—indicandent lamp, T—thermocouple, F—light filter, Mo—monochromator, TM—photomultiplier, D—cooling mixture, PA—pre-amplifier, PSA—synchronous phase amplifier, Me—meter.

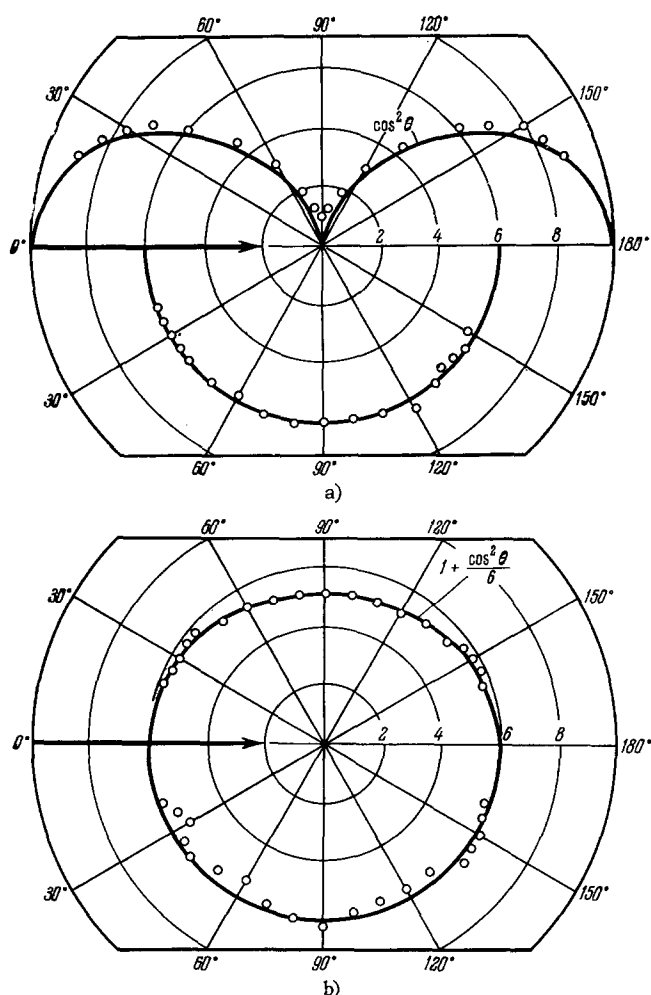


FIG. 19. Intensity indicatrix for benzene lines: a) 992 cm^{-1} (strongly polarized); b) 1586–1606 cm^{-1} (depolarized).

tering substance. The measurements were made in a scattering-angle interval from 20 to 160°, the registered light beam having an aperture of approximately 5°. The spectrum was recorded photoelectrically. Several lines of benzene were investigated.

The results of the measurements of the indicatrix for the benzene 992 cm^{-1} line (strongly polarized) and the 1586–1606 cm^{-1} lines (depolarized) as shown in Fig. 19. When the electric vector E of the exciting light beam was perpendicular to the scattering plane, the intensity was independent of the observation angle θ . When E was in the plane of the incident and scattered rays, the intensity was proportional to $\cos^2 \theta$ for the 992 cm^{-1} line and to $1 + \frac{1}{6} \cos^2 \theta$ for the 1586–1606 cm^{-1} lines, in agreement with the theory. It is interesting to note that the "front-back" asymmetry reported by the authors of earlier investigations of the scattering indicatrix^[37–39] was not observed in the angular dependence.

Reference^[36] gives also data on the ratio of the scattering cross sections of the Rayleigh line in benzene δ_0 and of the Raman lines of benzene δ_R (Table I). Using data on the cross section for Rayleigh scattering in benzene^[40], the authors of^[36] calculated the abso-

TABLE I

$\Delta\nu$, cm^{-1}	δ_0/δ_R	$\delta_r \cdot 10^{28}$, cm^{-2}
992	220	0.56
1586-1606	1980	0.062
3049-3062	250	0.50

lute scattering cross section of the benzene Raman lines investigated by them (last column of Table I). The measurements errors amount to approximately 20%.

For investigations of the line intensity in stimulated Raman scattering, the data on the scattering cross section in ordinary Raman scattering, obtained in [41], are of interest. Table II lists the data obtained in that reference for the quantity

$$K = \frac{d^3\sigma}{d\lambda d\Omega dV},$$

which is the differential scattering cross section divided by the wavelength interval $d\lambda$, the volume of the scattering substance dV , and the solid angle $d\Omega$. The measurements were made with a ruby laser the source, but under conditions when only ordinary Raman scattering was excited; the scattered light was observed in a direction perpendicular to the laser beam.

TABLE II

Substance	$\Delta\nu$, cm^{-1}	K , cm^2	Substance	$\Delta\nu$, cm^{-1}	K , cm^2
Nitrobenzene	1345	2.3	Benzene	1179	0.13
Benzene	991.6	3.9	Toluene	1002	1.1
			Toluene	1212	0.24

II. STIMULATED RAMAN SCATTERING

6. Excitation Methods

The phenomenon of stimulated Raman scattering (SRS), discovered more or less accidentally [42], has been attracting the interest of an increasing number of experimentors and theoreticians. Whereas in 1962-1963 work on SRS was devoted essentially to a qualitative investigation of the phenomenon, greater attention is being paid now to its quantitative study.

It is important to note that of principal significance for the excitation of stimulated Raman scattering spectra is not the energy of the exciting radiation, but its power. The required power can be obtained from "giant pulse" lasers (usually called Q-switched lasers). The operation of such a laser can be described approximately as follows.

It is known from the general theory of quantum generators that the generation intensity is determined essentially by the extent to which the population of the upper level can be raised relative to the minimum pop-

ulation that determines the start (threshold) of the generation. The generation threshold is determined by the resonator loss. Under ordinary conditions, however, it is impossible to produce a large population in excess of threshold, for as soon as the population of the upper level reaches the threshold value, generation sets in and lowers the population rapidly to a value below threshold, stopping the generation. If the pump pulse is sufficiently powerful and long, then several relatively weak radiation pulses are produced. An increase in the pump power leads essentially to an increase in the number of these pulses, so that the generation energy increases but the radiation power increases little. It follows therefore that to increase the population of the upper level it is necessary to raise the generation threshold, that is, to increase the resonator loss. But this is not all. In order for the generation power to be maximal, a device is necessary to turn off the loss as soon as the population reaches maximum. Such devices are constructed at present essentially by three methods: electro-optical, optomechanical, and optical.

In the electro-optical method a Kerr cell, placed between crossed polarizers acting as a shutter, is introduced in the system. A high voltage applied to the cell rotates the plane of polarization through the required angle, and allows the light to pass unhindered through the polarizers. Equipment of this kind calls for a complicated high-voltage device. In addition, this method is not convenient in SRS, since the substances used in the cell produce as a rule parasitic lines in the spectrum.

An example of an optomechanical shutter is one with a rotating mirror (total internal reflection prism). This calls for very large rotational velocities, but this method is simpler and more convenient than the preceding one.

Optical shutters have been finding increasing use recently. If radiation of sufficiently high power is incident on the absorbing medium, then all the molecules are excited and the substance becomes transparent. It remains transparent so long as the molecules are in the excited state. Shutters of this type are made, for example, of cryptocyanine or KS-19 glass. Powers on the order of a gigawatt were obtained with them.

The character of the SRS phenomenon depends essentially on the position of the active medium relative to the resonator [2]. Attempts were made recently to produce for SRS a resonator which is not connected with the resonator of the master generator. Thus, for example, Takuma and Jennings [44,45] investigated SRS in a resonator whose axis made a certain angle with the axis of the resonator for the ruby.

The master generator was a Q-switched ruby laser pulsed of approximately 20 MW output power. The effective cross section of the exciting beam in the cell was approximately 0.5 cm^2 . The mirrors of the SRS resonator (Fig. 20) were parallel within 20". The mirror M_1 reflected 99% of the light both at the frequency of the exciting radiation and at the Raman frequency. The reflection coefficients of the mirror M_2 were 2 and 18% for the exciting and Raman radiations respectively. The angle α between the axis of the SRS resonator and the axis of the master generator was approximately 2.5°. Under these conditions, lasing action was produced at the first Stokes frequency of benzene. As indicated by the authors, the least deviation mirrors M_1 and M_2 from parallelism stopped the generation. The loss of generation at the Raman

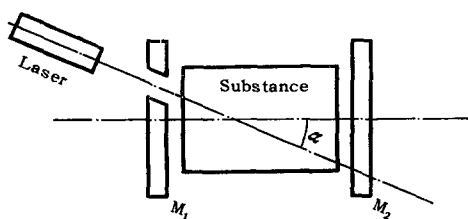


FIG. 20. Equipment for the investigation of SRS in an off-axis resonator (M_1 and M_2 —mirrors).

frequency when the angle α lies in the plane of polarization of the master radiation is of independent physical interest.

The authors of [45] confine themselves to an investigation at a small angle between the axes of the resonators. Dennis and Tannenwald^[46] obtained SRS under essentially different conditions—in a resonator whose axis was perpendicular to the axis of the master generator.

In this investigation they used a Q-switched ruby laser, which produced a power on the order of 5 MW at the pulse duration 30 nsec. Its radiation was focused by a cylindrical lens of 10 cm focal length onto a cell whose four walls were made of optically plane glass. No spherical lens was used because the very high energy densities produced in its focus disturbed the optical homogeneity of the medium and consequently decreased the resonator Q. The resonator consisted of two identical plane dielectric mirrors with transmission and absorption coefficients 0.3 and 0.6% at the first two Stokes frequencies of nitrobenzene (0.765 μ and 0.853 μ , respectively). The spectrum was registered photoelectrically with a double monochromator. The minimum power of the master generator necessary to excite SRS in the "perpendicular" direction was approximately 2 MW. When the maximum power of the master laser was used (~ 5 MW), the radiation power at the first Stokes frequency was 150 and 10 kW in the forward and perpendicular directions, respectively.

Besides the radiation at the first Stokes frequency in the perpendicular direction, radiation was observed also at the second Stokes harmonic (0.853 μ). The intensity of this radiation was $\sim 1\%$ of the intensity at the first Stokes frequency in the same direction. The authors believe that the second-harmonic radiation is due to a repetition process, that is, it is generated by the first Stokes frequency produced in the resonator.

The relatively simple geometry of the experiment has enabled the authors to obtain some numerical estimates of the gain at the first Stokes frequency. Assuming that at threshold the loss per pass should be compensated by the gain, they obtained a lower estimate

$$\alpha = \frac{1-R}{l} = 0.02 \text{ cm}^{-1};$$

here α is the gain, R the reflection coefficient ($R = 1 - 0.003 - 0.006 = 0.991$), and l the length of the light path in the active zone (width of the exciting-radiation beam), equal to ~ 0.5 cm. Dennis and Tannenwald assume correctly that the obtained value of the gain is indeed the minimum, for no account is taken of either the loss in the medium (for example, scattering) or the fiberlike structure of the exciting

radiation beam, which certainly reduces the dimensions of the active zone. They assume that the obtained value of the gain is in good agreement with theoretical estimates of the gain in the forward direction ($0.1-1 \text{ cm}^{-1}$). It must be noted, however, that the reasoning in [46] concerning the gain is not very well founded, since it is perfectly applicable also to the second harmonic, for which it yields the same value of the gain, which is somewhat doubtful. In addition, the gain, as will be shown below, depends both on the exciting-radiation power and on the radiation intensity at the investigated frequency.

The experiment described above is of interest from a different point of view. It has been customarily assumed that the Stokes components of SRS can be emitted only in the longitudinal direction with relatively low divergence ($4-5^\circ$). Moreover, Stoicheff^[47] has shown experimentally that beyond this angle the radiation intensity at the first Stokes frequency is practically equal to zero. Therefore SRS generation at 90° to the main beam makes it necessary to consider SRS somewhat differently, although from the point of view of the general theory of Raman scattering there is nothing extraordinary about it.

From the point of view of using the new source of exciting radiation, interest attaches to the work of Akhmanov et al. [48] They used as the exciting line the second harmonic of a glass laser activated with neodymium (wavelength $\sim 0.5 \mu$). They compared the thresholds of SRS of various substances excited with ruby radiation and with radiation at this second harmonic. It turned out that in excitation with the second harmonic the thresholds are lower, and the authors note that the lowering of the thresholds can apparently not be uniquely attributed to the increase in the intensity of the Raman scattering, which corresponds to a factor ν^4 .

7. Investigations of SRS of Substances in Different Aggregate States

In the first investigations, SRS was observed essentially in organic liquids. The development of experimental techniques and the great interest in the phenomenon have caused, first, an appreciable extension of the number of liquids active in SRS; second, stimulated Raman scattering of light was obtained in solids and with gases at different pressures and temperatures.

From among the investigations devoted to liquids, we shall mention two on SRS of styrene^[49,50]. It has been assumed prior to these investigations that only some vibrational frequency of the molecule and its harmonics are active in SRS. In styrene, SRS was observed at two different vibrational frequencies. Moreover, in addition to the fundamental frequencies $\nu_1 = 999 \text{ cm}^{-1}$ and $\nu_2 = 1626 \text{ cm}^{-1}$, the combination frequencies $2\nu_1 - \nu_2$, $\nu_2 - \nu_1$, and $3\nu_1 - \nu_2$ were observed in the SRS spectrum.

Somewhat more complicated from the experimental point of view are inorganic crystals. As a rule, the intensity of the lines of substances of this type is lower

in ordinary Raman scattering than that of organic liquids, calling for an increase in the power of the master generator.

The development of quantum generator techniques and a suitable choice of crystals have enabled Eckhardt, Bortfeld, and Geller^[51] to obtain SRS of single crystals of diamond, calcite, and sulfur.

Crystal vibrations are customarily classified as external and internal. By external vibrations are meant vibrations of individual molecules, or groups of molecules occupying different positions in the lattice. Internal vibrations take place inside the molecule or the molecule group.

The chosen object with strong external interaction was single-crystal diamond, the vibrational frequency of which is 1331.8 cm^{-1} and corresponds to the triply degenerate vibrations of two cubic sublattices relative to one another. A diamond crystal of type IIA was used, in the form of a disc of approximately 9 mm diameter and 2.95 mm thickness, cut perpendicular to the [111] axis. The authors observed in the SRS spectrum of diamond two Stokes lines (1325 and 2661 cm^{-1}) and one anti-Stokes line (1335 cm^{-1}).

Single crystals of calcite and α sulfur are characterized by strong internal vibrations. In particular, the spectrum of ordinary Raman scattering of calcite contains a strong and rather narrow (width 5.5 cm^{-1}) line of frequency 1085.6 cm^{-1} , pertaining to the fully-symmetrical vibration of the CO_3^{2-} ion. The orthorhombic crystal of α sulfur is molecular, made up of S_8 molecules. It is characterized by two fully-symmetrical molecule vibrations, which give in ordinary Raman scattering two intense lines with frequencies 216 and 468 cm^{-1} . The SRS spectra of these two crystals, reveal Stokes lines 1075 and 2171 cm^{-1} for calcite and 216 , 472 , and 946 cm^{-1} for sulfur, as well as anti-Stokes lines 1092 and 472 cm^{-1} for CaCO_3 and S respectively. (The authors note the relatively low accuracy of the measurements.) The work was carried out by the standard technique with the substance outside the resonator. Somewhat later, SRS of calcite was obtained by Chiao and Stoicheff^[52]. Their results will be discussed separately.

Almost simultaneously with the work on SRS of crystals, Minck, Terhune, and Rado^[53] reported an investigation of SRS spectra of gases. They obtained SRS of hydrogen, deuterium, and methane.

The excitation of the SRS spectra was produced, as above, in a setup with the substance outside the resonator. The power of the exciting radiation was of the order of 5 MW at a pulse duration 30 nsec. The investigated gas was placed in a specially constructed cell 15 cm long, capable of withstanding a pressure up to 100 atmospheres when cooled to 77°K .

The authors observed stimulated radiation at the Stokes and anti-Stokes frequencies in the spectral region 6000 – 30950 cm^{-1} . In the case of hydrogen, they measured the relative intensities of different harmonics. The results obtained in that investigation are listed in Table III.

Somewhat later, Dumartin, Oksengorn, and Vodar^[54] reported an investigation of SRS in gases at high pressures. The experimental setup was the same as in^[53]. They obtained SRS of hydrogen and nitrogen at pressures 50–500 atm. Apparently, owing to the use of a master generator power larger than in^[53] (10 MW), they were able to observe six har-

monics in the anti-Stokes region of hydrogen compressed to 100 atm. Thus, they obtained stimulated emission with approximate wavelength 2500 \AA . In the same work they investigated the dependence of the intensity of the SRS lines of nitrogen on the pressure. Experiment has shown that the scattering intensity increases with increasing pressure. An interesting result was obtained by the authors in a study of SRS of hydrogen mixed with argon, helium, and deuterium. In this case, at definite pressure ratios of the hydrogen and the impurity gas, the spectrum consists of an intense continuum on which weak SRS lines are superimposed. The short-wave boundary of the continuum lies in the region of 2300 \AA (the authors believe that it is determined by the transparency of the corundum windows). A further increase of the hydrogen pressure leads to the occurrence of SRS lines and to the disappearance of the background. This phenomenon is related by the authors with processes similar to ionization.

Summarizing the foregoing, we can state that the present development of experiment techniques makes it possible to obtain SRS of practically any substance in any aggregate state.

8. Spatial Distribution of SRS Radiation

The least understood effect which experimenters have encountered in the investigation of SRS was the somewhat unusual character of the spatial distribution of the radiation at the anti-Stokes frequencies (see, for example, ^[2]). Whereas the spatial distribution of radiation at the first Stokes frequency has a sharp minimum in the propagation direction of the exciting radiation, the directions of the maximum intensity of radiation at the anti-Stokes and Stokes frequencies of order higher than the first make a certain angle with this direction; this angle is characteristic of the given substance and of the number of the harmonic. This peculiarity of SRS was first explained more or less satisfactorily by Townes^[55]. An analysis of this theory is given in sufficient detail in ^[2] so that we present here only the fundamental relations.

It is shown in ^[55] that the rates of energy exchange between the field of the exciting radiation and the radiation at the first Stokes and first anti-Stokes frequencies are described respectively by

$$P_{-1} = \frac{1}{2R_0} \left(\frac{d\alpha}{dx} \right)^2 \frac{\omega_0 - \omega_r}{\omega_r} \{ (\mathbf{E}_0 \mathbf{E}_{-1})^2 + (\mathbf{E}_0 \mathbf{E}_1) (\mathbf{E}_0 \mathbf{E}_{-1}) \} \\ \times \cos [(2\mathbf{k}_0 - \mathbf{k}_1 - \mathbf{k}_{-1}) \mathbf{r} + \varphi_1 + \varphi_{-1}], \quad (1a)$$

$$P_1 = \frac{1}{2R_0} \left(\frac{d\alpha}{dx} \right)^2 \frac{\omega_0 + \omega_r}{\omega_r} \{ -(\mathbf{E}_0 \mathbf{E}_1)^2 - (\mathbf{E}_0 \mathbf{E}_1) (\mathbf{E}_0 \mathbf{E}_{-1}) \} \\ \times \cos [(2\mathbf{k}_0 - \mathbf{k}_1 - \mathbf{k}_{-1}) \mathbf{r} + \varphi_1 + \varphi_{-1}]; \quad (1b)$$

Here ω_0 is the frequency of the exciting light, ω_r the vibration frequency of the molecule, R_0 a phenomenological damping constant, $d\alpha/dx$ the derivative of the

TABLE III

Substance and experimental conditions	Observed frequency, cm ⁻¹	Intensity, %	Identification
Hydrogen, H ₂ : ν ₁ = 4155.21 cm ⁻¹ , T = 300° K, P = 35 atm	≈ 6 000 10 251 ± 4 (9755 Å) 14 404.1 ± 0.2 (6943 Å) 18 559.1 ± 0.2 (5388 Å) 22 714.4 ± 0.2 (4402 Å) 26 869 ± 3 (3721 Å) ≈ 30 950	0.3 25 100 2 2 0.2	ν ₀ - 2ν ₁ ν ₀ - ν ₁ ν ₀ (laser) ν ₀ + ν ₁ ν ₀ + 2ν ₁ ν ₀ + 3ν ₁ ν ₀ + 4ν ₁
Deuterium, D ₂ : ν ₁ = 2991 cm ⁻¹ , a) 140° K, 70.0 atm, b) 155° K, 38.7 atm:	a) 11 415 ± 3 14 405.3 ± 0.4 b) 17 218 ± 1 17 305 ± 3 a) 17 396.4 ± 0.3 a) 20 386.9 ± 0.2		ν ₀ - ν ₁ ν ₀ (laser) ν ₀ + ν ₁ ν ₀ + 2ν ₁
Methane, CH ₄ : ν ₁ = 2915 cm ⁻¹ , T = 300° K, P = 98.4 atm	11 488.9 ± 0.5 11 404.4 ± 0.2 17 319.5 ± 0.4 20 234.3 ± 0.3		ν ₀ - ν ₁ ν ₀ (laser) ν ₀ + ν ₁ ν ₀ + 2ν ₁

polarizability, E_0 , E_{-1} , and E_1 the amplitudes of the fields at the frequencies ω_0 , $\omega_{-1} = \omega_0 - \omega_R$, and $\omega_1 = \omega_0 + \omega_R$ of the exciting, first Stokes, and first anti-Stokes radiations, respectively, and k_0 , k_{-1} , and k_1 are the wave vectors of the radiation at the same frequencies.

Thus, in order for the field at the frequency ω_1 (first anti-Stokes component) to become amplified ($P_1 > 0$), it is necessary to have $|E_{-1}| > |E_1|$; as a rule, this is satisfied. In addition, the conditions $2k_0 = k_1 + k_{-1}$ and $\cos(\varphi_1 + \varphi_{-1}) < 0$ should be satisfied (φ_1 and φ_{-1} are the phases of the fields at the frequencies ω_1 and ω_{-1}). In this case $P_1 > 0$, but then (1a), (1b), and the relation $2k_0 = k_1 + k_{-1}$ determine the directions in which the field will be amplified at the frequency ω_1 , and the amplification at the frequency ω_{-1} decreases ("absorption" at frequency ω_{-1}).

Further development of the theory^[55] yields for the calculation of the angles more general relations, constituting the momentum conservation law:

$$k_0 + k_{n-1} = k_{-1} + k_n, \quad (2a)$$

$$k_0 + k_{-1} = k_{n-1} + k_n, \quad (2b)$$

where k_i are the wave vectors of the light waves with frequencies $\omega_i = \omega_0 \pm i\omega_R$, $i = 1, 2, 3, \dots$ (the minus sign corresponds to Stokes frequencies). These relations are quite simple for calculation, and no complicated equipment is necessary to verify them experimentally. All this has made it possible to carry out many experimental verifications of these relations.

Garmire^[56] investigated the angular dependence of SRS at anti-Stokes frequencies in several organic liquids placed in an unfocused beam of a Q-switched ruby laser. According to her measurements, the angles agree well with relations (2a) and (2b).

Chiao and Stoicheff^[52] confirmed the correctness of (2a) and (2b) for crystals.

These authors worked with calcite, whose refractive index has been thoroughly studied in a broad region of the spectrum. The investigated samples were calcite single crystals 5–10 cm long, oriented in such a way that the beam of the exciting radiation passed through the crystal as the ordinary ray. The excitation was with a Q-switched ruby laser whose power reached 10 MW at a pulse duration 30 nsec. Under these conditions, fully symmetrical oscillation of the ion CO_3^{2-} was excited, with frequency 1088.6 cm⁻¹. Five harmonics of this frequency were obtained. A set of filters was used to separate different wavelengths.

The angles were measured by a simple reliable method. The scattered radiation was photographed directly on a photographic plate placed in the path of the beam emerging from the crystal. When the exciting-radiation beam was perpendicular to the entrance and exit faces of the crystal, the anti-Stokes components produced on the plate dark concentric rings. The Stokes radiation produced a central dark spot with light rings on it, corresponding to the absorption of light at the first Stokes frequency (see Table IV). By varying the distance from the photographic plate to the crystal and by measuring the diameters of the rings produced on the plate, they could calculate not only the angles at which the radiation of different wavelengths diverge, but also the position of the vertices of the cones. Measurements of this kind have shown that when the beam of the exciting radiation is focused inside the crystal, the vertex coincides with the focus of the focusing lens. On the other hand, if the focus of the lens lies behind the crystal, then the apex of the cone is in the direct vicinity of the exit surface of the crystal.

A symmetrical picture was observed only when the exciting-radiation beam was perpendicular to the crystal faces. A slight tilt of the crystal caused the distribution of the intensity over the periphery of the rings to become inhomogeneous. The sections of the rings on which the maxima of the anti-Stokes radiation intensity fell were radially disposed on one side of the center, while the sections corresponding to the Stokes components of order higher than the first and to absorption of the first Stokes component were disposed along the radius on the opposite side of the center.

Analyzing the results obtained in the experiments with oblique incidence, the authors have concluded that the wave vectors of the Stokes and anti-Stokes radiations \mathbf{k}_{-1} and \mathbf{k}_1 lie in one plane, on opposite sides of the wave vector \mathbf{k}_0 of the exciting radiation. Further, it follows from (2a) and (2b) that the ring of the second Stokes component should be produced only in the presence of the second anti-Stokes ring, as was also confirmed by experiment. From the theory developed in [55] it follows that the gain of the radiation at the second Stokes frequency is accompanied by "absorption" of energy from the radiation at the first Stokes frequency in a direction governed by relations (2a) and (2b). In this case the emission of the second Stokes component and the absorption of the first Stokes component are observed on the photographic plate to one side of the exciting beam. This was also confirmed experimentally.

Investigations of the dependence of the angular distribution in SRS on different factors have shown that the angles are determined essentially by the scattering medium. The angles do not depend on the length of the scattering sample and depend very little on the temperature ($\approx 3\%$ at $\Delta T = 100^\circ\text{C}$). They do, however, depend strongly on the focal length of the focusing lens. Chiao and Stoicheff attribute this effect to the fact that \mathbf{k}_0 is somewhat smaller at the focus of the lens than for a plane wave. At the same time, the values of the angles are very sensitive to change in \mathbf{k}_0 . In this connection, lenses with different focal distances were used in the investigation (8, 20, 30, 50 and 127 cm). The results obtained were extrapolated to $f = \infty$ (plane wave).

The theoretical calculation was based on the relations

$$\theta_n = \beta_n \pm (\beta_n^2 + \delta_n - \gamma_n)^{1/2}, \quad (3)$$

where

$$\begin{aligned} \beta_n &= \frac{k_{n-1}\theta_{n-1}}{k_{-1} + k_n}, \\ \delta_n &= 2 \frac{k_{-1}}{k_n} \frac{k_n + k_{-1} - k_0 - k_{n-1}}{k_{-1} + k_n}, \\ \gamma_n &= \frac{(k_{n-1} - k_{-1})\beta_n\theta_{n-1}}{k_r} \end{aligned}$$

(in the case of calcite, $\omega_r = 1088.6 \text{ cm}^{-1}$). The angles determining the direction of the absorption at the first Stokes frequency were calculated from the formula

$$\theta_{-1}^{(n)} = \frac{k_{n-1}\theta_{n-1} - k_n\theta_n}{k_{-1}}. \quad (4)$$

The results of the measurements and of the calculations by formulas (3) and (4) are given in Table IV.

The good agreement between their theoretical calculations and experiment had enabled these authors to state that SRS proceeds in accordance with the stepwise scheme proposed in [55], and contradicts the four-photon scheme (see, for example, [57]) in which two photons of frequency ω_0 are annihilated simultaneously

with the production of two photons of frequency ω_1 and ω_{-1} . This process also leads to the condition $2\mathbf{k}_0 = \mathbf{k}_{-1} + \mathbf{k}_1$ (which is obtained from (2a) at $n = 1$), but in this case the radiation at both the first anti-Stokes and the first Stokes frequencies should propagate at an angle to the direction of the exciting radiation, something not observed in the experiment. This was pointed out earlier by Zeiger, Tannenwald et al. [58]. The experimental results of [52] disagree likewise with calculations by the Szoke formula [59], obtained by taking into account, besides volume effects, also processes on the surface. Calculation by the latter formula gives for the angles values much larger than those observed in experiment.

In spite of the good agreement obtained by Chiao and Stoicheff, between experiment and the theory of [55], no final conclusions can apparently be drawn concerning the processes that lead to the somewhat unusual spatial distribution of the SRS radiation. Hellwarth et al. [60], investigating the spatial distribution of IRS of nitrobenzene, found a considerable discrepancy between the experimental results and calculations based on relations (2a) and (2b). We note that Chiao and Stoicheff chose calcite for the investigation because its dispersion is well known in a wide spectral range. In [60], the refractive index of nitrobenzene was measured precisely. Calculation of the angles by the formulas given in [58] yields the following values: $\theta_{-1} = 2.5 \pm 0.2^\circ$, $\theta_{-2} = 12.4 \pm 1^\circ$, and $\theta_{-3} = 16$ or $12 \pm 1^\circ$ *. Experiment yields essentially different results: 3.1 ± 0.1 , 3.9 ± 0.1 , and 3.8 ± 0.1 respectively.

Summarizing the foregoing the results on the spatial distribution of stimulated Raman scattering, it can be stated that the qualitative picture of the phenomenon is more or less clear. It is also clear that the angles are determined by a macroscopic parameter of the investigated substance—dispersion. An exact quantitative theory of this process, however, calls for further development.

9. Some Energy Characteristics of SRS

We have already noted above a certain dependence of the SRS parameters on intensity of the exciting radiation. In this section we shall analyze this question in greater detail.

At the present time there are many theoretical papers devoted to a study of the dependence of SRS intensities and line widths on the power of the exciting radiation. We shall stop to discuss our own paper [61], where we presented an elementary theory of SRS and a comparison of the obtained theoretical results with experiment.

Let us consider a simplified model of SRS. Let a light pulse propagate along the axis of a cylindrical cell of finite length. The substance in the cell has ab-

*In different variants of the calculation.

TABLE IV

Frequency	Wavelength, Å	Radiation angles		Absorption angle for the first Stokes component	
		experiment	theory	experiment	theory
$\omega_0 - 2\omega_r$	8174.9	$5.2 \pm 0.1^*$	5.57	$1.8 \pm 0.1^*$	2.22
$\omega_0 + \omega_r$	6456.0	2.50 ± 0.03	2.49	2.90 ± 0.03	2.90
$\omega_0 + 2\omega_r$	6033.2	5.03 ± 0.08	4.91	3.26 ± 0.06	3.21
$\omega_0 + 3\omega_r$	5662.3	7.64 ± 0.2	7.29	3.50 ± 0.06	3.55
$\omega_0 + 4\omega_r$	5334.4	10.2 ± 0.4	9.61	3.77 ± 0.06	3.86

*The values were obtained at $f = 20$ cm. All the remaining results were extrapolated to $f = \infty$.

sorption coefficients α and α' for the exciting radiation and for the scattered radiation, whose frequencies are ν and ν' respectively. In this case the change in the number of photons n and n' of the exciting and scattered radiations, following the passage of a pulse through a layer dx , is given by the equations

$$\frac{dn}{dx} = -\alpha n - k_2 n - k_1 n n', \quad (5a)$$

$$\frac{dn'}{dx} = -\alpha' n' + k_2 n + k_1 n n'. \quad (5b)$$

The first terms in (5a) and (5b) describe the radiation loss in the medium (absorption, scattering, etc.), the second terms characterize ordinary Raman scattering, and the third are responsible for the induced Raman scattering.

We shall solve this system for the case of greatest practical interest—that of small absorption. We shall assume further that $\alpha = \alpha'$ and that the number of quanta n_0' with frequency ν' at the input of the cell ($x = 0$) is equal to zero. These conditions are as a rule satisfied in practice; then we obtain from (5a) and (5b)

$$n + n' = n_0 e^{-\alpha x}, \quad (6)$$

where n_0 is the number of quanta with frequency ν at the input of the cuvette ($x = 0$). Substituting (6) in (5b) we obtain after putting $n' = v(x)e^{-\alpha x}$ an equation of the form

$$\frac{dv}{dx} = v [q(n_0 - v) - k_2] + k_2 n_0, \quad (7)$$

where $q = k_1 e^{-\alpha x}$. At relatively small values of αx (that is, when the absorption over the cell length l is small) we have $q \approx k_1$ and $v(x) \approx n'$; then integration of (7) yields

$$\ln \left[\frac{k_2 + n'}{k_1 n_0 - n'} \right] = (k_1 n_0 + k_2) x + C. \quad (8)$$

Recognizing that $n'(0) = 0$ on the boundary and putting $k_2/k_1 = b$ and $k_1 l = a$, we obtain

$$\ln \left(1 + \frac{n'}{b} \right) - \ln \left(1 - \frac{n'}{n_0} \right) = a(n_0 + b), \quad (9)$$

hence

$$n' = \frac{b [e^{a(n_0+b)} - 1]}{1 + \frac{b}{n_0} e^{a(n_0+b)}}. \quad (10)$$

Let n'_π be the threshold observation of the stimulated Raman scattering, determined by the experimental conditions and attained at an exciting-light intensity $n_0 = \pi$. For the threshold value $n' = n'_\pi$ we obtain from (9)

$$\ln \left(1 + \frac{n'_\pi}{b} \right) - \ln \left(1 - \frac{n'_\pi}{\pi} \right) = a(\pi + b). \quad (11)$$

Subtracting (11) from (9) and discarding n'/n_0 , n'_π/π , and n'_π/b , we obtain the approximate formula

$$\ln \left[1 + \frac{1}{b} (n' - n'_\pi) \right] = a(n_0 - \pi). \quad (12)$$

This formula is convenient for comparison with experiment, since it contains the quantities $n' - n'_\pi$ and $n_0 - \pi$, which are directly measured in the experiments, but it must be borne in mind that formula (12) is valid for a small excess of intensity of the exciting light above the threshold, since at large values of n_0 the value of n' may reach 25% of n_0 .

Formulas (10) and (12) contain two parameters, a and b , the dependence of which on the properties of the scattering substance and the employed apparatus is essentially different. From the general formula for the scattering probability^[62] it follows that

$$a = I_0 c l A, \quad (13)$$

where c is the volume concentration of the scattering substance, A a constant, and I_0 a coefficient characterizing the intensity of the scattering relative to one (isolated) molecule. It must be noted that I_0 in (13) does not coincide with the intensity of the analogous line in the spectrum of ordinary Raman scattering (we shall return to a discussion of this question later).

It follows from (10) or (12) that the dependence of the Raman scattering lines on the values of I_0 , c , l , and n_0 is approximately exponential and only at low exciting-light intensity do we obtain a linear dependence of n' on the indicated variables, such as is characteristic for ordinary Raman scattering.

The meaning of the parameter b is such that it should not depend on I_0 , c , or l . Therefore, comparing two scattering media that differ in concentration or type of scattering molecules, we obtain from (11) (again neglecting $\ln(1 - n'_\pi/\pi)$)

$$a_1(\pi_1 + b) = a_2(\pi_2 + b), \quad (14)$$

hence

$$\frac{\pi_2}{\pi_1} = \frac{a_1}{a_2} \left[1 + \frac{b}{\pi_1} \left(1 - \frac{a_2}{a_1} \right) \right]. \quad (15)$$

We choose the threshold of the first substance π_1 as the standard; Then $r = b/\pi_1$ and is constant under the given experimental conditions (assuming that the spectral sensitivity of the plate is the same for the compared lines).

In the case of mixtures, putting $c_1 = 1$ and $c_2 = c$, we have $a_2/a_1 = c$ and we obtain in lieu of (15)

$$\frac{\pi_2}{\pi_1} = \frac{1+r(1-c)}{c}. \quad (16)$$

In comparing different substances, taking I_{01} as the comparison unit, we obtain

$$\frac{\pi_2}{\pi_1} = \frac{1+r(1-I_r)}{I_r}. \quad (17)$$

In the investigations cited, the stimulated Raman scattering was excited with a ruby laser Q-switched by a rotating prism. The experimental setup is shown in Fig. 21. The laser radiation was focused on a cell with the investigated substance by means of a lens of focal length 250 mm. Particular attention was paid in the measurements to strict standardization of all the experimental conditions. Consequently no easily-spoiled mirrors or other parts were used in the apparatus.

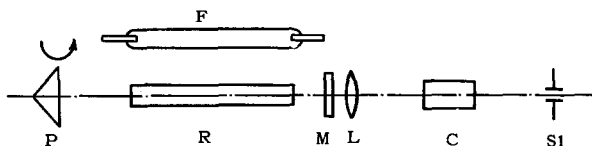


FIG. 21. Experimental setup. R—ruby crystal; F—flash lamp; P—Rotating prism; M—mirror; L—lens with 25 cm focus; C—cell with investigated substance; SI—spectrograph slit.

To measure the threshold, the beam of exciting radiation was attenuated with a stack of glass plates placed ahead of the cell with the investigated liquid. By varying the number of plates, it was possible to change the intensity of the incident radiation in small steps, the "threshold" being defined as that minimal intensity at which Raman scattering was still observed (following a single flash). This method, having the advantage of great simplicity, gave a sufficient measurement accuracy (approximately 10%).

The SRS spectra were registered photographically with the aid of the spectrograph with diffraction grating and with dispersion of approximately 13 Å/mm. Several series of experiments were carried out for each substance.

The parameters of the lines in the spectra of ordinary Raman scattering (integral intensity I_∞ , width δ , degree of depolarization ρ) were measured with a photoelectric spectrometer with approximate dispersion 5 Å/mm with the spectra excited by the 4358 Å mercury line.

The photographic photometry method was used for the intensity measurements. Density markers were produced with the aid of a stepwise attenuator. The source of light in this case was the laser flash, to avoid the influence of the Schwarzschild factor. In processing and measuring the spectrograms, standard methods were used, with all possible precautions. To broaden the range of the measured intensities, neutral filters were used, the transmission of which were measured with the same apparatus. It should be

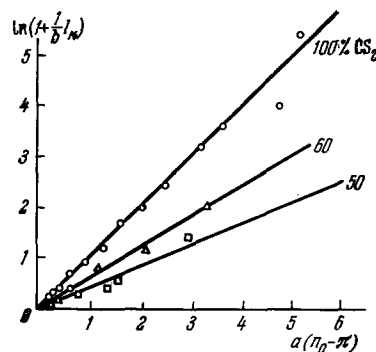


FIG. 22. Dependence of SRS intensity on the excess of intensity of the exciting light over the threshold for CS_2 and mixtures of CS_2 with benzene.

noted that the transmissivity of the optical filters for high-power pulsed radiation turns out to be much higher than when ordinary radiation of the same wavelength is used.

To vary the intensity of the exciting light, a stack of glass plates was used, just as in the measurements of the threshold.

The apparatus described above yielded SRS spectra of twelve different substances (benzene, bromo-benzene, chlorobenzene, toluene, pyridine, o-xylol, styrene, pentadiene-1,3, 2-methylbutadiene-1,3, carbon disulfide, carbon tetrachloride, nitrobenzene).

Principal attention was paid in the investigation of the spectra to quantitative measurements of the excitation threshold and of the SRS line intensity. The study was devoted essentially to the first Stokes component; all the data that follow pertain to this component.

To clarify the question of the ratio of the intensity of the exciting radiation to the stimulated Raman scattering, we measured the line intensities as functions of the excess of the exciting-light intensity over the threshold. The data obtained for carbon disulfide, benzene, and toluene are shown in Figs. 22 and 23. The straight lines on these figures are the theoretical line intensities in accord with (12). The constants a and b in this formula were determined in the following manner. From the experimentally obtained points for carbon disulfide (Fig. 22) or for benzene (Fig. 23), a plot of $\ln(1 + n'/b)$ against $n_0 - \pi$ was prepared, with n' measured in a certain arbitrary scale (that depended on the sensitivity of the plate in the region of the given spectral line), and $n_0 - \pi$ in a second arbitrary scale.

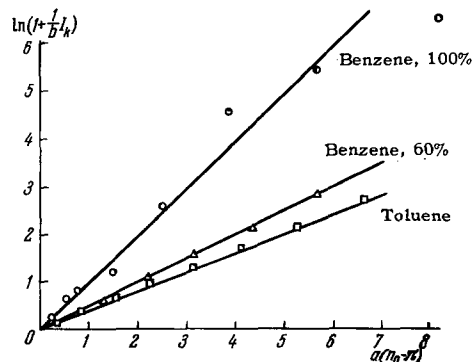


FIG. 23. Dependence of SRS intensity on the excess of intensity of the exciting light over the threshold for benzene, toluene, and mixtures of benzene with CS_2 .

TABLE V

Substance	$\Delta\nu$, cm ⁻¹	c	$\frac{a}{a_0}$	Substance	$\Delta\nu$, cm ⁻¹	c	$\frac{a}{a_0}$	$\frac{I}{I_{\text{benz}}}$
Carbon disulfide	656	1.0	1.0	Benzene	992	1.0	1.0	1.0
		0.6	0.6			0.6	0.5	—
		0.5	0.41			1.0	0.40	0.42
Toluene	1004	1.0	0.40					

By varying b it was possible to make this dependence linear. For the obtained value of b , the constant a was determined from the condition that the indicated line have a slope of 45° .

For the intensity of the same line in the mixture, or for some other substance with closely-lying Raman line, the constant b was assumed to be the same as before, and the constant a was determined from the slope of the experimental line. The data obtained from the constant a are listed in Table V. It must be noted that the measurement conditions were such that only comparisons of the relative values of these quantities are meaningful.

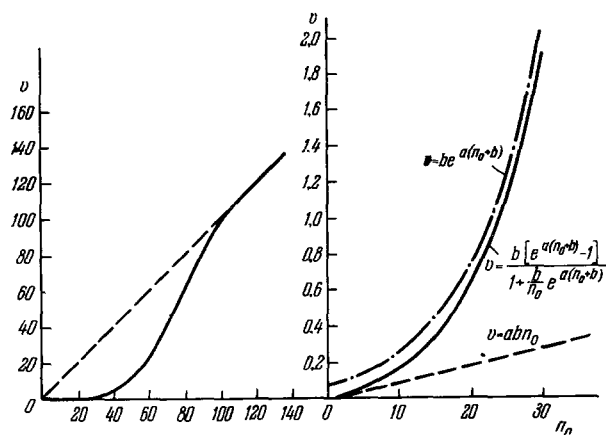


FIG. 24. General plot of SRS intensity against the exciting-radiation intensity in accord with formula (10) for $a = 0.1$ and $b = 0.1$. The initial section of the curve is shown enlarged on the right.

On the basis of Figs. 22 and 23 we can conclude that the approximate formula (12) describes quite well the observed dependence of the Raman line intensity on the excess of intensity of exciting light above threshold.

The values obtained for toluene agree quite well with the ratio of its intensity to the intensity of benzene in ordinary Raman scattering.

Formula (10) was used to plot the Raman line intensities against the exciting-line intensity. The plot obtained (Fig. 24) describes the phenomenon qualitatively at different values of excess excitation above threshold.

Table VI gives the data obtained for the excitation thresholds of different substances relative to the threshold for benzene. The parameters of ordinary Raman scattering lines are also given.

The data obtained lead to the following conclusions:

1. In SRS spectra with sufficiently low threshold, lines of compounds with conjugated C=C bonds are excited in the 1600 cm^{-1} region. The group of substances investigated by us constitutes a new class of compounds active in stimulated Raman scattering and possessing π electrons not in ring systems. We note that the lines investigated by us have considerable intensity both in ordinary Raman spectra and in infrared spectra.

2. The SRS threshold is determined essentially by the intensity of the lines in ordinary Raman scattering, whereas the degree of depolarization plays apparently an insignificant role. As a rough approximation, the reciprocal of the threshold is determined by the line intensity per unit width, but no strict proportionality is observed between these quantities. This may be connected with the fact that our data on the intensities pertain to a 4358 \AA exciting line, whereas in SRS was excited with the 6943 \AA line. However, as is well known, the dependence of the Raman line intensity on the exciting wavelength differs somewhat for different substances (see, for example [63]). Nor can we ignore the influence of differences in the shapes of the compared lines.

TABLE VI

Substance	$\Delta\nu$, cm ⁻¹	δ , cm ⁻¹	σ	I_∞	$\frac{I_\infty}{\delta}$	$1/\pi$
Benzene	992	2.8	0.06	1	1	1
Toluene	1004	1.6	0.07	0.38	0.42	0.40
Pentadiene-1,3	1655	15	0.31	1.6	0.2	0.5
2-methylbutadiene-1,3	1638	7	0.21	1.3	0.3	0.5
Carbon disulfide	656	1	0.25	1.6	3	1.4
Styrene	998	2	—	0.7	0.6	0.5
	1602	3	—	0.9	0.6	—
	1634	3	—	1.6	0.9	0.9

Measurements of the dependence of the SRS line intensity on the intensity of the exciting light were made also by Bret and Mayer.^[64] Starting from Placzek's general formula for the transition probability in Raman scattering^[62], they derived the dependence of the SRS intensity on the intensity of the exciting light and on the ratio n_0/n'_0 , where n'_0 is the intensity of radiation with frequency ν' at the input of the cell. Neglecting in Placzek's formula the term which determines the ordinary Raman scattering, we can write

$$\frac{dn'}{dx} = kn'n, \quad (18)$$

hence, taking into account the boundary conditions, we obtain at the output of the cell

$$n'_l = n'_0 e^{kn_0 l}. \quad (19)$$

From (19), assuming that n_0 does not depend on l , we obtain for the gain G

$$G = \frac{\int n'_0(t) e^{kn_0(t)l} dt}{\int n'_i(t) dt}. \quad (20)$$

Equation (20) contains integrals with respect to the time. The reason for it is that the widths of the exciting-radiation pulses and of the SRS pulses differ by a factor 2–3. The integration in ^[64] was carried out graphically. Experiments of two types were carried out.

In the experiments of the first type, G was measured as a function of n_0 at the entrance to the cell; n'_0 remained unchanged. To this end, type RG Schott filters were placed ahead of the cell. Plots of $\ln G$ against a quantity proportional to n_0 showed a clearly pronounced linear character, thus confirming the foregoing theoretical reasoning.

In the experiments of the second type, $\ln G$ was measured as a function of the ratio $\zeta = n'_0/n_0$ at the entrance to the cell, with n_0 kept constant. This was done by placing neodymium glass in front of the cell. The results presented in the paper show that $\ln G$ decreases with increasing ζ . The authors do not stop to interpret this result theoretically. Polarization measurements, carried out at the same time, have shown that the gain is zero when the polarizations of n_0 and n'_0 at the entrance to the cell are orthogonal. This result confirms the coherence of the SRS.

The experiments described above were made with the apparatus illustrated in Fig. 25, which is essentially a combination of the method in which the substance is placed inside the cavity with the method in which the substance is outside the cavity.

Mirrors M_1 and M_2 had respective transmissions 95 and 30%. Apparently to increase the ruby laser power, use was made of two rubies in tandem, illuminated by a straight flash lamp. A calorimeter was used to measure n_0 . Pulsed Q-switching was by means of an optical shutter. A semitransparent plate diverted part of the radiation to a photomultiplier PM_1 , with which n'_0 was measured. Photomultiplier PM_2 was used to measure n' at the exit from the cell. Filters F_1 and F_2 shielded both photomultipliers against the 6943 Å radiation (ruby). The telescopic system of lenses L_1 and L_2 decreased the cross section of the exciting beam to 0.075 cm², but approximately doubled the divergence at the same time. The time resolution of the radio apparatus was not worse than 3×10^{-9} sec. Birefringent plate D was used which made the polarizations at the frequencies ν and ν' orthogonal, and analyzer A , were used in the polarization measurements. Cells C_1 and C_2 were filled with nitrobenzene in experiments of the first type, and with benzene in the second case.

So far we have been dealing with amplification of SRS at the first Stokes frequency. Recently Tang and Deutsch^[65] demonstrated the feasibility of gain at the anti-Stokes frequency. Unfocused radiation from a Q-switched ruby laser passed through the active liquid parallel to two mirrors, the distance between which was ~ 6 mm. The typical concentric ring of anti-Stokes components were observed in the absence of these mirrors. The photographs obtained with the mirrors, show a strong increase in the intensity of the sections of the rings lying on the intersection with the plane passing through the exciting beam perpendicular to the mirrors. Such an experimental setup is equivalent to increasing the optical length of the beam path in the active medium.

We have discussed above the question of the dependence of the SRS intensity on the intensity of the incident radiation. The dependence of SRS on the concentration of the scattering molecules was investigated in ^[61,67].

The results of the measurements (see Fig. 23) show that the intensities of the SRS lines at constant concentration depend exponentially on the excess of exciting-light intensity above threshold. On the other hand, the dependence of the intensities of these lines on the concentration in mixtures deviates somewhat from theoretical, owing to a certain decrease in the scattering intensity in the mixtures as a result of intermolecular interactions. Similar changes in the intensity were observed many times in ordinary Raman scattering of light. In addition, the dependence of the excitation threshold on the concentration was measured in mixtures of CS₂ and benzene with concentrations 80, 60, 50, and 40%, and in pure CS₂ and benzene.

The results of measurements of the excitation

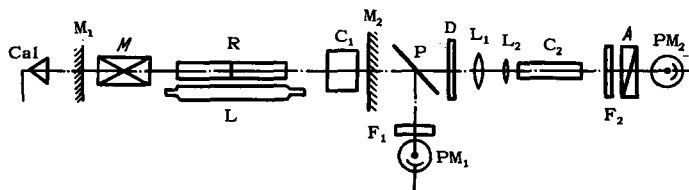


FIG. 25. Diagram of the apparatus of Bret and Mayer^[64]. R—Ruby, L—flash lamp, M_1 and M_2 —mirrors; Cal—calorimeter; M—obstacle shutter; C_1 and C_2 —cells with investigated substance; L_1 and L_2 —telescopic system of lenses; P—semitransparent plate; D—birefringent plate; A—analyzer; F_1 and F_2 —filters; PM_1 and PM_2 —photomultipliers.

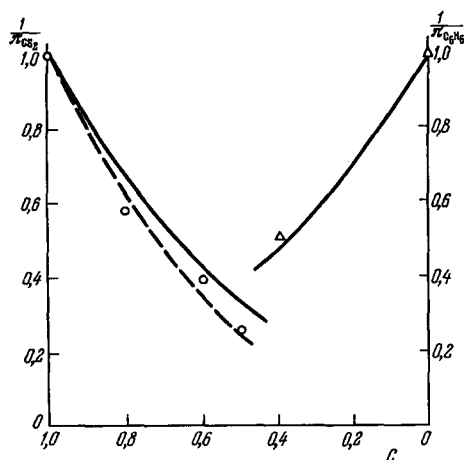


FIG. 26. Threshold of SRS excitation vs. concentration of the scattering molecules for mixtures of benzene and carbon disulfide. Left curve— 656 cm^{-1} line of CS_2 ; right curve— 992 cm^{-1} line of benzene; c —volume concentration of CS_2 in the mixture.

threshold of the 656 cm^{-1} line are shown in Fig. 26 (left-hand scale). This line could be excited at a volume concentration in the mixture ranging from 100 to 50%. At 40% concentration, excitation of the 992 cm^{-1} of benzene started (Fig. 26, right-hand scale).

The data show that the dependence of the excitation threshold on the concentration is not linear. For the 656 cm^{-1} line of CS_2 , this dependence is sufficiently well described by an empirical quadratic formula^[67] (dashed curve on Fig. 26). The solid lines in Fig. 26 show the curves obtained by formula (16) at $r = 1$ (656 cm^{-1} line of CS_2) and $r = 0.7$ (992 cm^{-1} line of benzene). A change in r corresponds to a change in the excitation threshold for these lines.

Kaiser, Maier, and Giordmaine^[66] also investigated the variation of the line intensities of benzene and nitrobenzene in mixtures. They reached the conclusion that an important role for SRS scattering in mixtures is played by intermolecular interaction. According to their data, SRS lines of benzene were observed in a benzene-heptane mixture up to 75% heptane concentration. The intensity of the first Stokes line of benzene remained constant with varying concentration, in first approximation, at heptane contents in the mixture up to 50% (Fig. 27). With further increase of the heptane concentration, the intensity of this line decreased rapidly. A characteristic feature is that no SRS lines of heptane were observed in the experiment at all. An entirely different picture was obtained when working with a mixture of benzene and nitrobenzene. Here the intensity of the SRS lines of benzene (or nitrobenzene) decreased somewhat with decreasing concentration. At concentrations of approximately 50%, the intensity decreased rapidly (by several orders of magnitude). At this concentration, there were observed the benzene line ν_1 , that of nitrobenzene ν_2 , and also lines with combination frequencies of the type $\nu = \nu_0 \pm (k_1\nu_1 + k_2\nu_2)$, where $k = \pm 1, \pm 2, \dots$. At a benzene

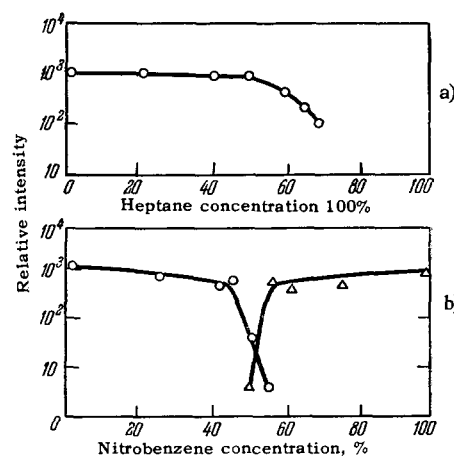


FIG. 27. SRS line intensity vs. concentration of the scattering molecules (from^[66]). a) Benzene-heptane mixture; b) benzene-nitrobenzene mixture.

(nitrobenzene) concentration of 40%, the SRS lines of benzene (nitrobenzene) vanished.

The dependence of the SRS intensity on the concentration, investigated by the authors of^[66], differs essentially from the theoretical dependence. They attribute this discrepancy between theory and experiment to intermolecular interactions. They refer to the work reported in^[65], where the possibility is indicated of a certain increase in the intensity of the SRS lines of benzene in mixtures containing polarized molecules. However, we do not regard this explanation as sufficiently convincing, all the more since we have obtained sufficiently good agreement between experiment and theory in our own work.

As is well known, Raman scattering of light is accompanied by absorption of the exciting radiation (more accurately speaking, by the transfer of energy from the exciting radiation to the Raman radiation). In ordinary Raman scattering, when the fraction of the scattered light is too small, it is practically impossible to measure absorption of this type. The situation is different with SRS, where the line intensity reaches in some cases 30% of the intensity of the exciting radiation. Brewer^[69] succeeded in experimentally proving the transfer of energy from the exciting radiation to the SRS.

A Q-switched laser was used in this investigation. Its radiation passed through semitransparent mirror SM_1 (Fig. 28), which reflected part of the exciting radiation to the first photomultiplier PM_1 , and transmitted the rest to cell C with the investigated substance. The radiation from the cell was split by a second semitransparent mirror, the reflected and transmitted parts going to multipliers PM_2 and PM_3 . Filters F_1 and F_2 , placed ahead of the first two photomultipliers, transmitted only the ruby radiation. A filter F_3 placed ahead of the third photomultiplier separated the first Stokes frequency of the benzene, the substance investigated in the experiment. The signals of the first two photomultipliers were fed to a differential amplifier, whose output signal was proportional to the difference between the signals from PM_1 and PM_2 , that is, proportional to the energy absorbed in the cell. The signals from the differential amplifier and from PM_3 were registered by a two-beam oscilloscope. Such a system has enabled the

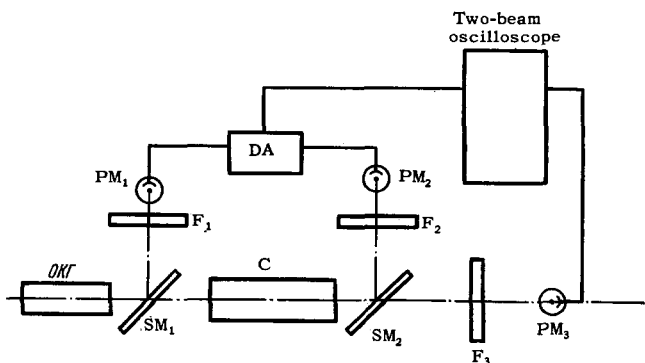


FIG. 28. Setup for investigating the "absorption" accompanying SRS. SM_1 , SM_2 —Semitransparent mirrors; C—cell with investigated substance; PM_1 , PM_2 , PM_3 —photomultipliers; F_1 , F_2 , F_3 —filters; DA—differential amplifier.

author to avoid the uncertainty connected with the fact that during the giant pulse there can be produced several pulses of unequal power, one of which may produce SRS and the others not.

Measurements made with the apparatus described above have shown that in the case of benzene 90% of the absorbed energy is pumped over into SRS.

The author has measured incidentally the distribution of the SRS intensity by components. If the entire SRS is taken to be 100%, then under the given experimental conditions 85% is transferred to the first Stokes line, 9.8% to the second, 0.1% to the third, 0.8% to the first anti-Stokes line, 0.7% to the second, and $\sim 0.002\%$ to the third. 3.5% of the energy goes to radiation at the first Stokes frequency in the opposite direction.

10. Some Nonlinear Effects Connected with SRS

It was shown above that Raman scattering of light is connected with the transfer of energy from one spectral region to the other. But it follows from the general theory that this process is reversible. Indeed, the probability of annihilation of a quantum with frequency ν_0 and creation of a quantum with frequency $\nu_1 = \nu_0 \mp \nu_r$ (where ν_r is the natural frequency of the molecule) is given by the formula

$$W = \frac{16\pi^4}{h^4} \int |\mu|^2 Q_0 \left(\frac{8\pi h \nu_1^3}{c^3} + Q_1 \right) d\nu_0. \quad (21)$$

Here $|\mu|^2$ is the square of the matrix element of the two-photon process, ρ_0 the density of radiation with frequency ν_0 , ρ_1 the density of radiation with frequency ν_1 , and the remaining symbols are standard. The probability of the inverse process (absorption of a quantum ν_1 and emission of a quantum $\nu_0 = \nu_1 \pm \nu_r$) is given by the same formula, except that ν_0 and ρ_0 are replaced by ν_1 and ρ_1 . It is essential that the matrix element $|\mu|$ is the same in both cases. Thus, if radiation with a continuous spectrum is incident on the system, then, generally speaking, some redistribution of the energy will take place, but the spectrum will remain continuous. On the other hand, if the continuous spectrum does not contain radiation at some particular frequency (for concreteness—at the frequency

ν_0), then the process will be only unilateral—energy will be transferred from the radiation with frequency $\nu_1 = \nu_0 \mp \nu_r$ to the radiation with frequency ν_0 . An "absorption" band will appear in place of the frequency ν_1 .

The first to perform an experiment of this type were Landsberg and Baryshanskaya^[70]. In their experiment, light from a source with a continuous spectrum (1,000 W incandescent lamp) was transmitted through a praseodymium-neodymium filter, which gave a sharp absorption band. This light was used to irradiate a quartz crystal. The radiation scattered by the quartz showed, in addition to the main band, also an absorption band whose frequency shift relative to the "main" absorption band coincided with the natural frequency of quartz ($\approx 465 \text{ cm}^{-1}$). Kastler^[71] later proposed to use this phenomenon in astrophysics, but, insofar as we know, nobody succeeded in repeating the experiment of Landsberg and Baryshanskaya, although, for example, Stoicheff did make such an attempt^[72].

It is obvious that the presence of the term $\rho_0\rho_0$ in (21) is not essential for the existence of inverted Raman scattering. However, the presence of the term gives rise to one more effect, characteristic only for the stimulated processes. A study of this effect is the subject of a paper by Jones and Stoicheff^[72]. The radiation of an ordinary Q-switched laser* was transmitted through two cells arranged in tandem, the focus being in the second cell. When the same substance (benzene) was poured in both cells, then self-inversion of the first anti-Stokes benzene line was observed. Even more interesting results were obtained when working with different substances in the cell. We note that under certain conditions of excitation, the anti-Stokes lines can have an appreciable width (up to 100 cm^{-1})^[47]. Thus, it is possible to apply to the second cell radiation consisting of a powerful monochromatic line ν_0 and a quasicontinuous background $\nu_1 = \nu_0 + \nu_r \pm \delta$. In this case a sharp ($\approx 2 \text{ cm}^{-1}$) absorption band was observed at the exit from the second cell in the region of the background, shifted relative to the "exciting" line ν_0 by exactly the natural frequency of the molecules of the substance in the second cell. The first cell was filled with toluene and the second with benzene or nitromethane. One flash was sufficient to observe the "absorption band" of the benzene, whereas registration of the "absorption band" of nitromethane necessitated ten flashes. This is easily explained by the fact that the nitromethane line is shifted relative to the toluene line by almost 85 cm^{-1} , whereas the same shift for the toluene-benzene system amounts to 11 cm^{-1} .

*It is interesting that the second mirror ($R \approx 20\%$) was a plane-parallel plate of "Corning 2-58" glass, which operated simultaneously as a mirror, as a filter, and as a mode selector.

The observed effect can be explained in the following manner. It is perfectly obvious that the transitions $\nu_0 \rightarrow \nu_1$ and $\nu_1 \rightarrow \nu_0$ ($\nu_1 = \nu_0 + \nu_R$) proceeds simultaneously, and at sufficiently high intensities of the "exciting" radiation with frequency ν_0 their probabilities are more or less the same. However, the intensity of the transition is proportional in first approximation to the number of particles that are in the initial state. For the transition $\nu_1 \rightarrow \nu_0$ the initial state is the ground state, while for $\nu_0 \rightarrow \nu_1$ it is the first excited state. Under ordinary conditions, practically all the molecules are in the ground state and thus the $\nu_1 \rightarrow \nu_0$ transition is much more intense than $\nu_0 \rightarrow \nu_1$. Consequently, a somewhat paradoxical energy transfer takes place from the relatively weak radiation at ν_1 ("absorption" at frequency ν_1) into powerful radiation at frequency ν_0 . It is easy to see that in order to observe this effect the product $\rho_0\rho_1$ in (21) should be sufficiently large, and at the same time the quantity ρ_0 should not be very large. When the density of the "exciting" radiation ρ_0 is large, an important role is assumed by the stimulated transition $\nu_0 \rightarrow \nu_0 - \nu_R$, which transfers the molecules to the excited state and by the same token increases the intensity of the transition. $\nu_0 \rightarrow \nu_0 + \nu_R$. This was observed in the experiment. An increase in the output power (ρ_0) of the master generator caused the absorption to vanish, and the absorption band gave way to the SRS line of the substance in the second cell. The reasoning presented above can be used also to explain the "self-inversion" of the anti-Stokes SRS line.

One of the interesting questions of nonlinear optics is that of optical mixing of frequencies. This phenomenon makes it possible to extend the spectral region in which stimulated emission appears. Martin, Thomas, and Wright^[73] obtained optical mixing of the Raman and the exciting-radiation frequencies. Radiation at three Stokes frequencies was observed at the exit of a cell with benzene at the ruby-laser powers which they employed. All this radiation and the so to speak residual radiation of the ruby were aimed at an optically-nonlinear ADP single crystal, which was used as a mixer. The result was a frequency spectrum ranging from 29000 to 11300 cm^{-1} . The authors propose the following frequency assignment: $\nu_0 - \nu_R$, ν_0 , $(\nu_0 - 2\nu_R) + (\nu_0 - 3\nu_R)$, $(\nu_0 - \nu_R) + (\nu_0 - 3\nu_R)$, or $2(\nu_0 - 2\nu_R)$, $(\nu_0 - \nu_R) + (\nu_0 - 2\nu_R)$, or $\nu_0 + (\nu_0 - 3\nu_R)$, $\nu_0 + (\nu_0 - 2\nu_R)$, or $2(\nu_0 - \nu_R)$, $\nu_0 + (\nu_0 - \nu_R)$, $2\nu_0$. Here $\nu_0 \approx 14404 \text{ cm}^{-1}$ is the ruby emission frequency and $\nu_R \approx 991 \text{ cm}^{-1}$ is the natural frequency of the benzene molecule.

The results of this investigation, together with the results obtained by other authors, show that stimulated Raman scattering of light makes it possible to extend greatly the spectral region in which stimulated emission can be used. Akanaev, Akhmanov, and Khokhlov^[74] called attention to the fact that SRS can be used also for amplification of an external signal. Here, as is well

known from general radio engineerings, the signal gain, say, at the first Stokes frequency should be larger by at least one order of magnitude than the gain of the signal at the ruby frequency when a ruby amplifier is used. The reason is that the widths of the typical Raman lines are one order of magnitude smaller than the spectral band amplified by the ruby amplifier. It is shown in ^[74] that the amplification of the signal at the first Stokes frequency of benzene can reach an order of ten. If two different lasers are used for amplification of the radiation at the combination frequency, then it is necessary to solve a very complicated technical problem, that of synchronizing two pulses with accuracy of the order of 10 nsec. Therefore the same laser was used in ^[74] as the master generator and the amplifier. A Q-switched ruby laser with dead-end resonator, whose axis passed through one of the arms of a cruciform cell half-filled with benzene, was used in the investigation. The beam emerging from the resonator, which contained the radiation at the first Stokes frequency, was split into two beams with the aid of semitransparent and fully reflecting mirrors and fed to the second arm of the same cell. One beam traveled in air, and the other through the active zone of the cell. Both beams were then incident on the upper and lower halves of the spectrograph slit. By measuring the ratio of the line intensities of the exciting radiation and the radiation at the combination frequencies, it was possible to estimate the gain. These measurements have shown that radiation at the first Stokes frequency of benzene is amplified by a factor 3–8 per passage through the cell.

Thus, new possibilities are uncovered for practical utilization of stimulated Raman scattering of light for amplification of light signals in a wide spectral region.

¹ Ya. S. Bobovich, UFN 84, 37 (1964), Soviet Phys. Uspekhi 7, 656 (1965).

² V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, UFN 83, 197 (1964), Soviet Phys. Uspekhi 7, 419 (1964).

³ L. P. Malyavkin A. N. Mogilevskiĭ, and I. S. Abramson, Materialy X Soveshchaniya po spektroskopii (Trans. Tenth Conf. on Spectroscopy), L'vov, L'vov Univ. Press, 2, No. 4(9), 129 (1957).

⁴ I. S. Abramson, É. Ya. Kononov, A. N. Mogilevskiĭ, S. N. Murzin, and V. A. Slavnyiĭ, Zavodskaya laboratoriya 28(7), 875 (1962).

⁵ V. A. Zubov, G. G. Petrash, and M. M. Sushchinskiĭ, PTÉ No. 5, 119 (1959).

⁶ V. A. Zubov and G. G. Petrash, Predovoĭ nauchno-tekhnicheskii i proizvodstvennyi opyt (Progressive Scientific, Technical and Manufacturing Experience), Topic 35, No. 5, Ser. 3 (1960).

⁷ A. N. Mogilevskiĭ, Paper at All-Moscow Colloquium on Molecular Spectroscopy (Moscow, April, 1965).

⁸ Simomura, Fukuda, Kida, Simadzu Rev 16(1), 5 (1959).

- ⁹H. W. Schrötter, *Zs. angew. Phys.* **12**(6), 275 (1960).
- ¹⁰P. Ransen, R. Dupeyrat, *J. Phys. et Radium* **22**(4), S15 (1961).
- ¹¹N. Brandmuller and H. Moser, *Introduction to Raman Spectroscopy* (Russ. Transl.) Mir, 1964.
- ¹²F. Valentin, *Compt. rend.* **244**(14), 1915 (1957).
- ¹³F. Valentin, M. Dumartin, M. Biron, *J. Phys. et Radium* **18**(11), 64 (1957).
- ¹⁴F. Valentin, *Ann. de phys.* **4**(11-12), 1239 (1959).
- ¹⁵M. Delhaye, *J. Phys. et Radium* **20**, 47 (1959).
- ¹⁶M. Delhaye, M. B. Delhaye-Buisset, *Rev. univers. mines* **15**(5), 480 (1959).
- ¹⁷M. Delhaye, *Adv. Mol. Spectr.* **3**, 1286 (1962).
- ¹⁸V. A. Zubov, G. G. Petrash, and M. M. Sushchinskiĭ, *Optika i spektroskopiya* **6**, 827 (1959).
- ¹⁹M. M. Sushchinskiĭ, *Izv. AN SSSR ser. fiz.* **22**, 1073 (1958), transl. *Bull. Acad. Sci.* p. 1062; dissertation, *Trudy, FIAN* **12**, 54 (1960).
- ²⁰N. Fuhrer, Hs. H. Günthard, *Helv. Chim. Acta* **44**(5), 1330 (1961).
- ²¹R. E. Kagarise, B. Whetsli Kermit, *Spectrochim. Acta* **17**(N8), 869 (1961).
- ²²G. Collier and F. Singleton, *J. Appl. Chem.* **6**, 495 (1956).
- ²³G. L. Collier and A. Panting, *Spectrochim. Acta* **14**, 104 (1959).
- ²⁴A. E. Martin, *Nature* **180** (No. 4579), 231 (1957); A. E. Martin, *Spectrochim. Acta* **14**, 97 (1959).
- ²⁵R. C. Sinith, *Rev. Sci. Instr.* **34**(3), 296 (1963).
- ²⁶E. C. Olson and C. D. Alway, *Anal. Chem.* **32**(3), 370 (1960).
- ²⁷V. I. Bunimovich, *Fluktuatsionnye protsessy v radiopriemnykh ustroĭstvakh* (Fluctuation Processes in Radio Receivers), *Soviet Radio*, 1951.
- ²⁸S. G. Rautian, *UFN* **66**, 475 (1958), *Soviet Phys. Uspekhi* **1**, 245 (1959).
- ²⁹V. A. Zubov, *Optika i spektroskopiya* **11**, 275 (1961).
- ³⁰S. P. S. Porto and D. L. Wood, *JOSA* **52**, 251 (1962).
- ³¹S. P. S. Porto, *Proceedings of the X Colloquium Spectroscopicum International*, Washington, 1963, p. 417.
- ³²B. P. Stoicheff, *Proceedings of the X Colloquium Spectroscopicum International*, Washington, 1963, p. 399.
- ³³G. E. Danil'tseva, V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, *JETP* **44**, 2193 (1963), *Soviet Phys. JETP* **17**, 1473 (1963).
- ³⁴R. C. C. Leite and S. P. S. Porto, *JOSA* **54**, 981 (1964).
- ³⁵J. A. Koningstein and R. G. Smith, *JOSA* **54**, 1061 (1964).
- ³⁶T. C. Damen, R. C. Leite, and S. P. S. Porto, *Phys. Rev. Letts.* **14**, 9 (1965).
- ³⁷G. J. Pokrowski and E. A. Gordon, *Ann. Phys.* **4**, 488 (1930).
- ³⁸I. I. Kondilenko, P. A. Korotkov, and V. L. Strizhevskii, *Optika i spektroskopiya* **8**, 471 (1960); **11**, 169 (1961); **17**, 451 (1964).
- ³⁹A. I. Soklovskaya and P. D. Simova, *ibid.* **15**, 622 (1963).
- ⁴⁰R. C. Leite, R. S. Moore, S. P. S. Porto, and J. E. Ripper, *Phys. Rev. Letts.* **14**, 7 (1965).
- ⁴¹F. J. McClung and D. Weiner, *JOSA* **54**(5), 641 (1964).
- ⁴²E. J. Woodbury and W. K. Ng, *Proc. IRE* **50**, 2367 (1962).
- ⁴³M. Geller, D. P. Bortfeld, W. R. Sooy, and E. J. Woodbury, *Proc. IEEE* **51**, 1236 (1963).
- ⁴⁴H. Takuma and D. A. Jennings, *Bull. Amer. Phys. Soc.* **9**, 499 (1964).
- ⁴⁵H. Takuma and D. A. Jennings, *Appl. Phys. Letts.* **4**(11), 185 (1964).
- ⁴⁶J. H. Dennis and P. E. Tannenwald, *Appl. Phys. Letts* **5**(3), 58 (1964).
- ⁴⁷B. P. Stoicheff, *International School of Physics "Enrico Fermi," XXXI Course*, August 19-31, 1963; B. P. Stoicheff, *Phys. Rev. Letts.* **7**, 186 (1963).
- ⁴⁸S. A. Akhmanov, A. I. Kovrigin, et al. *JETP* **48**, 1202 (1965), *Soviet Phys. JETP* **21**, 801 (1965).
- ⁴⁹V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, *JETP* **47**, 784 (1964), *Soviet Phys. JETP* **20**, 524 (1965).
- ⁵⁰D. P. Bortfeld, M. Geller, and G. Eckhardt, *J. Chem. Phys.* **40**(6), 1170 (1964).
- ⁵¹G. Eckhardt, D. P. Bortfeld, and M. Geller, *Appl. Phys. Letts.* **3**(8), 137 (1963).
- ⁵²R. Y. Chiao and B. P. Stoicheff, *Bull. Amer. Phys. Soc.* **9**, 490 (1964); R. Y. Chiao and B. P. Stoicheff, *Phys. Rev. Letts.* **12**(11), 290 (1964).
- ⁵³R. W. Minck, R. W. Terhune, and W. G. Rado, *Appl. Phys. Letts.* **3**(10), 181 (1963).
- ⁵⁴S. Dumartin, B. Oksengorn, and B. Vodar, *Compt. rend* **259**(25), 4589 (1964).
- ⁵⁵C. H. Townes, *International School of Physics "Enrico Fermi," XXXI Course*, August 19-31, 1963; E. Garmire, F. Pandarese, and C. H. Townes, *Phys. Rev. Letts.* **11**, 160 (1963).
- ⁵⁶E. Garmire, *Bull. Amer. Phys. Soc.* **9**, 490 (1964).
- ⁵⁷R. W. Terhune, *Bull. Amer. Phys. Soc.* **8**, 359 (1963).
- ⁵⁸H. J. Zeiger, P. E. Tannenwald, S. Kern, and R. Herendeen, *Phys. Rev. Letts.* **11**, 419 (1963).
- ⁵⁹A. Szöke, *Bull. Amer. Phys. Soc.* **9**, 490 (1964).
- ⁶⁰R. W. Hellwarth, F. J. McClung, W. G. Wagner, and D. Weiner, *Bull. Amer. Phys. Soc.* **9**, 490 (1964).
- ⁶¹V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, *Prikladnaya spektroskopiya* (Applied Spectroscopy) **3**, 10, 336 (1965).
- ⁶²G. Placzek, *Rayleigh and Raman Scattering*, Lawrence Lab. U. of Cal. Livermore, 1959.
- ⁶³M. M. Sushchinskiĭ and V. A. Zubov, *Optika i spektroskopiya* **13**, 766 (1962).
- ⁶⁴G. Bret and G. Mayer, *Compt. rend.* **258**(12), 3265 (1964).
- ⁶⁵C. L. Tang and T. F. Deutsch, *Phys. Rev.* **A138**(1), 1 (1965).

⁶⁶W. Kaiser, M. Maier, and J. A. Geordmain, Appl. Phys. Letts. **6**(2), 25 (1965).

⁶⁷V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, JETP **48**, 378 (1965), Soviet Phys. JETP **21**, 249 (1965).

⁶⁸R. W. Hellwarth, Phys. Rev. **130**, 1850 (1963).

⁶⁹R. G. Brewer, Phys. Letts. **11**(4), 294 (1964).

⁷⁰G. S. Landsberg, Izbr. trudy (Collected Works), AN SSSR, 1958.

⁷¹A. Kastler, J. Chem. Phys. **46**, 72 (1949).

⁷²W. J. Jones and B. P. Stoicheff, Phys. Rev. Letts. **13**, 22, 657 (1964).

⁷³M. D. Martin, E. L. Thomas, and J. K. Wright, Phys. Letts. **15**, 2, 136 (1965).

⁷⁴B. A. Akanaev, S. A. Akhmanov, and R. V. Kholov, JETP Letters **1**, No. 4, 4 (1965), transl. **1**, 103 (1965).

Translated by J. G. Adashko